Anonyme. The Journal of physical chemistry. Published at Cornell university [3puis3 Published under the auspices of the American chemical society, the Chemical society and the Faraday society]. 1896 [l]-. 1931 . July-sept..

1/ Les contenus accessibles sur le site Gallica sont pour la plupart des reproductions numériques d'oeuvres tombées dans le domaine public provenant des collections de la BnF.Leur réutilisation s'inscrit dans le cadre de la loi n°78-753 du 17 juillet 1978 :
*La réutilisation non commerciale de ces contenus est libre et gratuite dans le respect de la législation en vigueur et notamment du maintien de la mention de source.
*La réutilisation commerciale de ces contenus est payante et fait l'objet d'une licence. Est entendue par réutilisation commerciale la revente de contenus sous forme de produits élaborés ou de fourniture de service.

Cliquer ici pour accéder aux tarifs et à la licence

2/ Les contenus de Gallica sont la propriété de la BnF au sens de l'article L.2112-1 du code général de la propriété des personnes publiques.

3/ Quelques contenus sont soumis à un régime de réutilisation particulier. Il s'agit :

*des reproductions de documents protégés par un droit d'auteur appartenant à un tiers. Ces documents ne peuvent être réutilisés sauf dans le cadre de la copie privée sans l'autorisation préalable du titulaire des droits.
*des reproductions de documents conservés dans les bibliothèques ou autres institutions partenaires. Ceux-ci sont signalés par la mention Source Gallica.BnF.fr / Bibliothèque municipale de ... (ou autre partenaire). L'utilisateur est invité à s'informer auprès de ces bibliothèques de leurs conditions de réutilisation.

4/ Gallica constitue une base de données, dont la BnF est producteur, protégée au sens des articles L341-1 et suivants du code la propriété intellectuelle.

5/ Les présentes conditions d'utilisation des contenus de Gallica sont régies par la loi française. En cas de réutilisation prévue par un autre pays, il appartient à chaque utilisateur de vérifier la conformité de son projet avec le droit de ce pays.

6/ L'utilisateur s'engage à respecter les présentes conditions d'utilisation ainsi que la législation en vigueur, notamment en matière de propriété intellectuelle. En cas de non respect de ces dispositions, il est notamment passible d'une amende prévue par la loi du 17 juillet 1978.

7/ Pour obtenir un document de Gallica en haute définition, contacter reutilisation@bnf.fr.

Journal of physical chemistry

Tome 35

Volume 39

Washington 1931

DECOMPOSITION AND POLYMERIZATION OF THE OLEFINIC HYDROCARBONS*

BY GUSTAV EGLOFF, R. E. SCHAAD, AND C. D. LOWRY, JR.

This survey covers the changes occurring when olefins are subjected to heat or pressure, with or without the aid of catalysts, to a number of chemical reagents, to photolysis, to electric sparks or discharge, and to alpha particles. While these agencies are not alike in their effects on hydrocarbons of the ethylene series there are similarities in their action which justify their discussion together. The reactions occurring are of three types. There may be breakdown of the molecule consisting in some cases merely of hydrogen loss, and in others of more deep-seated change, which go so far as to produce carbon and hydrogen as sole products. As an alternative, the change can be one of synthesis giving rise to hydrocarbons with more atoms in their molecules than the starting substance. Or merely a molecular rearrangement takes place—usually a shift in the position of the double bond—without variation in molecular size. Under some conditions change of but one of these types occurs. But often changes of these three classes are brought about by the same means, either concurrently or simultaneously, the type of reaction changing with experimental conditions.

The action of heat, for example, may produce changes of the three types. With mild heating, rearrangement or polymerization reactions predominate, and may be the only ones occurring. They produce olefin or naphthene hydrocarbons of molecular weight greater than that of the starting substance. Change of this type is aided by superatmospheric pressure. At more elevated temperatures, while polymerization continues, there form simultaneously carbon, hydrogen, acetylene, and low molecular weight olefins and paraffins as a result of disruptive changes. At elevated temperatures the higher olefins produced by polymerization tend to become in part converted into aromatic hydrocarbons. At very high temperatures practically no polymerization takes place, and the primary products obtained from olefins are carbon and hydrogen. Catalysts notably lower the temperature at which changes in olefins take place. Some catalysts favor disruptive changes, while others aid polymerization.

The electric spark or arc causes changes in olefins similar to those occasioned by high temperature—a small amount of polymerization occurs, but, in the main, there is decomposition to carbon, hydrogen, and methane. The reactions caused by the silent discharge, on the other hand, are indicated to be almost exclusively polymerization.

The action of the chemical reagents discussed in this paper is largely polymerization, except that at elevated temperatures disruptive reactions occur.

---

* Presented before the Organic Division of the American Chemical Society, Cincinnati, Ohio, September, 1930.

With some hydrocarbons definite series of polymers of successively higher boiling points are obtained, which in some cases have proved to be dimers, trimers, etc. Among the reagents discussed, sulfuric acid is not included. While with olefins sulfuric acid produces polymerization, it also gives rise to a complex series of other reactions, and therefore its action has little similarity to that of the other substances described.

The action of light and of alpha particles on olefins has been but meagerly investigated. The information available indicates that light of short wave length causes dissociation and polymerization. The action of alpha particles appears to be similar to that of light.

Reaction Mechanism

From the work which has been done on olefin decomposition and polymerization, it appears that certain principles regarding the course of the reactions are of general application.

During breakdown, by heat of other agencies, methane is almost always formed, often in considerable proportion. It evidently arises by splitting off of a terminal carbon atom. Such splitting would first form two molecular fragments, a small group which would become methane by hydrogenation, and a larger residue which could rearrange to a diolefin, or add hydrogen to form a lower mono-olefin.

Dehydrogenation and hydrogenation go on during olefin reactions. As products of these changes diolefins, acetylene, and paraffins are formed. Probably free radicals form during decomposition, and are intermediate in many of the reactions occurring. The presence of radicals has been proved in positive ray work on hydrocarbons and the existence of free methyl is indicated in the work of Paneth.[124] Their existence offers the clearest explanation of many of the reactions of olefins, and is almost a necessity to a rational mechanism for some changes.

Polymerization, the available evidence indicates, begins with the addition of an olefin molecule to another of the same sort, forming a dimer of the original substance. In some investigations it has been possible to stop reaction at the dimer stage. By careful heating or by use of the electric discharge, ethylene has been converted into butylene and no other product. By addition of another olefin molecule to the dimer, a trimer would result. No doubt this sort of addition process continues until high boiling oils and tars, which have often been reported, are formed. As a preliminary to the addition of an olefin to another, it is quite probable, as postulated by Hurd and Spence,[65] that there is activation, creating from the double bond grouping a reactive radical with two free linkages.

Naphthenes have been reported only in work done with chemical reagents or under pressure. It is likely, however, that when olefins are heated, naphthenic substances are formed, and that careful study would reveal their presence.

Aromatic substances are abundantly formed by olefin pyrolysis at moderately high temperature. It seems most likely that they are formed from naphthenes which are produced from olefins by polymerization and ring closure. On the other hand, as postulated by Berthelot[5] and Lewes[95,96], acetylene may first form and by polymerization go directly to aromatic substances. While most workers favor the ethylene polymerization mechanism, some still support the Berthelot-Lewes theory. The absence of acetylene, or its occurrence in many studies in but small quantities, speaks against this mechanism.

In regard to the relationship of structure to stability among isomeric olefins, Hurd[64] has presented the generalization that hydrocarbons containing alkyl groups attached to saturated carbon atoms (which he termed olefins of the R-allyl type) are less stable than those containing alkyl groups attached to unsaturated carbon atoms (which he termed olefins of the R-vinyl type). Substances of the first class may pass, on heating, into isomers of the second variety. Thus 1-butene, an R-allyl type hydrocarbon, is somewhat less stable than 2-butene, of the R-vinyl type. Similarly iso propylethylene is less stable to heat than trimethylethylene, and is readily converted into it.

The change of iso propylethylene into trimethylethylene is also a shift of the double bond from alpha to beta position. Change of this type also appears in the ready conversion of 2,6-dimethyl-7-octene into 2,6-dimethyl-6-octene[159], and is probably a general reaction of olefinic hydrocarbons.

Sources of Olefins

The great significance of a study of olefin reactions is apparent when one considers the vast quantities of these hydrocarbons available in commercial gases, or that could be made available by cracking natural gas and hydrocarbon oils.

Below are given representative analyses of cracking still gas and other commercial gases containing olefins. Gas from the cracking process is available at the present time to the extent of approximately 250,000,000,000 cubic feet per year. Crack gas is now largely utilized as refinery fuel, although its olefin content makes it of more value for other uses. In Table I are representative analyses[30] of this gas, produced from a number of oils by cracking under diverse conditions.

TABLE I

Analyses of Gases from the Cracking Process (in per cent)
(Egloff and Morrell)

Hydrocarbon							
Ethylene	0.6	1.9	2.2	2.7	4.0	6.3	27.0
Propylene	11.7	0.8	15.2	7.6	6.8	12.0	16.0
Butylenes	4.7	7.4	3.9	6.5	2.6	7.1	9.0
Butadiene	—	—	—	—	—	—	1.0
Hydrogen	3.0	1.9	2.0	3.0	5.0	1.7	7.0
Paraffins	80.0	88.0	77.7	80.2	81.6	72.9	40.0

There is seen to be a great variation between different samples of gas. The cracking process can be regulated to produce a large or small volume of gas, and in some degree to control its composition.

Because of the divergence of analyses it is difficult to arrive at even an approximate figure for the proportions of olefin hydrocarbons in commercial gases. In Table II are given what are believed to be representative figures.

TABLE II

Olefin Content of Commercial Gases

	Olefin content in per cent			
	Ethylene	Propylene	Butylenes	Higher Olefins
Cracking still gas	6	8	4	2
Coke oven gas	2.7	—	—	—
Carburetted water gas	6.7	—	—	—

On the basis of these figures, and the 1929 production of these gases, there has been drawn up, in Table III, an estimate of the amounts of the lower olefins which they contain.

TABLE III

Volumes of Lower Olefins in Commercial Gases, 1929
(In 1000 cu. ft.)

	Production 1929	Ethylene	Propylene	Butylenes
Cracking still gas	250,000,000	15,000,000	20,000,000	10,000,000
Coke oven gas	540,000,000	14,580,000	———	———
Carburetted water gas	255,000,000	17,085,000	———	———

In addition to this supply a potential source of olefinic hydrocarbons is the lower paraffin hydrocarbons present in natural gas, cracked gases, gasoline, etc., which may readily be cracked to give olefins. Egloff, Schaad, and Lowry[31] have published estimates of the amounts of the gaseous paraffins available. If quantitative dehydrogenation of the paraffins to olefins is assumed, the data listed in Table IV are obtained.

TABLE IV

Potential Olefin Production from Paraffins in Commercial Gases, 1929
(In 1000 cu. ft.)

Source	Total produced	Ethylene	Propylene	Butylenes
Natural gas	1,800,000,000	162,000,000	54,000,000	18,000,000
Petroleum distillation gas	270,000,000	56,700,000	32,400,000	10,800,000
Natural gas gasoline[1]	45,463,000 barrels		2,050,000	14,830,000
Refinery gasoline[1]	390,810,000 barrels		4,300,000	16,350,000

---

[1] Propane and butane dissolved in gasoline are calculated to equivalents as gaseous propylene and butylenes.

Nor does this complete the possible sources of olefins. Hydrocarbon oils, such as fuel or gas oil, may be cracked to olefins. Oil gas, first made as an illuminant, still finds limited application for this use, but is also manufactured at the present time for the purpose of securing unsaturated hydrocarbons. The amount of olefins that can be made from this source is limited only by the production of crude oil, and is therefore enormous. Analyses reported by Brooks[17] of typical oil gas as made at different temperatures are given in Table V.

TABLE V

Analyses of Typical Oil Gases (Pintsch Gas)

Temp., °C.*	Ethylene per cent	Propylene per cent	Higher olefins per cent	Total olefins per cent
805-650	16.3	18.6	1.4	36.3
660-535	18.3	19.0	1.6	38.9
635-535	12.5	22.4	2.4	37.3
625-535	13.7	22.6	2.6	38.5
615-425	12.0	25.7	3.8	41.5

* The temperatures given are those at the beginning and end of the gas making period.

In Table VI are given figures for oil gas prepared under pressure.[17]

TABLE VI

Composition of Oil Gas produced under Pressure

Temp., °C.	Pressure pounds per sq. in.	Ethylene per cent	Propylene per cent	Higher olefins per cent	Total olefins per cent
600	57	19.3	28.0	3.2	50.5
650	72	19.0	28.4	4.2	51.6
700	83	17.7	23.9	3.5	45.1
730	95	17.5	20.0	3.1	40.6

Markowitsch and Pigulewski[108] have published analyses (Table VII) of three fractions of gas from the cracking of oil vapors primarily to produce gas.

TABLE VII

Gas from the Cracking of Oil Vapors (Markowitsch and Pigulewski)

	Composition, in per cent		
	I	II	III
Ethylene	17.1	25.2	—
Propylene	24.3	12.0	4.0
n-Butylene	9.0	2.9	35.0
Iso butylene	10.3	3.0	40.0
Amylene and higher	2.5	—	—
Butadiene	6.6	2.0	18.0
Total olefins	69.8	45.1	—
Paraffins	29.6	49.0	3.0
Hydrogen	0.2	2.4	—
CO, CO_2, and N_2	0.4	3.5	—

The supply of olefins, one may say, is inexhaustible. Their study to date is far from thorough. They offer to the student of pure science a field rich in its rewards of new facts. Their abundance gives great value to any process that can convert these substances into products commercially more useful.

I. THERMAL ACTION

1. Ethylene

When ethylene is exposed to heat at low temperatures, unless catalysts are employed, polymerization is the predominant reaction, and may be the only change which takes place. At temperatures from 350° to 800°, changes both of polymerization and of disintegration occur. At high temperatures, as above 950°, only decomposition goes on.

From their calculations of the free energies of various hydrocarbons, Francis and Kleinschmidt[40] concluded that lower olefins will polymerize at temperatures up to 425°, but crack at higher temperatures. "Similarly, the higher olefins tend to isomerize into naphthenes below about the same temperature, and do so in the presence of aluminum chloride."

As products of ethylene decomposition, there form mainly carbon, hydrogen, methane, ethane, and acetylene. Polymerization yields both liquid and gaseous products. The liquids produced contain higher olefins, of which several have been reported, and the aromatic hydrocarbons, benzene, naphthalene, anthracene, and styrene. In the gases formed are found propylene, butylene, amylene, and butadiene. Pressure greatly aids polymerization of olefins, causing ethylene to change even at room temperature, and yielding among the products naphthenic hydrocarbons, which have not been reported in work at atmospheric pressure.

A number of workers have suggested mechanisms by which some of these changes occur. Bone and Coward,[14] Nellensteyn,[118], and Walker[151] postulated the extensive formation of free radicals as intermediate products. Many investigators, notably Noyes[121], Zanetti, Suydam, and Offner,[158] Hague and Wheeler,[53] and Wheeler and Wood,[155] have presented theories to explain aromatic formation from ethylene. From the reaction products of ethylene reported, we consider the most probable course of the changes occurring when ethylene is subjected to the action of heat to be the following:

The first break of an ethylene molecule is probably in part at least to free methylene radicals, $:CH_2$. These lose hydrogen and form methine radicals, $\vdots CH$, or disintegrate completely to carbon and hydrogen—two products abundantly formed. Hydrogenation of methylene radicals gives methane. It is possible to write a simple reaction:

$$C_2H_4 \rightarrow CH_4 + C,$$

but that such a change would occur in one step is unlikely. Because of its stability, methane once formed does not usually undergo further change. It is therefore an abundant product of ethylene pyrolysis.

Ethane forms by direct hydrogenation of ethylene, the hydrogen being liberated by the simultaneous dehydrogenation of other molecules of ethylene or split from free radicals. Combination of a radical with an ethylene molecule forms propylene, or this hydrocarbon may arise by butylene breakdown. The most simple way in which acetylene could be formed from ethylene is by loss of hydrogen. Possibly it is formed by combination of free ⋮CH groups, or even by the union of carbon and hydrogen resulting from ethylene breakdown.

Polymerization of ethylene appears to commence with the formation of butylene. As butylene is the sole product obtained in careful work done at very low temperature, it undoubtedly is produced by the direct combination of two ethylene molecules, and does not involve any intermediate steps. Butadiene results by the dehydrogenation of butylene. Further polymerization can be confined to hexylene, formed by the addition of ethylene to butylene in the same way that ethylene adds to itself to form butylene. Continuation of this process gives the oils reported as "higher olefins" of undetermined structure.

In regard to the steps by which ethylene is converted into aromatic hydrocarbons, we favor the mechanism proposed by a number of workers involving the formation of butadiene, a cyclohexene (with perhaps the intermediate formation of a straight chain hexene), and benzene by dehydrogenation of the cyclic hydrocarbon. Perhaps ethylene is first converted into butylene, which adds ethylene to give a hexene, or dehydrogenates to butadiene, and then forms hexadiene. The ring closes and loss of hydrogen follows. This mechanism was stated by Hague and Wheeler[53] in the following equations:

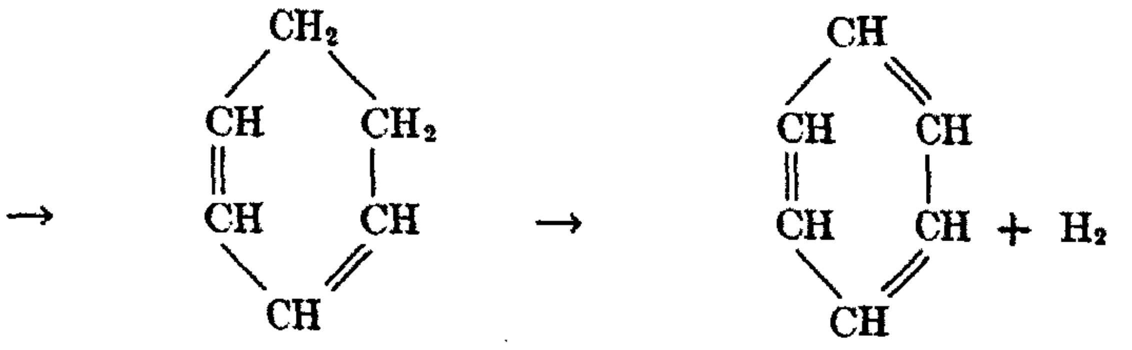
(a) $CH_2{:}CH_2+CH_2{:}CH_2 \rightarrow CH_3.CH_2.CH{:}CH_2 \rightarrow CH_2{:}CH.CH{:}CH_2+H_2.$

Butylene Butadiene

(b) $CH_2{:}CH.CH{:}CH_2 + CH_2{:}CH_2 \rightarrow$ either

$CH_2{:}CH.CH_2.CH_2CH{:}CH_2$ or $CH_2{:}CH.CH{:}CH.CH{:}CH_2 + H_2$

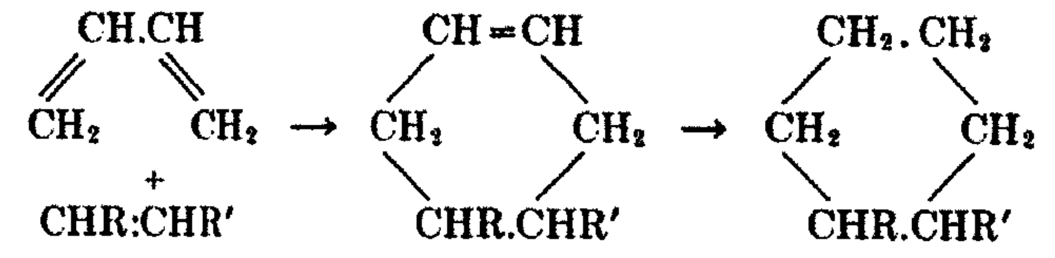
1,5-hexadiene 1,3,5-hexatriene



The same compounds might form in a simpler manner by union of three ethylene molecules to cyclohexane, followed by dehydrogenation to benzene. Further addition of ethylene to benzene probably accounts for the styrene reported, and it is likely that as postulated by Hague and Wheeler "butadiene can condense with benzene, hydrogen being eliminated, to form naphthalene; and that anthracene and phenanthrene can be formed from the naphthalene in a similar manner."

Upon the basis of work on ethylene, propylene, and the straight chain butylenes, Wheeler and Wood[155] modified the mechanism proposed by Hague and Wheeler. They wrote the following general equation for ring formation involving no intermediate formation of a hexene.

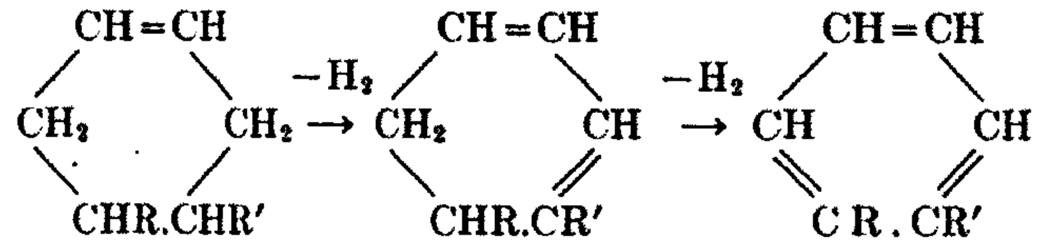
(A)



This reaction accords with the work of Diels and Adler[29a] who proved that the addition to butadiene of unsaturated substances, such as maleic anhydride, forms cyclic compounds.

According to equation A, equimolecular proportions of ethylene and butadiene combine at comparatively low temperatures to produce cyclohexane. Propylene and butylene similarly react with butadiene forming hydroaromatic hydrocarbons with side chains. This hypothesis is supported by the fact that Wheeler and Wood found cyclohexene and methylcyclohexene in considerable quantity in the liquid hydrocarbons formed from the olefins at low decomposition temperatures. At higher temperatures the liquids consisted mainly of aromatic hydrocarbons, with traces of cyclohexadiene. This accorded with the fact that cyclohexene was found to be dehydrogenated to benzene at 600°. The cyclohexadiene identified was considered to be an intermediate reaction product. This latter stage in the reactions, forming aromatic from hydroaromatic hydrocarbons, was represented by these workers by reaction B:

(B)



"Analogously to the formation of *cyclo*hexene from butadiene and ethylene, partly hydrogenated naphthalenes could be formed by the combination of butadiene and *cyclo*hexene. These products would then readily be dehydrogenated (compare Jones, J. Chem. Soc., 1915, **107**, 1582), giving rise to naphthalene, which is found in the liquid decomposition products of the olefins."

There is considerable uncertainty as to the temperature at which ethylene first decomposes. Some investigators have found no marked decomposition below 600°. As opposed to this observation it has been reported that continuous exposure of ethylene for twenty-four hours, in glass, to a temperature of 350° to 355° caused incipient decomposition. Others have claimed 380-400° to be the minimum temperature at which the gas decomposed (in quartz).

Formation of condensation products at 450° is readily shown, and breakdown at a considerable rate occurs at 525°. As in the case of the paraffins, many metals lower the temperature of initial change. In the presence of nickel or cobalt, decomposition has been stated to occur at 300°. The disagreement as to temperature of initial decomposition is to be attributed to differences in contact time.

a. *Under Atmospheric Pressure*

i. *Without Catalysts*

Deimann, Van Troostwyk, Lauwerenburg, and Bondt,[27] the first to recognize the difference between ethylene and methane, were also the first to study its pyrolysis. These were the men whose work gave to ethylene chloride the name, "Oil of the Dutch Chemists." They found that while in a red-hot glass tube ethylene did not decrease in volume, it, however, lost its ability to combine with chlorine to form an oily liquid. The tube in which the hydrocarbon was heated became blackened and covered by drops of an "empyreumatic oil."

On repeating some of the experiments of these workers, Hecht and Vauquelin[64] found that when passed through a red-hot porcelain tube, ethylene produced hydrogen and large quantities of carbon. De Carolles[26] observed that in a white-hot iron tube ethylene decomposed, and yielded as one product a black deposit—not carbon, however, but iron carbide.

Magnus,[105] the next worker on this subject, enlarged the list of products identified. Working at red heat he obtained as gaseous product a mixture equal to 90 per cent of the volume of the original olefin, containing hydrogen, methane, undecomposed ethylene, and tar vapor. He also separated a tar containing naphthalene. When ethylene was confined in a white-hot tube or passed through such a tube at this high temperature he found that it yielded, almost exclusively, carbon and hydrogen.

Berthelot[5] identified several aromatic hydrocarbons in the products of ethylene decomposition. He found that passage of the hydrocarbon through a red-hot glass or porcelain tube yielded benzene, styrene, naphthalene, and a residual gas, which he stated contained traces of acetylene and considerable amounts of ethane. Berthelot assumed that the primary decomposition of ethylene was its conversion in part into acetylene, and in part into ethane. The liquid products, were attributed to condensation or polymerization of the acetylene.

Norton and Noyes[120] went still further in the identification of the products. By passing ethylene slowly through a hard glass tube at a "low red heat," they obtained carbon, methane, ethane, propylene, butylene, divinyl (butadiene), benzene, naphthalene, and a crystalline substance thought to be anthracene. The absence of acetylene and the presence of butylene and butadiene in their products caused them to reject acetylene and turn to butadiene as the essential intermediate in the formation of aromatics.

In early studies the investigators knew only approximately the temperatures at which they worked. The first to accurately control the heating in the study of the thermal behavior of ethylene was Day.[25] He found that at 344° ethylene would remain for several hours without change of volume or odor. At 350° to 355° the gas contracted about one-twentieth in 24 hours, and acquired an odor of impure kerosene. As he could find no evidence of the formation of methane, or hydrogen, he considered the action exclusively one of polymerization. When heated at 400° to 408° for 171 hours, the contraction amounted to a little more than one-half, and visible drops of liquid were formed. This liquid combined readily with bromine, and did not contain benzene. The residual gas at this temperature contained 24.7 per cent olefins, 39.6 per cent ethane, 35.5 per cent methane, and no hydrogen. At 450° ethylene was acted upon still more readily. There was 44 per cent contraction of the gas in 72 hours, and a liquid was obtained which had the same charactertistics as that obtained at the lower temperature. The residual gas contained 8.4 per cent methane, 64.0 per cent ethane, and 27.6 per cent olefins. No hydrogen was obtained, but there was a slight deposition of carbon.

These figures give a rough picture of the rates at which ethylene decomposes at low temperatures. The data of Simmersbach[139] presented in Table VIII allow a more exact comparison of decomposition speeds at somewhat higher temperatures.

TABLE VIII

Rate of Decomposition of Ethylene at 500° to 1000°
(Simmersbach)

Temp., °C.	Heating time, sec.	Ethylene present after heating, per cent by volume	Temp., °C.	Heating time, sec.	Ethylene present after heating, per cent by volume
500	45	90.4	800	38	16.8
600	38	88.9	850	36	8.9
650	38	71.5	900	43	1.1
700	36	61.1	1000	40	0.3
750	45	34.3			

Pease[125] decomposed ethylene at several comparatively low temperatures, and compared the products obtained in an endeavor to analyze the steps in the reactions occurring. He found formation of butylene to be the only change which took place to any large extent when ethylene was passed through a pyrex tube heated at 450° to 500°. Above 525°, ethane, methane, a little hydrogen, and liquid products (which were not identified) began to appear. While the quantity of ethane formed was small it was regarded as a primary decomposition product because at low temperatures its amount was nearly proportional to the amount of ethylene decomposed. Methane was considered a secondary product, since its proportion increased as the heating time was prolonged. This only proves its stability however, and can hardly be considered positive evidence that it does not form at least in part from ethylene.

Bone and Coward[14] carried the temperature a little higher, passing ethylene with and without recirculation through a porcelain tube at 570° to 950°. At 570° to 580°, when recirculating the olefin, they obtained hydrogen, methane, ethane, acetylene, and aromatic hydrocarbons, with a negligible amount of carbon. They regarded acetylene as the principal primary product of the decomposition at these temperatures. At 700° to 800°, without recirculation, carbon separation was larger than at the lower temperatures, and formation of aromatic hydrocarbons smaller, while there was an increased production of methane. At 950° decomposition was very rapid, 90 per cent of the ethylene decomposed during an exposure of one minute, and there was a copious separation of carbon. Only a small proportion (4 per cent) of the olefin was here converted into condensable products.

Lewes[95] made a study under still more severe conditions. He passed ethylene rapidly through a platinum tube at temperatures from 800° to 1500°. At 800° the breakdown was negligible. The results at higher temperatures are summarized in Table IX.

TABLE IX

Decomposition of Ethylene
(Lewes)

Temp. of gas in tube, °C. Products	900	1000	1200	1500
		Per cent of gaseous products		
Unsatd. hydrocarbons	34.77	18.02	10.54	0.43
of which C_2H_2 was	0.82	0.60	3.60	0.00
Satd. hydrocarbons	59.73	76.48	55.26	27.80
Hydrogen	0.00	0.00	25.11	62.68
Oil, grams deposited per 100 cc. of gas	0.0024	0.0048	0.0038	0.00

At 900° and 1000°, as will be seen from the table, the gaseous products were largely saturated hydrocarbons. These were methane and probably some ethane. At 1200° hydrogen appeared in considerable volume and carbon deposited, no doubt in part at least because of the instability of methane itself at this temperature. Acetylene was formed in small amount even at 900°, and reached a maximum at 1200°. The yield of acetylene was increased when the ethylene was diluted with hydrogen.

Some benzene formed, particularly with long time of heating. Lewes attributed it to polymerization of acetylene. At 1000° aromatic substances of higher molecular weight than benzene were obtained, conspicuously naphthalene. At 1100° and above, these liquid products were not found, and it was assumed that they broke down to acetylene and finally to carbon and hydrogen. At 1500° the decomposition yielded almost exclusively carbon, hydrogen, and methane, with no acetylene and no oil.

Lewes[96] observed that the decomposition of ethylene was at first very rapid, but as it neared completion, it slowed down. This he attributed to secondary reactions which tended to reform ethylene. The chief agent of the thermal action was thought to be radiant heat rather than contact with heated surfaces.

In Walker's[151] study in glass and quartz at 500° to 650°, hydrogen, methane, ethane, acetylene, and oily products were reported. The acetylene yield at 650°, with 31 per cent decomposition of the ethylene, was 8 per cent of the gaseous products. Walker also obtained a small yield of oily material as a product of heating a mixture of ethylene and acetylene at 600°. Prunier[128] had earlier reported that butadiene resulted from the passage, through a red-hot porcelain tube of a mixture of equal volumes of ethylene and acetylene. Several patents[65, 73, 76] also cover the production of butadiene, benzene, and "oils" from mixtures of ethylene and acetylene. Walker believed that the polymerization of the ethylene could be attributed to the catalytic influence of some one or more of the constituents of his Jena glass tube. Accordingly, at temperatures up to about 600°, he passed ethylene over the raw materials of glass—silica, borax, caustic soda, calcium hydroxide, and ferric, zinc, and lead oxides. He obtained negative or indecisive results.

Frey and Smith[41] obtained a rather large yield of propylene when they heated ethylene in a silica flask at 575° for four minutes. Decomposition was slight, the analysis of the products being as follows (in per cent):

N_2	H_2	CH_4	C_2H_6	C_3H_8	C_2H_4	C_3H_6	C_4H_8	C_5H_{10} to C_8H_x	Higher H.C.
0.8	0.8	2.6	3.2	0.0	84.4	4.5	1.2	2.2	0.3

Less than 0.05 per cent of acetylene was present. "The liquid product was yellow, indicating the presence of highly unsaturated compounds."

Zanetti, Suydam, and Offner[158] paid particular attention to the formation of butadiene. They found that when ethylene was heated at several temperatures in each experiment for a period of three minutes, production of this diolefin began at 600°, reaching at 750° a maximum of about one per cent of the ethylene treated, and dropping to zero at about 850° to 900°. During the heating, most of the ethylene was converted into hydrogen, methane, and carbon.

TABLE X

Decomposition of Ethylene
(Hague and Wheeler)

Temp., °C.	Calcd. contact time secs.	Liquids, per cent by weight of ethylene		Gas analyses, per cent by volume				
		Total liquids	Benzene fraction	Higher olefins	C_2H_2	C_2H_4	H_2	CH_4
700	55	13.5	6.6	9.2	8.2	55.2	5.9	8.7
750	52.5	25.5	13.1	4.4	4.8	40.5	13.1	28.8
800	50	28.9	10.7	1.4	4.2	16.1	27.9	44.0
850	47.7	15.5	7.8	0.4	1.1	6.6	35.6	50.0

Hague and Wheeler[53] showed that considerably larger amounts of liquid products could be obtained than had previously been reported. By passing ethylene through a vertical, electrically heated quartz tube, at temperatures from 700° to 850°, they obtained conversion of as high as 30 per cent into oils. Their results are summarized in Table X.

In general, these gas analyses accord with the results of other workers. The yield of higher olefins and acetylene decreased, that of hydrogen and methane increased, with rise in temperature.

The gases obtained at 700° contained butylene and butadiene, and the latter was also present at 600° and 675°. As will be seen from the table, the temperature range most favorable to the formation of liquid products, which were chiefly benzene and a smaller amount of naphthalene, was 750° to 800°. Dilution with hydrogen decreased the yield of benzene and the temperature range over which the maximum yield could be obtained. The investigators stated that their figures for acetylene are too high, because the ammoniacal silver chloride solution used in its estimation dissolved some ethylene.

The results of Wood[157] (Table XI), obtained by heating ethylene for three hours in quartz bulbs at 400° to 700°, are of particular interest for the picture they give of the rise and fall in the yield of higher olefins. He found maximum production of olefins above ethylene at 500°. In addition, as the temperature rose, there was steady increase in the percentage of hydrogen and methane, accompanied by first a rise of the proportion of ethane, and then a decline.

TABLE XI

Decomposition and Polymerization of Ethylene
(Wood)

Temp., °C.	Composition of gaseous products, per cent by volume				
	Higher olefins	C_2H_4	H_2	CH_4	C_2H_6
400	3.5	96.5	—	—	—
450	8.0	92.0	—	—	—
500	13.7	76.0	—	—	10.3
550	7.9	55.1	2.9	12.0	22.1
600	6.0	30.0	2.7	25.4	35.1
650	4.2	19.0	11.2	52.7	12.9
700	1.9	16.5	15.4	57.5	8.7
750	0.7	8.2	18.7	67.0	5.4

Wheeler and Wood[155] went to higher temperatures, determining the yield of liquid products and carefully analyzing the gases produced. They carried out their preliminary work in quartz bulbs, and found that at 400 mm. pressure ethylene decomposition began at 380° to 400°. The greater part of their work was done in tubes, using the method of Hague and Wheeler, at temperatures of 650° to 900°. At intermediate temperatures, they obtained larger conversions of ethylene into liquid products, while as the temperature increased the liquid yield dropped, and there was a larger production of hydrogen and methane, with considerable carbon deposition. The results are presented in Table XII.

TABLE XII

The Decomposition of Ethylene
(Wheeler and Wood)

Temp., °C.	Calcd. contact time, secs.	Yields in per cent by weight of ethylene treated			Per cent change in volume
		Total liquids	Distillate up to 170°	Carbon	
650	58.2	1.5	—	Nil	− 2.7
700	55	12.2	8.0	Nil	−15.2
750	52.5	28.2	16.5	Trace	−16.4
800	50	36.1	17.7	1.4	−11.8
850	47.7	31.4	13.3	11.9	+ 1.3
900	45.7	13.4	5.4	13.4	+13.1

	Gas analyses, in per cent by volume of the ethylene treated						
	H_2	CH_4	C_2H_6	C_2H_4	C_3H_6	C_4H_8	C_4H_6
650	0.7	0.5	2.0	89.9	Nil	3.8	0.3
700	3.2	4.9	4.9	66.2	2.2	2.8	0.4
750	7.2	16.7	8.6	47.6	1.7	1.5	0.2
800	17.3	33.7	6.9	29.0	1.1	Nil	0.15
850	35.8	49.7	3.3	12.2	0.5		
900	51.0	55.2	2.2	4.6	Nil		

It will be noted that at 650°, butylene was the product present in largest amount. The proportion of the ethylene passed through the reaction tube that was recovered as gases containing four carbon atoms (butylene and butadiene) was 8.4 per cent by weight as compared with 1.5 per cent of liquid hydrocarbons. At 700°, the formation of butylene was less, but that of butadiene increased, and propylene appeared in the products. Propylene was regarded as derived from butylene. Acetylene was reported absent. The tests used would detect it in 0.2 per cent concentration.

Of the liquid product formed at 700°, "50 per cent boiled below 110° and was principally benzene, with some toluene and cyclohexene; neither naphthenes nor paraffins were present in this fraction."

Wheeler[164] stated that the carbon produced during decomposition of ethylene might be either a soft dull form or a hard and shiny kind, depending upon the character of the heated surface in contact with the gas, the rate of passage of the gas over that surface, and the temperature. At 760° he obtained shiny carbon.

Waterman and Tulleners[152] passed ethylene at ordinary pressure through a quartz tube heated electrically to temperatures between 600° and 900°, but did not make a complete analysis of their products. They reported at 700° to 800° considerable yields of a light oil boiling from room temperature to about 85° and a higher boiling tar. At 900° there was high carbon formation. Their results are given in Table XIII.

TABLE XIII

Decomposition of Ethylene

(Waterman and Tulleners)

	Yields on a single passage of the olefin* through a heated quartz tube				
Expt., No.	6	7	5	3	4
Temp., °C	600	650	700	800	900
Rate of ethylene flow, grams per min.	0.99	0.933	0.97	0.934	0.942
Contact time, secs. (Calcd.)	4.9	4.9	4.5	3.8	3.5
Total ethylene passed, grams	386	419.8	459.6	490.3	99
Effluent gas					
Total weight, grams	371.8	299.8	308	—	—
Unsatd. hydrocarbons, per cent	90	78	53	30.2	1.5
Light oil					
Yield in grams	Traces	38	58.8	63.2	7.0
Per cent by wt. of ethylene treated	—	9.1	12.8	12.9	7.1
Specific gravity	—	0.80	0.84	0.88	0.88
Bromine number	—	123	36.2	13.7	0
Tar					
Yield in grams	0	2.7	79.9	119.5	0
Per cent by wt. of ethylene treated	0	0.6	17.4	24.4	0
Carbon					
Yield in grams	0	0	1.6	13.7	58.1
Per cent by wt. of ethylene treated	0	0	0.35	2.8	58.7

* The gas used in experiments 3 to 6 contained about 90 per cent of ethylene, while that used in experiment 7 was more than 95 per cent ethylene.

The constituents of the light oil were not identified except that it was reported to contain considerable benzene. The higher boiling tar obtained at 800° was distilled with results as follows:

Fraction	Per cent
Distillate up to 100°	about 7
100–200°	14
200–300°	30
300–400°	26
Pitch and Carbon	20
Gas and loss	3

At 900° the ethylene produced carbon and a gas containing 74 per cent hydrogen, 19 per cent methane and homologs, and 1.5 per cent unsaturated hydrocarbons.

By the passage of ethylene over silica gel at 700° Mailhe with Renaudie[106] obtained, besides gaseous products, a liquid boiling up to 170° which consisted mainly of benzene mixed with small quantities of toluene, and a higher boiling (150–330°) brown liquid containing considerable naphthalene. The gases were mainly undecomposed ethylene with small amounts of methane.

When Frolich, Simard, and White[42] heated a mixture containing 27.3 per cent ethylene and 72.7 per cent nitrogen in a quartz tube at 734° to 816°, they obtained no products which they could condense with solid carbon dioxide, a result which they attributed to the fact that the large amount of nitrogen and ethylene present carried off condensables formed, such as butadiene.

Sinkinson[140] observed that deposition of free carbon occurred at 550° in a slowly moving stream of ethylene.

Smolenski[141] reported that ethylene decomposition at 700° to 750° yielded liquid and solid hydrocarbon products, equal to sixty per cent by weight of the original hydrocarbon, and hydrogen. He did not identify his products.

Hollings and Cobb[59] heated a mixture containing 11 per cent ethylene, 48 per cent methane, and 41 per cent hydrogen for 45 seconds at 800°. The content of ethylene dropped, that of methane increased, and some acetylene was formed. When the experiment was repeated at 1100° with an exposure of 35 seconds, the ethylene was decomposed in entirety, and the gaseous product was a mixture of methane and hydrogen.

The products which have been obtained by thermal treatment of ethylene are summarized in Tables XIV to XVIII inclusive. These outlines do not include the substances claimed in patents.

TABLE XIV

Thermal Decomposition of Ethylene
Products obtained at Different Temperatures in Quartz Bulbs and Tubes

Temp., °C.	Heating tube diam., etc.	Rate of gas flow or time of heating	Products	Yields, per cent of gaseous products*	References (by number)
400	Bulb	3 hrs.	"Higher olefins"	3.5	157
450	Bulb	3 hrs.	"Higher olefins"	8.0	157
500	Bulb	3 hrs.	Ethane	10.3	157
			"Higher olefins"	13.7	
550	Bulb	3 hrs.	Hydrogen	2.9	157
			Methane	12.0	
			Ethane	22.1	
			"Higher olefins"	7.9	
550	Tube	"Slowly moving gas"	Carbon	Not stated	140
600	Bulb	3 hrs.	Hydrogen	2.7	157
			Methane	25.4	
			Ethane	35.1	
			"Higher olefins"	6.0	
650	Bulb	3 hrs.	Hydrogen	11.2	157
			Methane	52.7	
			Ethane	12.9	
			"Higher olefins"	4.2	
650	Tube, 2.2 cm.	4 l./hr., 58.2 secs., (calcd.)	Hydrogen	0.7 **	155
			Methane	0.5 **	
			Ethane	2.0 **	
			Butylene	3.8 **	
			Butadiene	0.3 **	
			Total liquids	1.5 ***	

* Unless stated otherwise.

** Per cent by volume of the ethylene entering the reaction tube.

*** Per cent by weight of ethylene treated.

TABLE XIV (Continued)

Temp., °C.	Heating tube diam., etc.	Rate of gas flow or time of heating	Products	Yields, per cent of gaseous products*	References (by number)
650	Tube	0.93 g./min., 4.9 secs. (calcd.)	Light oil	9.1 ***	152
			Tar	0.6 ***	
700	Bulb	3 hrs.	Hydrogen	15.4	157
			Methane	57.5	
			Ethane	8.7	
			"Higher olefins"	1.9	
700	Tube 2.2 cm.	4 l./hr., 55 secs., (calcd.)	Hydrogen	5.9	53
			Methane	8.7	
			Acetylene	8.2	
			Butylene	Not stated	
			Butadiene	Not stated	
			"Higher olefins"	9.2	
			Total liquids	13.5 ***	
			Benzene fraction	6.6 ***	
700	Tube 2.2 cm.	4 l./hr., 55 secs., (calcd.)	Hydrogen	3.2 **	155
			Methane	4.9 **	
			Ethane	4.9 **	
			Propylene	2.2 **	
			Butylene	2.8 **	
			Butadiene	0.4 **	
			Total liquids	12.2 ***	
700	Tube	0.97 g./min., 4.5 secs., (calcd.)	Light oil	12.8 ***	152
			Tar	17.4 ***	
			Carbon	0.35 ***	
750	Tube 2.2 cm.	4 l./hr., 52.5 secs., (calcd.)	Hydrogen	13.1	53
			Methane	28.8	
			Acetylene	4.8	
			"Higher olefins"	4.4	
			Total liquids	25.5 ***	
			Benzene fraction	13.1 ***	
			Naphthalene	Not stated	

TABLE XIV (Continued)

Temp., °C.	Heating tube diam., etc.	Rate of gas flow or time of heating	Products	Yields, per cent of gaseous products*	References (by number)
750	Bulb	3 hrs.	Hydrogen	18.7	157
			Methane	67.0	
			Ethane	5.4	
			"Higher olefins"	0.7	
750	Tube 2.2 cm.	4 l./hr., 52.5 secs., (calcd.)	Hydrogen	7.2 **	155
			Methane	16.7 **	
			Ethane	8.6 **	
			Propylene	1.7 **	
			Butylene	1.5 **	
			Butadiene	0.2 **	
			Total liquids	28.2 ***	
			Carbon	Trace	
800	Tube, 2.2 cm.	4 l./hr., 50 secs., (calcd.)	Hydrogen	27.9	53
			Methane	44.0	
			Acetylene	4.2	
			"Higher olefins"	1.4	
			Total liquids	28.9 ***	
			Benzene fraction	10.7 ***	
800	Tube, 2.2 cm.	4 l./hr., 50 secs., (calcd.)	Hydrogen	17.3 **	155
			Methane	33.7 **	
			Ethane	6.9 **	
			Propylene	1.1 **	
			Butadiene	0.15 **	
			Total liquids	36.1 ***	
			Carbon	1.4 ***	
800	Tube	0.934 g./min., 3.8 secs. (calcd.)	Light oil	12.9 ***	152
			Tar	24.4 ***	
			Carbon	2.8 ***	

TABLE XIV (Continued)

Temp., °C.	Heating tube diam., etc.	Rate of gas flow or time of heating	Products	Yields, per cent of gaseous products*	References (by number)
850	Tube, 2.2 cm.	4 l./hr., 47.7 secs., (calcd.)	Hydrogen	35.6	53
			Methane	50.0	
			Acetylene	1.1	
			"Higher olefins"	0.4	
			Total liquids	15.5 ***	
			Benzene fraction	7.8 ***	
850	Tube, 2.2 cm.	4 l./hr., 47.7 secs., (calcd.)	Hydrogen	35.8 **	155
			Methane	49.7 **	
			Ethane	3.3 **	
			Propylene, butylene, and butadiene	0.5 **	
			Total liquids	31.8 ***	
			Carbon	11.9 ***	
900	Tube, 2.2 cm.	4 l./hr., 45.7 secs., (calcd.)	Hydrogen	51.0 **	155
			Methane	55.2 **	
			Ethane	2.2 **	
			Total liquids	13.4 ***	
			Carbon	13.4 ***	
900	Tube,	0.942 g./min., 3.5 secs., (calcd.)	Light oil	7.1 ***	152
			Carbon	58.7 ***	

TABLE XV

Thermal Decomposition of Ethylene

Products obtained at Different Temperatures in Glass Bulbs and Tubes

Temp., °C.	Rate of gas flow or time of heating	Products	Yields	References (by number).
350-355	24 hrs.	"Odor of impure kerosene"	*	25
400-408	171 hrs.	Unsatd. liquid	Few drops	25
		Gaseous products	24.7% olefins 39.6% C_2H_6 35.5% CH_4	
450	72 hrs.	Unsatd. liquid	*	25
		Carbon	*	
		Gaseous products	8.4% CH_4 64.0% C_2H_6 27.6% olefins	
450-500	Flowing gas **	Butylene	*	125
"Above 525"	Flowing gas **	Hydrogen	"A little"	125
		Methane	*	
		Ethane	"Small"	
		Unidentified liquids	*	
"Low red heat"	"Slow" rate of flow	Carbon	*	120
		Methane	*	
		Ethane	*	
		Propylene	*	
		Butylene	*	
		Butadiene	*	
		Benzene	*	
		Naphthalene	*	
		Anthracene (?)	*	
"Red-hot"	Confined ** gas	Carbon	*	27
		"Empyreumatic oil"	Few drops	
"Red-hot"	**	Ethane	*	5
		Acetylene	*	
		Benzene	*	
		Styrene	*	
		Naphthalene	*	

* The yield was not stated.

** Time of heating was not stated.

TABLE XVI

Thermal Decomposition of Ethylene

Products obtained at Different Temperatures in Porcelain Tubes

Temp., °C.	Rate of gas flow or time of heating	Products	Yields, per cent of C_2H_4 treated	References (by number)
570–580	Gas recirculated	Hydrogen	*	14
		Methane	*	
		Ethane	*	
		Acetylene	*	
		"Aromatic H.C."	*	
		Carbon	Nearly negligible quantity	
700–800	Flowing gas without recirculation	Carbon Methane	Larger than at 570–580°	14
		"Aromatic H.C."	Smaller than at 570–580°	
950	One minute	Carbon	"Copious"	14
		Liquids	4	
"Red-hot"	Flowing gas **	Carbon	Large quantity	54
		Hydrogen	*	
"Red heat"	**	Tar, mainly naphthalene	*	105
		Gas consisting of hydrogen, methane, ethylene, and tar vapors	90	
"Red-hot"	Flowing gas **	Ethane	*	5
		Acetylene	*	
		Benzene	*	
		Styrene	*	
		Naphthalene	*	
"White-hot"	"Confined gas"	Carbon Hydrogen	Almost exclusive products	105
"White-hot"	Flowing gas **	Carbon Hydrogen	Almost exclusive products	105

* The yield was not stated.

** Time of heating was not stated.

TABLE XVII

Thermal Decomposition of Ethylene

Products obtained at Different Temperatures in Platinum Tubes*

(Lewes)

Temp., °C.	Products	Yields	
900	"Satd. H.C." **	59.7%	of gaseous product
	Acetylene	0.8%	
	"Other unsatd. H.C."	34.0%	
	"Oil"	0.0024 g./ 100 cc. of C_2H_4	
1000	"Satd. H.C."	76.5%	of gaseous product
	Acetylene	0.6%	
	"Other unsatd. H.C."	17.4%	
	"Oil"	0.0048 g./ 100 cc. of C_2H_4	
1200	"Satd. H.C."	55.3%	of gaseous product
	Hydrogen	25.1%	
	Acetylene	3.6%	
	"Other unsatd. "H.C."	7.0%	
	"Oil"	0.0038 g./ 100 cc. of C_2H_4	
1500	"Satd. H.C."	27.8%	of gaseous product
	Hydrogen	62.7%	
	"Unsatd. H.C."	0.4%	

* The ethylene was passed "rapidly" through platinum tubes 2 mm. in diameter.

** The abbreviation H.C. is here used for the term "Hydrocarbons".

TABLE XVIII

Products obtained by the Decomposition of Ethylene in Heated Tubes

	Reference numbers for tubes of			
Products	Quartz	Glass	Porcelain	Platinum
Carbon	140, 152, 155	25, 27, 120	14, 105	—
Hydrogen	53, 152, 155, 157	125	14, 105	—
Methane	53, 152, 155, 157	24, 120, 125	14, 105	—
Ethane	155, 157	5, 25, 120, 125	5, 105	—
"Satd. H.C."	—	—	—	95
Propylene	155	120	—	—
Butylene	53, 155	120, 125	—	—
Butadiene	53, 155	120	—	—
"Higher olefins"	53, 157	—	—	—
"Olefins"	—	25	—	—
"Unsatd. H.C."	—	—	—	95
Acetylene	53	5	5, 14, 105	95
Cyclohexene	155	—	—	—
Benzene	53, 152, 155	5, 120	5	—
Toluene	155	—	—	—
Styrene	—	5	5	—
Naphthalene	53	5, 120	5	—
Anthracene	—	120 (?)	—	—
"Aromatic H.C."	—	—	14	—
"Liquids"	53, 155	125	14	—
"Oil"	152	27	—	95
"Tar"	152	—	105	—

ii. *With Catalysts*

1. Metals

Most substances having catalytic effect during the heating of ethylene stimulate its breakdown. Only a few aid polymerization. Thus all metals which have been studied, except iron and sodium, encourage the formation of saturated hydrocarbons (chiefly methane), carbon, and hydrogen. In the presence of cobalt or nickel decomposition begins even at 300°, while without these catalysts breakdown is very slow below 500°. Aluminum and magnesium are reported to also aid scission, but are less active. Copper, palladium, and platinum appear inactive at 400°, but when glowing are said to catalyze decomposition to carbon and hydrogen.

Sodium and iron aid the polymerization of ethylene to oily products. Sodium is active from 150° upward, but it is reported to have no lasting action because it is readily converted into sodium ethylene carbide. Iron is active at 350° and above, and at the temperature mentioned causes both breakdown to carbon and hydrogen and polymerization. Deposition of carbon upon it early stops its condensing activity, but it is said to continue to exert an influence favoring the dissociation. However, this dissociation may really be the result of catalysis due to carbon.

The metals are discussed in alphabetical order.

Aluminum—Kusnetsov[86] found that ethylene was converted quantitatively into carbon and hydrogen when it was passed over this metal at its melting point (659°). Some of the carbon produced formed an aluminum carbide.

Cobalt—At temperatures up to 200° cobalt was found by Sabatier and Senderens[135, 136] to have no action on ethylene, but at 300° and upward there was slow decomposition. A gas sample collected at 360° contained 67.4 per cent ethylene, 13.4 per cent ethane, 4.4 per cent methane, and 14.8 per cent hydrogen. Acetylene was not produced. Much carbon deposited on the catalyst.

Walker[151] found that ethylene decomposed rapidly when passed over cobalt at 400°, giving mainly carbon and hydrogen, with some ethane and "traces" of methane. Neither acetylene nor liquid products were formed. The results were similar at 500° to 545°, the gaseous product at the higher of these temperatures consisting of 82.7 per cent hydrogen, 13.0 per cent methane and 1.9 per cent ethane. The addition of 10 per cent of potassium hydroxide to the cobalt increased the speed of decomposition.

Copper—Marchand[107] found that ethylene on passage through a red-hot porcelain tube filled with copper wire was converted almost completely into methane, while at white heat the exit gas was largely hydrogen.

Sabatier and Senderens[135] reported that copper did not effect the decomposition of ethylene below 400°.

The I. G. Farbenindustrie A.-G.[70] claimed that liquid hydrocarbons of low boiling point could be obtained when gases containing ethylene, propylene, butylene, and methane were conducted through a copper tube, which might contain copper gauze, heated to 850°.

This work gives no conclusive proof of the activity of copper, as similar results were obtained by heating in the absence of this so-called catalyst.

Iron—That reduced iron had a catalytic action upon ethylene resembling that of cobalt, but less intense, was observed by Sabatier and Senderens.[136] In their work, in the presence of iron, ethylene decomposition was first noticeable at about 350°, whereas with cobalt it began at about 300°. Walker[151] reported that ethylene polymerized to a colorless oil in the presence of iron at 360°. However, only a small yield of oil was obtained before the catalyst lost its condensing action. The metal appeared, however, to retain an ability to assist the breakdown of ethylene into carbon, hydrogen, and methane.

Treatment of the iron with one per cent of potassium hydroxide did not strengthen its catalytic action. A mixture of iron with from 10 to 100 per cent of its weight of chromium oxide was less active than iron alone.

In the presence of iron at 700°, Smolenski[141] obtained carbon and a gaseous product containing 80 to 85 per cent hydrogen.

Bradley and Parr,[16] who used ethylene as an "atmosphere" in which to pyrolyze xylenes, found that in contact with iron surfaces at temperatures above 725°, the olefin was completely decomposed. They did not report the products into which it was converted.

Magnesium.—On passing ethylene over magnesium powder heated to redness, Lidov and Kusnetsov[97] found that practically the entire carbon content of the hydrocarbon combined with the metal, forming a carbide. Hydrogen was liberated, although its evolution was not quantitative. These workers studied the decomposition of a number of the hydrocarbons, and suggested comparison of the per cent of hydrogen produced by their breakdown over magnesium as a means of distinguishing methane, ethane, ethylene, and acetylene.

Nickel.—Sabatier and Senderens[135] reported that while nickel had no action on ethylene at ordinary temperature, at 300° and above it caused breakdown almost exclusively to carbon, hydrogen, and methane. The carbon and methane were thought to be primary products, and the hydrogen to result from secondary changes. This accords with the known fact that methane is decomposed to its elements at low temperature by nickel. Higher olefins and acetylene were found, but because of the presence of an odor like that of petroleum report was made of traces of higher paraffin hydrocarbons. As the temperature was increased the proportion of hydrogen to methane increased. At 400° hydrogen made up but one-tenth of the gaseous product; at "dull red heat" it was one-half.

The reaction was most rapid if the nickel had been prepared for use by reduction at a temperature near 300°, but nickel obtained by reduction at red heat was also very active. During the decomposition the nickel swelled to a voluminous black material. Nickel fillings had some catalytic activity, but were active only at a temperature higher than that necessary with nickel obtained by reduction.

In further experiments carried out at 320° ethane as well as hydrogen and methane were identified. Here also higher paraffin hydrocarbons were believed present in the products because of a kerosene-like odor. During slow passage of the olefin, decomposition was almost exclusively to methane and hydrogen.

Cantelo[23] attempted a study of the methane-carbon-hydrogen equilibrium by decomposing ethylene (96-98% C_2H_4) at 150° to 350° over a nickel catalyst. The analyses of his products from 300° to 350° are shown in Table XIX.

As shown in this table, methane and a large proportion of ethane, reaching forty per cent of the final gas, formed above 300°. Differences between the results obtained at 325° and those at other temperatures are probably due to

TABLE XIX

Decomposition of Ethylene over Nickel reduced from the Oxide (Cantelo)

Temp., °C.	Percentage composition of the products						
	CO_2	C_2H_4	O_2	CO	CH_4	C_2H_6	H_2
300	0.6	1.6	0.0	1.3	32.9	47.0	16.6
325	0.8	18.4	0.0	0.8	33.1	29.9	17.0
325	0.4	5.9	0.4	0.8	30.5	40.4	21.6
325	0.4	6.0	0.4	0.9	30.5	40.4	21.4
350	0.0	0.9	0.0	1.3	42.3	34.1	21.4
350	0.9	0.0	1.7	0.0	40.2	36.7	20.5

different time factors. Cantelo's efforts to measure the methane equilibrium were frustrated by the stability of ethane. After 8.5 hours at 360° in the presence of nickel the gaseous product still contained a large amount of ethane, as is shown by its analysis below:

Gas	CO_2	C_2H_4	O_2	CO	CH_4	C_2H_6	H_2
Per cent	0.0	0.0	0.0	0.7	68.2	25.2	5.6

At higher temperatures, however, ethane is less stable, and at 500° to 670° equilibrium measurements were successfully carried out, and gave results in conformity with those of Mayer and Altmayer[111], who started with methane.

Walker[151] decomposed ethylene over nickel-coated pumice at 400°, obtaining carbon, hydrogen, methane, ethane, and acetylene. He believed that hydrogen atoms were split off "to yield acetylene from which in turn more hydrogen was liberated to produce the carbon. At the same time molecules of ethylene or acetylene separated between the carbon atoms to give $:CH_2$ or $\vdots CH$ groups which became hydrogenated to methane."

In the presence of nickel at 700° Smolenski[141] found ethylene decomposed to carbon and hydrogen, the latter at the end of a run being of 80 to 85 per cent purity.

Palladium—Wöhler[156] found that ethylene was decomposed into its elements in the presence of palladium sponge at a temperature at which glass glowed. But according to Sabatier and Senderens[135] this metal had no action below 400°.

Platinum—Platinum also has little, if any, catalytic action on ethylene. When the hydrocarbon is passed over a heated platinum wire decomposition results, but is not notably different in character or amount from that produced by heating alone, a fact giving rise to some doubt as to whether any real influence is exerted by the metal. Grove[49] noted that on exposure to an electrically heated platinum wire ethylene contracted slightly, deposited carbon, and gave a residual gas containing hydrogen. A glowing platinum wire in ethylene was found by Buff and Hofmann[18] to cause a considerable separation of carbon, but caused practically no change in gas volume. The chief result was the formation of methane.

Sabatier and Senderens[135, 136] found that finely divided platinum black or spongy platinum did not affect ethylene below 400°. Mylius and Hüttner[116] observed that no carbonization took place when an illuminating gas, a mixture of ethylene, methane, carbon monoxide, and hydrogen, was exposed to platinum or platinum-iridium at 600°.

2. Compounds of Metals

Engelder[32] reported that passage of ethylene over titania at 490° caused its decomposition to carbon, hydrogen, and methane, although the olefin was stable to above 500° in the absence of this catalyst. It should be pointed out, however, that other workers have reported decomposition of ethylene in the absence of catalysts at temperature below 490°.

Taylor and Jones[146] observed the formation of liquid products when ethylene was bubbled through mercury dimethyl or lead tetraethyl and then passed through a tube heated at 325°. Passage of the olefin alone through the tubes yielded no condensable products. They thought the polymerization was induced by the decomposing metallic alkyl. The degree of polymerization was roughly proportional to the pressure, and the amount of liquid polymer formed increased with the volume of the ethylene in the original mixture. The reaction was considered to occur in the gas phase and not merely at the walls of the reaction vessel, since results obtained using the reaction tube filled with glass wool were in close agreement with those obtained in an empty tube.

The I. G. Farbenindustrie A.-G.[70] claimed that liquid hydrocarbons of low boiling point could be obtained by passing gases containing ethylene and propylene over granulated dipotassium phosphate at 700° under ordinary pressure.

3. Summary

Products obtained by the decomposition of ethylene by heat in the presence of catalysts are summarized by Tables XX and XXI.

TABLE XX

Catalytic Thermal Decomposition of Ethylene
Products obtained with varying Temperatures and Catalysts

Temp., °C.	Catalysts	Products	Yields, per cent of gaseous products	References (by number)
300	Nickel	Carbon	*	135
		Hydrogen	*	
		Methane	*	
		"Higher Paraffins"	"Traces"	
300–350	Nickel	Hydrogen	16–20	22
		Methane	30–43	
		Ethane	35–47	

TABLE XX (Continued)

Temp., °C.	Catalysts	Products	Yields, per cent of gaseous product	References (by number)
320	Nickel	Hydrogen	*	135
		Methane	*	
		Ethane	*	
325	Mercury dimethyl or lead tetraethyl	Liquids	*	146
350	Iron	Carbon	*	151
		Hydrogen	*	
		Methane	*	
		Oil	"Very small"	
360	Cobalt	Carbon	*	135, 136
		Hydrogen	14.8	
		Methane	4.4	
		Ethane	13.4	
400	Nickel	Hydrogen	10	135
400	Cobalt	Carbon	*	151
		Hydrogen	*	
400	Nickel-coated pumice	Carbon	*	151
		Hydrogen	*	
		Methane	*	
		Ethane	*	
		Acetylene	*	
490	Titania	Carbon	*	32
		Hydrogen	*	
		Methane	*	
545	Cobalt	Carbon	*	151
		Hydrogen	82.7	
		Methane	13.0	
		Ethane	1.9	
659	Aluminum	Carbon	*	86
		Hydrogen	*	
700	Iron or nickel	Carbon	*	141
		Hydrogen	80–85	
725	Iron	Carbon	Decompn. complete	16
		Hydrogen		

* The yield was not stated.

TABLE XX (Continued)

Temp., °C.	Catalysts	Products	Yields, per cent of gaseus product	References (by number)
"Dull red heat"	Nickel	Hydrogen	50	135
"Red heat"	Magnesium	Magnesium carbide Hydrogen	* *	97
"Red-hot"	Copper wire	Methane	Main product	107
"White-hot"	Copper wire	Hydrogen	Main product	107
"Glowing temp." of glass	Palladium sponge	Carbon Hydrogen	* *	156
?	Platinum wire electrically heated	Carbon Hydrogen	* *	49
"Glowing temp" of platinum	Platinum wire electrically heated	Carbon Methane	"Considerable" *	18

*The yield was not stated.

TABLE XXI

Catalytic Thermal Decomposition of Ethylene
Products obtained in the Presence of Metal Catalysts

Products	References for metals used							
	Al	Co	Cu	Fe	Mg	Ni	Pd	Pt
Carbon	86	135, 151	—	151	97*	135, 151	156	18, 49
Hydrogen	86	135, 151	107	151	97	22, 135, 151	156	18, 49
Methane	—	135, 151	107	151	—	22, 135, 151	—	—
Ethane	—	135, 151	—	—	—	22, 151	—	—
"Higher paraffins"	—	—	—	—	—	135	—	—
Acetylene	—	—	—	—	—	151	—	—
"Oil"	—	—	—	151	—	—	—	—

* The carbon reacted with the magnesium and formed magnesium carbide.

b. *Under Superatmospheric Pressure*

With or without catalysts, the condensation of ethylene to products of higher boiling point is aided by pressure. Ipatiev[78,79] found that under pressure of 70 atmospheres polymerization readily took place at temperatures at which under atmospheric pressure, change was very slight. Reaction began at about 325° and proceeded with considerable speed at 380° to 400°. The product consisted of a small amount of solid and grayish green liquid made up of paraffin, olefin, and polymethylene hydrocarbons. The fractions of this liquid boiling below 100° were chiefly paraffin and olefin hydrocarbons, while polymethylene hydrocarbons were thought to be the main constituents of the portions boiling from this temperature to about 280°.

From the boiling ranges of the fractions (each of which as a rule covered 2° to 10°), densities, and carbon and hydrogen analyses, he reported pentane, hexane, heptane, octane, nonane, amylene, hexylene, nonanaphthene, alpha- and beta-decanaphthene, hendeca-, dodeca-, tetradeca-, and pentadecanaphthenes. It seems possible, however, that the fractions he studied were not individual hydrocarbons, but mixtures, since wide ranges of boiling points, coupled with the small differences in carbon and hydrogen content of successive numbers of a homologous series, his criteria, are insufficient for the identification of pure hydrocarbon fractions. Between octane to nonane, for example, the carbon analysis changes only 0.16 per cent, and the difference becomes still less between two consecutive members of a homologous series as they increase in molecular weight. Ipatiev also obtained a mixture of hydrocarbons containing less hydrogen than polymethylenes, and another unidentified hydrocarbon fraction boiling above 280°. Benzene derivatives were not found.

In the presence of alumina, in further work[79] under 70 atmospheres pressure at 375°, there was increased formation of high boiling products. Almost twice as much of the fraction boiling above 280° was obtained when using this catalyst as was formed without it, even at a slightly higher temperature. The corresponding fractions of the product in the two cases were reported to contain, in general, the same hydrocarbons, largely polymethylenes.

Walker[151] observed that ethylene underwent slight decomposition to carbon and hydrogen when heated in the presence of reduced iron at 340° to 430° and under a final pressure of 10 to 30 atmospheres. The fact that there was no formation of liquid polymers was attributed to poisoning of the catalyst by carbon.

Stanley[142] recently found that in the absence of catalysts in a steel autoclave under pressures up to 60 atmospheres, ethylene did not polymerize until the temperature reached 325°. "The condensation to liquid hydrocarbons was fairly rapid at 350°."

Ipatiev's[78] mechanism of reaction includes the formation of polymethylenes through conversion of ethylene to hexamethylene. Higher open chain olefins were thought to arise either by direct polymerization or by ring opening from the polymethylenes. Production of saturated hydrocarbons was considered due either to hydrogenation of the cyclanes, causing ring opening, or to splitting of side chains attached to a polymethylene nucleus.

The I. G. Farbenindustrie A.-G.[74] claimed the production of carbon black by dehydrogenating ethylene or its homologs by treatment at 100° to 600° (usually 300° to 450°) under pressures of 30 to 100 atmospheres or more with such catalysts as iron, nickel, or cobalt, alone or with additions of metal oxides, hydroxides, or carbonates, such as the oxides of cadmium, copper, aluminum, vanadium, uranium, thorium and zinc, manganous oxide, caustic alkalies, alkaline earth oxides, or salts such as silicates, chromates, molybdates, or tungstates. This organization[71] also reported that products consisting largely of aromatic hydrocarbons can be obtained by passing ethylene or gases containing it under pressure through tubes of tinned copper and aluminum-coated iron at 750° and 800°, respectively. It was stated that no deposition of carbon occurred.

The I. G. Farbenindustrie A.-G.[69] patented a two-stage process for converting olefins such as ethylene, propylene, and butylene into aromatic hydrocarbons. In the first step the olefin was polymerized, for example, by passage under 40 atmospheres pressure over active charcoal kept at 400°. In the other stage, the bulk of the liquid polymerization product was converted into benzene and its homologs by passing under five atmospheres pressure over a dehydrogenating catalyst as ammonium molybdate maintained at 600°.

Ramage[131] claimed to produce butylene from gases containing ethylene by compressing the gases into kerosene or other heavy hydrocarbon solvent under a pressure of 80 to 200 pounds per square inch and at about 0°, and recovering the polymerization product from the charged solvent by distillation. Besides butylene, the distillate was reported to contain small amounts of amylene, octylene, and decylene.

2. Propylene

Under the influence of heat in quartz tubes, propylene undergoes decomposition very similar to that of ethylene. From the work which has been done to date on this hydrocarbon the major products appear to be methane, propane, ethylene, butylene, and liquids containing benzene and toluene. In lower amounts, carbon, hydrogen, ethane, and acetylene have been reported. In one study butadiene formed in considerable quantity, and in another investigation during the heating of propylene under pressure a large conversion into cyclopropane was reported. Not enough work has been reported to show fully the variation of the products formed with changing time of exposure and temperature.

The predominant reaction appears to be loss of the terminal carbon atom, with the formation of methane and ethylene (this involves, of course, the addition of hydrogen coming from other reactions). Carbon and hydrogen are often abundantly formed, either from breakdown of propylene, itself, or of radicals formed from it. Butylene perhaps arises through the combination of a free ⋮CH group with a propylene molecule. Butadiene is most likely a product of butylene dehydrogenation, though it may form by combination of two radicals remaining after propylene has split off methane. Propane is no doubt a hydrogenation product of propylene, and ethane similarly forms from ethylene. The unidentified liquid products are formal by polymerization reactions.

Wheeler and Wood[155] observed that in a quartz bulb 350° to 375° was the lowest temperature at which propylene decomposed. Dissociation has also been reported by others[56] to be "almost negligible" in pyrex below 525°. In the presence of metals it begins much lower, becoming appreciable over nickel at 210°.

a. *Without Catalysts*

Berthelot[12] reported that although propylene was stable when exposed for 20 minutes at 550°, it was decomposed at a bright red heat.

Frey and Smith[41] partially decomposed propylene by heating for four minutes in a silica flask at 575°, with the formation mainly of methane and ethylene, together with some hydrogen, ethane, propane, and butylene. The analysis of their products was as follows (in per cent):

N_2	H_2	CH_4	C_2H_6	C_3H_8	C_2H_4	C_4H_6	C_3H_8	C_5H_{10} to C_8H_x
0.4	1.7	10.7	1.9	3.0	8.0	68.9	2.8	2.6

Liquid products, apparently polymeric hydrocarbons, were also obtained. The yellow color of the liquid was considered to indicate the presence of highly unsaturated substances. When propylene was heated in the presence of hydrogen the products were colorless.

Engler and Rogowski[34] stated that when propylene was heated in a sealed tube at 400° to 405° more than 50 per cent of the olefin was converted into cyclopropane. Between 450° and 505° there was separation of carbon and formation of a dark yellow liquid.

Trautz and Winkler[148] reported that polymers formed from propylene at about 650°. Higher temperatures caused deposition of carbon and formation of polymers of higher boiling point.

By passing a mixture of 13.2 per cent propylene and 86.8 per cent nitrogen through a quartz tube at 728°, Frolich, Simard, and White[42] obtained a yield of 3.3 per cent butadiene based on the olefin treated.

Wheeler and Wood[155] showed that large amounts of liquid products could be obtained by the action of heat on propylene. When passing the gas through a vertical quartz tube heated electrically at 650° to 900°, oil yields were as high as 40 per cent. Table XXII summarizes the results of these tests.

The liquids of lower boiling point obtained from the decomposition at 650° were reported to be mainly monocyclic hydroaromatic hydrocarbons with one double bond in the ring, while those produced at 700° were chiefly benzene and toluene. "At the higher temperature of formation, the proportion of liquids of high boiling point had increased, showing that the more complex hydrocarbons had been formed at the expense of the simpler. The

TABLE XXII

The Decomposition of Propylene (Wheeler and Wood)

Temp., °C.	Calcd. contact time secs.	Yields, in per cent by weight of propylene treated			Per cent increase in volume
		Total liquids	Distillate up to 170°	Carbon	
650	58.2	5.2	3.2	Nil	4.0
700	55	20.3	12.9	Trace	10.0
750	52.5	35.6	20.4	Trace	20.1
800	50	40.6	19.0	1.7	30.1
850	47.7	33.8	14.6	9.5	46.2
900	45.7	11.9	6.8	Not detd.	64.2

	Gas analyses, in per cent by volume of the propylene treated						
	H_2	CH_4	C_2H_6	C_2H_4	C_3H_6	C_4H_8	C_4H_6
650	0.5	2.1	2.5	7.7	86.9	4.1	0.2
700	7.0	18.9	7.9	23.5	45.6	6.5	0.6
750	14.4	49.1	6.8	37.0	10.4	2.0	0.4
800	23.6	70.7	5.4	28.1	1.5	0.5	0.3
850	36.7	85.9	4.5	18.6		0.5	
900	66.5	86.1	3.1	8.0		0.5	

proportion of toluene to benzene formed from propylene at 700° was greater than from ethylene at the same temperature. Naphthenes and paraffins were absent from the liquids boiling below 110°, and were presumably absent also from the liquids of higher boiling point."

Studies of Hurd and Meinert[64a] show propylene to be decomposed rapidly at temperatures above 600° in pyrex or quartz tubes. The larger part of the propylene which disappeared in the reaction was broken down into carbon, hydrogen, methane, paraffins higher than methane (principally ethane), and ethylene. In pyrex or in quartz 20 to 25 per cent of the propylene used was converted into aromatic liquids. "Benzene and toluene were identified and more complex substances, such as naphthalene and phenanthrene, were indicated. The last two are not considered to be primary products of the pyrolysis, since they could arise by interaction of the simpler aromatic hydrocarbons with olefins at the high temperatures in question."

Propylene[64a] and iso butylene[65] were found to undergo about the same amount of pyrolysis when subjected to the same temperature and contact time.

Some of the data obtained in pyrex tubes at 600° to 700° and in quartz at 950° and 955° are given in Table XXIIA.

TABLE XIIA

Thermal Decomposition of Propylene
(Hurd and Meinert)

Experiment	11	3	7	4	8	28	29
Temp., °C.	600	650	650	700	700	950	955
Contact time, secs.	125	30	120	25	53	0.513	0.471
Decomposition, per cent of entering propylene	26.7	16	59.3	50.8	72.5	90.3	95.2
Liquids formed							
Wt. in grams	2.37	Trace	1.7	6.9	3.8	—	6.7
Per cent by wt. of propylene decomposed	21	—	15.4	27.6	24	—	20.8

Gaseous products, in cc. per liter of propylene entering

Acetylenes	13	5	4	6	—	31.8	34.8
Ethylene	91	50	192	202	318	343.0	354.5
Hydrogen	32	13	76	76	111	318.0	359.0
Paraffins	104	67	378	283	420	593	628

Gaseous products, in cc. per liter of propylene decomposed

Acetylenes	49	32	6	11	—	35.2	36.6
Ethylene	340	314	323	396	438	379.6	372.7
Hydrogen	119	83	127	149	152	352.3	377.3
Paraffins	388	415	637	558	580	356.5	659.9

Comparison of experiments 28 and 29 "with the others shows that pyrolysis at 950° in quartz with a hot contact time of 0.5 second gives about the same results as pyrolysis at 700° in pyrex with a contact time of 53 seconds. The percentage of propylene pyrolyzed is about 90 instead of 73, but the products formed are very much the same. There is about the same percentage of unrecovered propylene which is converted into liquids in each case; viz., 20-25%. In both cases liquids are aromatic hydrocarbons and in both the gaseous products are the same. More hydrogen and methane are formed at the higher temperatures, but this would be expected, since the secondary reactions would also be more rapid at higher temperatures.

"The liquids obtained from the 950° experiments were fractionally distilled as carefully as the small volume would permit with these results.

Fraction	Volume, cc.	B.P. °C.	n_D^{20}
A	2.0	78–97	1.5025
B	0.8	97–130	1.5140
C	1.0	130–180	1.5465

"Fraction A had an odor very much like that of benzene, fraction B an odor somewhat resembling that of toluene and fraction C smelled like tar. The properties of these liquids are almost identical with those of the liquids obtained from propylene in pyrex at 700°. Nitration of fraction A yielded *m*-dinitrobenzene."

b. *With Catalysts*

Sabatier and Senderens[137, 138] found that with propylene, as with ethylene, reduced nickel notably lowered the temperature at which decomposition occurred. Breakdown was appreciable at 210°, and rapid at 350°. At the higher temperature large quantities of carbon deposited on the catalyst and the gaseous products were largely methane, ethane, and propane, as is shown by the following analysis (in per cent by volume):

Gas	H_2	CH_4	C_2H_6	C_3H_8	C_2H_4	C_3H_6
Per cent	2.1	13.4	38.1	39.7	4.6	2.1

Platinum black, platinum sponge, and reduced copper did not cause ethylene decomposition below 400°.

The pyrolytic behavior of propylene in tubes of monel metal was also investigated by Hurd and Meinert.[64a] "The almost exclusive change was a decomposition into hydrogen and a sooty form of carbon. Moreover, the rate of decomposition was much greater than when pyrex or quartz tubes were employed. Thus, with the same hot contact periods, much more propylene decomposed in monel at 350° than in pyrex at 650°.

"A peculiarity about the reaction in monel metal was that it was autocatalytic. The carbon formed and deposited on the walls of the tube near the beginning of the experiment catalyzed the reaction so that it proceeded much more rapidly after about twenty minutes. A number of experiments at different temperatures showed conclusively that this was the case.

"The pyrolysis in monel metal tubes started at a temperature of 350°. At 375°, with a contact time of about half a minute, it was practically complete. No liquids or tarry products were formed in the reaction at any temperature from 300° to 650°. About one liter of hydrogen and one-half liter of a mixture of paraffin hydrocarbons resulted from each liter of propylene consumed at 375°. With increasing temperature, the amount of hydrogen formed per liter of propylene increased to 1.7 liters at 650°, while the amount of paraffins (chiefly methane) formed decreased to 0.2 liters.

"The fact that the production of hydrogen increased with increasing temperature while the production of paraffins decreased indicates that the first step in the reaction is probably a splitting into compounds that are simpler than propylene, but which are themselves unstable at higher temperatures and also break down into their elements."

3. Butylenes

Of the butylenes, iso butylene is the only one whose behavior has been at all thoroughly investigated. 1-Butene and 2-butene have each been the subject of but one investigation.

a. *1-Butene*

A conversion of as much as 40 per cent to liquid products was effected by Wheeler and Wood[155] by passing 1-butene through a vertical quartz tube heated electrically to temperatures from 600° to 900°. As in the decomposition of the lower olefins, there was high methane and hydrogen production at the higher temperatures. Table XXIII summarizes their results, which will be discussed following review of their work on 2-butene.

TABLE XXIII
The Decomposition of 1-Butene
(Wheeler and Wood)

Temp., °C.	Calcd. contact time secs.	Yields in per cent by weight of 1-butene treated: Total liquids	Distillate up to 170°	Carbon	Per cent change in volume
600	61.5	12.9	6.5	Nil	− 23.4
650	58.2	29.8	20.3	Nil	− 10.7
700	55	35.8	23.6	Trace	+ 30.0
750	52.5	39.6	22.4	Trace	+ 43.9
800	50	39.4	19.9	1.0	+ 57.0
850	47.7	35.0	16.2	4.7	+ 73.9
900	45.7	13.9	7.8	7.1	+104.0

Gas analyses, in per cent by volume of the butene treated

Temp., °C.	H_2	CH_4	C_2H_6	C_2H_4	C_3H_6	C_4H_8	C_4H_6
600	0.8	8.1	1.9	3.2	7.6	54.1	0.9
650	6.2	37.2	7.1	14.2	24.5	19.8	1.7
700	11.9	62.1	10.6	22.3	19.6	2.1	1.4
750	17.3	78.5	9.7	31.4	5.6	1.3	0.2
800	27.2	89.0	7.6	30.2	2.0	1.0	
850	50.5	95.7	6.1	20.6	1.0		
900	85.2	103.3	5.0	9.6	0.9		

Calingaert[20, 21] found that pure 1-butene on pyrolysis at 600° yielded hydrogen, methane, propylene, and butadiene. Acetylene was not observed. Butadiene can be considered a product of the dehydrogenation of butylene. Methane and propylene formation indicates loss of a terminal carbon atom, perhaps to giving two free radicals which add hydrogen to form these products.

According to a patent of Perkin, Weizmann, Matthews, and Strange[127] butadiene may be obtained by passing 1-butene through a tube containing metallic copper heated to redness.

b. *2-Butene*

By passing 2-butene through a vertical quartz tube heated electrically at 600° to 900° Wheeler and Wood[155] were also able to obtain high yields of liquid products, running to as much as 40 per cent, from this hydrocarbon. Their results reported are summarized in Table XXIV.

Table XXIV
The Decomposition of 2-Butene
(Wheeler and Wood)

Temp., °C.	Calcd. contact time, secs.	Yields, in per cent by weight of 2-butene treated			Per cent change in volume
		Total liquids	Distillate up to 170°	Carbon	
600	61.5	5.2	1.4	Nil	− 25.4
650	58.2	27.0	17.2	Nil	− 7.5
700	55	37.0	25.8	Trace	+ 27.4
750	52.5	39.6	23.2	Trace	+ 38.9
800	50	37.9	18.6	1.4	+ 52.8
850	47.7	31.6	14.2	4.7	+ 68.3
900	45.7	12.4	6.1	5.4	+100.0

<table>
<tr><th></th><th colspan="7">Gas analyses in per cent by volume of the butene treated</th></tr>
<tr><th></th><th>H_2</th><th>CH_4</th><th>C_2H_6</th><th>C_2H_4</th><th>C_3H_6</th><th>C_4H_8</th><th>C_4H_6</th></tr>
<tr><td>600</td><td>0.9</td><td>2.8</td><td>1.2</td><td>1.3</td><td>2.6</td><td>65.0</td><td>0.8</td></tr>
<tr><td>650</td><td>4.9</td><td>31.4</td><td>7.8</td><td>8.9</td><td>17.8</td><td>20.0</td><td>1.7</td></tr>
<tr><td>700</td><td>11.1</td><td>62.0</td><td>11.8</td><td>19.8</td><td>19.2</td><td>2.6</td><td>0.9</td></tr>
<tr><td>750</td><td>17.6</td><td>76.5</td><td>9.1</td><td>27.9</td><td>5.3</td><td>2.1</td><td>0.4</td></tr>
<tr><td>800</td><td>28.4</td><td>90.0</td><td>7.9</td><td>24.4</td><td>1.6</td><td colspan="2">0.5</td></tr>
<tr><td>850</td><td>48.4</td><td>96.1</td><td>5.7</td><td>16.9</td><td colspan="3">1.2</td></tr>
<tr><td>900</td><td>83.3</td><td>103.1</td><td>3.7</td><td>8.3</td><td colspan="3">1.6</td></tr>
</table>

Although 2-butene was somewhat more stable than 1-butene, the decomposition products from the two isomers at 600° were similar. Approximately equal volumes of methane and propylene were produced, which was interpreted to indicate rupture of the terminal carbon-carbon bonds, followed by hydrogenation of the radicals so formed. The hydrogen needed for this change was considered to arise by simultaneous decomposition of part of the butene to form butadiene.

In the liquids formed at 600° (the product from decomposition of a mixture of the two butenes was studied) cyclohexane and methylcyclohexene predominated. From results of stream experiments with mixtures of ethylene and butadiene it was concluded that these cyclohexenes were produced by the combination of butadiene with an olefin. Benzene and toluene were present "in comparatively small proportion. Cyclohexadiene and methylcyclohexadiene were also present. Only 18.5 per cent of the liquids produced at this temperature boiled above 117°. Of the liquids formed (from 2-butene) at 650°, however, 29.6 per cent boiled above 110° and 16.6 per cent above 150°, and aromatic hydrocarbons now predominated. As with propylene, therefore, an increase in the temperature of formation of the liquids resulted in a greater proportion of higher-boiling hydrocarbons and caused the conversion of hydroaromatic into the more stable aromatic hydrocarbons. Naphthenes and paraffins were absent from the liquids boiling below 110°."

c. *Iso butylene*

As with lower olefins, the heating of iso butylene causes competing reactions of two types—decomposition and polymerization. Prolonged exposure at 200° causes polymerization alone, with reported formation of triisobutylene. At 600° to 700° both types of change occur simultaneously. At this temperature the decomposition gives rise to carbon, hydrogen, methane, iso butane, ethylene, butadiene, and a very small amount of acetylene. Some investigators have reported butadiene, while others have challenged its occurrence. Polymerization produces benzene, toluene, xylene, naphthalene, methylnaphthalene, diphenyl, anthracene, and phenanthrene. The formation of styrene and ditolyl has been reported but not proved. Under pressure, higher paraffins and olefins are reported to form.

A possible series of steps by which these products may be produced is as follows: Loss of a terminal carbon atom forms radicals, which by addition of hydrogen become methane and propylene, or by loss of hydrogen, go to carbon and hydrogen. There is no way apparent for ethylene to form by a simple reaction. Perhaps it forms by further loss of a carbon atom from the radical formed by the break of iso butylene at a terminal carbon. Butadiene has been considered by some workers to be produced from ethylene. It may also form by rearrangement and dehydrogenation of iso butylene. The formation of aromatic hydrocarbons, following the mechanism outlined in discussing ethylene, takes place by polymerization reactions commencing with ethylene, or butadience, which forms cyclohexane, loses hydrogen to give benzene, and undergoes further polymerization to more complex aromatics.

Iso butylene is one of the few olefins whose resistance to breakdown by heat has been accurately compared with that of the corresponding paraffin. Hurd and Spence[65] found that at 600° iso butylene decomposed but slowly, so that but 1.2 per cent breakdown took place during 18 seconds contact time, and 20 per cent changed in an exposure of 3.3 minutes. In comparison iso butane underwent from 20 to 25 per cent decomposition at 600° during a contact time of 24 to 26 seconds. Iso butylene, it will be noted, belongs to the more stable R-vinyl type of olefin. Its stability does not indicate greater stability for olefins in general than for paraffins.

These workers made a series of decomposition runs with iso butylene at temperatures of 600°, 650°, and 700°. The main products were propylene, methane, iso butane, and hydrogen, with smaller amounts of acetylene and ethylene, and a considerable proportion of liquid. A portion of their data is given in Table XXV.

The table shows the rate of change to be quite slow at 600°, and to increase rapidly with increasing temperature. Methane was the most abundant substance formed, and its amount grew larger with time and with increase in temperature. At 700° it made up 46 to 55 per cent of the gaseous products. Propylene and iso butane appeared in greatest amounts when low temperature and long heating time were used, while the concentration of acetylene was

TABLE XXV

Thermal Decomposition of Iso butylene
(Hurd and Spence)

Experiment	1	2	10	11	7	4
Temperature, °C.	599	599	652	652	700	700
Contact time, secs.	200	18	27	13	12	18
Decomposition, per cent of entering iso butylene	20	1.2	22.7	11.1	30.2	47.7
Oil formation						
Per cent by wt. of entering iso butylene	—	—	9	7	14.1	30
Per cent by wt. of iso butylene decomposed	—	—	39.6	63	46.6	63
Gaseous products, in cc. per liter of iso butylene entering						
Propylene	61	4	39	16	66	109
Methane	118	—	65	15	177	312
Iso butane	54	—	40	22	40	29
Hydrogen	35	—	34	6	73	124
Acetylene	3	3	8	12	13	28
Oxides of carbon	7	4	10	9	12	6
Ethylene and aromatics	18	2	7	11	20	32
Gaseous products, in cc. per liter of iso butylene decomposed						
Propylene	305	—	172	144	218	228
Methane	590	—	286	135	586	655
Iso butane	270	—	176	198	133	61
Hydrogen	175	—	150	54	242	260
Acetylene	15	—	35	108	43	59
Ethylene and aromatics	90	—	31	99	66	69

greatest at intermediate temperature and with short contact time. In molecular proportions, each 100 moles of iso butylene decomposed at 700° produced 59 to 83 moles of methane, 20 to 30 moles of hydrogen, 20 to 25 moles of propylene, smaller quantities of iso butane and ethylene, and nearly negligible quantities of acetylene. No butadiene was found, the work of Hurd and Spence differing in this respect from that of Noyes.[121]

The oil formed at 700° was higher in density the longer the time of heating. This was taken to indicate an increase in aromatic hydrocarbons. By fractional distillation benzene and toluene were shown to make up more than half of this oil; the remainder appeared to consist of xylene, naphthalene, methyl naphthalene, diphenyl, anthracene, phenanthrene, and possibly ditolyl.

When the iso butylene was diluted with nitrogen before passing into the hot tube, the yield of liquid products was decreased. Dilution with hydrogen had a similar effect, and in addition served to increase the yield of methane and of propylene and apparently the yield of gaseous saturated hydrocarbons above methane.

The rate of decomposition was unchanged by dilution of the olefin with nitrogen or with hydrogen. The rate was also unchanged when the hot surface to which the gas was exposed was increased to twice its original value by packing the tube with small pyrex tubing. The decomposition was therefore termed, homogeneous and "unimolecular."

In 1888 A. A. Noyes[121] studied the action of heat on iso butylene primarily to determine whether butadiene, which was known to be a product of the pyrolysis of ethylene, would be formed. In iso butylene pyrolysis ethylene is produced at a temperature sufficiently high to lead one to expect it to undergo this change. By decomposing iso butylene by slow passage through a hard glass tube heated to low redness, he obtained among the products, carbon, hydrogen, methane, ethylene, propylene, butadiene, benzene, toluene, and naphthalene. Styrene was thought also to be formed, but no acetylene was identified. Noyes regarded butadiene as an intermediate in the formation of benzene and naphthalene from ethylene, and its formation in this work appeared to him to support his ideas.

Nef[117] stated that over pumice iso butylene (prepared by heating tertiary butyl chloride) began to decompose at 570° into methane, hydrogen, propylene, and some carbon.

Lebedev and Kobliansky[91] reported the formation of polymerized products to the extent of 6 to 8 per cent of the decomposed iso butylene when the hydrocarbon was heated at 200° in tubes of hard glass for 14 days, and claimed the identification of triisobutylene. Higher polymers were thought to have formed, but were not isolated, possibly because of their easy decomposition.

Ipatiev[77, 81] also found that in the presence of alumina at 550° to 600° iso butylene was converted into hydrogen, propylene, and paraffins. At lower temperatures alumina and also zinc chloride had no effect.

Subjection of iso butylene to 70 atmospheres pressure and a temperature of 380° to 400° was reported by Ipatiev[79] to convert it into a mixture of higher paraffin, olefin, and naphthene hydrocarbons. These resembled the products he obtained by similar treatment of ethylene, except that the fraction boiling below 150° was richer in olefins in this case. The olefins present were thought to be a dimer and trimer of iso butylene.

d. *Unidentified Butylene*

Mailhe[106] observed that in contact with nickel butylene decomposed almost quantitatively at 350° into methane and hydrogen with slight formation of carbon, ethylene, and propylene, and from 350 liters of butylene, 5 cc. of liquid was obtained which consisted mainly of aromatic hydrocarbons.

4. Amylenes

The behavior on heating of three of the amylenes—2-pentene, iso propylethylene, and trimethylethylene has been studied. Iso propylethylene is converted into trimethylethylene. The other two hydrocarbons give large amounts of methane, a considerable proportion of lower olefins, and small amounts of liquid products. Free hydrogen appears only at high temperatures. Apparently the predominant reaction is loss of a terminal methyl group as methane, followed by secondary changes converting the remainder of the molecule by dehydrogenation into a diolefin, by hydrogenation into a lower olefin, or by the coupling of two radicals into a higher unsaturate.

a. *2-Pentene*

By the decomposition of 2-pentene in a silica tube at 600°, Norris and Reuter[119] obtained products which they separated into two fractions: one, making up 33 per cent, composed of hydrocarbons with molecular weight greater than the pentene; the other, 67 per cent, of hydrocarbons of lower molecular weight. The higher boiling fraction appeared to be unsaturated, but its full investigation has not been reported. Free hydrogen was not found. Carbon deposited in the heating tube.

In the mixture of low molecular hydrocarbons "the components were found to be present approximately in the molecular ratios: methane, 100; butadiene, 30; butene, 27; propylene, 21; and ethylene, 15. The number of moles of methane was approximately equal to the sum of the number of moles of other hydrocarbons present. This fact indicates that the decomposition consists in the removal of a methyl group from the end of the chain of pentene-2 and a similar removal in the case of the decomposition of the products formed as the cracking progressed."

The main decomposition of 2-pentene was formulated as consisting in an initial break to a methyl group and a radical derived from butylene, followed by hydrogenation, as shown in the equation:

$$CH_3CH_2CH:CHCH_3 \rightarrow CH_3- + -CH_2CH:CHCH_3 \xrightarrow{+2H} CH_4 + CH_3CH:CHCH_3.$$

The hydrogen required by this reaction was thought to come in part from conversion of the larger radical into butadiene, and in part from other dehydrogenations occurring simultaneously.

b. *Iso propylethylene*

According to Norris and Reuter,[119] iso propylethylene is less stable than 2-pentene or trimethylethylene. When its vapor was passed with a contact time of 16 seconds, through a silica tube containing alumina at 450°, it rearranged to trimethylethylene to the extent of ten per cent. With a similar heating period, phosphoric acid at 500° caused 29 per cent conversion to the isomer, and aluminum sulfate at 425° produced 47 per cent change. In the presence of these catalysts at 450° to 500° trimethylethylene was unchanged, nor was 2-pentene affected even at 525°.

Ipatiev[77] had earlier reported the same arrangement. He found that while iso propylethylene was not appreciably changed by passage through a glass tube at 500° to 550°, it underwent about 80 per cent conversion into trimethylethylene by passage over silica at 500° to 505°, or over alumina at

525° to 535°. An attempt to reverse the reaction by conducting trimethylethylene over alumina at 520° to 550° was not successful, the only isolable product being about 10 per cent of a hydrocarbon, insoluble in sulfuric acid, which boiled at 28° to 32°.

c. *Trimethylethylene*

Norris and Reuter[119] found trimethylethylene the most stable of the three pentenes they investigated. They wrote: "At 625° the extent of decomposition of trimethylethylene was about one-half that of 2-pentene at 600°, and at 650° the decomposition was slightly more." As in the case of 2-pentene, the gaseous product contained no hydrogen and was about fifty per cent methane. No butadiene was found. Both the gaseous and liquid products were analysed "for the proportions in which compounds containing the grouping $(CH_3)_2C^=$ were present. Such compounds react rapidly with 60% sulfuric acid and with concentrated hydrochloric acid." From its solubility in concentrated hydrochloric acid the gaseous product was reported to consist of about 30 per cent of olefins containing two methyl groups attached to a doubly bonded carbon. Twenty per cent was considered to be straight chain olefins. Of the liquid products, seventy per cent was absorbed by sixty per cent sulfuric acid, and was therefore reported to contain the mentioned grouping.

The initial decomposition of trimethylethylene was formulated by these workers as follows:

$$(CH_3)_2C{:}CHCH_3 \longrightarrow (CH_3)_2C{:}CH- \;+\; -CH_3 \xrightarrow{+2H} (CH_3)_2C{:}CH_2 + CH_4.$$

Staudinger, Endle, and Herold[143] found isoprene to be an important product of the pyrolysis of trimethylethylene under 15 mm. pressure at 750° to 770°. Of 50 grams of the amylene treated, 32.3 grams was decomposed and 8.3 grams of isoprene and 0.2 grams of butadiene were formed. The gaseous product was mainly a mixture of ethylene and propylene, the combined yield of these being about 1.1 grams. Under atmospheric pressure at 750°, however, the decomposition was quite different. Fifty grams of trimethylethylene then yielded 1.2 grams of liquid olefins boiling below 80°, and 14.5 grams of higher boiling liquids, mainly aromatic. In the gases, ethylene was the only gaseous olefin observed, and was present to the amount of 1.6 grams.

The investigation of Haber and Oechelhäuser[51,52] on the decomposition of trimethylethylene over the temperature range of 600° to 1060° was the first made on this hydrocarbon. At 600° on passage of vapors of the hydrocarbon through a porcelain tube, they found that decomposition was slight and noted particularly that neither carbon nor hydrogen was liberated. At higher temperatures decomposition was more extensive, as shown by Table XXVI, which gives the products obtained at 750° to 790° and 930° to 940°.

At 750° to 790° about one methane molecule was formed for each molecule of trimethylethylene treated. The nearly complete absence of higher paraffins indicated that hydrogenation of olefinic products did not occur. The tar consisted mainly of high molecular weight unsaturated substances.

TABLE XXVI

Decomposition of Trimethylethylene
(Haber and Oechelhäuser)

Temp., °C. Products, per cent of original olefins	750° to 790°	930° to 940°
Methane	22.5	27.7
Olefins (mostly ethylene)	26.8	8.5
Acetylene	0.09	0.3
Hydrogen	0.3–1.3	1.7
Other gaseous products	—	4.5
Carbon	Trace	5.1
Benzene	—	8.0–13.0
Tar (containing a little benzene)	45.2	33.7–39.1

At 930° to 940° more than one molecule of methane formed per molecule of the original olefin, and a considerable amount of benzene was produced.

At 1050° to 1060° the gaseous products contained 50 per cent hydrogen, 30 per cent methane, and 5 per cent ethylene. Heavy tars containing benzene and naphthalene were formed, and carbon separation was so great that the porcelain tube soon became stopped. Only a trace of acetylene, estimated as 0.005 per cent, was found.

By heating trimethylethylene in sealed glass tubes at 320° to 325° Engler and Routala[36] converted it almost completely into a mixture of products reported to consist largely of paraffins and naphthenes, with a small proportion of unsaturates. Thus 350 grams of the olefin which was heated for 32 days, produced about 10 liters of gas and 270 grams of liquid product. The gas consisted of 7.4 per cent by volume of hydrogen, 91.1 per cent of saturated hydrocarbons, and 1.5 per cent of unsaturated hydrocarbons.

Upon the basis of the boiling ranges, specific gravities, and refractive indices of different fractions, the constituents of the liquid product were identified as pentane, iso pentane, hexane, heptane, octane, nonane, cyclohexane, hepta-, octo-, nono-, α- and β-deca-, hendeca-, dodeca-, trideca-, tetradeca-, and pentadeca-naphthene. The proportion of cyclomethylene compounds increased with rise of the boiling point, so that these were almost the only constituents of the higher boiling fractions.

d. *Unidentified Amylenes*

Berthelot[5] reported that when amylene was heated in a glass bulb until the glass softened, it produced the normal paraffins from methane to pentane, ethylene, propylene, butylene, a trace of acetylene, and tarry hydrocarbons.

Perkin, Weizmann, Matthews, and Strange[126] claimed to produce isoprene by passing one or more of the amylenes through a tube heated to "dull redness."

5. 2-Hexene

Engler and Eberle[33] heated this hydrocarbon in sealed glass tubes at 360° to 365° for a period of 14 days, and obtained a liquid product distilling between 67° and 240°. Similar experiments in which Engler and Routala[38] heated the olefin for 30 days at 325° yielded gaseous saturated hydrocarbons and a liquid similar to that produced by the action of heat on amylene. From the boiling points, densities, and refractive indices of the fractions of the liquid, they were stated to contain hexane, undecane, methylpentamethylene, decanaphthene, and dodecanaphthene. Carbon was not formed. At 360° the decomposition was more rapid, and there was deposition of carbon.

6. Octene

Hugel and Szayna[63a] investigated the pyrolysis of *n*-octene in quartz tubes (2 × 75 cm. heated portion) over the temperature range 290° to 600°. The octylene pyrolyzed, a mixture of 40 per cent 1-octene and 60 per cent 2-octene as shown by oxidation with neutral potassium permanganate, resulted from the dehydration with five volumes of 45 per cent sulfuric acid of methylhexylcarbinol which was obtained by treating castor oil with three moles of sodium hydroxide (about 30 per cent solution) and slowly distilling the mixture at 150° to 160° while water was introduced drop by drop at the bottom of the iron retort to prevent pyrogenation of the alcohol.

TABLE XXVI A

Decomposition of *n*-Octene
(Hugel and Szayna)

Temp., °C.	Octene charged, g./hr.	Octene cracked, per cent of charge	Liquid recovered		
			Per cent of charge	Initial b.p. °C.	Per cent boiling below octene (121.5°)
287-295	7.5	0	100	119	1
364-369	8.0	0.4(?)	100	117	3.3
438-444	6.8	7.3	96.4	35	14.8
480-490	8.0	27	87.8	35	26.5
540-549	7.0	72.3	45.7	35	57.5
600	6.3	100	30	35	49

	Gas produced moles/mole of octene cracked	Gas analyses, per cent by volume			
		Satd. H.C.	Olefins	Acetylenes	H_2
438-444	1.01	87	8.5	—	4.5
480-490	1.54	73	17.5	3	6.5
540-549	2.63	69	19.5	5	6.5
600	2.70	67	15	4.5	13.5

As evidenced by Table XXVIA the lowest temperature which caused any change in *n*-octene was between 295° and 365° where the boiling range of the olefin was widened from 121.5°-124° to 117°-130° without any appreciable evolution of gas. This result was suggested as due to isomerization of the *n*-octene to branch chain octenes with lower boiling points. Above 400° the octene which was decomposed yielded gas and a low-boiling liquid. The liquid produced at 440° gave indications of the presence of unsaturated cyclic hydrocarbons (by conversion into a solid formolite), while that obtained at 540° and 600° contained benzene. Tar formation was observed at 440°, and carbon deposition occurred from 480° upward.

The results obtained were interpreted as evidencing three cracking reactions: isomerization; rupture of the carbon chain with formation of radicals; probably followed by condensation and cyclization, appearance of double bonds, and loss of hydrogen.

By heating *n*-octene in sealed pyrex tubes at 405° for one hour McKee and Szayna[109] observed a rise in the critical temperature (287.5° to 306°) of the liquid indicating initial polymerization as a dominant reaction. However, after exposure to 420° for 30 minutes, cracking was evidenced by a drop of 5° in the critical temperature. The octylene also became yellow during the heat treatment, and gave a deposit of carbon on the walls of the pyrex tube.

Hugel and Cohn[62] reported that 1-octene at 400° and under a pressure of 500 kg. per sq. cm. gives polymerization products which are liquid under the conditions of the experiment resulting in a considerable decrease in volume.

7. Decene

Zelinskii and Levina[169] found that 2,6-dimethyl-7-octene when passed in a slow current of carbon dioxide over palladized asbestos at 200° was completely converted into 2,6-dimethyl-6-octene.

8. Hexadecene

In order to cast light on the chemical reactions occuring during the cracking of petroleum, Gault and his coworkers have carried out an extensive series of researches on the pyrolysis of hexadecene. Gault and Altchidjian[43,45] working in the temperature range 350° to 725° with hexadecene, prepared by distilling cetyl palmitate under reduced pressure, found that the product was a complex mixture of hydrocarbons of the paraffin, olefin, and aromatic series, with hydrogen, and a small amount of acetylene. At low temperatures the olefins predominated. At higher temperatures aromatic hydrocarbons and tars were present in greatest proportions. It was thought that in an intermediate temperature range cyclic compounds more or less unsaturated were present, which by loss of hydrogen were converted into the aromatics. The maximum production of unsaturated hydrocarbons was about 66 to 68 per cent of the gaseous products, at 575° to 700°. Coincident with this maximum was the production of 26 per cent of saturated hydrocarbons, their minimum formation. In the gases there were identified by means of their bromine derivatives, ethylene, propylene, butylene, amylene, and butadiene, the last at 500° being equal to about 1 per cent of the original hexadecene. Some carbon was deposited at temperatures above 600°. At 650° naphthalene was isolated from the liquid products, and there was evidence of the formation of benzene.

These investigators considered that the main steps in the decomposition were the breaking of methane from the ends of hexadecene molecules, thus forming olefinic residues which themselves broke into smaller fragments. Olefins of diolefins were thought to form cyclic compounds by the steps shown below:

$CH_3CH_2CH_2CH_2CH{:}CH_2$ → cyclohexane → cyclohexene → cyclohexadiene → benzene + hydrogen,

or by a direct cyclization of a diolefin:

$CH_2{:}CHCH_2CH_2CH{:}CH_2$ → cyclohexene → cyclohexadiene → benzene + hydrogen.

Gault and Bargmann[44] extended this work by a study of the breakdown of hexadecene under elevated pressure. They found that pressure at 500° to 600° caused ring formation and the production of saturated hydrocarbons, both gaseous and liquid, some of the liquid paraffins in the products having a molecular weight greater than hexadecene. The total quantity of gas increased as the pressure was raised up to 3 kg. per sq. cm., and then remained constant with further pressure increase up to 9 kg. per sq. cm., while the amount of liquid products decreased with increasing temperature and pressure.

Hexadecene was subjected to still higher pressures, rising to 1000 kg. per sq. cm., by Hugel and Artichevitch.[61] The carbon chain then appeared to break near the double bond, forming an unsaturated radical and a long chain saturated group. Two of the saturated groups were thought then to combine to form a paraffin. The unsaturated radicals were believed to polymerize to oily products.

Hugel and Cohn[62] reported that polymerization of hexadecene to $C_{32}H_{64}$ and $C_{48}H_{96}$ was the only reaction observed when the hydrocarbon was heated to 300° under pressures varying between 5 and 1000 atmospheres. The polymerization reaction "was the more accentuated as the pressure rose, particularly above 500 atm. The study of this reaction as a function of time shows that it is probably an equilibrium reaction. The equilibrium appears to depend on the pressure and the temperature."

Other experiments by Hugel[60] were carried out by heating hexadecene (a) in a tube incompletely filled with the hydrocarbon so that a gas space was present when cracking conditions were reached, and (b) in a tube completely filled with the liquid olefin. When the desired pressure was reached in the latter case, the excess oil was allowed to escape. "Distillation of the final product shows that where the gas is present, a series of compounds boiling from 40° to above 360° is obtained, whilst in the completely liquid phase polymers of the original substance only are formed, indicated by the distillation curve, which shows three flat stages corresponding to the polymers of hexadecene,

$$C_{16}H_{32},\ C_{32}H_{64} \text{ and } C_{48}H_{96},$$

thus demonstrating the necessity for a gas phase, in order to produce normal cracking. These polymers of hexadecene are solid products like paraffin wax. Although the molecular structure of the polymers is yet undetermined, it was stated that "the dimer seems to form from two molecules of hexadecene by elimination of the double bond, whilst the trimer results from the union of three molecules with the disappearance of two double bonds."

Hugel and Goldthorpe[63] continued the work on hexadecene by introducing the use of catalysts. These noticeably lowered the temperature at which decomposition commenced. Under conditions as nearly like those of Gault and Altchidjian[43] as possible, they found that whereas in the presence of pumice alone, which appeared to have no catalytic action, carbon deposition was first noticeable at 500°, in the presence of pumice coated with iron, carbon formed at 425°, and with nickel at 350°. Gault and Altchidjian had reported initial decomposition at 450° to 550°, depending upon conditions. When using the nickel catalyst, deposition of carbon on the metal was so copious that the heating tube became obstructed after 100 cc. of hexadecene had been passed through it.

Besides the temperature lowering, the catalysts caused a distinct change in the products obtained. Nickel appeared to decompose the gaseous olefins which were thought to be among the primary pyrolysis products, and caused the appearance of carbon, hydrogen, and methane. Iron, on the other hand, induced the formation of ethylene and of saturated hydrocarbons above methane, so that there was a lower gas production than with pumice alone. It also increased the formation of acetylene. The liquid products decreased with increase in temperature, becoming almost negligible at 650°.

9. Diolefins

a. *Allene*

When Lebedev and Mereshkovski[92] heated allene at 140° to 145° in Ipatiev's high pressure apparatus, the pressure fell in three days from 58 to 16 atmospheres, and the hydrocarbon was in part converted into a semi-solid yellowish mass similar to caoutchouc. As this polymer did not resemble those obtained from the other allenic hydrocarbons, it was thought that possibly the metal of the apparatus exerted a catalytic influence. To avoid this, allene was condensed in glass tubes at −80°, the air in the tubes was replaced by nitrogen, and they were then sealed and heated in Ipatiev's apparatus, which was filled with hydrogen under 100 atmospheres pressure to prevent bursting of the tubes. After 3.5 days at 140°, 50 per cent of the allene was polymerized. The reaction product on distillation in a current of hydrogen under varying diminished pressures gave the following approximate yields of the different polymers: dimer 5, trimer 15, α-tetramer 5, β-tetramer 22, pentamer 18, hexamer 10, and 25 per cent of a colorless gum-like solid.

Hurd, with Spence[68] and with Meinert[110], has also studied the pyrolysis of allene. They passed the hydrocarbon through a vertical pyrex tube at temperatures of 400° to 600° and thus made the hot contact time a matter of seconds rather than days as in Lebedev's experiments. At the lower temperatures the main product was liquid, believed to be formed by a polymerization process.

To Meinert and Hurd[110] a temperature of 500° seemed best for the formation of liquids from allene. At lower temperatures, the reaction was too slow, while at higher temperatures less liquid polymers and more gas were formed, although the percentage of allene pyrolyzed was greater. A summary of their results is given in Table XXVII.

TABLE XXVII

Products obtained from the Pyrolysis of Allene
(Meinert and Hurd)

Experiment	2	3	1	5	4
Temp., °C.	400	450	500	500	600
Contact time, secs.	60.8	52.0	54.7	86	50
Extent of pyrolysis, per cent	13.8	28.8	66.2	80.5	83.5
Liquid products, Per cent yield on basis of allene pyrolyzed	32	75	—	90	43
Gaseous products, in cc. per liter of allene entering					
Acetylenes	—	—	11.9	18.5	0
Ethylene	—	—	11.9	15.3	65
Hydrogen	—	—	5.9	21.8	130
Paraffins	—	—	20.2	50.9	146
Gaseous products, in cc. per liter of allene pyrolyzed					
Acetylenes	—	—	18	23	0
Ethylene	—	—	18	19	78
Hydrogen	—	—	9	27	156
Paraffins	—	—	32	63	175

The above results show that allene when pyrolyzed was converted mainly into liquids. The conversion approached completion more nearly when the diolefin was heated for a long time and when the temperature was between 500° and 600°. At the latter temperature the formation of gas was about five times greater than that observed at 500°, while the yield of liquids was considerably less. The gases produced in the pyrolysis of allene were hydrogen, methane, ethane, ethylene, and small amounts of acetylenes. "Methane represented the larger part at 500°, but at 600° the volumes of methane and hydrogen were almost equal. . . . Carbon and tar formation played a major role in the 600° experiments, whereas at 500° almost no tar or carbon was formed."

b. *Methylallene*

Hurd and Meinert[64b] "found that methylallene resembled allene in its mode of pyrolysis. At temperatures from 500 to 550° (Table XXVII A), a complete decomposition was effected in 36 seconds and three-fourths of the methylallene was converted into liquids of a polymeric nature. Some tarry material and a little carbon were deposited on the walls of the reaction tube."

TABLE XXVII A

Thermal Decomposition of Methylallene
(Hurd and Meinert)

Experiment	1	2	3	4
Temp., °C.	405	500	500	550
Methylallene used,				
Grams.	13.1	20.1	20.1	11.2
Cc. as gas	5420	8340	8340	4640
Contact time, secs.	46.3	36.6	36.1	37.0
Decomposition,				
Per cent of entering methylallene	28	95-100	95-100	95-100
Liquids formed, Wt. in grams	3	14.6	14.8	8.0
Per cent by wt. of methylallene decomposed	22	72.7	73.6	73.2
Gaseous products, total volume in cc.				
Acetylenes	—	72	82	13
Propylene, allene, etc	—	410	577	349
Ethylene	—	175	246	105
Hydrogen	—	260	398	138
Paraffins	—	1018	1204	806
Gaseous products, in cc. per liter of methylallene entering				
Acetylenes	—	8.6	9.9	3.0
Propylene, allene, etc	—	49.2	69.2	75.8
Ethylene	—	21.0	29.5	22.6
Hydrogen	—	31.2	47.8	29.9
Paraffins	—	122.0	145.0	173.4

"The liquids were separated as efficiently as possible into fractions containing but one polymer. The lowest boiling fraction was obtained in a state of fairly high purity. It boiled at 110-115° and a molecular weight determination showed that it was a dimer of methylallene. Attempts to prove its structure by permanganate oxidation or by ozonization were not fruitful.

"Inasmuch as allene was found[110] to pyrolyze 66 and 81% in 55 and 86 seconds, it is evident that it is more resistant to heat than methylallene which was almost completely altered in 36 seconds. Although the gaseous products from both allene and methylallene were the lesser products of the reaction, it is interesting to note that methylallene, even with its considerably shorter contact time, gave more than twice the volume of gaseous products. As compared with 77-132 cc. of gas from each liter of allene pyrolyzed, methylallene gave rise to 235-308 cc. Evidently the methyl group is the responsible factor for much of the increased volume was due to methane. Paraffin hydrocarbons made up about half of the total volume of the gases, and the n in C_nH_{2n+2} was considerably nearer unity in the gases from methylallene."

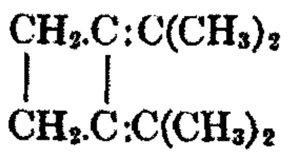
c. sym-*Dimethylallene*

Experiments of Lebedev and Mereshkovski[92] showed that at 150° polymerization of sym-dimethylallene was complete in four to five days. The product contained (a) about 90 per cent of the dimer, 1,2-dimethyl-3,4-diethylidenecyclobutane, $\underbrace{CHMe{:}C.CH(Me)CH(Me).C}{:}CHMe$, which was a colorless liquid boiling at 163°; and (b) 5 per cent of a trimer which was a colorless, odorless liquid boiling at 108° to 110° under 17 mm. pressure.

d. unsym-*Dimethylallene*

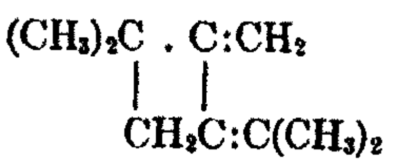
Lebedev[89] reported that when unsym-dimethylallene was heated in sealed tubes at 100° to 225° for two to twenty days, most of the diolefin polymerized to diisopropylidene-1,2-cyclobutane and dimethyl-1,1-methylene-2-isopropylidene-3-cyclobutane. The structures of these polymers are shown by formulas (I) and (II), respectively.

(I)



$$\begin{array}{l} CH_2.C{:}C(CH_3)_2 \\ |\quad\ | \\ CH_2.C{:}C(CH_3)_2 \end{array}$$

(II)

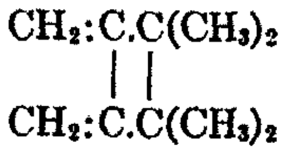


$$\begin{array}{l} (CH_3)_2C\ .\ C{:}CH_2 \\ \qquad\quad |\quad | \\ \qquad CH_2C{:}C(CH_3)_2 \end{array}$$

The first was a colorless liquid of aromatic odor boiling at 61° to 62° under 9 mm. pressure and at 179° to 181° under 753 mm. The second liquid (II) which was also colorless had an odor resembling that of kerosene and boiled at 37° to 39° under 9 mm. and at 149° to 150° under 752 mm.

In further work Lebedev[89, 92] obtained a third dimer

(III)



$$\begin{array}{l} CH_2{:}C.C(CH_3)_2 \\ \qquad |\ \ | \\ CH_2{:}C.C(CH_3)_2 \end{array}$$

by slowly heating dimethylallene to 120-125°. This dimer was a colorless liquid of a terpene-like odor boiling at 140-141° which polymerized within a few hours at ordinary temperature, depositing a colorless substance.

At 130° the relative amounts of polymerization products obtained from dimethylallene were: 40 per cent of that boiling at 179° to 181° (I), 18 per cent of that boiling at 149° to 150° (II), 3 per cent of (III), 33 per cent of a trimer boiling at 100° under 8 mm. pressure, and 6 per cent of a vaseline-like residue which contained much of (III) and some of the dimer boiling at 149° to 150°.

e. *Trimethylallene*

Lebedev and Mereshkovski[92] reported that trimethylallene, when heated in a sealed tube at 150°, underwent polymerization and isomerization. The mixture of dimers formed consisted mainly of 1,2-dimethyl-3,4-diisopropylidene-cyclobutane, a colorless liquid with the odor of kerosene and boiling at 190°-191°. Higher polymers were formed to the extent of 10 per cent, but no individual compounds were isolated.

f. *Butadiene*

Lebedev and Skavronskaya[88,93] found that butadiene when heated in a sealed tube at 150° for 10 days, polymerized to ethenyl-1-cyclohexane-3, $CH_2{:}CH\,\underline{CH\ CH_2\ CH_2\ CH{:}CH\ CH_2}$, a liquid of sharp mustard-like odor boiling at 129.5 = 130.5°, and a resin-like polymer designated by the formula:

$$[CH_2\ CH{:}CH\ CH_2\ CH_2\ CH{:}CH\ CH_2]_x.$$

Staudinger, Endle, and Herold[143] observed that butadiene at 800° yielded tar which contained aromatic hydrocarbons.

Patents of F. Bayer and Company[3a] cover the polymerization of butadiene to a caoutchouc-like material by heating the diolefin alone in an autoclave for four days at 90° to 100°, or by heating in benzene solution for 10 hours in an autoclave at 150°.

g. *Isoprene*

Formation of a dimer is one of the first results of continued heating of isoprene at temperatures below about 300°. Ostromislensky and Koschelev[122a] reported that isoprene when maintained at 80° to 90° for three to five days yielded an open-chain, myrcene-like hydrocarbon ($C_{10}H_{16}$, termed β-myrcene) which contained three double bonds, two of them in conjugated positions.

Earlier than this Bouchardat,[15] Tilden,[147a] and Wallach[151a] independently converted isoprene into dipentene (which boiled between 170° and 185°) and higher boiling viscous products (termed "colophene" by Tilden) by heating the diolefin in sealed tubes at 250° to 290° during six to twelve hours.

Lebedev[88, 93] also observed that isoprene when heated in sealed tubes at 150° for six or seven days yielded dipentene, an isomeric hydrocarbon boiling at 160° to 161°, and a resin-like polymer.

Under similar conditions a higher olefin termed diisoprene, produced a polymer thought to be a dimer.

A patent of Bayer[3b] covers the production of artificial rubber by heating synthetic isoprene with or without the addition of neutral, alkaline, or acid catalysts, at a temperature under 250°.

The changes taking place when isoprene was subjected to higher temperatures were studied by Staudinger, Endle, and Herold.[143] At temperatures of 400° and 500°, polymerization reactions were foremost, with the production of higher unsaturates and terpenes resembling those formed in the polymerization of isoprene to rubber. Some amylene appeared, and a very small amount of gas. At 600° to 700° decomposition was rapid, and a mixture of unsaturated hydrocarbons resembling crude petroleum was formed, along with a considerable quantity of gas in which ethylene, propylene, and butadiene were identified. Above 700°, aromatic hydrocarbons began to appear.

At 750° the decomposition yielded 33.7 per cent by weight of gas, 56.1 per cent of tar, and 4.8 per cent of carbon. The gases consisted of 13.6 per cent unsaturated hydrocarbons (mainly ethylene with smaller amounts of butadiene), 58 to 60.3 per cent of methane, and 19.9 to 23.5 per cent of hydrogen. The tar, which closely resembled coal tar in appearance and composition, was separated by fractional distillation into 5.3 per cent benzene, 27.8 per cent toluene, 11.2 per cent naphthalene, 9.8 per cent α-methylnaphthalene, 8 per cent of anthracene and phenanthrene, 9.2 per cent of chrysene, and 28.7 per cent of pitch, coke, and oil from which no individual compounds could be separated.

At 800° aromatic hydrocarbons were the only products identified. Under 20 to 25 mm. pressure at 700° considerable amounts of highly unsaturated compounds, and much gas were produced, but no tar.

The polymerization of isoprene and closely related diolefins by other agencies than heat, is a subject too extensive to treat except in a paper devoted to that subject, and will therefore not be considered here.

h. *Hexadienes*

Lebedev and Mereshkovski[92] reported that diallyl (1,5-hexadiene) when heated for eight days at 140° to 200° remained unchanged, but after 10 days at 250°, 40 per cent of the hydrocarbon was polymerized and isomerization occurred to some extent. The crude product of the reaction was a mixture of about 15 per cent of a liquid dimer (b_{20} 97-98°) and 85 per cent of a colorless insoluble polymer resembling caoutchouc.

Similarly, 2,4-hexadiene when heated at 150° yielded a dimer (b_{20} 86° to 90°), and after 10 days at 250° a dimer boiling mainly at 96° to 98° under 20 mm. pressure.

Methylisoprene (2,3-dimethylbutadiene) which Harries[53a] maintained at 100° during about 23 days yielded a viscous mass, which, when freed from small quantities of terpene-like substances (related to dipentene) by vacuum distillation, contained 32 per cent of dimethylbutadiene caoutchouc, $(C_{12}H_{20})_x$.

Hofmann, Coutelle, Meisenburg, and Delbruck[56b] claimed to obtain a caoutchouc-like substance by heating diisopropenyl (2,3-dimethylbutadiene) at 80° to 90° for two months; or by heating with an equal quantity of benzene in an autoclave at 200° for 10 hours. Mixtures of butadiene, isoprene, and diisopropenyl were said[56a] to yield a rubber-like material when kept in an autoclave at 70° to 75° for three months.

10. Summary

Tables XXVIII and XXIX summarize the substances which have been reported as thermal decomposition products of individual olefins and diolefins. In some cases the blanks of these tables, no doubt, represent gaps in present knowledge, and do not indicate that the substances referred to cannot be formed from the olefinic hydrocarbons.

TABLE XXVIII

Products of the Action of Heat on Olefins

Substances identified	C_2H_4	C_3H_6	EtCH:CH$_2$	MeCH:CHMe	i-C_4H_8	EtCH:CHMe	i-PrCH:CH$_2$
Carbon	+	+	+	+	+	+	—
Hydrogen	+	+	+	+	+	—	—
Methane	+	+	+	+	+	+	—
Ethane	+	+	+	+	—	—	—
Propane	—	+	—	—	—	—	—
Isobutane	—	—	—	—	+	—	—
"Satd. H.C."	+	—	—	—	—	—	—
Ethylene	—	+	+	+	+	+	—
Propylene	+	—	+	+	+	+	—
Butylene	+	+	+	+	—	+	—
Trimethylethylene	—	—	—	—	—	—	+
Triisobutylene	—	—	—	—	+	—	—
Butadiene	+	+	+	+	+	+	—
"Higher olefins"	+	+	—	—	—	—	—
"Unsatd. H.C."	+	—	—	—	—	—	—
Acetylene	+	+	—	—	+	—	—
Cyclopropane	—	+	—	—	—	—	—
Cyclohexene	+	—	+	+	—	—	—
Methylcyclohexene	—	—	+	+	—	—	—
Cyclohexadiene	—	—	+	+	—	—	—
Methylcyclohexadiene	—	—	+	+	—	—	—
Benzene	+	+	+	+	+	—	—
Toluene	+	+	+	+	+	—	—
Xylene	—	—	—	—	+	—	—
Styrene	+	—	—	—	+(?)	—	—
Naphthalene	+	—	—	—	+	—	—
Methylnaphthalene	—	—	—	—	+	—	—
Diphenyl	—	—	—	—	+	—	—
Ditolyl	—	—	—	—	+(?)	—	—
Anthracene	+(?)	—	—	—	+	—	—
Phenanthrene	—	—	—	—	+	—	—
"Aromatic H.C."	+	—	—	—	—	—	—
"Oil" or "tar"	+	+	+	+	—	—	—
"Liquid and solid H.C."	+	+	—	—	—	—	—

Products reported in patents are not included here, but are given in the text.

TABLE XXVIII (Continued)

Substances identified	$Me_2C:CHMe$	C_6H_{12}	C_8H_{16}	i-$C_6H_{13}CMe:CHMe$	$C_{16}H_{32}$
Carbon	+	+	+	—	+
Hydrogen	+	—	+	—	+
Methane	+	—	—	—	+
Pentane	+	—	—	—	—
Isopentane	+	—	—	—	—
Hexane	+	+	—	—	—
Heptane	+	—	—	—	—
Octane	+	—	—	—	—
Nonane	+	—	—	—	—
Undecane	—	+	—	—	—
"Satd. H.C."	—	+	+	—	+
Ethylene	+	—	—	—	+
Propylene	+	—	—	—	+
Butylene	—	—	—	—	+
Amylene	—	—	—	—	+
2,6-Dimethyl-6-octene	—	—	—	+	—
$C_{32}H_{64}$	—	—	—	—	+
$C_{48}H_{96}$	—	—	—	—	+
Butadiene	+	—	—	—	+
Isoprene	+	—	—	—	—
"Unsatd. H. C."	—	—	+	—	+
Acetylene	+	—	+	—	+
Methylpentamethylene	—	+	—	—	—
Cyclohexane	+	—	—	—	—
Heptanaphthene	+	—	—	—	—
Octonaphthene	+	—	—	—	—
Nononaphthene	+	—	—	—	—
Decanaphthene	+	+	—	—	—
Undecanaphthene	+	—	—	—	—
Dodecanaphthene	+	+	—	—	—
Tridecanaphthene	+	—	—	—	—
Tetradecanaphthene	+	—	—	—	—
Pentadecanaphthene	+	—	—	—	—
Benzene	+	—	+	—	+
Naphthalene	+	—	—	—	+
"Aromatic H.C."	—	—	—	—	+
"Liquid polymer"	—	—	+	—	—

TABLE XXIX

Products of the Action of Heat on Diolefins

Substance identified	$CH_2:C:CH_2$	$CH_2:C:CHMe$	$CH_2:C:CMe_2$	$CHMe:C:CHMe$	$CHMe:C:CMe_2$	$CH_2:CH\text{-}CH:CH_2$	$CH_2:CHMe\text{-}CH:CH_2$
Carbon	+	+	—	—	—	—	+
Hydrogen	+	+	—	—	—	—	+
Methane	+	+	—	—	—	—	+
Ethane	+	—	—	—	—	—	—
Ethylene	+	+	—	—	—	—	+
Propylene	—	+	—	—	—	—	+
Amylene	—	—	—	—	—	—	+
Dipentene	—	—	—	—	—	—	+
Butadiene	—	—	—	—	—	—	+
"Highly unsatd. and terpene H.C."	—	—	—	—	—	—	+
Acetylene	+	+	—	—	—	—	—
Benzene	—	—	—	—	—	—	+
Toluene	—	—	—	—	—	—	+
Naphthalene	—	—	—	—	—	—	+
Methylnaphthalene	—	—	—	—	—	—	+
Anthracene	—	—	—	—	—	—	+
Phenanthrene	—	—	—	—	—	—	+
Chrysene	—	—	—	—	—	—	+
"Aromatic H.C."	—	—	—	—	—	+	—
Dimer	+	+	+	+	+	+	—
Trimer	+	—	+	+	+	—	—
Tetramer	+	—	—	—	—	—	—
Pentamer	+	—	—	—	—	—	—
Hexamer	+	—	—	—	—	—	—
High polymers	+	—	—	—	+	—	—
"Resin-like" polymer	—	—	—	—	—	+	+
"Vaseline-like" residue	—	—	+	—	—	—	—
"Oil" or "tar"	+	+	—	—	—	—	+
"Non-aromatic liquids"	+	—	—	—	—	—	—

II. ELECTRICAL ACTION

1. Ethylene

A considerable amount of study has been given to the action of electrical forces on ethylene, and a little work has been done in this field with higher olefins.

A sharp distinction must be made, as has been mentioned earlier, between the action of spark or arc, which closely resembles that of heat, and the predominantly polymerizing action of the silent discharge.

The main products obtained from ethylene exposed to spark or arc are carbon and hydrogen, with some methane, ethane, and acetylene. A small amount of condensation to liquid products also occurs.

The silent discharge largely produces condensation products ranging from simple substances such as butene and hexene to heavier oils and resins of undetermined composition. The mechanism by which these products are formed is apparently much like that through which polymerization occurs under the influence of heat.

a. *By Sparks or Arc*

Dalton and Henry[24] observed that ethylene increased in volume when electric sparks between platinum points were passed through it. They found that the sole products were hydrogen and carbon, and that the increase in volume amounted to twice the volume of ethylene which disappeared. Similar results were obtained by Quet[130] using induction sparks between copper electrodes.

Ludeking[104] also decomposed ethylene completely between copper electrodes. He noted at the positive pole a very thick thread of hard and highly conductive carbon, and at the negative a loose deposit. The hard deposit was attributed to "electrical," the loose to "thermal" action of the sparks Under the same conditions, more carbon was produced from ethylene than from methane.

Miller[113] found that the decomposition of ethylene by electric sparks was "extremely intense" when aluminum electrodes were used, but "comparatively slight" with gold.

Buff and Hofmann,[18] employing a flaming arc between platinum electrodes, found that the expansion incident to reaction reached a maximum in about ten minutes, and that the sole gaseous product was hydrogen.

Berthelot[7] reported that the action of electric sparks on ethylene gave a mixture of one volume of acetylene and six volumes of hydrogen. The action of induction sparks on a mixture[11] of equal volumes of ethylene and argon yielded hydrogen with a small proportion of methane.

De Wilde[29] reported that under the same conditions the decomposition of ethylene by induction sparks was slower than that of acetylene. The dissociation of ethylene was believed to take place in two phases: conversion of the olefin into acetylene and hydrogen, and of acetylene into carbon and hydrogen. This investigator later found that induction sparks also caused ethylene to polymerize, forming a colorless oil which smelled like petroleum or turpentine.

Patents of Gros[48] cover the manufacture of acetylene and hydrogen by the action on ethylene of electric sparks between moving points in an annular reaction chamber. The production of small amounts of polymerization products is also claimed.

According to the I. G. Farbenindustrie A.-G.,[72] products containing 9.1 per cent of propylene, 7.7 per cent of butadiene, and 1.4 per cent of butylene resulted when ethylene was passed at the rate of 20 liters per hour through a spark discharge between copper electrodes 8 cm. apart and supplied with about 60 watts.

b. *By Electrical Discharge*

The work of Mignonac and de Saint-Aunay[112] is the most clean-cut that has been done on the action of the electric discharge on ethylene. They allowed but brief exposure of the hydrocarbon to the discharge, and obtained as sole products, 1-butene and 1-hexene. This indicates that these substances are primary products, and probably the first intermediates in the polymerization of ethylene to substances of high molecular weight, of unknown structure, which are the only products most workers on this field have reported.

In carrying out their experiments Mignonac and de Saint-Aunay circulated ethylene through a Berthelot electrical discharge tube connected to several condensers maintained at −60°. From 90 to 95 per cent of the gas was converted into colorless polymerization products, for the most part liquid at ordinary temperatures. The condensate was separated by distillation into two main fractions, one boiling at −2° and the other at 70°, which were identified by their ozonides as 1-butene and 1-hexene. No hexene was formed when the condensation apparatus was at −80°, which prevented butene from re-entering the discharge chamber with the stream of ethylene.

The reaction was considered to take place through activation of ethylene molecules, each of which then added as $H^{\cdot}$ and $^{\cdot}CH{:}CH_2$ to the double bond of an ordinary ethylene molecule to form butylene, or to a butylene molecule to form hexene.

P. and A. Thénard[147] were first to observe that in the silent electric discharge ethylene condensed rapidly to a liquid. Berthelot[9] obtained a similar liquid and stated that its composition corresponded to the formula $C_{10}H_{16.6}$. Later[10,13] he represented the composition by $(C_8H_{14})_n$. Hydrogen, ethane, acetylene, and resins were formed at the same time.

By subjecting a "large amount" of ethylene to the silent electrical discharge at −20° for two weeks, Collie[23] obtained 10 grams of polymerized products, which boiled from "below 100°" to 250°, and left a resinous residue. The main constituent of the polymerized product had a boiling point near that of a decene. The residue, a polymer similar to india-rubber, had a composition close to $(C_5H_8)x$.

Losanitsch and Jovitschitsch[103] observed that ethylene exposed to the silent electrical discharge (3 to 5 amperes at 70 volts) yielded a thick yellow oil boiling above 200°. Later, Losanitsch[100] obtained in the same way a similar oil which boiled above 260°. This latter product appeared to have an empirical composition $C_{12}H_{22}$. It combined rapidly with oxygen of the air. Upon the basis of further experiments Losanitsch[102] stated that a liquid and two solids were formed by the action of the silent electrical discharge on ethylene. The formulas proposed and the boiling or melting points of these substances were: $C_{14}H_{26}$, b.p. 100° to 110° under 14 mm. pressure; $(C_{12}H_{26})_9$, m.p. 105°; and $(C_{16}H_{26})_n$, m.p. 110°.

Jovitschitsch[82] stated that the liquid produced in this way was a cyclic condensation product very reactive toward oxygen, having as probable formula $C_{30}H_{54}$. His analytical figures for carbon plus hydrogen content totaled only 93 per cent, however. Jovitschitsch reported this polymer to be strongly "radioactive," but Losanitsch[101] said that this assertion was an error. In further work, from two liters of ethylene exposed to the discharge for 32 hours Jovitschitsch[83] obtained 1.67 grams of liquid whose analysis he reported as 68.95 per cent carbon and 10.26 per cent hydrogen. He accounted for the remainder by suggesting a combination of the product with oxygen, nitrogen, or water. It is to be regretted that complete analysis of the product was not made.

A small proportion of a mobile, yellowish brown liquid was formed when Dem'yanov and Pryanishnikov[28] passed ethylene for 24 hours through a modification of the ordinary Siemens ozonizer. The velocity of polymerization as well as the properties of the products depended on the potential drop, the size of the reaction chamber of the ozonizer, and the thickness of the glass and its quality. Ethylene polymers (reported to be C_6H_{12} to $C_{12}H_{24}$), and also small amounts of saturated hydrocarbons were found in the fractions of the liquid boiling between 90° and 210°.

Lind and Glockler[99] reported that the condensation of ethylene by the electrical discharge was similar to the reaction observed when the hydrocarbon was exposed to alpha rays.[98] Both condensations showed a pressure decrease to about 1/3 of the initial pressure. Hydrogen and methane appeared in the same relative amounts, the quantity of free hydrogen produced was of the same order in both types of condensation, and there were similarities in the proportions (93 to 96 per cent) of hydrocarbon converted into liquid products, as well as in the composition of the liquids.

Patents of Epner[39] cover the polymerization of ethylene by means of the silent electric discharge, preferably of high tension and high frequency at ordinary or increased temperatures and with or without the use of catalyst, to obtain products containing both saturated and unsaturated hydrocarbons of which fractions are suitable for use as motor fuel and lubricating oil.

2. Propylene

Berthelot[10] observed that propylene condensed in the electrical discharge to a product whose analysis corresponded to the formula $C_{15}H_{26}$. It was suggested that this might be a polymer of allyl, $(C_3H_5)_n$. Hydrogen and methane were also formed.

Pryanishnikov[129] found that under the action of the silent electrical discharge propylene yielded a liquid product of density 0.824, index of refraction 1.4578, and mean molecular weight 233. From these data the presence of a pentamer and higher polymers was assumed.

3. Butylenes

a. *Iso butylene*

The silent electric discharge converts iso butylene into liquid products of considerable complexity, which apparently consist largely of paraffin and olefin hydrocarbons.

By this means Dem'yanov and Pryanishnikov[28] obtained a liquid of density 0.822 and mean molecular weight 141, of which the largest fractions corresponded in boiling point to di- and tri-isobutylene, while a lower fraction boiling between 30° and 42° was thought to be amylene.

By a discharge at 12,000 volts A.C., Pryanishnikov[129] quantitatively converted iso butylene into a yellowish oily liquid of specific gravity 0.807 and mean molecular weight 182. Of this liquid about 22.8 per cent distilled below 150° at atmospheric pressure and an additional 46.2 per cent below 150° under 8 mm. pressure.

By further fractionation Pryanishnikov obtained two fractions boiling from 32° to 52° and 75° to 85°, having molecular weights corresponding to C_6 and C_7 hydrocarbons, respectively. These fractions appeared to contain 20 to 30 per cent of olefin and 70 to 80 per cent of paraffin hydrocarbons. The 75° to 85° fraction was thought to be made up of dimethylpentane, 2,2-dimethylpentane, 2,2,3-trimethylbutane, and the corresponding pentenes and butenes. The first fraction (32°-52°) of the liquid was reported to contain 2,2-dimethylbutane and 2,2-dimethylbutene. With such wide boiling ranges, of course, accurate identification of compounds was not possible.

Fractions boiling higher than these two were richer in unsaturated hydrocarbons, and also contained naphthenes. No aromatic compounds were reported, and physical constants of the liquids were said to indicate their absence.

The character of the products depended greatly on the length of the experiment; prolongation increased the yield of highly polymerized, nonvolatile products. Increase in the voltage accelerated the polymerization, but appeared not to change the character of the product.

b. 2-*Butene*

Pryanishnikov[129] subjected 2-butene to the action of the silent electric discharge and obtained an oily product which he did not identify. It had an average molecular weight of 202, density of 0.831, and iodine number 156, with thirty per cent boiling below 150°.

4. Amylenes

Losanitsch[102] reported that from the action of a silent electrical discharge in vacuum on trimethylethylene there was obtained colorless liquid "diamylene," "tetraisoamylene," and "nonaisoamylene," $C_{45}H_{76}$ or $(C_5H_{10})_9$-14H), a brownish yellow mass.

Truchot[149] observed that induction sparks passing between platinum electrodes immersed in amylene caused separation of traces of carbon and evolution of a gas consisting of hydrogen, methane, ethylene, acetylene, and probably a small quantity of ethane. The amylene was kept near its boiling point so as to prevent the gases formed from dissolving in the liquid and being exposed repeatedly to the action of the sparks.

5. Summary

The products obtained by the action of electric sparks and electrical discharge on the individual olefins are listed in Table XXX.

TABLE XXX

Products of the Action of Electric Sparks and of Silent Electric Discharge on Olefins

Substances identified	Electric Sparks		Electrical Discharge				
	C_2H_4	C_5H_{10}	C_2H_4	C_3H_6	iso C_4H_8	2-C_4H_8	C_5H_{10}
Carbon	+	+	—	—	—	—	—
Hydrogen	+	+	+	+	—	—	—
Methane	+	+	+	+	—	—	—
Ethane	—	+	+	—	—	—	—
2,2-Dimethylbutane	—	—	—	—	+	—	—
2,2-Dimethylpentane	—	—	—	—	+(?)	—	—
2,2,3-Trimethylbutane	—	—	—	—	+(?)	—	—
Ethylene	—	+	—	—	—	—	—
1-Butene	—	—	+	—	—	—	—
Amylene	—	—	—	—	+	—	—
1-Hexene	—	—	+	—	—	—	—
2,2-Dimethylbutene	—	—	—	—	+	—	—
2,2-Dimethylpentene	—	—	—	—	+	—	—
2,2,3-Trimethylpentene	—	—	—	—	+	—	—
Decene	—	—	+	—	—	—	—
Pentapropylene	—	—	—	+	—	—	—
Diisobutylene	—	—	—	—	+	—	—
Triisobutylene	—	—	—	—	+	—	—
Diisoamylene	—	—	—	—	—	—	+
Tetraisoamylene	—	—	—	—	—	—	+
Nonaisoamylene	—	—	—	—	—	—	+
Acetylene	+	+	+	—	—	—	—
Naphthenes	—	—	—	—	+	—	—
"Oil"	+	—	+	—	+	+	—
"Liquid polymers"	—	—	+	+	—	—	—
"Solid polymers"	—	—	+	—	—	—	—
"Resins"	—	—	+	—	—	—	—

Products reported in patent are not included here, but are given in the text.

III. CHEMICAL ACTION

Several chemical reagents, notably aluminum chloride, boron fluoride, earths such as fluoridin, sodium, and zinc chloride cause rapid polymerization of olefin hydrocarbons, and effect little, if any, other change. No attempt is made to decide in any case whether the action is due to a chemical reaction in which the polymerizing agent takes part, or to its catalytic properties. The products usually include gases, volatile liquids containing low paraffin, olefin, and naphthene hydrocarbons, and liquids and resins whose constituents have not been positively identified, but which are thought to be largely naphthenes and olefins of higher molecular weight. Some reactive substances besides those mentioned—sulfuric acid, for example—cause the formation of higher boiling products from olefins, but at the same time, they produce changes of other types, such as the formation of addition products and other derivatives. Because the action of these other substances is not limited to polymerization, they will not be dealt with in this paper.

In a study of the polymerization of olefins by floridin (Florida earth) Lebedev and Filonenko[90] set forth the following general rules:

1. Of the olefin hydrocarbons only those polymerize in the presence of activated floridin which are derivatives of asymmetrical doubly or triply substituted ethylenes ($RR'C{:}CH_2$, $RR'C{:}CHR''$).

2. Mono-substituted, and symmetrical di- and tetra-substituted olefins do not polymerize even over periods of as long as two years.

1. Ethylene

a. *Aluminum Chloride*

Szayna[144] reported that ethylene reacted with anhydrous aluminum chloride at temperatures of 100° to 150°, but with some difficulty. A small amount of liquid was formed which he reported to contain a small proportion of unsaturated hydrocarbons, but to be composed largely of low boiling paraffins and higher boiling naphthenes. The gaseous product was said to be exclusively butane.

By the action of freshly prepared aluminum chloride under 70 atmospheres pressure Ipatiev and Rutala[80] polymerized ethylene at ordinary temperature, producing a greenish fluorescent oil containing unsaturated hydrocarbons paraffins boiling below 200°, and naphthenes distilling above this temperature. When the reaction was carried out at 200°, liquid polymerization products were not obtained and only a charred residue remained in the apparatus.

With commercial aluminum chloride under the same high pressure ethylene was scarcely affected at 240°. At 280° were obtained a carbonaceous residue, and a gas containing 10 per cent hydrogen, 4.0 per cent olefins, and 86 per cent paraffins.

Stanley[142] studied the polymerization of ethylene in the presence of anhydrous aluminum chloride at temperatures up to 180° under an initial pressure of 50 to 55 atmospheres. "At ordinary temperatures the products were of two types, (1) a free oil, and (2) a double compound of aluminum chloride and liquid hydrocarbons, from which the combined oil was extracted by decomposition with ice water.

"The free oil consisted of liquid hydrocarbons, mostly of a saturated nature and containing from about 10 to 45 carbon atoms in their molecules. The lower boiling fractions contained proportions of paraffin hydrocarbons, but the main part of the oil consisted of saturated compounds, presumably cycloparaffins.

"The combined oil, liberated from the pasty aluminum chloride additive compound, also consisted of a complex mixture of hydrocarbons with from 10 to more than 50 carbon atoms per molecule." Those hydrocarbons from the "combined" oil appeared to be unsaturated and contained less hydrogen than was required by the formula C_nH_{2n}. Stanley suggested that these oils are probably composed of olefins mixed with hydrocarbons of lower hydrogen content (probably unsaturated cyclic hydrocarbons). The amount of "combined" oil obtained was limited by the quantity of aluminum chloride used, but the quality of "free' oil increased steadily with the duration of the experiment.

"At higher temperatures the condensation of ethylene under pressure in the presence of aluminum chloride was much more rapid, but the life of the catalyst was considerably curtailed. As before, free oil and aluminum chloride double compounds were formed, but those differed considerably from the products obtained at lower temperatures. The aluminum chloride complex tended to become more and more carbonaceous as the temperature was increased, and above 100 to 150°C. it was not possible to obtain oil from this material at all, but only a relatively small amount of a heavy black tar.

"The free oil produced at higher temperatures was a pale yellow, clear oil, containing large proportions of low-boiling constituents in contrast to the viscous free oil produced at lower temperatures. The low-boiling fractions consisted of paraffin hydrocarbons from pentane upwards, whilst the higher boiling fractions were deficient in hydrogen and corresponded to the formulae C_nH_{2n-6}, C_nH_{2n-8}, C_nH_{2n-10}. These latter substances probably belong to the class of polynuclear naphthenes. At higher temperatures lower paraffin hydrocarbons appeared in the residual gases from the experiments, their amount increasing with rise in temperature.

"Briefly, it was believed that the formation of the numerous products by the action of aluminium chloride could be explained on the basis of three well-known reactions, namely: (1) Polymerisation of ethylene to higher olefins; (2) isomerisation of those olefins to produce the corresponding cycloparaffins; and (3) cracking of the latter under the influence of aluminium chloride to produce light paraffin hydrocarbons and heavy oils less rich in hydrogen."

Ricard[132] and Ricard, Allenet, and Cie[133],[134] claimed to convert gaseous olefinic hydrocarbons as ethylene, propylene, and butylene, into liquid hydrocarbons by passage into a suspension of anhydrous aluminium chloride in gasoline or petroleum ether. In carrying out the process ethylene was circulated under a pressure of about three atmospheres through gasoline containing in suspension, 20 per cent of its weight of aluminium chloride.

b. *Boron Fluoride*

Otto,[123] polymerized ethylene to oils, claimed valuable as lubricants, by contact with boron fluoride under pressure. The reaction was carried out at temperatures up to 300° under an initial pressure of 130 atmospheres and using halide equal to 10 per cent by weight of the hydrocarbon. After eight hours the pressure had dropped to about 20 atmospheres, and the conversion to oil was as follows.

Temp., °C.	0	"Room Temp."	100	200	300
Oil, per cent by wt. of C_2H_4 treated.	10	85-95	37	60	73

Nickel deposited on the walls of the reaction bomb greatly accelerated the polymerization and increased the yield of oily products, while the presence of only 0.75 per cent of carbon monoxide almost completely prevented the formation of higher products. It was possible to make the process continuous by recovering the boron fluoride from the oil produced and using it repeatedly.

The oils resembled petroleum lubricating oils in viscosity, temperature coefficient of viscosity, and flash point. The viscosity decreased with increase in the temperature at which the oil was produced. Oils obtained in the presence of nickel were less viscous than those prepared with boron fluoride alone.

Hofmann[56] stated that to assist the action of the boron fluoride, besides nickel, traces of water, hydrogen fluoride, or Florida earth activated by the addition of hydrochloric acid were employed.

Hofmann, Otto, and Stegermann[58] patented the process of polymerizing ethylene by treatment with boron fluoride in the presence of water, hydrofluoric acid, hydriodic acid, ethyl fluoride, or ethyl chloride.

Hofmann and Otto[57] have also covered the polymerization of ethylene, propylene, and butylene to liquid products by boron fluoride, with or without the presence of finely divided metals under pressure at ordinary or elevated temperatures. As an example, twenty per cent of ethylene treated with boron fluoride at 70 atmospheres pressure was stated to have been polymerized in 12 hours, and in 3 to 4 hours when nickel was present on the walls of the reaction vessel.

The I. G. Farbenindustrie A.-G.[75] claimed to obtain 200 cc. of 2-butene per hour by passing liquid ethylene with 0.5-2 per cent of gaseous boron fluoride at a rate of 0.5 to 1 liter per hour of under pressure (amount not stated) through a tube containing one liter of a catalyst consisting of finely divided nickel on a carrier such as iron sponge, rings of refractory material, or burnt bauxite. It was said that up to one liter per hour of butylene was produced when the ethylene was saturated with water.

c. *Sodium*

Walker[151] found that in the presence of molten sodium at 150°, ethylene was polymerized to a colorless liquid. He stated that in the process the metal was changed into sodium ethylene carbide, which was inert toward ethylene. At 200° a similar polymerization occurred, accompanied by decomposition of the ethylene into acetylene, carbon, and hydrogen. At 400° to 550° a small amount of methane was produced.

d. *Zinc Chloride*

In the presence of zinc chloride Ipatiev and Rutala[60] found that ethylene began to polymerize at 275° under 70 atmospheres pressure. During 50 to 60 hours exposure the pressure decreased to 30 to 35 atmospheres. The residual gas consisted of 3.0 per cent hydrogen, 36 per cent olefins, and 61 per cent paraffins. A liquid reaction product resembling naphtha was obtained equivalent to 44 per cent of the ethylene treated. This liquid was reported to be a mixture of the same hydrocarbons as had been obtained without the catalyst, namely, pentane, hexane, heptane, octane, nonane, decane, undecane, dodecane, tridecane. tetradecane, hexylene, heptylene, octylene, nonylene, nona-, deca-, hendeca-, dodeca-, trideca-, tetradeca-, and pentadeca-naphthene.

Stanley[142] recently reported that under pressures up to 60 atmospheres in the presence of zinc chloride the polymerization of ethylene to liquid products took place at temperatures of 230° to 275°.

e. *Summary*

The substances which have been obtained from the action of chemicals upon ethylene are summarized by Tables XXXI and XXXII.

TABLE XXXI

Products Formed by the Action of Chemicals upon Ethylene

Temp., °C.	Chemical present	Products	Yields	References (by number)
100-150	$AlCl_3$	Butane	"Only gaseous product"	144
		Liquid paraffins, olefins, and naphthenes	*	
150	Sodium**	"Colorless oil"	"Small amount"	151
200	Sodium**	"Oil"	*	151
		Carbon	*	
		Hydrogen	*	
		Acetylene	*	
400-500	Sodium**	Carbon	*	151
		Hydrogen	*	
		Methane	*	

* The yield was not stated.

** Ethylene was passed over the sodium at atmospheric pressure.

Table XXXII

Thermal Decomposition of Ethylene

Products obtained under Superatmospheric Pressure with and without Chemicals

Temp., °C.	Chemical present	Initial pressure, atms.	Products	Yields, per cent by wt. of C_2H_4 treated	References (by number)
"Ordinary temp."	$AlCl_3$	70	Greenish oil contg. unsatd. H.C., paraffins b. below 200°, naphthenes b. above 200°	Not stated	80
0–20	$AlCl_3$	50–55	Oil contg. paraffins and naphthenes	Not stated	142
200	$AlCl_3$	70	Charred residue	Not stated	80
230–275	$ZnCl_2$	Up to 60	Liquid products	Not stated	142
275	$ZnCl_2$	70	Liquid product*	44	80
0	BF_3**	130	Lubricating oil	10	123
"Room temp."	BF_3**	130	Lubricating oil	85–95	123
100	BF_3**	130	Lubricating oil	37	123
200	BF_3**	130	Lubricating oil	60	123
300	BF_3**	130	Lubricating oil	73	123
325–350	None	Not stated	Liquid H.C.	Not stated	142
375	Al_2O_3	70	"Satd. H.C."	Main product***	79
			"Higher olefins"	Not stated	
			Polymethylenes	Not stated	
380–400	None	70	Solid and liquid H.C. contg. paraffins, olefins, and polymethylenes	Not stated	78,79

* The liquid product was reported to contain: pentane, hexane, heptane, octane, nonane, decane, undecane, dodecane, tridecane. tetradecane, hexylene, heptylene, octylene, nonylene, nona-, deca-, hendeca-, dodeca-, trideca-, tetradeca-, and pentadeca-naphthene.

** The action of the boron fluoride was said to be assisted by the presence of nickel, hydrogen fluoride, traces of water, or floridin activated by the addition of hydrochloric acid.

*** The fraction boiling above 280° was about twice as great as that obtained in the absence of the catalyst.

2. Propylene

a. *Aluminum Chloride*

When propylene was caused to react with anhydrous aluminum chloride at 100° to 150°, Szayna[144] observed the formation of a little propane, considerable butane, a liquid containing paraffin, olefin and naphthene hydrocarbons, and a metallo-organic addition product containing aluminum chloride.

b. *Boron Fluoride*

Butlerov and Goriainov[19, 47] stated that the polymerization of propylene in the presence of boron fluoride at ordinary temperature yielded only products more complex than a trimer.

Otto[123] reported that a viscous yellow oil formed by polymerization when propylene was treated under high pressure (amount not stated) at room temperature with 10 per cent by weight of boron fluoride. Under 15 mm. the oil produced began to boil at 120° and half distilled off up to 300°.

Hofmann, Otto, and Stegermann[58] covered in their patent the polymerization of damp propylene with boron fluoride, alone or in the presence of hydrofluoric acid.

c. *Floridin*

Lebedev and Filonenko,[90] in line with their generalizations already stated, found that propylene was unaffected by floridin, while iso butylene polymerized in its presence.

Following this Van Winkle[150] attempted to use this silicate to remove impurities, thought to be higher olefins, from propylene to be used for anesthetic purposes. He showed that although propylene was reported by Lebedev and Filonenko not to polymerize in the presence of activated floridin at atmospheric pressure, it did change in the presence of this silicate when the pressure was increased. After contact for two months, polymers were isolated which corresponded in boiling points to a dimer and a trimer. There was also a higher boiling residue. At the end of a year's contact of the propylene with the silicate, no dimer was present, and from fractional distillations and molecular weight determinations by the freezing point method in benzene, the products appeared to consist of a trimer, tetramer, and a high boiling residue believed to be composed of still higher polymers. Control cylinders of propylene containing no floridin showed no polymerization.

3. Iso butylene

a. *Aluminum Chloride*

Weizmann and Legg[163] claimed to produce naphthenic hydrocarbons from butene (said to be a mixture of 2- and 3-butene (?)) by liquifying the olefin and bringing the liquid into contact with anhydrous aluminum chloride or ferric chloride while the temperature was maintained at about −10°.

b. *Boron Fluoride*

Otto[123] found that iso butylene polymerized rapidly at its boiling point in the presence of 10 per cent by weight of boron fluoride, and produced a thick colorless oil of which about 50 per cent distilled between 200° and 300°. Butlerov and Gorianov[19,47] previously reported this polymerization to progress rapidly at ordinary temperature.

c. *Floridin*

Lebedev and Kobliansky[91] found that iso butylene polymerized readily, even at −80°, in the presence of floridin which had been activated by ignition at about 300°, and that the reaction went on more rapidly at room temperature. Passage of the olefin gas over the unheated catalyst caused a temperature rise to between 110° and 135°, followed by a drop. When the floridin temperature was raised to 200°, polymerization was slow, and at 290° the iso butylene was decomposed, with deposition of carbon on the catalyst.

Contact of the olefin in the liquid state with floridin for a number of days at room temperature gave products of which 4 per cent boiled below 170°, 25 per cent between 170° and 185°, and 71 per cent above 185°. By passing the iso butylene as gas and removing the polymers as rapidly as formed from further action of the floridin, the proportion of low boiling material was increased. The oil then produced contained, on the average, 18 per cent boiling below 170°, 51 per cent boiling between 170° and 185°, and a residue of 31 per cent boiling above 185°. This liquid was further fractionated, and upon the basis of boiling points, specific gravities, molecular refractions, and molecular weights, its composition was stated to be as follows:

	Per cent of total liquid	Boiling point, °C.	Specific gravity, d_4^{20}
Diisobutylene	17	101–2 at 762 mm.	0.7195
Triisobutylene	50	178.5–9.5 at 760 mm.	0.7600
Tetraisobutylene	17	106 at 7 mm.	0.7944
Pentaisobutylene	5	148 at 7 mm.	0.8176
Hexaisobutylene	1	158–61 at 2.5 mm.	0.8340
Heptaisobutylene	0.5	183–6 at 2 mm.	0.8455
High boiling residue	9.5		

The diisobutylene, which could be hydrogenated easily, slowly passed into tetraisobutylene when kept into contact with floridin. The triisobutylene, tetraisobutylene, and pentaisobutylene did not further polymerize in the presence of the silicate, and they could be hydrogenated only very slowly. From a mixture of di- and triisobutylene in the presence of floridin, pentaisobutylene appeared to be formed. The residue remaining after the separation of the individual polymers was colorless and very viscous. These investigators believed that there was little prospect of isolating higher polymers from it, since the temperature required for distillation even under greatly reduced pressure was sufficiently high to cause breakdown.

To determine how these polymers formed, the reverse reaction "depolymerization," was investigated, as it was supposed that a polymer would decompose entirely or in part into the smaller molecules from which it was formed. Depolymerization of the polymerized product from iso butylene was effected by distillation with floridin or preferably by passing the substance over a short layer of the earth in a glass tube heated at 175° to 200°. The pentamer decomposed into the dimer and trimer, the tetramer into two molecules of the dimer, the trimer into the monomer and dimer, and the dimer into two molecules of iso butylene. Certain amounts of iso butylene were formed in every case. Inherent experimental difficulties prevented these investigators from determining whether iso butylene was a primary depolymerization product of the higher polymers or resulted from progressive depolymerization of the dimer and trimer.

The depolymerization of the mixture of average molecular weight 840 obtained by distilling off the lower forms (including the heptamer) of the polymerized iso butylene gave a dissociation product containing over 30 per cent of the trimer.

From the summary (Table XXXIII) of results obtained from the different polymers under the same conditions of temperature, catalyst, and rate of flow of the polymers, it is evident that diisobutylene is the most stable of the polymers, and that the stability decreases rapidly with increasing molecular weight.

TABLE XXXIII

Depolymerization of Iso butylene Polymers by Passage through Glass Tubes containing Floridin at 200°

(Lebedev and Kobliansky)

Polymer treated	Per cent of polymer not decomposed	Depolymerization products obtained, per cent				Loss, per cent
		Monomer	Dimer, b.p. 101°-110	Trimer, b.p. 110°-180°	Higher boiling material	
Diisobutylene	78.5	8	—	4	—	9.5
Triisobutylene	40	10	37	—	3	10
Tetraisobutylene	21	11	53	—	—	15
Pentaisobutylene	0	9	43	35	—	15
Polyisobutylene	0	9	25.2	37.9	2.7	16.7

As has already been stated, Lebedev and Filonenko,[90] in an extensive investigation of the polymerizing action of Florida earth, activated by heating, on olefins, found that unsymetrical di- and trisubstituted ethylenes polymerized readily, at ordinary temperature, while mono-, symetrical di-, and tetra-substituted derivatives did not change even in two years. They found that polymers were formed when iso butylene and the other olefins given below remained in contact with the silicate during the periods of time listed:

	Time of contact, days
$CH_2{:}C(CH_3)_2$, iso butylene	30
$CH_2{:}C(CH_3)\,(C_2H_5)$, 2-methyl-1-butene	7
$CH_2{:}C(CH_3)\,(C_6H_5)$, 2-phenylpropene	9
$CH_2{:}C(C_6H_5)_2$, unsym-diphenylethylene	30
$CH_2{:}C(CH_3).CH_2.C(CH_3)_3$, 2,4,4-trimethyl-1-pentene	17
$CH_2{:}C(CH_3).CH{:}CH_2$, 2-methyl-1, 3-butadiene	10
$CH_2{:}C(CH_3)C(CH_3){:}CH_2$, 2,3-dimethyl-1,3-butadiene	10
$CH_2{:}C(CH_3).CH_2.CH_2C(CH_3){:}CH_2$, 2,5-dimethyl-1,5-hexadiene	20
$(CH_3)_2C{:}CH.CH_3$, trimethylethylene	7
$(CH_3)_2C{:}CH.C(CH_3)_3$, 2,4,4-trimethyl-2-pentene	10
$(CH_3)_2C{:}CH.CH{:}C(CH_3)_2$, 2,5-dimethyl-2,4-hexadiene	15

Van Winkle's[160] work was similar to that of Lebedev and Filonenko. By passing iso butylene at ordinary temperature through a cooled column of floridin he obtained "several liters" of polymers, which fractional distillation and molecular weight determinations indicated to contain a dimer, trimer, and tetramer, along with a residue considered to "contain several polymers of isobutylene higher than a tetramer." The cylinders containing the olefin and silicate were maintained under a "slight" pressure, which increased the rate of reaction.

4. Amylene

a. *Aluminum Chloride*

Aschan[1] found that the action of anhydrous aluminum chloride on amylene (b.p. 42°, prepared by Wurtz method of treating amyl alcohol of fermentation with 1.5 times its weight of coarsely powdered zinc chloride, and apparently trimethylethylene as may be inferred from recent data of Young and Lucas[157a]) at about 0° during a period of five weeks produced a mixture of saturated hydrocarbons. From fractions of this mixture boiling below 200° Aschan obtained a hexane corresponding in boiling point to 2,3-dimethylbutane or 2-methylpentane, a mixture of paraffins apparently decane, undecane, and dodecane, and two other hydrocarbons closely resembling methylcyclobutane and cyclohexane.

When pure trimethylethylene, of boiling point 37° to 39°, was used in these experiments, the 55° to 60° fraction of the product was thought to contain a branched chain hexane. The fraction 260° to 265° consisted mainly of naphthenes mixed with small quantities of pentadecanes. A hydrocarbon designated by the formula $C_{38}H_{66}$, boiling at 190° to 220° under 30 mm. pressure was obtained when the tarry residues of the fractionation were distilled under diminished pressure.

Commercial amylene (trimethylethylene) boiling at 37° to 38° which Engler and Routala[35] treated for five weeks at ordinary temperature with an equal weight of anhydrous aluminum chloride yielded a product from which the isolation of the following substances was reported: pentane, iso pentane, probably diisopropyl and ethylisobutyl, hexane, heptane, octane, and decane.

Similar results were obtained with trimethylethylene prepared by Wurtz method, and also with Kahlbaum's preparation produced by the dehydration of dimethylethylcarbinol with oxalic acid. Little, if any naphthenes were produced, as Aschan had shown previously. Later these investigators[38] obtained lubricating oils by the reaction of trimethylethylene and aluminum chloride at ordinary temperature.

By heating this amylene with aluminum chloride, under varied conditions, gases were formed, but the other products boiling up to about 200° consisted mainly of paraffin hydrocarbons.

b. *Floridin*

Gurvitsch[60] observed that when freshly distilled "amylene" (its boiling point 39.0°-40.5° and specific gravity 0.6654 at 17° indicated it to be trimethylethylene) was mixed with an equal weight of dehydrated floridin, polymerization occurred, accompanied by a considerable rise of temperature. In two hours, about 15 per cent of the hydrocarbon was converted into polymerized products boiling above 100°, and in two days conversion was about 85 per cent complete. The polymers consisted largely of a "diamylene," a product which could also be obtained by the action of sulfuric acid on amylene. Polymerization of amylene was also brought about by carbon and by alumina. In the latter case the development of heat was greater than with floridin.

Lebedev and Vinogradov-Volzynski[94] treated a mixture of trimethylethylene and methylethylethylene with floridin at room temperature. The gas consisted of 8.25 per cent of methane and 91.4 per cent of a mixture of iso butylene and 2-butene, with possibly a trace of propylene. The liquid products were reported to consist of iso pentane, iso propylethylene, trimethylethylene, 3-methyl-2-pentene (b.p. 67° to 69°), heptylene, octylene, and nonylene.

c. *Zinc Chloride*

Kondakov[85] stated that trimethylethylene gave a considerable quantity of diamylene when heated with zinc chloride at 70°.

5. Octene

Szayna[144] reported that the reaction of *n*-octene with aluminum chloride at 100° to 150° yielded butane and a liquid product composed of paraffins and naphthenes with a small proportion of unsaturated hydrocarbons.

6. Decene

Szayna[144] found that when allowed to react with aluminum chloride at 100° to 150° "diamylene" was converted into butane and a liquid fraction consisting of paraffins, naphthene hydrocarbons of high molecular weight, and small proportion of unsaturated.

7. Summary

The products which have been obtained by the action of chemicals upon olefins higher than ethylene are summarized by Table XXXIV.

TABLE XXXIV

Products formed by the Action of Chemicals upon the Olefins above Ethylene

Olefin treated	Temp., °C.	Chemicals	Products	Yields	References (by number)
Propylene	100–150	$AlCl_3$	Propane Butane A liquid contg. paraffin, olefin, and naphthene hydrocarbons	"A little" "Considerable" *	144
Propylene	"Ordinary temp."	Activated floridin[1]	A dimer and a trimer	*	150
Propylene	"Ordinary temp."	Activated floridin[2]	A trimer, tetramer, pentamer, and a high-boiling residue	*	150
Propylene	"Ordinary temp."	BF_3	Other products more complex than a trimer	*	19,47
Prcpylene	"Room temp."	BF_3 Under high pressure —amount not stated)	Viscous yellow oil	*	123
Iso butylene	-80	Floridin; vapor phase treatment	Polymers formed readily	*	91
Iso butylene	200	Floridin; vapor phase treatment	Polymers formed slowly	*	91

* The yield was not stated.

[1] Propylene was on contact with floridin for two months at "slightly increased pressure."

[2] Propylene was on contact with floridin for one year at "slightly increased pressure."

TABLE XXXIV (Continued)

Olefin treated	Temp., °C.	Chemicals	Products	Yields	References (by number)
Iso butylene	"Room temp."	Floridin; liquid phase treatment	Liquid products[3]	*	91
Iso butylene	"Room temp."	Floridin; vapor phase treatment	Liquid products[4]	*	91
			Diisobutylene	17%[5]	
			Triisobutylene	50%[5]	
			Tetraisobutylene	17%[5]	
			Pentaisobutylene	5%[5]	
			Hexaisobutylene	1%[5]	
			Heptaisobutylene	0.5%[5]	
			Higher boiling residue	9.5%[5]	
Iso butylene	"Ordinary temp."	Floridin; pressure slightly above atmosphere	Dimer, trimer, tetramer, and residue contg. higher polymers	*	150
Amylene	"Ordinary temp."	Floridin[6]	Liquid boiling above 100°, largely "diamylene"	15% of the amylene treated	50
Amylene	"Ordinary temp."	Floridin[7]	Liquid boiling above 100°, largely "diamylene"	85% of the amylene treated	50
Amylene[8]	"Room temp."	Floridin	Methane	8.2% of gaseous products	94
			Propylene	Trace	
			Iso butylene 2-Butene	91% of gaseous products	
			Liquid[9]	*	

* The yield was not stated.

[3] The liquids consisted of 4 per cent boiling below 170°, 25 per cent boiling between 170° and 185°, and 71 per cent boiling above 185°.

[4] The liquids consisted of 18 per cent boiling below 170°, 51 per cent boiling between 170° and 185°, and 31 per cent boiling above 185°.

[5] Per cent of the total liquid products.

[6] Amylene was in contact with floridin for two hours.

[7] Amylene was in contact with floridin for two days.

[8] The amylene used in this test was a mixture of trimethylethylene and methylethylethylene.

[9] This liquid was reported to consist of iso pentane, iso propylethylene, trimethylethylene, 3-methyl-2-pentene, heptylene, octylene, and nonylene.

TABLE XXXIV (Continued)

Olefin treated	Temp. °C.	Chemicals	Products	Yields	References (by number)
Trimethylethylene (from isopropyl alcohol)	0	$AlCl_3$	A hexane, apparently decane, undecane, and dodecane Methylcyclobutane (?) Cyclohexane (?)	* * *	1
Trimethylethylene (pure)	0	$AlCl_3$	A branched chain hexane Pentadecanes Naphthenes $C_{38}H_{66}$	* * * *	1
Trimethylethylene (commercial)	0	$AlCl_3$	Pentane Iso pentane Heptane Octane Decane	* * * * *	35
Trimethylethylene (commercial)	"Ordinary temp."	$AlCl_3$	Lubricating oils	*	38
	200	$AlCl_3$	Paraffin H.C. and gas	*	38
Trimethylethylene	70	$ZnCl_2$	Diamylene	*	85
Octene	100–150	$AlCl_3$	Butane Liquid composed of paraffin, unsatd., and naphthene H.C.	* *	144
"Diamylene"	100–150	$AlCl_3$	Butane Liquid composed of paraffin, unsatd., and naphthene H.C.	* *	144

* The yield was not stated.

IV. PHOTOSENSITIZED DECOMPOSITION

Several workers have reported that ethylene may be polymerized by ultra-violet light to liquid products. It has also been found that mercury atoms, excited by light of short wave length, cause polymerization, and the study of the photosensitized conversion of ethylene has been enlivened by discussion as to whether the workers on the action of light on ethylene did not, all unknowingly, employ excited atoms.

D. Berthelot and H. Gaudechon[4] stated that ethylene exposed to ultraviolet light polymerized to a waxy, rancid-odored liquid which boiled at about 100° and resembled octylene.

Similar results were obtained by Landau,[87] using light from a mercury lamp. Ethylene was changed to the extent of 85 per cent in 134 hours when using a 100-volt lamp, while with long exposure to a 500-volt mercury lamp, there was full conversion into higher boiling products.

When ethylene was exposed to mercury atoms, excited by light from a quartz mercury-vapor arc, Olson and Meyers[122] found that the pressure of confined ethylene increased approximately 25 per cent, and then dropped slowly.

Bates and Taylor[2, 145] reported that ethylene could be polymerized by the agency of excited mercury atoms, but was not changed by ultra-violet light alone. They attributed the results of Berthelot and Gaudechon to excitation of mercury, in the apparatus which they used, by the ultra-violet light, and the action of the excited mercury on the ethylene. Bates and Taylor found a pressure increase immediately upon exposure of the olefin to the excited mercury and believed that this was caused by the formation of hydrogen, acetylene, and a very small amount of saturated hydrocarbons.

Ethylene was also polymerized, these workers[3] reported, at 225° to 260° by exposure to light from a cadmium quartz lamp in the presence of cadmium vapor.

In a patent, Taylor[145] claimed that ethylene on exposure to the resonance radiation of a metal such as mercury polymerized at room temperature or temperatures even lower to a "heavy oily hydrocarbon." The resonance radiation from cadmium was also said to be effective for polymerizing ethylene, but in this case it was said to be necessary to carry out the reaction at about 250° in order to secure an acceptable concentration of cadmium vapor.

According to Mooney and Ludlam[114] light of wave length shorter than 210 $\mu\mu$ can cause the decomposition of ethylene to acetylene. They reported no other product. They found, contrary to the assertion of Bates and Taylor, that the presence of mercury vapor was not essential to decomposition.

Klemenc and Patat[84] also observed that acetylene and a volatile liquid product of petroleum-like odor were formed, but no smooth hydrogenation took place, when ethylene mixed with hydrogen was exposed to the radiation from a mercury-vapor lamp.

The ethylene was thought to be decomposed to hydrogen and acetylene, and the latter to polymerize to the volatile liquid. It is also possible, particularly since no analysis of the polymer was given, that the ethylene itself polymerized.

V. DECOMPOSITION BY ALPHA PARTICLES

From the small amount of study that has been made of the action of alpha particles on ethylene, it appears that they exert, like other sources of energy, both a decomposing and a condensing action. Mund and Koch[116] obtained liquid droplets with a petroleum-like odor when ethylene was exposed to radiation from radon, and also reported hydrogen and methane equivalent to about 10 per cent of the ethylene decomposed.

Lind, Bardwell, and Perry[98] by a similar method produced hydrogen, methane, a small amount of ethane, and a similar oil.

As mentioned in the section of this paper on the action of electrical discharge, Lind and Glockler[99] found that similar condensations of ethylene are produced by the ionization due to α-particles and by electrical discharge. These similar results "lead to the belief that they both are brought about by the same agency."

References

[1] Aschan: Ann., **324**, 1-39 (1902).

[2] Bates and Taylor: J. Am. Chem. Soc., **49**, 2438-56 (1927); cf. Taylor and Hill: **51**, 2922-36 (1929).

[3] Bates and Taylor: J. Am. Chem. Soc., **50**, 771-3 (1928).

[3a] Bayer and Co.: Brit. 15,254, June 25, 1910; J. Soc. Chem. Ind., **29**, 1215 (1910); Hofmann and Coutelle: Can. 143,942; 143,943, Oct. 22, 1912; Chem. Abs., **7**, 427 (1913); U. S. 1,069,951, Aug. 12, 1913; Chem. Abs., **7**, 3424 (1913).

[3b] Bayer and Co.: Brit. 17,734 (1910).

[4] D. Berthelot and H. Gaudechon: Compt. rend., **150**, 1169-72 (1910); **155**, 521-2 (1912); Rev. gen. sci., **22**, 330 (1911).

[5] M. Berthelot: Compt. rend., **50**, 805 (1860); **66**, 624 (1868); Ann. Chim. Phys., (3) **67**, 52 (1863); (4) **9**, 442 (1866); (4) **16**, 144 (1869); (5) **30**, 539 (1883); Bull., (2) **5**, 405 (1866); (2) **9**, 457 (1868).

[6] M. Barthelot: Ann. Chim. Phys., (4) **9**, 442-3 (1866); Bull., (2) **5**, 413 (1866).

[7] M. Berthelot: Compt. rend., **67**, 1188-90 (1868); Ann. Chim. Phys., (4) **18**, 156-162 (1869); Bull., (2) **11**, 442 (1869).

[8] M. Berthelot: Bull., (2) **11**, 4-35 (1869); Ann. Chim. Phys., (4) **20**, 519-20 (1870).

[9] M. Berthelot: Bull., (2) **26**, 103-4 (1876); Compt. rend., **82**, 1360-3 (1876); Ann. Chim. Phys., (5) **10**, 73 (1877); "Essai de Mécanique chimique," **2**, 379 (1879).

[10] M. Berthelot: Compt. rend., **126**, 567-75 (1898).

[11] M. Barthelot: Compt. rend., **129**, 74 (1899).

[12] M. Berthelot: Compt. rend., **129**, 490 (1899).

[13] M. Berthelot: Ann. Chim. Phys., (7) **16**, 31-41 (1899); "Les Carbures d'Hydrogène." **2**, 341-51 (1901).

[14] Bone and Coward: J. Chem. Soc., **93**, 1197-1225 (1908); Proc. Chem. Soc., **24**, 167 (1908); J. Gas Lighting, **103**, 319-26 (1908); J. Gasbel., **51**, 803-6, 828-31, (1908); Chem. News, **98**, 20 (1908).

[15] Bouchardat: Bull., (2) **24**, 108 (1875); Compt. rend., **80**, 1446 (1875).

[16] Bradley and Parr: Chem. Met. Eng., **27**, 737 (1922).

[17] Brooks: Chem. Reviews, **2**, 369 (1926), see pp. 370-1.

[18] Buff and Hofmann: Ann., **113**, 144-5 (1860).

[19] Butlerov: Ann., **189**, 44-83 (1877); Ber., **9**, 1605 (1876).

[20] Calingaert: J. Am. Chem. Soc., **45**, 134 (1923).

[21] Calingaert: Reference (64), p. 78.

[22] Cantelo: J. Phys. Chem., **31**, 124-30, 246-50 (1927).

[23] Collie: J. Chem. Soc., **87**, 1540 (1905); Proc. Chem. Soc., **21**, 201 (1905).

[24] Dalton and Henry: Phil. Trans., **99**, 446 (1809).

[25] Day: Am. Chem. J., **8**, 153-67 (1886).

[26] De Carolles: Compt. rend., **12**, 339 (1841).

[27] Deimann, van Troostwyk, Lauwerenburg, and Bondt: Ann. Chim. Phys., **21**, 58 (1797); Ann. Physik, **2**, 208 (1799).

[28] Dem'yanov and Pryanishnikov: J. Russ. Phys.-Chem. Soc., **58**, 462-73 (1926), Chem. Abs., **21**, 3344 (1927).

[29] De Wilde: Bull., (2) **6**, 267-8 (1866); Ber., **7**, 357 (1874); Bull. Acad. roy Belg., (2) **37**, I, 77-80 (1874); Bull., (2) **21**, 444 (1874).

[29a] Diels and Adler: Ann., **460**, 98, see 102 (1928).

[30] Egloff and Morrell: Ind. Eng. Chem., **22**, 1080 (1930).

[31] Egloff, Schaad, and Lowry: J. Phys. Chem., **34**, 1617 (1930).

[32] Engelder: J. Phys. Chem., **21**, 676-704 (1917).

[33] Engler and Eberle: Engler, "Neueren Ansichten über die Entstehung des Erdöles," p. 23, (1907).

[34] Engler and Rogowski: Engler, "Neueren Ansichten über die Entstehung des Erdöles,' p. 24 (1907); Routala, Diss., Karlsruhe, p. 49 (1909).

[35] Engler and Routala: Ber., **42**, 4613-20 (1909); Routala, Diss., Karlsruhe, pp. 24-48 (1909).

[36] Engler and Routala: Ber., **42**, 4620-31 (1909); Routala, Diss., Karlsruhe, pp. 49-74 (1909).

[37] Engler and Routala: Ber., **42**, 4628-31 (1909); Routala, Diss., Karlsruhe, pp. 77-84 (1909).

[38] Engler and Routala: Ber., **43**, 388 (1910); Routala, Diss., Karlsruhe, pp. 85-110 (1909).

[39] Epner: Brit. 294,099; 294,100, Conv. date, July 16, 1927. not yet accepted; Brit. 295,705, Conv. date, Aug. 18, 1927, not yet accepted.

[40] Francis and Kleinschmidt: Proc. Am. Petroleum Inst., **11**, Sect. III, 93-9 (1930).

[41] Frey and Smith: Ind. Eng. Chem., **20**, 948 (1928).

[42] Frolich, Simard, and White: Ind. Eng. Chem., **22**, 240 (1930).

[43] Gault and Altchidjian: Compt. rend., **178**, 2092 (1924); Ann. chim., (10) **2**, 209-68 (1924); Bull. Inst. Petrole Strasbourg, **1**, 419, 531-78 (1924); Mat. grasses, **16**, 7006 (1924); **17**, 7038, 7071 (1925); Chem. Abs., **19**, 1695 (1925).

[44] Gault and Bargmann: Ann. combustibles liquides. **1**, 77-142 (1926); Chem. Abs., **20**, 3685 (1926).

[45] Gault, Hessel, and Altchidjian: Compt. rend., **178**, 1562 (1924).

[46] Goldthorpe: Ann. combustibles liquides, **3**, 219-39 (1928).

[47] Gorianov and Butlerov: Ann., **169**, 147-9 (1873); Ber., **6**, 561 (1873).

[48] Gros: Brit. 211,125, Conv. date, Feb. 7, 1923; Ger. 434,831, Oct. 5, 1926.

[49] Grove: Phil. Mag., (3) **31**, 23 (1847).

[50] Gurvitsch: J. Russ. Phys.-Chem. Soc., **47**, 827-30 (1915); J. Chem. Soc., **108i**, 933 (1915).

[51] Haber: Ber., **29**, 2691 (1896).

[52] Haber and Oechelhäuser: J. Gasbel, **39**, 799, 805, 813, 830 (1896).

[53] Hague and Wheeler: J. Chem. Soc., **1929**, 390-1.; Fuel Science Practice, **8**, 560-87 (1929.)

[53a] Harries: Ann., **383**, 157-227 (1911); Chem. Abs., **5**, 3519 (1911).

[54] Hecht and Vauquelin: Ann. Physik Chem., **2**, 210 (1799).

[55] Heinemann: Brit. 21,772, Oct. 2, 1907.

[56] Hofmann: Petroleum Times, **23**, 508 (1930).

[56a] Hofmann, Coutelle, Delbrouck, and Meisenburg: U. S. 1,062,828; 1,062,914; 1,062,915, May 27, 1913; Chem. Abs., **7**, 2485 (1913).

[56b] Hofmann, Coutelle, Meisenburg, and Delbruck: U.S. 1,074,432, Sept. 30, 1913; Chem. Abs., **7**, 3849 (1913); Can. 143,489, Oct. 22, 1912; Chem. Abs., **7**, 426 (1913).

[57] Hofmann and Otto: Brit. 293,487, April 8, 1927; cf. Fr. 632,768, Chem. Abs., **22**, 3417 (1928).

[58] Hofmann, Otto, and Stegermann: Brit. 313,067, July 31, 1929.

[59] Hollings and Cobb: J. Gas Lighting, **126**, 924-8; Gas World, **60**, 879-83 (1914).

[60] Hugel: World Power Conference, 1930, J. Inst. Petroleum Tech., **16**, 390A (1930).

[61] Hugel and Artichevitch: Ann. combustibles liquides, **3**, 985-1027 (1928), Chimie et Industrie, **21**, 953 (1929).

[62] Hugel and Cohn: J. Inst. Petroleum Tech., **15**, 744-5 (1929); Chimie et Industrie, Special No. 201-2 (March 1930); Chem. Abs., **24**, 5714 (1930).

[63] Hugel and Goldthorpe: Ann. combustibles liquides, **3**, 613-47 (1928).

[63a] Hugel and Szayna: Ann. combustibles liquides, **1**, 781-836 (1926).

[64] Hurd: "Pyrolysis of Carbon Compounds," p. 83, (1929).

[64a] Hurd and Meinert: J. Am. Chem. Soc., **52**, 4978-90 (1930).

[64b] Hurd and Meinert: J. Am. Chem. Soc., **53**, 289 (1931).

[65] Hurd and Spence: Reference (64), p. 79; J. Am. Chem. Soc., **51**, 3561-72 (1929).

[66] Hurd and Spence: Reference (64), p. 77.

[67] Hurd and Spence: J. Am. Chem. Soc., **51**, 3353 (1929).

[68] Hurd and Spence: Reference (64), p. 85.

[69] I. G. Farbenindustrie A.-G.: Brit. 261,393, Conv. date (Germany) Nov. 12, 1925, Acc. April 11, 1928.

[70] I. G. Farbenindustrie A.-G.: Brit. 291,137, July 18, 1928.

[71] I. G. Farbenindustrie A.-G.: Brit. 309,199, May 29, 1929.

[72] I. G. Farbenindustrie A.-G.: Brit. 315,249, Sept. 4, 1929; Fr. 666,014, Dec. 18, 1928; Chem. Abs., **24**, 1304 (1930).

[73] I. G. Farbenindustrie A.G.: Brit. 316,422, July 13, 1928.

[74] I. G. Farbenindustrie A.-G.: Brit. 324,959, April 2, 1930; Brit. 325,207, April 9, 1930.

[75] I. G. Farbenindustrie A.-G.: Brit. 326,322, April 30, 1930.

[76] I. G. Farbenindustrie A.-G.: Fr. 666,611, Jan. 2, 1929; Chem. Abs., **24**, 1389 (1930).

[77] Ipatiev: Ber., **36**, 2003-4 (1903); J. Russ. Phys.-Chem. Soc., **34**, 839-42 (1902); Bull., (3) **30**, 1115-6 (1903).

[78] Ipatiev: J. Russ. Phys.-Chem. Soc., **38**, 63-75 (1906); Chem. Zentr., **1906**, II, 86; J. Chem. Soc., **92i**, 5(1907).

[79] Ipatiev: Ber., **44**, 2978-87 (1911); J. Russ. Phys.-Chem. Soc., **43**, 1420-30 (1912), Chem. Abs., **6**, 736 (1912); Chem. Zentr., **1911**, II, 1777.

[80] Ipatiev and Rutala: Ber., **46**, 1748 (1913); J. Russ. Phys.-Chem. Soc., **45**, 995-1003 (1913), Chem. Abs., **7**, 3972 (1913).

[81] Ipatiev and Sdsitovetsky: J. Russ. Phys.-Chem. Soc., **39**, 897-901 (1907), Chem. Abs.. **2**, 259 (1908).

[82] Jovitschitsch: Monatshefte, **29**, 1-14 (1908); Chem. Zentr., **1908**, I, 1153; Sitz. Akad. Wiss. Wien, **116IIb**, 1241-5, 1245-54 (1907).

[83] Jovitschitsch: Bull. Sci. Acad. roy. Belg., **13**, 365-70 (1927); Chem. Abs., **22**, 2114 (1928).

[84] Klemenc and Patat: Z. physik. Chem., Abt. B, **3**, 289-98 (1929).

[85] Kondakov: J. Russ. Phys.-Chem. Soc., **24**, 309-17 (1893); J. Chem. Soc., **64**, 382 (1893).

[86] Kusnetsov: Ber., **40**, 2871-3 (1907).

[87] Landau: Compt. rend., **155**, 402-6 (1912).

[88] Lebedev: J. Russ. Phys.-Chem. Soc., **42**, 949-61 (1910); J. Chem. Soc., **100i**, 26 (1911).

[89] Lebedev: J. Russ. Phys.-Chem. Soc., **43**, 820-34 (1911); J. Chem. Soc., **100i**, 774 (1911); Chem. Abs., **6**, 478 (1912); J. Russ. Phys.-Chem. Soc., **43**, 1735-9; Chem. Abs., **6**, 1373 (1912).

[90] Lebedev and Filonenko: Ber., **58B**, 163-8 (1925).

[91] Lebedev and Kobliansky: Ber., **63B**, 103-12, 1432-41 (1930); J. Russ. Phys.-Chem. Soc., **61**, 2175-87 (1929), Chem. Abs., **24**, 2423 (1930).

[92] Lebedev and in part with Mereshkovski: J. Russ. Phys.-Chem. Soc., **45**, 1249-1388 (1913); J. Chem. Soc., **104i**, 1285-93 (1913); Chem. Abs., **8**, 320 (1914); **9**, 799 (1915).

[93] Lebedev and Skavronskaya: J. Russ. Phys.-Chem. Soc., **43**, 1124-31 (1911); Chem. Abs., **6**, 855 (1912); J. Russ. Phys.-Chem. Soc., **45**, 1296-1331 (1913); J. Soc. Chem. Ind., **33**, 1224 (1915); Chem. Abs., **9**, 798 (1915).

[94] Lebedev and Vinogradov-Volzynski: J. Russ. Phys.-Chem. Soc., **60**, 41-52 (1928), Chem. Abs., **23**, 1384 (1929).

[95] Lewes: J. Soc. Chem. Ind., **11**, 586 (1892); J. Chem. Soc., **61**, 329 (1892); Proc. Roy. Soc., **55**, 90-107 (1894); Chem. News, **69**, 87, 103, 111, 125 (1894).

[96] Lewes: Proc. Roy. Soc., **57**, 394 (1895); Chem. News, **71**, 273, 286, 298 (1895).

[97] Lidov and Kusnetsov: J. Russ. Phys.-Chem. Soc., **37**, 940-3 (1905); J. Chem. Soc., **90ii**, 201 (1906); Chem. Zentr., **1906**, I, 329, Bull., (4) **2**, 1269 (1907); Chem. Ztg., **29**, 402 (1905).

[98] Lind, Bardwell, and Perry: J. Am. Chem. Soc., **48**, 1563 (1926).

[99] Lind and Glockler: J. Am. Chem. Soc., **52**, 4450-61 (1930).

[100] Losanitsch: Ber., **40**, 4664 (1907); **42**, 4394 (1909).

[101] Losanitsch: Sitz. Akad. Wiss. Wien, **117IIb**, 467-76 (1908); Monatshefte, **29**, 753-62 (1908).

[102] Losanitsch: Bull. Soc. stiin. Bucharest, **23**, 3-33 (1914); Chem. Abs., **11**, 254 (1917); Chem. Zentr., **1914**, II, 611-2.

[103] Losanitsch and Jovitschitsch: Ber., **30**, 135-9 (1897).

[104] Ludeking: Phil. Mag. (5). **33**, 521-40 (1892); Jahresber., **1892**, 439-40.

[105] Magnus: Ann. Physik, **90**, 1-11 (1853); Phil. Mag. (4), **6**, 420-7 (1853); Ann., **88**, 319 (1853).

[106] Mailhe: J. usines gaz., **54**, 289-92 (1930); Brennestoff-Chem., **11**, 441 (1930); Mailhe and Renaudie: Compt. rend., **191**, 265-7 (1930).

[107] Marchand: J. prakt. Chem., **26**, 478 (1842).

[108] Markowitsch and Pigulewski: Neft. Choz., **18**, 425-44, (1930); Chem. Zentr., **1930** II, 503-4.

[109] McKee and Szayna: Ind. Eng. Chem., **22**, 953-6 (1930).

[110] Meinert and Hurd: J. Am. Chem. Soc., **52**, 4540-9 (1930).
[111] Meyer and Altmayer: Ber., **40**, 2134 (1907).
[112] Mignonac and de Saint-Aunay: Compt. rend., **189**, 106 (1929).
[113] Miller: J. Chem. Soc., **17**, 85 (1864).
[114] Mooney and Ludlam: Trans. Faraday Soc., **25**, 442-5 (1929); Sci. Abs., **33A**, 224 (1930).
[115] Mund and Koch: Bull., **34**, 125, 241 (1925).
[116] Mylius and Hüttner: Z. anorg. Chem., **95**, 257-83 (1916).
[117] Nef: Ann., **318**, 24-5 (1901).
[118] Nellensteyn: J. Inst. Petroleum Tech., **10**, 311 (1924).
[119] Norris and Reuter: J. Am. Chem. Soc., **49**, 2624 (1927).
[120] Norton and Noyes: Am. Chem. J., **8**, 362-4 (1886).
[121] A. A. Noyes: Mass. Inst. Technology Quarterly, **1**, 278-81 (1888).
[122] Olson and Meyers: J. Am. Chem. Soc., **48**, 389-96 (1926); cf. **49**, 3131-4 (1927).
[122a] Ostromislensky and Koschelev: J. Russ. Phy.-Chem. Soc., **47**, 1928-31 (1915); J. Soc. Chem. Ind., **35**, 368 (1916).
[123] Otto: Brennstoff-Chem., **8**, 321-3 (1927).
[124] Paneth: Ber., **62B**, 1335 (1929).
[125] Pease: J. Am. Chem. Soc., **52**, 1158 (1920); cf. Pease and Chesebro: Proc. Nat. Acad. Sci., **14**, 472 (1928).
[126] Perkin, Weizmann, Matthews, and Strange: Brit. 5932, 1910; U.S. 991,453, May 2, 1911.
[127] Perkin, Weizmann, Matthews, and Strange: Brit. 9722, April 21, 1911.
[128] Prunier: Bull., **20**, 72 (1873).
[129] Pryanishnikov: Ber., **61B**, 1358 (1928).
[130] Quet: Compt. rend., **46**, 903 (1858).
[131] Ramage: U.S. 1,527,079, Feb. 17, 1925.
[132] Ricard: U.S. 1,745,028, Jan. 28, 1930.
[133] Ricard, Allenet, and Cie: Brit. 202,311, Conv. date (Belgium) Aug. 9, 1922, Acc. Nov. 10, 1924; Ger. 402,990, July 6, 1923, published Nov. 13, 1924.
[134] Ricard, Allenet, and Cie: Brit., 202,393, Conv. date (Belgium) Aug. 9, 1922, Acc. Nov. 10, 1924.
[135] Sabatier and Senderens: Compt. rend., **124**, 616, 1358 (1897); Ann. Chim. Phys. (8), **4**, 436-8 (1905).
[136] Sabatier and Senderens: Compt. rend., **131**, 267-9 (1900).
[137] Sabatier and Senderens: Compt. rend., **124**, 1128 (1897).
[138] Sabatier and Senderens: Ann. Chim. Phys. (8), **4**, 436 (1905).
[139] Simmersbach: Stahl Eisen, **33**, 242 (1913).
[140] Sinkinson: Ind. Eng. Chem., **17**, 30 (1925).
[141] Smolenski: Przemysl Chem., **11**, 146-82 (1927); Chem. Abs., **23**, 2929-30 (1929).
[142] Stanley: J. Soc. Chem. Ind., **49**, 349-54T (1930); Stanley and Bowen: Petroleum Times, **24**, 799-802 (1930).
[143] Staudinger, Endle, and Herold: Ber., **46**, 2466-77 (1913).
[144] Szayna: Przemysl Chem., **12**, 637-47 (1928), B.C.A.-B., **1929**, 117.
[145] Taylor and Bates: Proc. Nat. Acad. Sci., **12**, 714-7 (1926); Taylor: U.S. 1,746,168, Feb. 4, 1930.
[146] Taylor and Jones: J. Am. Chem. Soc., **52**, 1111-21 (1930).
[147] P. Thénard and A. Thénard: Compt. rend., **76**, 1508-14 (1873).
[147a] Tilden: J. Chem. Soc., **45**, 410, see 414 (1884).
[148] Trautz and Winkler: J. prakt. Chem., **104**, 53 (1922), J. Chem. Soc., **122i**, 926 (1922), Chem Abs., **17**, 722 (1923).
[149] Truchot: Compt. rend., **84**, 714-6 (1877).
[150] Van Winkle: J. Am. Pharm. Assocn., **17**, 544-7 (1928).
[151] Walker: J. Phys. Chem., **31**, 961-96 (1927).
[151a] Wallach: Ann. **227**, 295 (1885); J. Chem. Soc., **48i**, 550 (1885).
[152] Waterman and Tulleners: Brennstoff-Chem., **11**, 337-40 (1930).
[153] Weizmann and Legg: Brit. 165,452, March 7, 1916, Acc. July 7, 1921; Can. 203,408, Aug. 31, 1920; U.S. 1,395,620, Nov. 1, 1921.
[154] Wheeler: Chaleur et industrie, **9**, 160-1 (1928); Fuel Science Practice, **8**, 121-2 (1929).
[155] Wheeler and Wood: J. Chem. Soc., **1930**, 1819-28.
[156] Wöhler: Ber., **9**, 1713-5 (1876).
[157] Hague and Wheeler, J. Chem. Soc., **1929**, 391.
[157a] Young and Lucas: J. Am. Chem. Soc., **52**, 1964 (1930).
[158] Zanetti, Suydam, and Offner: J. Am. Chem. Soc., **44**, 2036-41 (1922).
[159] Zelinski and Levina: Ber., **62B**, 1861-3 (1929).

Universal Oil Products Company,
Research Laboratories,
Chicago, Illinois.

HOW TO RIPEN TIME*

BY WILDER D. BANCROFT

On the dedication of a Science Hall or of a scientific laboratory, it is customary to stress the importance of research in connection with teaching, because the teaching has to be done anyhow and the research is liable to be crowded out. I agree with everything that can be said in regard to the importance of research in connection with teaching; but I wish today to emphasize the importance of teaching in connection with research.

Most of us feel that we have done our duty when we get our research work brought to some sort of a conclusion and published. How it may strike the scientific or the lay world is not supposed to be of special interest to us. Such a position is not tenable in these days of the popularization of science; but research men may and do say that they are not interested in the popularization of science and that they do not believe in it.

I am therefore basing my argument on entirely different grounds. Each of us hopes to make important discoveries. Some of us will probably be successful. It is a matter of distinct importance to the world at large and to each of us individually that our important discovery should become useful at once and not be buried for fifty years or even for centuries.

The danger of an idea not being accepted is greater than most people realize. Leonardo da Vinci had in the fifteenth century what appears to us as a fairly clear idea of the phenomenon of combustion.[1] "The element of fire consumes continuously the air as concerns that portion which nourishes it, and there would be formed a vacuum, if other air did not come in to take its place."

This could easily be interpreted as meaning that air consists of two portions, one of which nourishes the flame. If what we call the oxidation product were not volatile—Leonardo da Vinci did not know about carbon dioxide—a partial vacuum would occur. It is by no means certain that this is exactly what Leonardo had in mind. It is very easy to read our knowledge into the other man's words. For instance, Spengler[2] says definitely and explicitly that Leonardo da Vinci discovered the circulation of the blood; but I doubt whether Dr. Welch would endorse that statement.

In 1630 Jean Rey[3] printed a treatise in which he accounted for the increase in weight when tin and lead are calcined on the ground that "this increase of weight comes from the air, which has been condensed, made heavy, and rendered somehow adhesive by the vehemence and long-continued heat of the

---

* Expanded from an address given at the dedication of the Science Hall of the University of Southern California, June 6, and published in "The Semicentennial Celebration of the Founding of the University of Southern California," 87 (1930).

[1] J. M. Stillman: "The Story of Early Chemistry," 408 (1924).

[2] "The Decline of the West," 1, 278 (1926).

[3] J. M. Stillman: "The Story of Early Chemistry," 408 (1924).

furnace, which air mixes with the calxes (frequent addition aiding) and attaches to their more minute parts, not otherwise than water makes sand heavy by moistening and adhering to the smallest of its grains."

"This theory of Rey's, of course, did not explain the function of the air as now known; but it was an approach to the truth, in so far as it recognized air as the contributing source of the increase of weight instead of fire material absorbed by the calx, which was the explanation offered by Boyle and Lémery nearly half a century later. Rey's work seems to have made no impression on his times. This is in part explained by very much in his treatise which shows a curious lack of understanding of elementary physics. His work was forgotten and his little book was extremely rare, when it was recovered from oblivion by Bayen in a communication to the Journal de Physique in 1775."

While there may be some question as to just how much Leonardo da Vinci and Jean Rey really knew about the composition of the air, Alexander Smith, in his presidential address before the American Chemical Society, claims that Mayow anticipated most of the later work.[1] "A hundred years before Priestley's time, Mayow (1669) had shown by conclusive experiments that atmospheric air was made up of two components, of which the active one formed twenty-five percent of the whole. In measuring the amount, he employed the same reaction subsequently used by Priestley, namely removal of the oxygen by the introduction of nitric oxide and absorption of the product in water. But, whereas Priestly was thereby estimating the 'goodness' of the air and had no idea that he was dealing with a mixture, Mayow was perfectly clear as to the interpretation of the results. The latter demonstrated that the same component was removed in combustion, by rusting metals, by the alcohol in vinegar-making, and by the blood in respiration. He traced the animal heat of the body to a process analogous to that which heated the mass when marcasite rusted in the air. He identified this active component of the air as a constituent of saltpeter, and particularly of the acid part of this substance, and (like Lavoisier more than a century later) held that it was contained in all acids. Finally, he considered it to be an element, in the modern sense of the word. Unfortunately, circumstances conspired to relegate to obscurity all his wonderful work and magnificently clear reasoning. Mayow was a young physician, and the divergent view-point of Boyle, as an older man and an eminent philosopher, received more attention. Again, the logical conclusiveness of Mayow's proof of the existence of oxygen as a distinct substance was entirely over the head of his contemporaries, and his way of thinking quite out of harmony with theirs. In this point of view he came a century and a half too soon. Such a proof, if offered today, would be accepted as conclusive. The final isolation of the element would now be considered a matter of mere routine that would be assigned to a beginner in research, as the basis of his dissertation for the degree of doctor of philosophy. Finally, the clouds of the phlogistic theory soon began to darken the sky of science, and before long the spread of this remarkable notion, diligently

---

[1] Stillman is a bit more cautious. "The Story of Early Chemistry," 416 (1924).

fostered by Stahl, who had been born nine years before the appearance of Mayow's work, enveloped chemistry and the whole chemical world in an impenetrable fog. Since the believers in phlogiston started always with one absurd idea as the major premise, namely, that in combustion and oxidation some kind of matter *left* the burning or rusting material, the more rigorous the logic of the subsequent steps in the reasoning, the more certain was the attainment of uniformly false conclusions. The inveterate phlogistian, and everybody down to the time of Lavoisier, not excluding Priestley and Scheele, was forthwith an inveterate phlogistian, saw in simple, almost modern, modes of thought like those of Mayow only the sheerest nonsense. If we all stood habitually on our heads, naturally anyone caught persisting in a tendency to view the universe in the normal way would be instantly judged insane. For these various reasons, Mayow's work was first neglected and then forgotten."

An extraordinary case of a great man, whose work had apparently no influence, was that of Michael Wassiliewitsch Lomonossoff.[1] "He lived from 1711 to 1765. He thus was educated, did his life-work and died in the most virulent period of the phlogistic epidemic. Heat, light, and weight were then forms of matter, yet, when he notices them at all, he combats these views and makes experiments to disprove them. In a day when the jargon of the phlogistian was the only language of polite intercourse among chemists, he speaks and writes the language of modern chemistry—of the most modern chemistry, for he was a physical chemist. Needless to say, he lived at a time far removed from the psychological moment for a man holding such a view-point. Naturally, credit for his discoveries, and they were many, has all been distributed among others. It is quite likely that some of you have never happened to hear his name—the name of Michael Wassiliewitsch Lomonossoff.

"Even in Russia, although his work in literary and linguistic lines, his success as a man of affairs, and his investigations as a geographer and a meteorologist has won for him enduring fame, the fact that he was primarily a chemist had been completely forgotten. It was Menschutkin who, a few years ago, rediscovered him as a chemist, reprinted in Russian his scattered memoirs, and collected all that could be found of his manuscripts, letters, and laboratory note-books.

"Although trained—chiefly in Germany—by, and along with, men who ardently supported the current views, he seems to have thrown off the prejudices of his contemporaries with astonishing ease, and to have achieved a perfectly independent view-point of his own. At that time, the emission of light-matter explained the phenomena of light. Largely through the enormous influence of Newton's selection of the emission theory in preference to the wave theory (first developed by Huyghens in 1690), this remained the accepted explanation until, after a hard struggle against the influence of Laplace (1817) and others, who were unconvinced with the explanation of the phenomenon of polarization by Fresnel, the ether-wave theory finally triumphed. But Lomonossoff discusses (1753-56) the possible motions of ether—progres-

---

[1] Alexander Smith: J. Am. Chem. Soc., **34**, 112 (1912).

sive, rotatory, and wave-like—identifies the last as the basis of light, and goes in great detail into the nature of ether and the properties of light-waves and the anode of their propagation.

"In Lomonossoff's day, heat was also a form of matter. The classical experiment of Rumford was made (1798) thirty years after his death. But so strong was the prejudice that, even then, the proof (by qualitative experiments) that heat could be generated without limit from friction, under conditions such that the addition of any substance or form of matter was impossible did not carry conviction. Lavoisier believed (with some hesitation it is true) in an imponderable *matière de chaleur*. It was not until after the work of Mayer (1842), who was at first persecuted for his views, and especially after the demonstration by Joule (1855-60) that heat and work were mutually and quantitatively interconvertible, that the theory that heat was matter finally disappeared, yet Lomonossoff, more than a century earlier (1744-47), in a paper on "The Causes of Heat and Cold," discusses in detail the experimental evidence that motion is a source of heat, and that molecular motions are caused by heating. Radiant heat, of which then little was known, was transmitted by motions of the ether, which he believed to be of the rotatory variety. In all his papers, heat is always a mode of motion. The paper named was the subject of vigorous discussion, particularly in Germany, and, after the views contained in it had been sufficiently abused, they were consigned to oblivion.

"The kinetic molecular theory of gases used to be attributed to Krönig (1856) and Clausius (1857). But Lord Rayleigh discovered in the archives of the Royal Society a very complete form of it, contributed by Waterston in 1845. The state of public opinion among physicists, even then, a century after Lomonossoff's work, may be judged from the fact that the committee of the Society considered the content of the paper to be nonsensical, and refused to permit its public presentation. Lomonossoff's paper, read before the Academy of St. Petersburg in 1744, nearly suffered the same fate, for it was withheld from publication for three years. Starting with the view of Daniel Bernoulli (1738) to the effect that the pressure of gases was due to the impacts of their particles, Lomonossoff proceeded to develop ideas very much like those now held. According to him, for example, a rise in temperature caused increased motion of the particles, and resulted therefore in increased pressure. His theory differs from ours mainly in the fact that rotatory motions played a large part, and that the molecules had rough surfaces. Incidentally he points out that there is no limit to the possible amount of motion, and therefore no maximum of temperature; but that there a minimum of motion, when the latter becomes zero, and there must therefore be a minimum of temperature. In a later paper (1750) he proves by his hypothesis that the pressure *should* be, as it was then known to be, inversely proportional to the volume. And he goes further, for, with surprising insight, he shows that with increasing pressure, this relation will no longer hold, since the volumes of the particles themselves are not diminished. The reputed discoverer of this consequence of the theory is Dupré (who was thus anticipated by 115 years), and in 1873 van der Waals finally put the same fact into definite form. . . .

"Up to the end of the eighteenth century, there was utter confusion of thought in regard to the composition of materials. In considering the make-up of a specimen and the changes occurring during an experiment, heat-matter, light-matter, and weight-matter, as well as phlogiston were taken into account. As we have seen, even Scheele interpreted the phenomena he observed upon the theory that heat was an oxide of phlogiston. The composition was often stated in terms of salt, sulphur, and mercury, whether there was evidence of their presence or not. The 'elements' of Aristotle, and cognate ideas, were used in describing and in thinking about chemical phenomena. In consequence, Priestley thought he had a method of measuring the 'goodness' of air—as a quality—when in point of fact he was measuring the amount of oxygen as a component. With the basal conceptions thus in a state of utter chaos, it is no wonder that the simplest chemical situations were wholly misunderstood, and that the simplest experimental results, being described in terms of non-existent entities, and thought of in terms of non-existent relations, failed of their object. It was Lavoisier who received credit for setting our ideas permanently in order, by his emphasis upon the significance of the evidence of the balance, and by his setting forth clearly the idea of chemical compounds and their component elementary substances, and by giving a classified list of the latter.

"The chemical reformation might have come half a century sooner, however, if Lomonossoff's papers had been more widely known. As we have seen, to him heat and light were not forms of matter and phlogiston had no existence. His forms of matter were the same as ours, and his ideas of chemical composition, what it included and what it excluded, the same as ours. . . . In the paper on "Heat and Cold" (1744-47) he refers to Boyle's experiment, in which lead was sealed up in a retort and heated, when the lead and calx, upon removal, were found to have increased in weight. According to Boyle, this result showed that the heat, which alone could enter through the glass, had weight. Lomonossoff, of course, will not accept this conclusion and points out that the increase in weight of metals when heated in air must be due to union with material from the air, just as their increase in weight when placed in the flame of burning sulphur is due to union with 'acid' from the sulphur. Later, in 1756, he repeats Boyle's experiment, and finds that an increase in weight is observable when the retort is opened and air rushes in. He thus performed one of Lavoisier's most fundamental and convincing experiments eighteen years in advance, and interpreted it correctly. It is apparent that Lomonossoff's sound views were based upon many quantitative experiments on combustion, although the laboratory note-books containing the details have not yet been found."

Berthoud[1] points out that "already in the seventeenth century such thinkers as Bacon and Descartes realised that heat must be a movement of

---

[1] "The New Theories of Matter and the Atom," 23 (1924).

the ultimate particles of bodies. This idea was revived, and was developed in a way very remarkable for that date (1738) by Daniel Bernoulli. He was the first to conceive the idea that the molecules of a gas are in rapid motion, the speed of their movement increasing with the temperature; and he supposed that the pressure which a gas exercises upon the walls of the container is due to the multiple concussions of these particles. Bernoulli was even able to show that Boyle and Mariotte's law could be deduced from this hypothesis. Here is a precise formulation of the fundamental principles of the kinetic theory of gases, and the only reasonable application of the ancient doctrine of atoms to the interpretation of an experimental law. But the ideas came before their time, and were ignored. Indeed, they had been completely forgotten when, a century later, they sprang to life once more in the mind of Joule."

In 1842 J. R. Mayer published his calculation of the mechanical equivalent of heat and in 1845 he wrote a pamphlet on the subject; but it was not until about 1847 that anybody became interested in his work, and then chiefly because of the publications of Joule and of Helmholtz. It was six years before much of any attention was paid to the work of Joule.[1]

"That the obscure and scattered manner in which Joule's papers were published must have hindered his work from becoming as well known as it might otherwise have been is certain; but the fact that it called forth no comment does not show that it was not read, or if read was rejected. Two of the most important of his papers were read at the British Association and with several others published in full in the *Philosophical Magazine*. These were doubtless heard or read, and the complete silence with which they were received shows not that they were rejected, but that the views they contained were so much in advance of anything accepted at this time that no one had sufficient confidence in his own opinion or was sufficiently sure of apprehending the full significance of the discoveries on which these views were based, to venture an expression of acceptance or rejection. The 'angels feared to tread,' and perhaps the most remarkable thing is that in this case there were no fools. The position, however, is not without ample precedent besides that of Kepler. And although Joule, compelled against his will to remain the only individual in the world possessing the knowledge of and realizing the significance of this fundamental law of the universe, was, as he says, very anxious to convince the scientific world of the truth of the positions he maintained, he was in no way discouraged by the silence in which his papers were received, though this silence remained unbroken for six more years."

Nowadays all students in the introductory course in chemistry are taught Avogadro's law that equal volumes of gases at the same temperature and pressure contain equal numbers of molecules. While this law was formulated by Avogadro in 1813, it was over forty years before trained chemists really understood it and believed in it.[2] "It might have been expected that Avo-

---

[1] Osborne Reynolds: "Memoirs of James Prescott Joule," 77 (1892).

[2] Berthoud: "The New Theories of Matter and the Atom," 22 (1924).

gadro's hypothesis would have been well received. This was far from being the case. Dalton failed completely to recognise the support it could give to his own theories, and he opposed strenuously, not only Avogadro's hypothesis, but also the law of gaseous volumes. It seemed to him that the distinction between the atom and the molecule of a simple gas was a needness complication. Besides, there are some apparent exceptions to the laws of volumes, and chemists were loath to build up their theories upon a foundation which seemed to them unduly hypothetical. Renouncing the use of an instrument which, though it was not by itself competent to solve all the enigmas of the molecular structure of bodies, could nevertheless have done yeoman service in this direction, they sought for other methods."

Duhem has shown[1] that Georges Aimé anticipated by about thirty years the classical work of Sainte-Claire Deville on dissociation pressure. "Among the writings of Georges Aimé there is one which would have secured his fame if the ideas which it contains had been understood when they were published; we refer to his researches on the influence of pressure upon chemical reactions. The thesis of Georges Aimé indeed shows clearly that he had arrived at the notion of dissociation thirty years before Debray by his experiments established its existence. . . . H. Sainte-Claire Deville and H. Debray never knew of the discoveries of Georges Aimé concerning the influence of pressure upon chemical reactions; if they had, with their scrupulous honesty, they would not have failed to have mentioned them. Their ignorance is in no way surprising. When they took up the study of dissociation, Aimé's thesis, the only place in which these ideas had been recorded, had doubtless become very rare, and no voice was raised in support of the claims of their author, long since dead."

Smee[2] comments as follows on Ohm's law, one of the relatively few absolutely accurate laws. "Ohm, in an elaborate and obscurely worded paper, has given the mathematical formula for the galvanic current. . . . The value of this formula would have been appreciated long since, had he not discarded the terms quantity and intensity, but modeled them to suit his new views. Had he restricted the term quantity to the amount of electricity passing at each point, and intensity to the power which that had of overcoming obstacles, in which sense I shall use these terms throughout this work, then would his doctrines have immediately had their due weight amongst scientific men, instead of requiring years slowly but surely to work their way."

People have considered the prediction of isotopes[3] as a case of an idea that fell flat; but this is not correct. "I have said that the original *protyle* contained within itself the potentiality of all possible atomic weights. It may well be questioned whether there is an absolute uniformity in the mass of every ultimate atom of the same chemical element. Probably our atomic weights merely represent a mean value around which the actual atomic

---

[1] J. Phys. Chem., 3, 364 (1899).

[2] "Elements of Electrometallurgy," 11 (1843).

[3] Crookes: Report Brit. Ass. Adv. Sci., 1887, 569.

weights of the atoms vary within certain narrow limits. Each well-defined element represents a platform of stability connected by ladders of unstable bodies. In the first accreting together of the primitive stuff, the smallest atoms would form, then these would join together to form larger groups, the gulf across from one stage to another would gradually be bridged over, and the stable element appropriate to that stage would absorb, as it were, the unstable rungs of the ladder which led up to it. I conceive, therefore, that when we say the atomic weight of, for instance, calcium is 40, we really express the fact that, while the majority of calcium atoms have an actual atomic weight of 40, there are not a few which are represented by 39 or 41, a less number by 38 or 42, and so on. We are here reminded of Newton's 'old worn particles.' Is it not possible, or even feasible, that these heavier and lighter atoms have been subsequently sorted out in some cases by a process resembling chemical fractionation? This sorting out may have taken place in part while atomic matter was condensing from the primal state of intense ignition, but also it may have been partly effected in geological ages by successive solutions and reprecipitations of the various earths."

This was a very brilliant and fairly accurate guess; but it was only a guess, because there were at that time no experiments to confirm the guess and no method of testing it.

The usual way of accounting for good ideas falling flat is to say that the time was not ripe for them. Lecky[1] says that "the history of the Cabalists furnished, I think, a striking instance of the aberrations of a spirit of free thinking in an age which was not yet ripe for its reception."

James Walker[2] writes: "Although Avogadro published his hypothesis in 1811, the times were not ripe for it; and it was only in the fifties that its application became at all general."

Speaking of Lomonossoff, Alexander Smith[3] says: "Had only the times been ripe, had only the atmosphere been healthy for the propagation of such ideas as his, instead of being virulently poisonous to them, our science might easily, by now, have been a hundred years ahead of its present position, and we might today have been listening to papers which as it is, will not be read for a century. If Dante's *Divina Commedia* were to be revised by a chemist and brought up to date, the chief change he would make would be the provision of some horrible and revolting torment, calculated to give Stahl his just deserts."

If we accept the phrase, the problem becomes how can we ripen time or how can we present a new idea so that it will be accepted promptly? This is important both to the individual and to science. It has been discussed by James Harvey Robinson;[4] but what he has to say is not helpful at all.

"Those to whom the commonplace and ordinary appear to be startling and extraordinary are very rare, but they are very precious, since they, and

---

[1] Lecky: History of Rationalism, 67.

[2] "Introduction to Physical Chemistry," 12 (1909).

[3] J. Am. Chem. Soc., 34, 118 (1912).

[4] "The Humanizing of Knowledge," 25 (1926).

they alone, have built up our minds. It is they who for thousands of years have been gradually enriching human thought and widening the gap that separates man from his animal relations. Without them the mind as we know it would never have come into existence. They are the creators of human intelligence. The mass of mankind must perforce wait for some specially wide-eyed individual to point out to them what they have hitherto accepted as a matter of routine or failed altogether to notice.

"These mind-makers are the questioners and seers. We classify them roughly as poets, prophets, moralists, story-tellers, philosophers, theologians, artists, scientists, inventors. They all are discoverers and pointers-out. What eludes the attention of others catches theirs. They form the noble band of wonderers. Things commonly unnoticed excite a strange and compelling curiosity in them, and each new question sets them on a fresh quest. They see where others are blind, they hear where others are deaf. They point out profundities, complexities, involutions, analogies, differences and dependencies where everything had seemed as plain as a pike staff.

"In short, poets, philosophers, religious geniuses, artists, and scientists are all rare variants of the human species, who emerge here and there through the ages. Sometimes they make a wide appeal to their fellow men; often they stir their resentment or horror; most frequently they suffer neglect and contempt. A discovery to which no one listens is obviously of little or no importance. It is a mere private gratification which concerns only the discoverer himself. So the great question arises as to what determines the *success* of a new idea; what establishes its currency and gives it a social significance by securing its victory over ignorance and indifference or over older rival and conflicting beliefs?

"To be received by the multitude of non-discoverers an idea must obviously be *acceptable* to them in some way or other. And what are the kinds of acceptability which promote the wide dissemination and the firm and prolonged tenure of beliefs? This is one of the most fundamental of all questions involved in human progress and at the same time one of the most difficult to answer. Indeed I scarcely think that anyone is in a position as yet to answer it."

George Santayana[1] is more concise and more interesting. "All living souls welcome what they are ready to cope with; all else they ignore or pronounce to be monstrous and wrong, or deny to be possible.

As might have been expected, Ostwald[2] has discussed this question at considerable length. "When the prospective genius has done his great work and has communicated it to the world, one likes to think that he can go quietly to bed and wake up famous the next morning. There are one or two cases in which that is about what has happened, as in the case of Darwin, whose fundamental book was sold out within a few weeks of its appearance. This is a very rare case, however, and belongs rather in a class by itself, be-

---

[1] "Dialogues in Limbo," 62 (1926).

[2] "Grosse Männer," 366 (1909).

cause it was a piece of work which had been going on for years and which was written up because of the external reason that Wallace had reached the same general conclusion. Also, the world was to some extent ready for it.

"In the overwhelming majority of cases, the earth continues to revolve at its normal rate even when the most startling thought has been put forward, and very often the work of getting the new idea accepted is scarcely less than that of originating it. In many cases the man who had the idea is not able to get it accepted and this task falls to the lot of another man who may be less clever, but who speaks a language which makes the world conscious of the treasure which had been offered to it in obscure words.

"The judging of the value of a new advance is more difficult, the more considerable the advance. If one thinks how easily and how definitely one can evaluate an idea coming from a well-known person and standing in obvious relation to previously known generalizations, one sees what difficulties will confront a new idea which is not vouched for in this way. We have already seen that we are often dealing with a young and unknown man, whom we are inclined to distrust because of the superstition that the quality of a man's work improves as he grows older. If one keeps in mind the unceasing stream of scientific nonsense which pours into the literary markets from all sorts of amateurs and crazy people; if one keeps in mind that the young man, probably from lack of practical experience, often does not choose the best possible way of presenting his idea, one sees that the important new idea is so blocked by stones and thorns, that it is not so surprising that its value is often overlooked. We ought therefore to recognize that ideas which will be highly prized later, often have a hard time in getting accepted, and we ought to train ourselves to recognize a brilliant idea when we see it.

"Actually the acceptance of a great discovery depends entirely upon the way in which the scientific and lay publics have been prepared to understand it. If the new discovery has some surprising feature which brings it in sharp contradiction with ordinary views or phenomena, it may count on a quick acceptance. Thus the extraordinarily rapid spread of the knowledge of X-rays was due to the fact that it made visible what had hitherto been invisible. What was new in the result—not what was new in the method—was sufficiently clear to the ordinary newspaper reader to excite his interest. Since it dealt with experimental results, there was no chance for some of the normal, adverse criticism. In the same way the discovery by Hertz of the similarity of his electrical oscillations and of light was grasped readily, because the undulatory theory of light was more or less familiar to everybody and because Maxwell's electromagnetic theory of light had made the result plausible.

"On the other hand, the discovery of the Phase Rule by Gibbs produced no effect for ten years and then made progress slowly only through the efforts of several other investigators. Here it was not a question of a new experiment but of a new way of looking at well-known facts. In addition, the new point of view was so strange that those who wished to adopt it pretty nearly had to distort certain parts of their brain in order to get the concept in. It consequently took a good while to get people so familiar with the phase rule that they could use it as an instrument of research. And yet this discovery was quite as important scientifically as the others which have been mentioned.

"Much the same thing happened with respect to the law of the conservation of energy. Joule made progress much more easily than Mayer because he made experiments and his apparatus was easily understood, while Mayer's acute discussion of the ratio of the specific heats of gases, though just as convincing, called for a fairly profound knowledge which was not to be found in the general public. Perhaps the most striking case of the disadvantage of purely mental work which establishes relations between sets of facts without accompanying it with experiments is to be found in Faraday's concept of lines of force. We have already seen how obstinately Faraday's theoretical views were rejected by the same men who were enthusiastic over his experimental results. The same situation crops up in the continual warnings of Liebig to his pupil Gerhardt to keep clear of theoretical papers (Liebig had quarreled with Berzelius solely on account of their differing theoretical views).

"The reason for this fundamental behavior towards theory and experiment is nervousness. The novelty of an experiment is easy enough for anybody to see who is familiar with the subject, and the unexpectedness and strikingness of the experiment gives an approximate, though sometimes deceptive, measure of its importance. The correctness and usefulness of a new idea is much harder to determine, and if it comes in conflict with any self-evident propositions—meaning assumptions which one does not test—its fate is sealed for the time being. In addition there is a peculiar psychological reaction. One is not envious of a brilliant new experiment because it often involves apparatus which few have available and consequently one does not reproach oneself for not having done it oneself. To bring forth a striking thought is a matter which almost anybody interested in that line of work believes himself capable of doing, and consequently he is a bit grieved that somebody else had the good idea. Consequently many people feel envious over a theoretical discovery and consequently are prejudiced against accepting it. These antagonisms may take the form of showing that the new idea is scientifically untenable. If not, there is a passive resistance to acceptance and the new idea finds general adoption only when those who believe in it have achieved obvious and distinct successes by means of it.

"For this reason the discoverer, who supplements his purely theoretical ideas by experiments, invariably gets his ideas accepted more rapidly than the man who does not. Helmholtz would probably have had to wait decades for recognition, just as Mayer did, if his discovery of the ophthalmoscope had not demonstrated his ability to a large number of people. I do not have to complain of lack of appreciation of what I have been fortunate to do in the field of general chemistry; but the purely mental feat of recognizing catalytic phenomena as acceleration of existing and occurring reactions, a conception which opened the enormous field of catalysis to exact measurement, was so far outside the ordinary scientific thinking that it is still, after two decades, in the incubation stage so far as many investigators are concerned. Presumably this progress will eventually become so much an integral part of scientific thought that the resistance to it will disappear, and I shall receive the share of praise to which I am personally entitled for what I have done in developing this point of view."

We shall find more that is helpful to us in a book by Gustave LeBon[1] even though he is nominally discussing crowds and not groups of scientific men. Actually, the two have a good deal in common, because the scientific men form a specialized or scientific crowd. It is time in particular that prepares the opinions and beliefs of crowds, or at least the soil on which they will germinate. That is why certain ideas are realizable at one epoch and not at another. "It is time that accumulates that immense detritus of beliefs and thoughts on which the ideas of a given period spring up. They do not grow at hazard and by chance; the roots of each of them strike down into a long past. . . .

"When, however, it is proposed to imbue the mind of a crowd with ideas and beliefs—with modern social theories, for instance—the leaders have recourse to different expedients. The principal of them are three in number and clearly defined—affirmation, repetition, and contagion. Their action is somewhat slow, but its effects, once produced, are very lasting.

"Affirmation pure and simple, kept free of all reasoning and all proof, is one of the surest means of making an idea enter the mind of crowds. The conciser an affirmation is, the more destitute of every appearance of proof and demonstration, the more weight it carries. The religious books and the legal codes of all ages have always resorted to simple affirmation. Statesmen called upon to defend a political cause, and commercial men pushing the sale of their products by means of advertising are acquainted with the value of affirmation.

"Affirmation, however, has no real influence unless it be constantly repeated, and so far as possible in the same terms. It was Napoleon, I believe, who said that there is only one figure in rhetoric of serious importance, namely repetition. The thing affirmed comes by repetition to fix itself in the mind in such a way that it is accepted in the end as a demonstrated truth.

"The influence of repetition on crowds is comprehensible when the power is seen which it exercises on the most enlightened minds. This power is due to the fact that the repeated statement is embedded in the long run in those profound regions of our unconscious selves in which the motives of our actions are forged. At the end of a certain time we have forgotten who is the author of the repeated assertion, and we finish by believing it. To this circumstance is due the astonishing power of advertisements. When we have read a hundred, a thousand, times that X's chocolate is the best, we imagine we have heard it said in many quarters, and we end by acquiring the certitude that such is the fact. When we have read a thousand times that Y's flour cured the most illustrious persons of the most obstinate maladies, we are tempted

---

[1] "The Crowd," 77, 126, 136 (1896). He does not distinguish, as most psychologists would, between 'catching attention' and 'convincing.'

at last to try it when suffering from an illness of a similar kind. If we always read in the same papers that A is an arrant scamp and B a most honest man we finish by being convinced that this is the truth, unless, indeed, we are given to reading another paper of the contrary opinion, in which the two qualifications are reversed. Affirmation and repetition are alone powerful enough to combat each other."

The leaders of crowds often owe their position to personal prestige. "Its nature is very different from that of artificial or acquired prestige, with which I have just been concerned. It is a faculty independent of all titles, of all authority, and possessed by a small number of persons whom it enables to exercise a veritably magnetic fascination on those around them, although they are socially their equals, and lack all ordinary means of domination. They force the acceptance of their ideas and sentiments on those about them, and they are obeyed as is the tamer of wild beasts by the animal that could easily devour him.

"The great leaders of crowds, such as Buddha, Jesus, Mahomet, Joan of Arc, and Napoleon, have possessed this form of prestige in a high degree, and to this endowment is more particularly due the position they attained. Gods, heroes, and dogmas win their way in the world of their own inward strength. They are not to be discussed: they disappear, indeed, as soon as discussed.

"The great personages I have just cited were in possession of their power of fascination long before they became illustrious, and would never have become so without it. It is evident, for instance, that Napoleon at the zenith of his glory enjoyed an immense prestige by the mere fact of his power, but he was already endowed in part with this prestige when he was without power and completely unknown. When, an obscure general, he was sent, thanks to influential protection, to command the army of Italy, he found himself among rough generals who were of a mind to give a hostile reception to the young intruder dispatched them by the Directory. From the very beginning, from the first interview, without the aid of speeches, gestures, or threats, at the first sight of the man who was to become great they were vanquished."

Starting twenty years after Ostwald and thirty-odd years after LeBon it should be an easy matter to formulate the problem of how to ripen time more definitely than they did.

A new discovery is accepted:—

1. Because made or advocated by a man of recognized authority or of personal magnetism.
2. Because it clears up points over which people have puzzled or because it shows what to do next.
3. Because of extensive proofs.
4. Because results are useful or striking.

Everybody appreciates the importance of recognized authority and of personal magnetism. Einstein could probably get anything accepted by the world at large that he cared to put forward. Millikan is in practically the same position so far as the American lay public is concerned. Ostwald is a striking case of personal magnetism. Most of his former pupils accept what Ostwald has said because he said it and without any reference to whether it is true or not. Most people from the Leipzig laboratory believe that methyl orange is a strong-acid indicator in spite of the fact that they would know that it is a weak-base indicator if they were willing to look the facts in the face.

Langmuir is the most convincing lecturer that I have ever heard. I have heard him talk to an audience of chemists when I knew that they did not understand more than one-third of what he was saying; but they thought they did. It is very easy to be swept off one's feet by Langmuir. You remember in "Kim" that the water-jar was broken and Lurgan Sahib was trying to hypnotize Kim into seeing it as whole again. Kim saved himself by saying the multiplication table.

"The jar had been smashed—yess, smashed—not the native word, he would not think of that—but smashed—into fifty pieces and twice three was six and thrice three was nine, and four times three was twelve. He clung desperately to the repetition. The shadow-outline of the jar cleared like a mist after rubbing eyes. There were the broken shards; there was the spilt water drying in the sun, and through the cracks of the verandah showed, all ribbed, the white house—walk below—and thrice twelve was thirty-six."

I have heard Langmuir lecture when I knew he was wrong; but I had to repeat to myself: "He is wrong; I know he is wrong; he is wrong," or I should have believed like the others.

A second reason for accepting a new discovery is that it clears up points over which people have puzzled or because it shows what to do next. In 1858 Cannizzaro[1] insisted on the distinction, imperfectly realized till then, between molecular and atomic weights, and showed how the atomic weights of elements of whose compounds the vapour densities are unknown can be ascertained from a knowledge of their specific heats." Cannizzaro doubled the atomic weight of mercury and halved those of silver, potassium, sodium, and lithium.

I can remember back to the time when an indicator was a substance which changed color when the solution changed from alkaline to acid or vice-versa. On this basis, a solution must be either acid or basic regardless of what the indicator we used. This was not true, since milk was alkaline to litmus and acid to phenolphthalein; but we did not know why. Ostwald's theory of indicators seemed to clear up the whole subject and consequently there was very little hesitation about accepting it.

In the last decade of the nineteenth century, most physical chemists thought that the existing discrepancies between theory and experiment for aqueous solutions would disappear when more accurate measurements were made. In the first decade of this century it became evident that this was not to be the case. G. N. Lewis, now of the University of California, introduced

---

[1] "Encyclopaedia Britannica," 14th Ed., 4, 751 (1929).

the activity concept to meet the difficulty. We can always make the experimental data agree with the theoretical values by multiplying the data by the ratios of the theoretical values to the experimental data. Of course it was not done as crudely as that. The multiplying ratio was called the activity coefficient and the expression was put in the form of a thermodynamic function. At first this was not hailed with enthusiasm; but there came a time when many of the physical chemists did not quite know what to do. There was no point in collecting data unless one could do something with them. To these people the activity concept was a blessing. They could determine the data and then determine the activity coefficients, thereby making the data agree with the theoretical values. A large number of physical chemists are now engaged in this edifying task. Of course, by this method any set of data can be made to agree absolutely with any theoretical values one pleases; but, so far, people have confined themselves to one set of activity coefficients.

We might consider Mrs. Eddy and G. N. Lewis as the Gold Dust Twins of Christian and Physical Science. Mrs. Eddy eliminates sickness but admits error. Lewis admits sickness but eliminates error.

Sufficiently intensive proofs will cause the recognition of a discovery. While one might consider that Darwin's theory of the survival of the fittest came under the second heading, in that it cleared up points over which people have puzzled, it seems to me wiser to consider that the enormous number of proofs was the chief reason for its general adoption. The way in which the proofs were presented by Huxley and Lyell was very helpful.

Pasteur was both a genius and a fighter. Nothing could be more gorgeous than his challenge in regard to the anthrax vaccine.[1] "The twenty-five unvaccinated sheep will all perish and the twenty-five vaccinated ones will survive. . . . Of six vaccinated and four unvaccinated cows, there will be six survivors." In a letter to his children written June 2, 1881, Pasteur says: "It is only Thursday, and I am already writing to you; it is because a great result is now assured. A wire from Melun has just announced it. On Tuesday last, May 31, we inoculated all the sheep, vaccinated and unvaccinated, with virulent splenic fever. It is not forty-eight hours ago. Well, the telegram tells me that, when we arrive at two o'clock this afternoon, all the non-vaccinated subjects will be dead; eighteen were already dead this morning and the others dying. As to the vaccinated ones, they are all well; the telegram ends by the words '*stunning success;*' it is from the veterinary surgeon, M. Rossignol."

"When Pasteur arrived, at two o'clock in the afternoon at the farmyard of Pouilly le Fort, accompanied by his young collaborators, a murmur of applause arose, which soon became loud acclamation, bursting from all lips. Delegates from the Agricultural Society of Melun, from medical societies, veterinary societies, from the Central Council of Hygiene of Seine et Marne, Journalists, small farmers who had been divided in their minds by laudatory or injurious newspaper—all were there. The carcases of twenty-two un-

---

[1] Vallery-Radot: "The Life of Pasteur" (1923).

vaccinated sheep were lying side by side; two others were breathing their last; the last survivors of the unvaccinated lot showed all the characteristics of splenic fever All the vaccinated sheep were in good health. . . . The one remaining unvaccinated sheep died that same night. . . . Amongst the cattle, those which had been vaccinated showed no sign whatever of any disturbance; the others presented enormous oedemata."

The electrolytic dissociation theory was adopted enthusiastically by the younger chemists because of the enormous number of applications and because of the research problems that it opened up. On the other hand the Phase Rule applied to problems with which people were not working much and consequently it appealed only to a few. It was a godsend to Roozeboom because he had accumulated an enormous mass of data which he could not classify and the Phase Rule enabled him to bring order out of chaos at once.

I can remember when Donnan published his first paper on the now-famous Donnan equilibrium. It was an ingenious calculation, apparently of academic interest only. Jacques Loeb got hold of it and showed that he could account quantitatively for many properties of gelatine by making use of the Donnan equilibrium. Now it is a working tool for all biologists. It is of no importance from our view-point that Loeb did not fully understand the Donnan equilibrium and that he failed to see the possible flaws in his proofs.

In 1884 Haecker, a German biologist, gave the true explanation for the blue color of non-iridescent feathers, there being no blue pigment. He showed that the blue was due to the scattering of light by small air-bubbles in the feather, the dark back-ground cutting out all transmitted light. Haecker proved in a way that should have been conclusive that the blue was what we now call a Tyndall blue. His arguments appealed to a few physicists and chemists and to practically no biologists. So far as I can judge, Haecker failed to get the recognition that he should have received because he never made a blue feather or anything like one. People felt unconsciously that if he did not duplicate artificially some of the tints of blue feathers, there might be something wrong with his reasoning. After Mason at Cornell had made the equivalent of a blue feather, by heating a piece of combustion tubing to the desired degree of devitrification and painting the inside of the tube black, there could be no further question as to the accuracy of Haecker's explanation.

While one can establish a theory by getting sufficient facts, one should remember that it is impossible to overthrow a theory by means of facts. This is not generally realized and one often reads about trying to find crucial experiments which will disprove a particular theory. Nobody ever finds one, because there is no such thing. There have been many cases of apparently insuperable objections to a theory, which have turned out to be striking confirmations of the theory when worded a little differently. Consequently people will not discard a theory no matter how discredited until there is something to take its place. In other words, a theory can only be overthrown by another theory and never by facts alone. It seems to us as though the phlogiston theory had been utterly discredited experimentally before Lavoisier; but it staggered along, bolstered by new assumptions, until the oxygen theory was brought forward. It was not new facts which overthrew the phlogiston theory. It was a new explanation of the old facts.

In 1851 William Thomson, afterwards Lord Kelvin, worked out what appeared to be a thermodynamical proof of the numerical equality between the heat of reaction and the electrical energy of a reversible cell. He tested this relation on the Daniell cell, which was the only one available at the time and found a good agreement. Unfortunately he had picked by sheer accident one of the few cells that did give a good agreement. As time went on, more and more data were collected to show the inaccuracy of Thomson's law; but these data convinced only the people who got them. So far as the scientific world was concerned, Thomson's thermodynamics must be and were unimpeachable, and that was that. Thirty years later Helmholtz published the true formula for the relation between heat effect and electromotive force, and Thomson's law went out of existence. Helmholtz did not bring forward a single new fact; but he gave a more adequate theory.

The fourth reason for immediate recognition of a new discovery is that the results shall be useful or striking. The immediate popularity of the Daguerreotype is perfectly natural. Inadequate as the process now seems to us, it was the first thing of its kind and everybody was interested. Similarly the X-rays enabled one to see and to photograph the skeleton of a living person and of course everybody was interested.

Graham is known as the father of colloid chemistry and Baudrimont is not; although Baudrimont knew a great deal more about colloid chemistry than Graham ever did. It is of course simple to say that in Baudrimont's day the time was not ripe for colloid chemistry, which is true enough; but the time was also not ripe in Graham's day. The real development of colloid chemistry did not come until more than forty years after Graham, and yet Graham ripened time, presumably unconsciously, to such an extent that he is known as the originator of colloid chemistry, with Baudrimont and Selmi solely of antiquarian interest. What did he do that they did not do? My answer is that he invented dialysis, which was of practical importance to people. By means of diffusion through a parchment membrane, Graham was able to separate arsenic, for instance, from the organic materials of the body which interfered with the analysis. Dialysis was useful and it carried colloid chemistry with it as a tag.

Another less striking case, but still an interesting one, is that of electrometric titration. The first work was done by Behrend in Ostwald's laboratory. Later, Böttger tried in vain to make it popular. It was a process which interested physical chemists but that was all it was. At that time, nobody in a chemical laboratory except the physical chemists had ever made measurements of electromotive forces. The other chemists had no equipment and would not have known what to do with it if they had. The remarkable development of electrometric measurements is due primarily to J. H. Hildebrand, then of the University of Pennsylvania and now of the University of California. In addition to making a lot of measurements himself, he devised a simple and compact form of apparatus, which anybody could use. He ripened time and now electrometric titrations are made in all sorts of analytical work and there is no biological laboratory so humble that it does not make pH determinations.

The general conclusion is that to ripen time we must establish our view by many proofs; we must discover something for which the world is ready; we must educate the world up to our discovery; or somebody else must educate the world for us.

The last method is the one that has happened surprisingly often in the past. The theory of stereochemistry was developed independently by van't Hoff in Holland and by LeBel in France; but it is very much of a question whether either of these men could have got the theory accepted in any reasonable time. Nobody will dispute that the work essential to the adoption of the theory was done by Johannes Wislicenus in Germany. The experiments of Pfeffer on osmotic pressure and of Raoult on the lowering of the freezing-point were very interesting; but nobody knew just what they meant. It was van't Hoff who furnished the theoretical explanation which was lacking and who thereby enabled Raoult and Pfeffer to get the credit which was properly due them.

The theory of osmotic pressure was due to van't Hoff, the theory of electrolytic dissociation to Arrhenius, and the modern theory of electromotive force to Nernst; it was Ostwald who fought the battles which resulted in the acceptance of these views. Avogadro was put across by his countryman Cannizzaro; Gibbs by Roozeboom and Ostwald; Donnan by Jacques Loeb; and Darwin to a great extent by Huxley.

One cannot count on having somebody else exploit one's discoveries and the worker in pure science will not and should not limit himself to discovering only those things which the world knows that it wants. Consequently, he must make up his mind to sell himself to the scientific world if he is not going to run the risk of being classified as a man whose ideas, though excellent, came when the time was not ripe for them. This doctrine will horrify many of my friends and I admit that it horrified me at first; but I see no escape from it. We do not expect the scientific man to develop the financial possibilities of his ideas and, as a rule, he does not do it. When it comes to the purely scientific side of a man's work, he should not rank below the cuckoo and the cow-bird which at least pick out foster-mothers for its young, while the scientific man casts his ideas out into the world to shift for themselves.

Since the greatest discoveries are likely to be ones for which the world is least ready, we see that the greatest scientific men should really be super-salesmen. It is for this reason that I hope that, in this Science Hall, which is to be dedicated today, people will emphasize both the importance of research in connection with teaching and the importance of teaching in connection with research.

Cornell University.

THE DISSOCIATION OF STRONG ELECTROLYTES*

IV. Miscellaneous Properties

BY MORRIS B. JACOBS AND CECIL V. KING

It is really remarkable that no known property of electrolytes is unquestionably connected with the concentration of the undissociated molecules in such a way that it can be used as a completely satisfactory test for the presence of these in solutions of strong electrolytes. Conductivity measurements have admittedly failed to give a measure of the concentration of ions; there seem to be no absorption bands characteristic of the undissociated molecules; vapor pressure measurements, valuable in the case of volatile weak electrolytes fail for strong electrolytes because they are non-volatile (salts) or because they are probably highly hydrated (hydrogen halides) in which case the vapor pressure could give little idea of the actual concentration of undissociated molecules or of ion-pairs. It will be remembered that solutions of hydrochloric acid do have a very small, but appreciable, vapor pressure down to a concentration of 0.3N; but whether the extreme smallness of this vapor pressure and the lack of measurable vapor pressure at higher dilutions mean practically complete dissociation or not, is problematical.

The absence of properties undisputably assignable to undissociated molecules is one of the chief arguments of the supporters of complete dissociation, who feel that while perhaps no single piece of evidence is conclusive for the theory, the entire mass of data is best explained by this theory. The writers feel that it is unfair to neglect the possibility of incomplete dissociation; just as unfair as it would be to neglect the possibility of compound formation in studying the deviations from the ideal laws in the case of non-electrolytes. The best evidence for complete dissociation is probably agreement with the Debye-Hückel and related laws; but at present exact comparison of these with the experimental is possible only for highly dilute solutions. On the other hand, the best argument of those who do not accept complete dissociation except as a limiting law, seems to be the lack of evidence of any quantitative distinction between strong and weak electrolytes. It apparently behooves the latter to find some property which belongs undisputedly to the undissociated molecule or to show convincingly that the deviations from the Debye-Hückel theory or other theories based on inter-ionic attraction and complete dissociation are caused by incomplete dissociation.

In the meantime, there remain a few more points commonly adduced in favor of complete dissociation whose evidence in this direction seems to the writers to be greatly over-rated. In this paper we wish to discuss critically the evidence offered by: (1) crystal structure data; (2) transference number

---

* Contribution from the Department of Chemistry of Washington Square College, New York University.

and conductance; (3) certain electrical cells; (4) some of the experimental data which have been compared with the Debye-Hückel theory; and (5) the additivity of some properties not mentioned before.

First we should again raise the question of the exact meaning of *ionization* and *dissociation* and the distinction, if any, between the two terms. By an ion we understand, according to the picture of the atomic physicist (if he can be said to have any picture) an atom or group of atoms in which one or more electrons are completely missing, or which have full possession of one or more extra electrons. Two such ions of opposite charge might "associate" to form an "electrical molecule" as suggested by Noyes in 1904 (an idea treated in detail by Bjerrum[1] in 1926) or more than two such ions might form a group; in fact, such grouping, to a limited degree, in the sense that any ion will have more ions of the opposite charge near it, on the average, than ions of like charge, is postulated in the Debye-Hückel theory. It is not clear to the writers whether or not close grouping of two ions of opposite charge, perhaps to form "electrical molecules," is actually taken into account in the Debye-Hückel theory. At any rate, there should be a quantum difference between a true molecule and even an ion-pair or "electrical molecule"; but perhaps there can be all stages between, in which the ions are deformed or the valence electrons are in distorted orbits or orbits of exceptional energy levels. It has been assumed, at least as a simplifying picture, that in the case of weak electrolytes we deal with only two conditions—complete ionization and complete molecule formation[2]—although this is not necessarily correct.[3]

1. Crystal Structure Data

The X-ray evidence that the atoms of several salts exist as ions in the crystal has seemed to fit in perfectly with the complete dissociation theory. For instance, LaMer[4] says: "The studies of the Braggs and others on the structure of crystals by means of X-rays furnishes more conclusive evidence for the new point of view. They find that no molecules of NaCl are present in the solid salt; instead the crystal structure consists of sodium and chlorine ions arranged in a cubic lattice, such that each sodium ion is surrounded at equal distances by six chloride ions and similarly each chlorine ion by six sodium ions. That the forces holding a crystal of salt together are due to electrostatic forces between the charged ions, has since been established by the calculations of Born, Debye and Scherrer, Fajans, Madelung and others upon the magnitude of the so-called space lattice energy."

It should be noted that X-ray spectra can be used to fix the positions of the atoms in the crystal lattice (for instance the cubic lattice of NaCl), but do not themselves indicate with certainty whether the atoms are charged or uncharged. The intensity of the X-ray lines depends on the number of

---

[1] Det. Kgl. Danske Vidensk. Selskab., Math.-fys.Medd., 7, No. 9 (1926).

[2] Rördam: Dissertation, Univ. of Copenhagen (1925). Also, other work on activity coefficients of slightly soluble weak electrolytes.

[3] See Fajans, Fowler: Trans. Faraday Soc., 23, 410, 411 (1927).

[4] Trans. Am. Electrochem. Soc., 51, 507 (1927).

external electrons, it is true; and, theoretically, intensity measurements should indicate whether a crystal consists of charged or uncharged atoms. Practically, however, such intensity measurements cannot be made with the necessary accuracy. For this reason, the argument that simple crystals as NaCl and KCl consist of equally spaced *ions* depends on the calculations mentioned above, which show that the electrostatic forces of such charged ions are of the correct order of magnitude to hold the crystal structure together.

However, it is obvious that many other substances form stable crystal lattices, with symmetrical spacing of the various atoms or groups of atoms involved, without such forces to stabilize the lattices. Also, all salts of symmetrical valence types each of whose radicals consists of a single atom, should crystallize in a cubic lattice, if held together by electrostatic forces alone. It is hard to reconcile the apparently molecular form of gaseous sodium chloride with a completely non-molecular form in the crystal. It seems possible that in the crystal, the electron from each sodium atom, instead of being possessed by a single chlorine atom, might be equally shared by all the six nearest chlorine atoms.

Now consider the solution of a crystal of sodium chloride; it must be admitted that we can have absolutely no idea of what happens in this process. Partington[1] says that "in solution such a crystal would simply fall apart into its ions." On the next page, however, Partington questions such a process of ionization for molecules. Such a picture is undoubtedly too simple. When a salt is melted it might be supposed that the ions would simply remain as such, with the added freedom of motion other than vibration. That this is not the case is well known. The conductivity of molten salts indicates a high "association factor" but the interpretation of this factor is not altogether clear. Great dilution with water should, of course, tend to break up any groups formed in concentrated solutions. It is evident that the structure of the crystal gives no indication of what is to happen when the crystal is dissolved in some solvent.

The enormous difference between such substances as the hydrogen halides and the common salts, all of which take equal places in the complete dissociation theory, make it quite evident that the previous history of the electrolyte is of questionable significance with respect to its dissociation in water.

2. Transference Number and Conductance Data

The conductance of an electrolyte at a given dilution is, according to the law of Kohlrausch

$$\lambda_v = nF\alpha (U + V) \qquad (1)$$

where U and V are the mobilities of the anion and cation. At infinite dilution the conductivity is

$$\lambda_\infty = nF (U + V) \qquad (2)$$

---

[1] Taylor: "Treatise on Physical Chemistry," 2nd Edition, 634 (1931).

since $\alpha = 1$. Dividing (1) by (2) we get $\alpha = \lambda_v/\lambda_\infty$, the classical expression for the degree of ionization. This obviously depends on the assumption that the mobilities of the ions do not change with the dilution.

This we now know is erroneous. It is probable that the mobilities change with the viscosity of the solution, with the electrostatic environment and perhaps with other factors, as changing hydration of the ions. However, the effect of these factors is difficult, if not impossible, to calculate; and the simplest way out seems to be to follow MacInnes:[1] "So far as conductivity and transference data are concerned it appears, therefore, that the assumption of complete dissociation results in a simplification of the theory of monovalent strong electrolytes, since one variable, ion mobility, is substituted for two, i.e., the number and mobilities of the ions. The phenomena can otherwise only be explained by more or less indefinite distribution of the effects observed between these two variables."

MacInnes thus states the problem very clearly, and proceeds to attack the problem from the standpoint of the old rule of Kohlrausch, the additivity of ion conductances. He shows that in a number of univalent metal chlorides, the chloride ion has, at any one dilution, nearly the same equivalent conductance ($T\lambda$, transport number of the chloride ion multiplied by the equivalent conductance of the salt.). $T\lambda$ is not satisfactorily constant unless multiplied by an empirical viscosity correction (the relative viscosity raised to the 0.7 power) but with this correction the rule holds well at concentrations as high as 1M.

MacInnes was inclined to interpret this as indicating that all these chlorides were completely dissociated. However, McBain and Rysselberge[2] have shown that this constancy fails for bi-valent metal chlorides. MacInnes and Cowperthwaite[3] later found no such constancy for nitrates of the univalent metals, and McBain and Rysselberge showed that the values of $T\lambda$ vary enormously for metallic sulfates. If constancy of $T\lambda$ is any indication of complete dissociation, most salts are not completely dissociated even at rather low concentrations. Obviously, a satisfactory explanation is not available at present. All the alkali halides seem to show additivity in several properties as we shall show later in this paper; but if this indicates complete dissociation, other salts are not completely dissociated.

It is not quite clear to the writers whether electroendosmosis has been adequately considered in connection with conductivity and transference number experiments. Conductance through a membrane is usually abnormal, the water moving through the membrane in a direction determined by the sign of the charge between the membrane and the water. The effect is usually pronounced in very dilute solutions. The conductivity of very thin surface films has been shown to be highly abnormal. It is possible that there is more movement of water in the usual transport number apparatus than has been expected, due to a difference in charge of the glass and the solution.

---

[1] J. Am. Chem. Soc., 43, 1217 (1921).

[2] J. Am. Chem. Soc., 50, 3009 (1928).

[3] Trans. Faraday Soc., 23, 400 (1927).

The high mobilities of hydrogen and hydroxyl ions have sometimes been explained as being due to a sort of "Grotthuss conductivity"; i.e., a single ion may move until it collides with a water molecule, when it will stick and a corresponding ion leave the other side of the water molecule. The experiments of McBain and Rysselberge,[1] showing that the transference number of almost any positive ion, in low concentration in the presence of a high concentration of another salt having a common anion, is abnormal, merit more investigation. Sata[2] states that he can account for the conductivity of acetic acid in acetone only by assuming that undissociated molecules as well as ions conduct.

Onsager[3] has pointed out that in addition to the Debye-Hückel interionic attraction and electrophoretic effects an ion moving under a potential difference will be influenced by its own Brownian movement. Onsager's final conductivity equation has been used by some investigators as a criterion of complete dissociation (with proper regard to its limitations). Davies[4] has shown that, by assuming deviations from Onsager's equation (in quite dilute solution) to be due to incomplete dissociation, a mass-action (activity) constant can be calculated for some bi-bivalent salts as well as some strong uniunivalent acids.

Another method of attacking the problem of degree of dissociation has been discussed by Davies.[5] Wien has measured the conductivity of solutions of electrolytes at such high voltages that the migration speed of ions is of the order of several meters per second. The equivalent conductance rises above the normal and at sufficiently high voltages seems to reach a maximum. If we can assume that at such high migration velocities interionic attraction and electrophoretic effects are negligible, this maximum conductivity should give $\alpha\lambda_\infty$; in fact, for salts which may be considered completely dissociated Wien considers the maximum value to be equal to λ_∞. Davies shows that for 0.001 M $MgSO_4$, for which he has calculated a dissociation of 92.4% from the deviations from Onsager's equation, the maximum conductance increase should be 11%, which agrees well with Wien's value of 9% for 0.00093M $MgSO_4$. Objections to this interpretation of Wien's experiments have been raised by Gyemant.

The multitude of factors which may influence ion mobilities and transference numbers, and the diversity of opinion in interpreting experimental results with respect to complex ion formation[6] and with respect to the true mobilities when the moving boundary method is used[7] leave much to be desired in the use of this type of data in support of complete dissociation.

---

[1] J. Am. Chem. Soc., 50, 3009 (1928); 52, 2336 (1930).

[2] Bull. Chem. Soc. Japan, 1, 245 (1926).

[3] Trans. Faraday Soc., 23, 341 (1927).

[4] Davies: "The Conductivity of Solutions," Chapters VII and IX (1930)

[5] "The Conductivity of Solutions," Chapter XI.

[6] See Schneider and Braley: J. Am. Chem. Soc., 45, 1121 (1923); MacInnes: 47, 1922 (1925); Dewey: 47, 1927 (1925); Bjerrum and Ebert: Det Kgl. Danske Vidensk. Selskab, Math.-fys. Medd., 6, No. 9 (1925).

[7] See Mukherjee: Nature, 122, 608 (1928).

3. The Concentration Cells of Brönsted

In 1919-1920 Brönsted[1] published measurements on the electromotive force of cells which have often been quoted in support of complete dissociation. With two cadmium amalgam electrodes in solutions containing M/10 to M/320 and M/20 to M/640 cadmium sulfate, respectively, with the ratio always ½, both solutions made up to 2 M with magnesium sulfate, the electromotive force ratio was in agreement with that calculated from the Nernst equation, using the total cadmium concentrations. With two silver chloride electrodes in solutions containing 0.0032 M and 0.1 M magnesium chloride and made up to 4 M with magnesium sulfate, the e.m.f. ratio was nearly in agreement with the Nernst equation. Considering the 0.0032 M magnesium chloride completely dissociated, the 0.1 M magnesium chloride would be 99.3% dissociated.

At first glance it seems that the simplest explanation of these results is that the cadmium sulfate and magnesium chloride are completely, or nearly completely, dissociated at all concentrations. However, this need not be the case. The experiments simply prove that the *activity coefficients* of these salts are the same, or nearly the same, in the two solutions in the presence of the large excess of magnesium sulfate. Brönsted has demonstrated that this is true in general, in showing that the velocity of reaction of ions at low concentrations in solutions of high ionic strength follows the classical reaction velocity laws. These experiments do not involve the degree of dissociation of the salts in question. It seems probable that even on the basis of the Arrhenius theory, in the presence of a constant ionic environment (high concentration of inert salt) the percent ionization of a salt present in comparatively low concentrations would remain appreciably constant over a considerable concentration range. One of the weak points in the application of conductivity to the study of salts with respect to the ionization theory has always been that the conductivity of one salt cannot be measured independently of other salts present. Nevertheless, it is evident that the experiments of Brönsted are suitable to determine activity ratios but not degrees of ionization, or dissociation.

4. The Debye-Hückel Theory

This theory has without doubt come very close to explaining the behavior of electrolytes in rather dilute aqueous solutions. It assumes, in its simplest forms, that all deviations from the ideal behavior are due to interionic forces. Thus it neglects any lack of complete dissociation and also any specific peculiarities of ions no matter what their cause. Experimental agreement with the theory substantiates the underlying assumptions. Unfortunately, there is reasonably good agreement of experiment and theory only in solutions sufficiently dilute so that any reasonable modern theory of ionization must postulate nearly complete dissociation. It is in the region of deviation from the simpler form of the theory that we must look for incomplete dissociation.

---

[1] Medd. Vetenskapsakad. Nobelinst., 5, No. 25, 1 (1919); Kgl. Danske Vidensk. Selskab., Math.-fys. Medd., 3, No. 9 (1920); Trans. Faraday Soc., 24, 727 (1928).

Very few non-electrolytes follow the ideal laws closely. The deviations have not in every case been satisfactorily explained; there are some very clear-cut reasons for non-ideality, such as association of the solute, compound formation with the solvent, etc., while others are difficult to measure quantitatively, such as chemical dissimilarity of solvent and solute, differences in internal pressure, polarity, and other factors. In the case of electrolytes we should expect deviations from some of these causes to persist to very high dilutions, compound formation between the two parts of the solute (the two ions) being pronounced because of the high electrostatic attraction.

The simple form of the Debye-Hückel theory would seem to bear to the "ideal" theory of the behavior of ions the same relation as the van't Hoff equations for dilute solutions to the ideal equations derived from Raoult's law or the van't Hoff isochore. The simple theory ascribes all deviations of the ions from Raoult's law to inter-ionic attraction; and even in doing this makes simplifying assumptions which invalidate it except for high dilutions. Some progress has been made in extending it; Debye and Hückel themselves added a factor necessary to account for a finite size of the ions. Gronwall, LaMer and Sandved[1] have improved the mathematical treatment for ions of higher valence types. Otherwise the chief modifications have been in the addition of empirical terms which have some qualitative justification but are of a type which cannot be submitted to quantitative treatment.

A weak link in any form of the Debye-Hückel theory is in the manner in which the dielectric constant of the medium is used. Bjerrum[2] concludes that anomalies in heats of dilution, partition coefficients, Soret effect, and other properties are due to variations in the dielectric constant. Fowler[3] says "the introduction of the dielectric constant makes use of a process of averaging in steps, which is illegitimate though probably not seriously in error, and should be replaced if possible by a deeper investigation, including a study of saturation effects in the polarization of the medium."

Hückel[4] has attempted to take into account the variation of the dielectric constant with salt concentration. He concluded that the dielectric constant should show a linear decrease with concentration, which seems probable at low concentrations but is contrary to experiment at high concentrations. Walden and his co-workers[5] have found indications that the dielectric constant first decreases, goes through a minimum and then increases. This effect has been found correct in general, although experiments are not checked[6] exactly.

---

[1] Physik. Z., **29**, 358 (1928).

[2] Trans. Faraday Soc., **23**, 445 (1927).

[3] Trans. Faraday Soc., **23**, 435 (1927).

[4] Physik. Z., **26**, 93 (1925).

[5] Z. physik. Chem., **110**, 43 (1918).

[6] Walden, Ulick and Werner: Z. physik. Chem., **116**, 261 (1925); Schmidt: Phys. Rev., (2) **30**, 925 (1927); Hellman and Zahn: Z. physik. Chem., **132**, 399 (1928); Carman and Schmidt: Phys. Rev., (2) **31**, 157 (1928).

Gronwall and LaMer[1] outline a theory for the variation of the dielectric constant with concentration which is in substantial agreement with the experimental results of Walden.

On the whole, the original Debye-Hückel theory or the extended forms seem satisfactory at low concentrations, especially for uni-univalent salts, although even here small specific variations for individual salts may persist to very high dilutions.[2] Brönsted,[3] even before the original papers of Debye and Hückel appeared (1923) published papers on "the specific interaction of ions." In these papers he showed that the solubility effects of un-univalent salts have marked individual characteristics even in 0.1 M solution and presented a simple method of dealing with these specific effects. The theory has been well established.[4] Whether "specific interaction" is connected with molecule or ion-pair formation is not known and is not necessary to the theory.

The agreement with the Debye-Hückel theory in non-aqueous solution is far from being as good. Water happens to be an excellent solvent for the theory in that its polarity and dielectric constant are such that the valence of ions plays a predominating role and specific salt effects are low.[5] Data on solubilities and ion mobilities in solvents of low dielectric constant do not agree so well with the theory. Part of this may be due to lack of correct dielectric constants; some writers[6] are inclined to favor incomplete dissociation as one reason.

The Debye-Hückel theory thus seems to be obeyed as a limiting law over a small range of concentration of strong electrolytes in solvents with a small range of dielectric constants and ionizing powers. In this range its validity is of utmost importance. Too little is known of the deviations at present to say what role lack of complete dissociation plays.

5. Additivity of Properties

In the preceding papers of this series we have pointed out that a number of properties of strong electrolytes which from the older experimental work were thought by the exponents of complete dissociation to be additive for positive and negative ions, have been shown on careful investigation to deviate from this rule. The deviations have been interpreted variously in favor of incomplete dissociation and otherwise. We shall point out some other deviations from additivity which make the interpretation of such data in favor of complete dissociation questionable.

---

[1] Science, **64**, 122 (1926).

[2] LaMer, King and Mason: J. Am. Chem. Soc., **49**, 363 (1927).

[3] Det Kgl. Danske Vidensk. Selskab, Math.-fys. Medd., **4**, No. 4 (1922); J. Am. Chem. Soc., **44**, 877 (1922); **45**, 2898 (1923).

[4] See Güntleberg: Z. physik. Chem., **123**, 199 (1926); LaMer and Cook: J. Am. Chem. Soc., **51**, 2622 (1929).

[5] See Hammett and Dietz: J. Am. Chem. Soc., **52**, 4795 (1930).

[6] Robinson: J. Phys. Chem., **32**, 1089 (1928); Ulich and Birr: Z. angew. Chem., **41**, 1075 (1928); Hartley and Bell: Trans. Faraday Soc., **23**, 396 (1927); Frazer and Hartley: Proc. Roy. Soc., **109A**, 351 (1925); Woolcock and Hartley: Phil. Mag., (7) **5**, 1133 (1928); Kraus and Seward: Trans. Faraday Soc., **23**, 488 (1927).

We have already mentioned the usual close additivity of properties for the *alkali halides* and the usual deviation for other electrolytes. We have discussed the "additivity" of ion conductances.

LaMer and Gronwall[1] have calculated the partial molal volumes of most of the alkali halides in water solution and their data show good agreement with the additivity principle even at rather high concentrations. Data for other salts are probably too meager to be of much use, but it is unlikely that the same additivity will be found.

Haeseler,[2] working with LaMer, investigated carefully the additivity of the effect of ions on the solubility of benzoic acid in water. For the nine alkali halides (Li, Na, K – Cl, Br, I) the results indicate independence of the effect of individual ions within experimental error up to a concentration of 1M, aside from minor deviations at low concentrations probably due to the ionization of benzoic acid. Above this concentration there is a regular deviation which presumably persists to a very slight extent even to low concentrations. Experiments with other salts, however, showed pronounced deviations at lower concentrations. The mechanism of such a salting-out effect is, of course, problematical; as before, the alkali halides seem to be a limiting case, but whether we should consider them completely dissociated and the nitrates and sulfates not depends on a more complete interpretation of the data.

The experimental data on other properties such as partial volumes, specific heats, etc., are so meager that it is doubtful if they offer any convincing evidence for or against the theory.

In concluding this series let us point out again that we are not trying to discourage legitimate use of the complete dissociation theory. The chemist should keep an open mind, accepting such a theory when it seems valuable, trying to find its limitations and the reasons for these limitations. In the present situation it would seem very important to try to find some property unquestionably due to undissociated molecules, and then look for this property in solutions of strong electrolytes in aqueous and other solutions. In addition, deviations from the limiting laws based on the assumption of complete dissociation should be systematically studied and the attempt made to learn if any or all of them are unquestionably caused by incomplete dissociation.

New York, N. Y.

---

[1] J. Phys. Chem., 31, 393 (1927).

[2] Dissertation, Columbia University (1929).

A MICRO-METHOD FOR THE MEASUREMENT OF SURFACE TENSION*

H. MOUQUIN AND S. NATELSON

The instructive character of the information available from the Sugden Parachor is responsible for its increasing application in Organic Analysis. But lack of a satisfactory micro-method for surface tension has limited the utility of this tool in micro-work. Such a method, to be successful, should be as precise and as easy to operate as the current macro-methods, e.g. the du Noüy ring, the stalagmometer, etc; and, like the latter, not necessarily absolute but readily standarized with liquids of known surface tension.

The sole method previously developed worthy of the appellation "micro" is the ingenious one due to Kiplinger,[1] more recently modified by Ferguson.[2] The fact, however, that their apparatus has found no place in the microchemical armamentarium would seem to indicate some practical insufficiency.

At this late date a brief statement of the major difficulties may suffice:

1.—If the capillary be held vertically, as in all the original experiments, the pressure values depend on an exact measure of column height. This, as noted by Kiplinger, is obviously impossible for volatile liquids like ether, chloroform, or carbon bisulphide.

Furthermore, any attempt to correct for this by placing the tube horizontally must fail since, as admitted by Ferguson, "it is impossible in an inclined tube to obtain an accurately plane meniscus", i.e. the end-point becomes indefinite.

2.—Since the total pressures measured are of the order of 1 cm. of water, superprecise manometer readings become necessary in order to keep the experimental error within reasonable limits.

The method adopted is based on an entirely different principle, and, other than a common microscope, requires only the simplest materials and technique. It is not subject to errors resulting from evaporation, gives much larger pressure readings, and has a stable, precise, and easily determined end-point.

The principle involved may be formulated thus: A definite pressure will be required to advance a short column of liquid along a tube of conical bore in the direction of the larger cross section, provided the contact angle is less than 90°. In addition, the effect of a gravitational field on the said force will be negligible for the case where the axis is horizontal; the applied pressure being counteracted only by capillarity, and hence completely defined by the difference between the radii of curvature at the two ends of the liquid column and the surface tension of the liquid.

---

* Contribution from the Chemical Laboratory of the Washington Square College of New York University.

[1] Kiplinger: J. Am. Chem. Soc., 42, 472 (1920).

[2] Ferguson: Proc. Phys. Soc. London, 36, 37-44 (1923).

Among the combinations investigated, that found most convenient was to have a constant difference in terminal radii, i.e. at equilibrium external pressure is directly proportional to surface tension. This was achieved experimentally by employing a capillary with a small bulb-shaped enlargement blown near one end, Fig. 1.

Since the position of meniscus A will not affect its radius of curvature while it remains in the cylindrical portion of the capillary, any alteration of A by evaporation is of no consequence; it being only necessary to localize B in some arbitrary manner. This was effected by etching a fine line of reference on the tube about one third of the distance from the end of the bulb. Although the exact position of the line is immaterial, more convenient readings will be obtained if it be first approximated by trial.

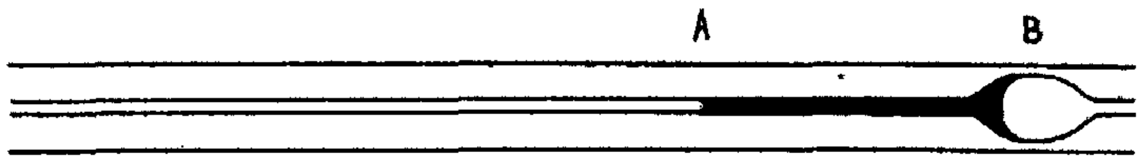


Fig. 1

A broken thermometer stem was found to make an excellent tube. Inasmuch as these already have a small bulb blown in at the upper end during the sealing process, the tube requires only to have its tip broken off (to be open at both ends), and is ready for use. The experimental capillary—employed with organic liquids whose surface tension varied from 15 to 45 dynes/cm.—had an internal diameter of 0.0229 cm. B was observed through a low power microscope fitted with a cross hair ocular; the instrument being first focussed on the reference scratch, and then lowered vertically with the focussing screw the short distance necessary to bring the bottom of the meniscus into the field.

The two other essential parts of the set-up are: a means of procuring variable pressures; and a manometer to measure them.

The first was improvised from an atomizer bulb, secured in a large laboratory clamp. By revolving the thumb screw on the latter any desired pressure could be produced; and released at will through an exit tube and stop-cock communicating with the free end of the bulb, or at some other convenient point.

As for the second, contrivances such as Roberts'[1] micro-manometer, even with an index of carbon disulphide between water columns, are out of the question because of the length of time required for equilibrium to be established. The device decided on was designed for its sensibility, simplicity, and ease of manipulation. It combines the "Inclined Side-Arm" and "Volume Change" principles, thereby gaining sensitivity without complication. It is constructed by fusing a straight glass tube, of 0.35cm. bore and 60 cm. long, on the arm of a side-arm test tube 1.75 cm. in diameter; mounting upright on veneer board; and levelling the whole until the lateral tube makes an angle

---

[1] Proc. Roy. Soc., A. 78, 410 (1907).

of about 3° with the horizontal. A spirit level permanently fixed at the appropriate angle leaves no uncertainty in reproducing the desired inclination, while a centimeter scale behind the side-arm extension serves as a reading device. With the thermometer stem used (which, of course, occupies a horizontal position on the microscopic stage) there was no difficulty in making each centimeter correspond to 1 dyne/cm. of surface tension by appropriate levelling.

The accompanying diagram, Fig. 2, is self-explanatory.

The apparatus is calibrated in terms of reference liquids with known surface tensions. Specially purified ether and acetone were used for our instrument; and a du Noüy ring was simultaneously calibrated with the same liquids. Our other liquids, as indicated by the results, were contaminated in varying degrees.

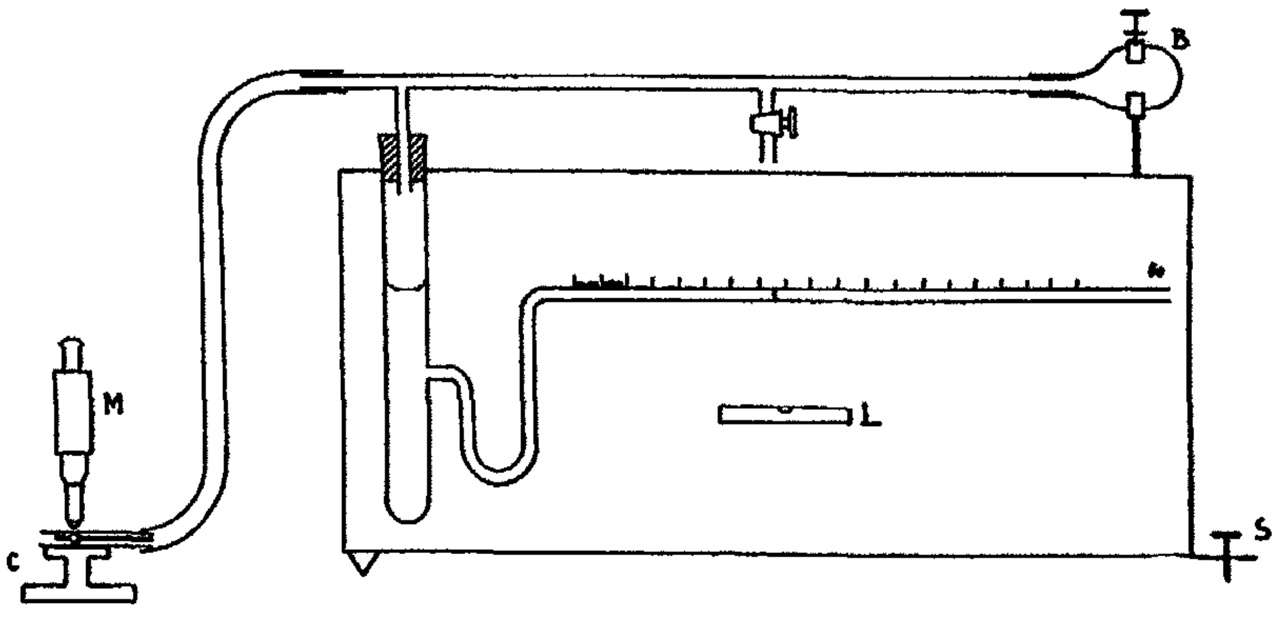


FIG. 2

C—capillary tube
M—microscope
B—rubber bulb and pressure clamp
L—spirit level
S—levelling screw

A word as to the method of measurement. The capillary, after ordinary cleaning, is touched to the liquid under examination, and then emptied and dried by drawing air through it. Another index is drawn up by capillarity and the cylindrical end of the tube connected with the manometer. Meniscus B is next brought to the etch mark and the new pressure read.

Fig. 3 gives a plot of the values obtained by each method (du Noüy and micro). The tensions for the ring have been reduced to a scale which makes them correspond to the pressures; the numerical values for ether being identical on both scales. The zero point on the manometer was arbitrarily fixed at 15 dynes/cm. in order not to unduly increase the length of the side-arm.

Three points should be noted:

1. Plotting pressure against surface tension for the micro-apparatus gives a satisfactory straight line.

2. The values can readily be checked by this method to 0.1 dyne/cm.; which is somewhat better than can be done with the ring in some cases.

3. With only one drop of liquid a surface tension determination is readily performed.

Finally, we should like to direct attention to a somewhat unrelated but conceivably important application of this instrument; to wit, with liquids of known surface tension, it is feasible to investigate the shape and dimensions of small bulbs similar to the one used in the set-up, by displacing the fluid from the ends to the center of the opening and taking corresponding pressure readings.

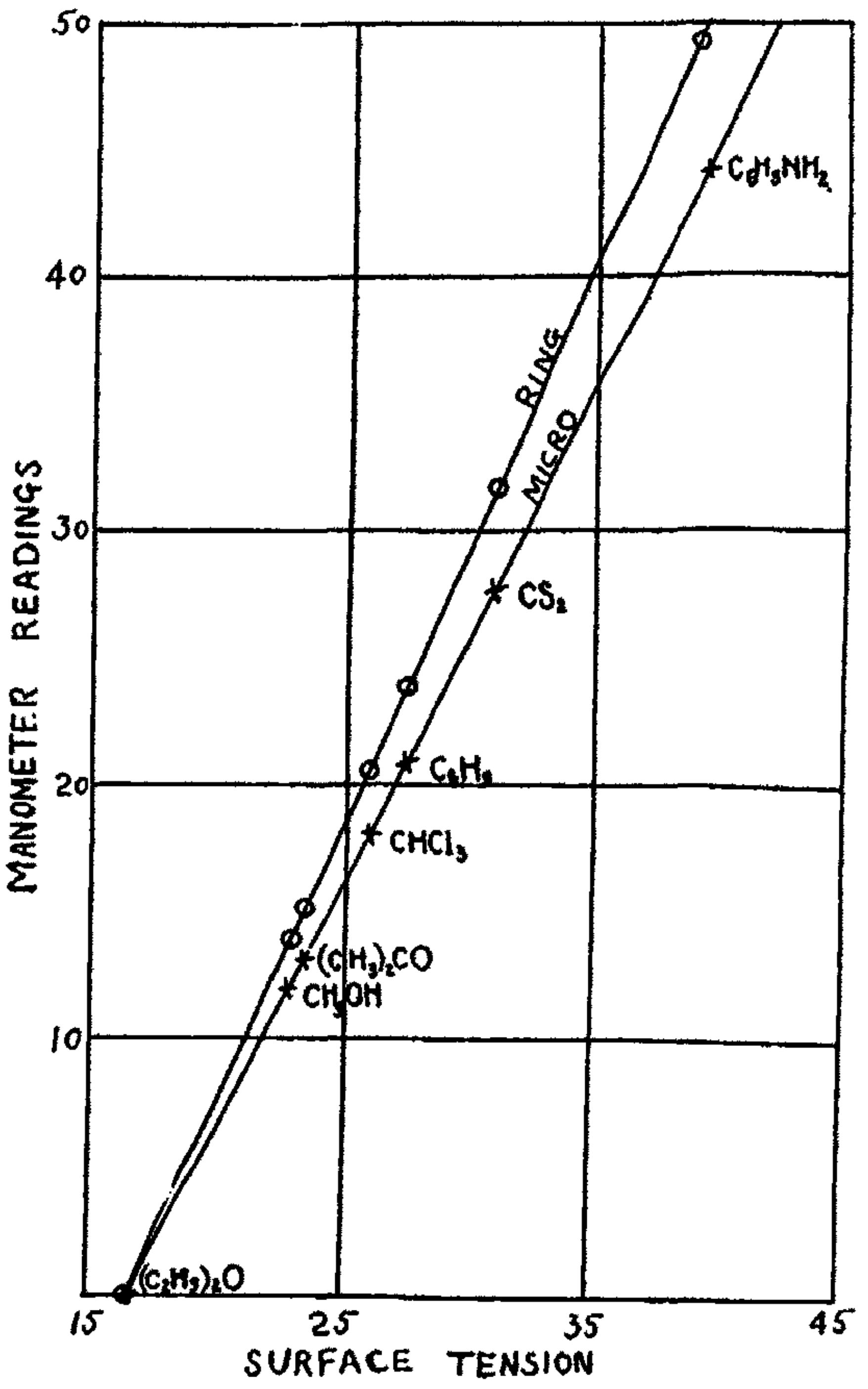


Fig. 3

Abstract

A new micro-method for the determination of surface tension is described in detail. The apparatus and technique are so simple as to make it universally applicable. The accuracy obtainable with it equals that of any of the current macro-methods.

New York, N. Y.

1935

THE SPECIFIC HEATS OF FIVE PURE ORGANIC LIQUIDS AND OF ETHYL ALCOHOL-WATER MIXTURES*

BY FRANCIS E. BLACET, PHILIP A. LEIGHTON AND EDWARD P. BARTLETT

1. Introduction

Apparatus and Method

Although many measurements of the specific heats of such organic liquids as ethyl alcohol and aniline have been reported, few of these have been made by methods which permit of measurement over small temperature intervals. At elevated temperatures in particular, the applications of methods of calorimetry which permit measurements over a continuous chain of small temperature intervals are singularly few. Williams and F. Daniels[1] have made measurements over 5° intervals in the range 30°-80° on fifteen pure organic liquids. Parks[2] and collaborators, employing the Nernst method, have made similar measurements at temperatures up to 30° on a number of liquids.

In the present work, an adiabatic calorimeter with a capacity of 150 cc. was employed (Fig. 1), in which heat was added to the liquid at a constant rate from an electrical heating coil, and the *time interval* between each five-degree rise, and in some cases between each two-degree rise in temperature was measured.

In this way an unbroken chain of specific heat readings could be obtained, without the necessity of waiting for temperature equilibrium before each reading.

The calorimeter was constructed for use up to 300°C. No solder was employed. The containers were built of thin copper, and all joints were either welded or held by screws. The lid was made tight with an asbestos-graphite gasket. The inner calorimeter was equipped with a single stirrer, provided with a long close fitting bearing to reduce evaporation error, while the surrounding adiabatic bath had three stirrers placed symmetrically around the inner container. For heating units, a single coil of nichrome, completely surrounding the stirrer, served for the inner liquid, and three coils, symmetrically placed between the stirrers, were used in the outer bath. One degree per minute was chosen as the standard rate of temperature rise. The stirrers were all driven by a single cord from a constant-speed motor. Experiments with various speeds of stirring resulted in 2.5 revolutions per second being chosen as the optimum rate. Temperatures were read to 0.01° by means of thermometers calibrated by the U. S. Bureau of Standards. Two ranges of thermometers, 0-100° C. and 100-200° C. were employed. By using the

---

* Contribution from the Chemistry Laboratories of Pomona College and of Stanford University.

[1] J. Am. Chem. Soc., 46, 903, 1569 (1924).

[2] J. Am. Chem. Soc., 47, 338, 2089 (1925); 48, 1506, 2788 (1926); 51, 1969 (1929); 52, 1032, 1547 (1930).

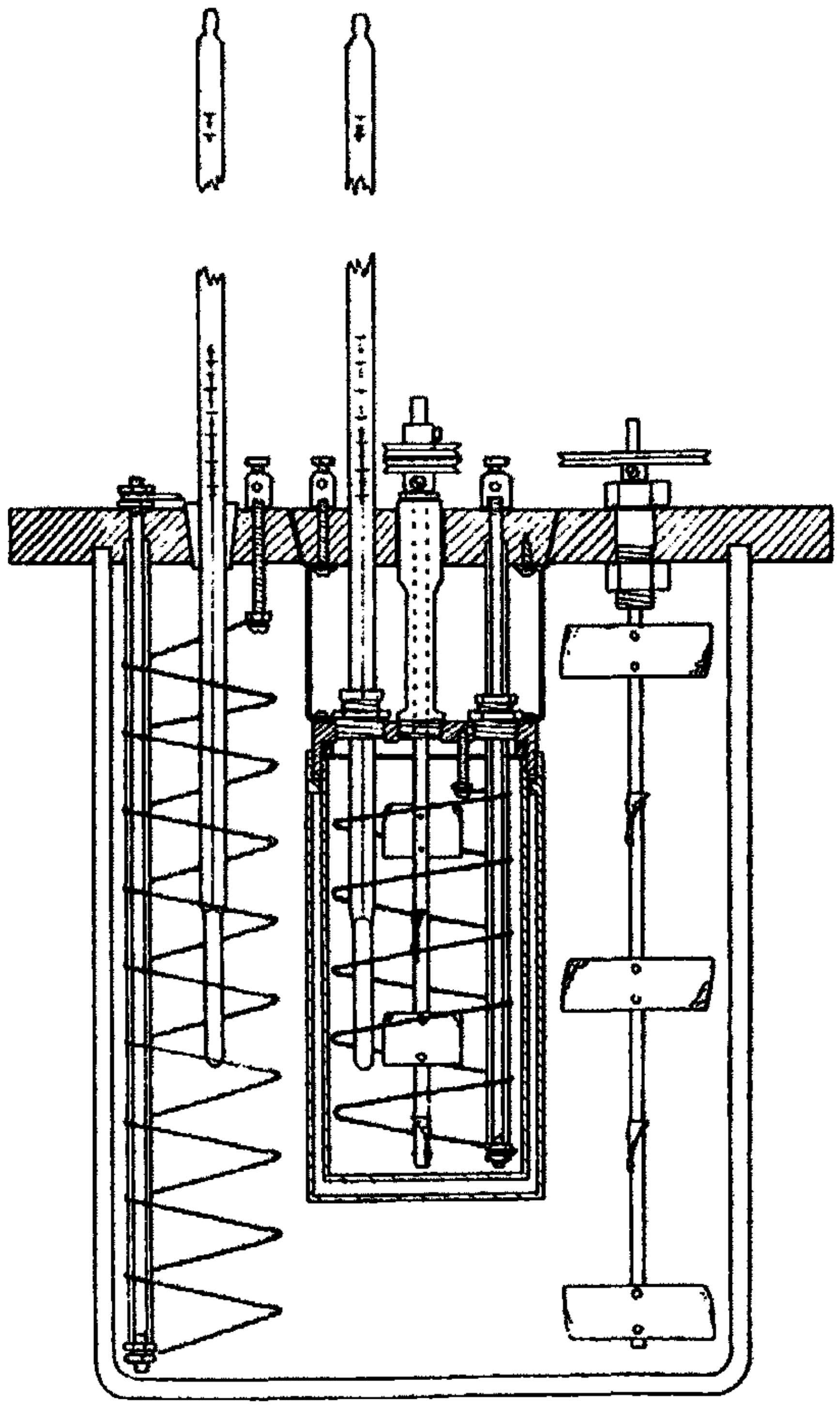
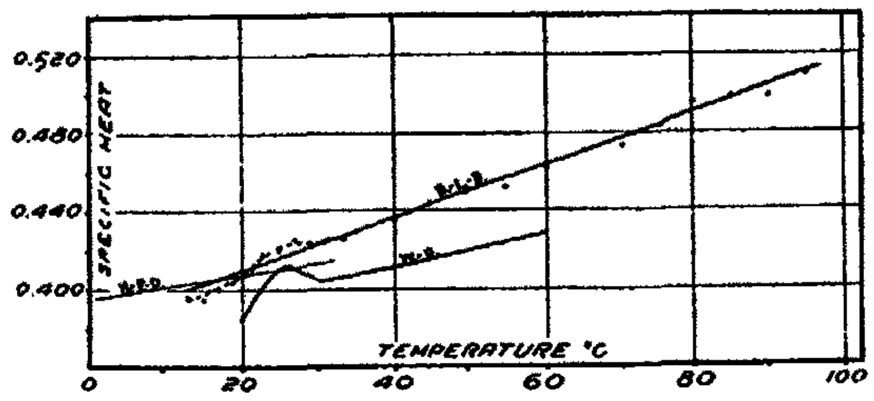


Fig. 1
Complete Calorimeter



Graph 1
Specific Heat of Ethyl Benzene

method of constant heat input and its corresponding constant rate of temperature rise, it was quite easy to keep the inner and outer temperatures equal.

When dissimilar liquids, e. g., water and kerosene, were used in the inner and outer containers, an interesting effect was observed. For example, the calorimeter constant, or correction for heat capacity of the calorimeter itself, was increased 10% at 30° C., and 25% at 90° C., by using kerosene instead of water in the adiabatic bath, water being used in the calorimeter proper in both cases. This effect was no doubt due to the greater heat-carrying capacity (a function of specific heat, density, and thermal conductivity) of water as compared to kerosene. When using water in the inner and kerosene in the outer compartments, the water would heat more than its share of the calorimeter, due to more rapid transfer of heat from coil to walls, resulting in a 10% to 25% error in the calorimeter constant. For this reason, the same liquid, or a liquid with specific heat per cc. and thermal conductivity very nearly equal to that of the liquid being measured, was always placed in the surrounding adiabatic compartment.

Every possible source of error known to us was carefully checked. Thermometer calibrations were corrected for emergent stem; voltmeter and ammeter were calibrated over their entire scales; and the errors due to heat of stirring, evaporation, variation in thermal head, inaccuracy in calibration, inaccuracy in reading instruments, etc., were investigated. As a result, we believe the maximum error to be expected in any specific-heat reading is about 3%.

2. Specific Heats of Ethyl Benzene, Diphenyl Methane, Aniline, and Naphthalene

a. *Materials*

Ethyl Benzene: Refluxed over mercury, shaken with conc. H_2SO_4, dilute NaOH, and water, allowed to stand 30 days over P_2O_5. B. P. = 135.5° – 136.5°; N_D^{25} = 1.49695; $N_f - N_c$ = 0.01531. Sp. gr. 0.8904. It was necessary to use the large boiling range indicated in order to obtain enough material to fill the calorimeter.

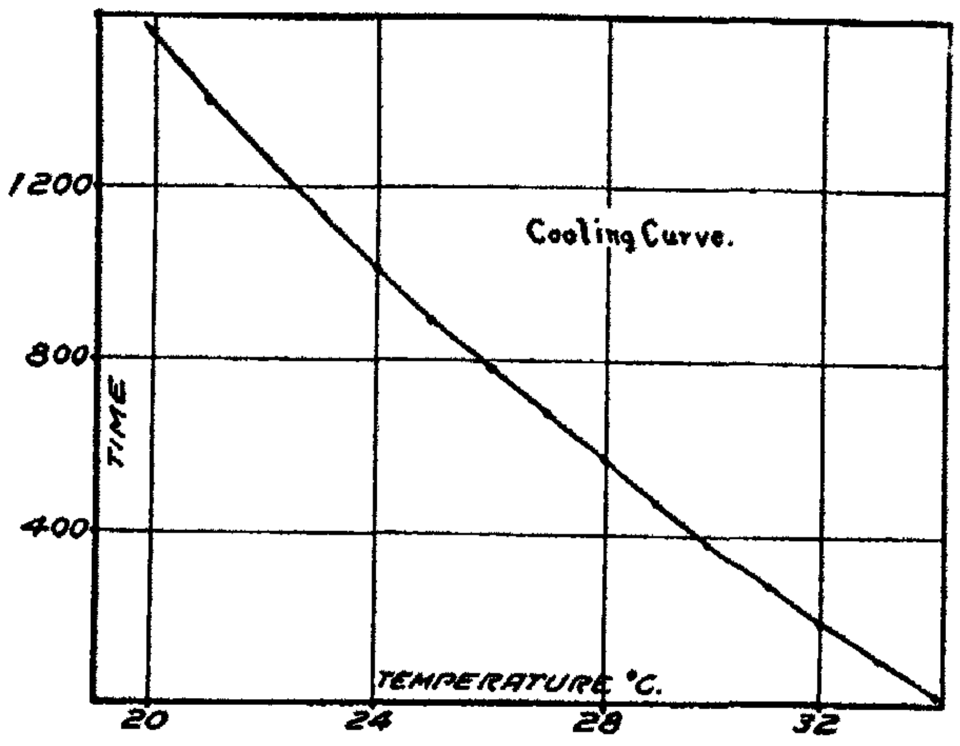
Diphenyl Methane: purified in same manner as ethyl benzene, except dilute H_2SO_4 used instead of concentrated. B. P. = 261°-262° C., N_D^{25} = 1.57390; $N_f - N_c$ = 0.02079.

Aniline: fractionated from Baker's aniline. B. P. = 182.0°, Sp. gr. = 1.027

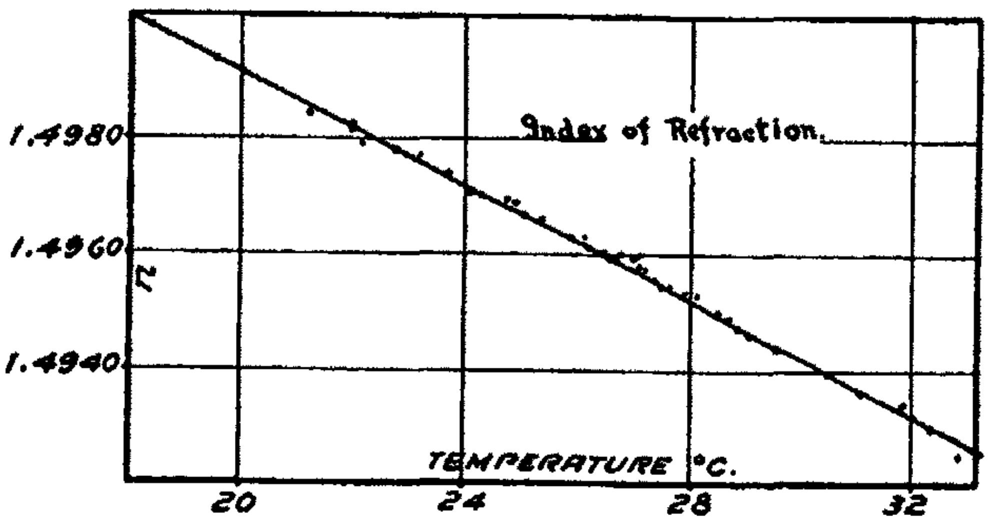
Naphthalene: Redistilled from c.p. naphthalene. M. P. = 80.0°, B. P. = 217.9°, Sp. gr. = 1.110.

b. *Results*

The specific heats obtained are reproduced in Table I and on the accompanying graphs. Each set of figures and each graph represents the mean of from two to four individual series of determinations.



GRAPH 2
Cooling Curve for Ethyl Benzene



GRAPH 3
Index of Refraction for Ethyl Benzene

Wherever possible, the graphs also include the results of other investigators, which are marked by letters denoting the references as given below[3]

The comparison of specific heat curves for ethyl benzene is of especial interest (Graph 1). Williams and F. Daniels[4] observed a marked irregularity

---

[3] *On Ethyl Benzene*

B-L-B,-this paper.
H-P-D,-Huffman, Parks and A. C. Daniels: J. Am. Chem. Soc., 52, 1547 (1929).
W-D,-Williams and F. Daniels: J. Am. Chem. Soc., 46, 903, 1569 (1924).

On Aniline

B-L-B,-this paper.
B,-Bartoli: Nuovo Cimento, (4) 2, 347 (1895).
G,-Griffiths: Phil. Mag., (5), 39, 47, 143 (1895).
L,-Louguinine: Ann. Chim. Phys., (7) 27, 105 (1902).
P,-Penot: Arch. sci. phys., (3) 32, 145 (1894).
Pe,-Petit: Ann. Chim. Phys., (6) 18, 145 (1889).
S,-Schiff: Z. physik. Chem., 1, 376 (1887).
S,-Schlamp: Ber. Ges. Naturw. Heilk., 31, 100 (1895).
T,-Timofijew: Dissertation, Kiew (1905).

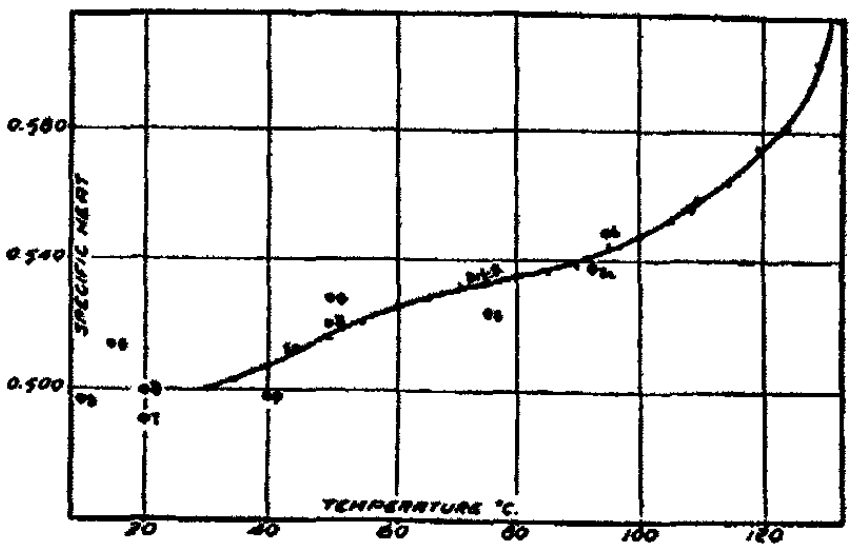
[4] Loc. cit.

Table I

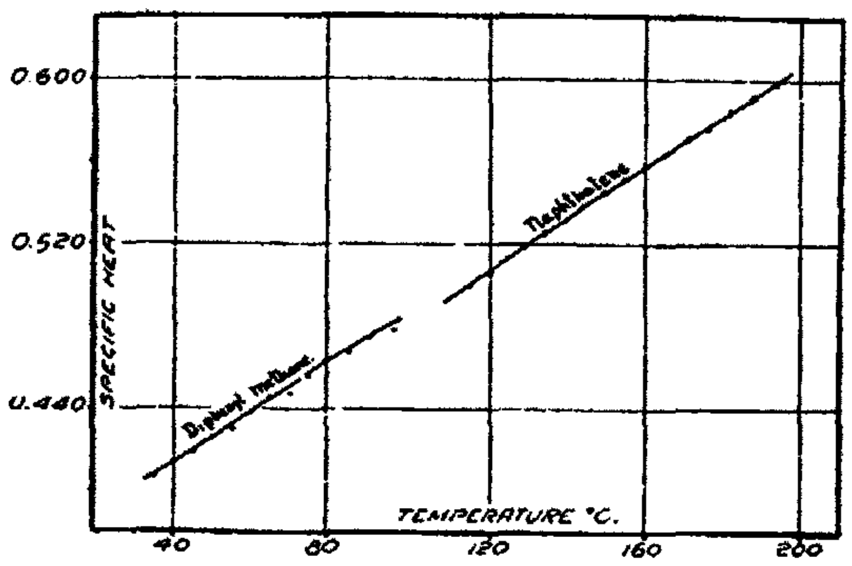
Specific Heats of Organic Liquids

Temp. C°	Ethyl Benzene	Diphenyl Methane	Aniline	Naphthalene
13	0.396			
15	.395			
17	.400			
19	.405			
21	.411			
23	.418			
25	.420			
27	.426			
29	.422			
30	.424		0.500	
31	.426		—	
33	.426		—	
35	.430	0.406	0.503	
40	.435	.414	.507	
45	.444	.419	.512	
50	.450	.426	.515	
55	.452	.430	.520	
60	.462	.438	.526	
65	.471	.446	.528	
70	.473	.447	.532	
75	.483	.455	.533	
80	.495	.464	.535	
85	.498	.467	.536	
90	.496	.475	.538	
95	.510	.478	.545	
104.8			.552	
108.8			.559	0.494
113.8			.564	.500
118.9			.575	.506
124.0			.581	.513
129.2			.601	.519
134.4			.627	.526
139.6			.665	.532
144.8				.539
150.0				.545
155.3				.552
160.4				.558
165.6				.564
170.9				.572
176.1				.578
181.6				.585
187.1				.592
192.7				.598

in the specific heat between 20° and 30° C. Huffman, Parks and A. C. Daniels[5] on the other hand obtained a smooth curve from the melting point to 32° C. Our values show a tendency toward the same variation as observed by Williams and Daniels, although less marked. Some experiments we made on benzene show a tendency toward irregularity in almost the same temperature range (25°-35° C. for benzene, 20°-30° for ethyl benzene). No such irregularity was found for any of the other liquids examined.



GRAPH 4
Specific Heat of Aniline



GRAPH 5
Specific Heats of Diphenyl Methane and Naphthalene

Williams and Daniels found no variation in the density or in the vapor pressure of ethyl benzene throughout the temperature range in question; we find no variations in the cooling curve, (Graph 2). There is possibly a variation in the index of refraction-temperature curve in the region 26°-28°, (Graph 3.) but it is scarcely beyond the limit of accuracy of the refractometer used.

The specific heat curve for aniline, (Graph 4), shows several marked changes in slope. The rapid rise beyond 115° is probably due to a chemical

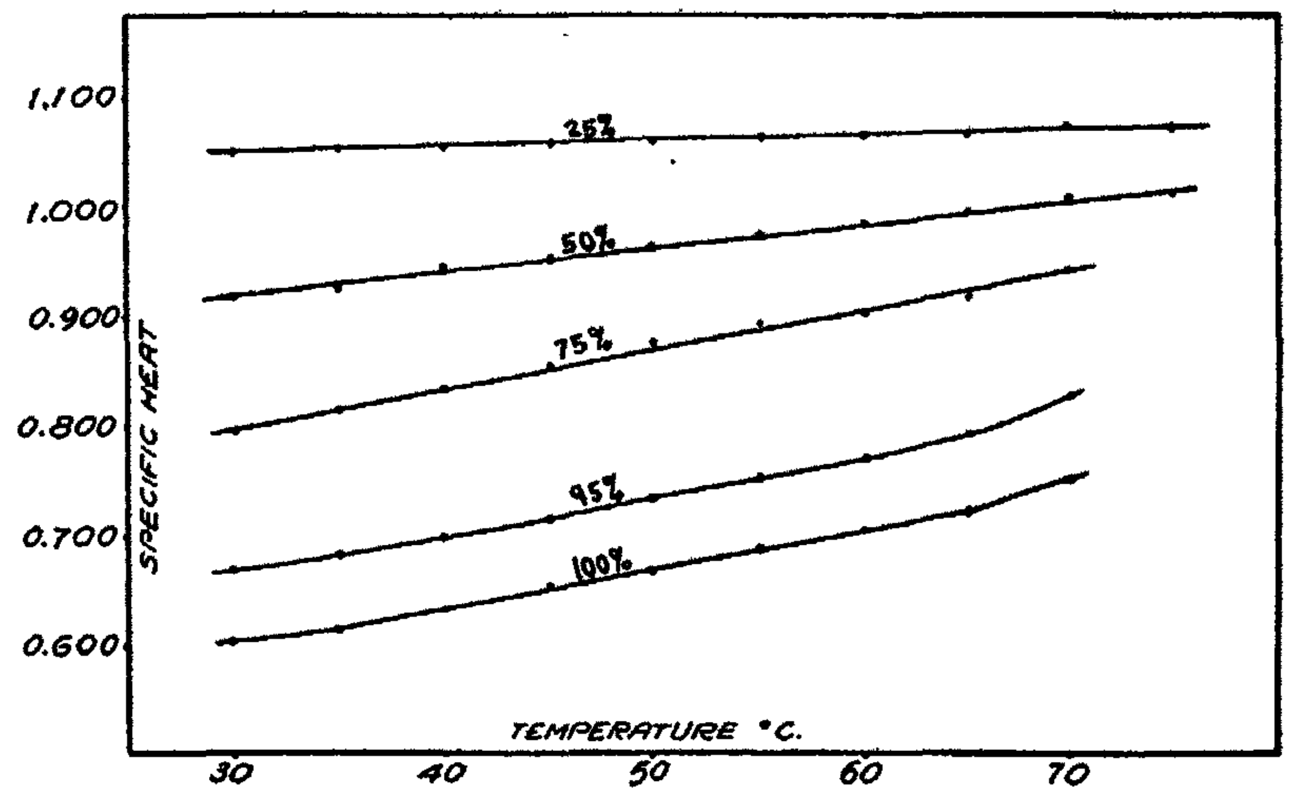
---

[5] Huffman, Parks and A. C. Daniels: J. Am. Chem. Soc., 52, 1547 (1929).

decomposition of the aniline, induced by the metal walls of the container or by electrolysis from the heating coil. When heated above this temperature in the calorimeter the aniline rapidly turned black.

The specific heats of diphenyl methane and of naphthalene, (Graph 5), are straight line functions of the temperature. Indeed, they are directly proportional to the absolute temperature throughout the range measured.

Diphenyl methane, Sp. Heat = 1.312 T.
Naphthalene, Sp. Heat = 1.289 T.



GRAPH 6

Specific Heats of Ethyl Alcohol-Water Mixtures. Weight-percentage of alcohol in the mixtures are given.

3. Specific Heats of Ethyl Alcohol and of Ethyl Alcohol-Water Mixtures

Isolated measurements of the specific heats of various ethyl alcohol-water mixtures have been reported for sixty years.[6]

Bose made the first attempt to correlate change in specific heat with relative concentrations. His measurements showed that the specific heats of alcohol-water mixtures are higher than would be expected for an ideal or perfect mixture. The amount of this variation changed with the temperature but the way in which it changed was not clear. Bose correlated this variation in specific heats with the heat of mixing and its temperature coefficient.

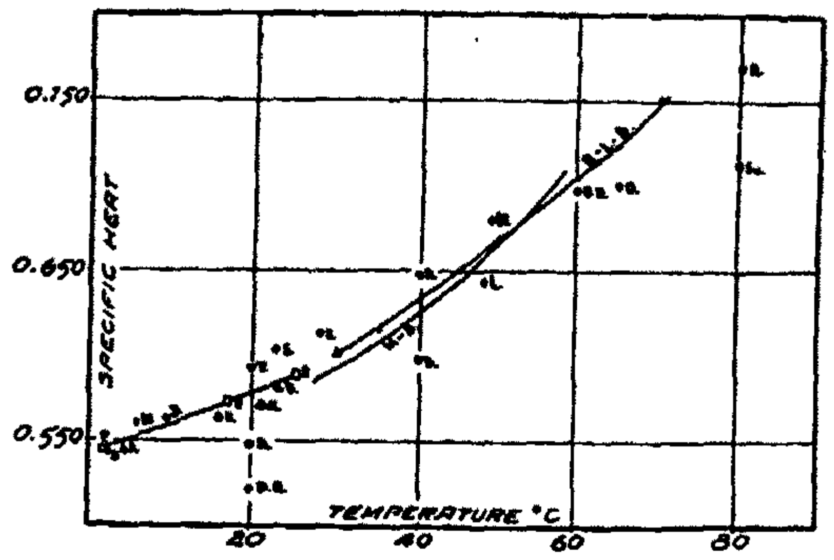
Doroshevskii and Rakovskii, as well as Kolosovskii, have derived empirical formulae for the specific heats of alcohol-water mixtures. These formulae, however, fail to take account of the change in specific heat with temperature.

---

[6] Schüller: Pogg. Ann., V, 116, 192 (1871); Blümcke: Wied. Ann., 25, 154 (1885); Magie: Phys. Rev., 9, 65 (1899); Zettermann; Bose: Z. physik. Chem., 58, 585 (1907); Doroshevskii and Rakovskii: J. Russ. Phys. Chem. Soc., 40, 860 (1908); Kolosovskii: 48, 84 (1916).

The relations between the three variables, specific heat, temperature, and concentration can in fact only be obtained by measuring a number of concentrations over a series of short temperature intervals. We have made such measurements.

Absolute ethyl alcohol was prepared by the usual method of distillation after standing 30 days over pure calcium oxide. The various mixtures were made by diluting this alcohol with pure water. The specific heats found are given in Table II and on Graph 6. As before, each figure in the tables and each point on the curves represents the average of several independent determinations. Our values for the specific heat of pure ethyl alcohol are compared with others found in the literature on Graph 7.*



Graph 7
Specific Heat of Ethyl Alcohol

On Graph 8, the specific heat is plotted against relative concentration for two temperatures. The same bow-shaped curves as observed by Bose are obtained. The curve at 30° is flattened on the side of high alcohol concentration. As the temperature increases, this side builds up until at 70° the curve is almost a perfect bow shape.

This relation is emphasized on Graph 9, where the departure of the specific heats from those of an ideal mixture are plotted against relative concentration.

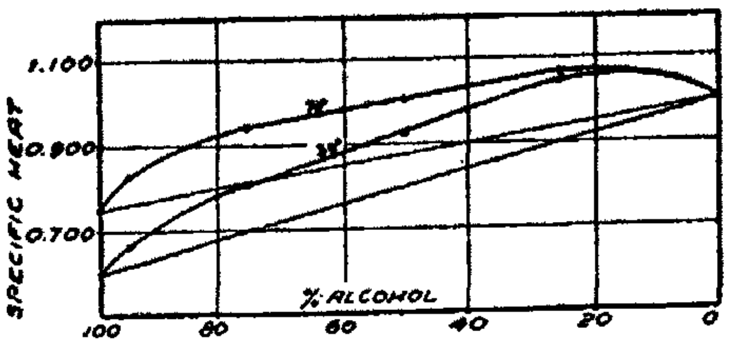
---

* References for pure ethyl alcohol, corresponding to initials on Graph 7.
B,-Bose: Z. physik. Chem., **58**, 585 (1907).
Bl,-Blümcke: Wied. Ann. **25**, 154 (1885).
B-L-B,-Blacet, Leighton and Bartlett: this paper.
D,-DeHeen and Deruyts: Bull. de Belg., (3) **15**, 168 (1888).
D-R,-Doroshevskii and Rakovskii: J. Russ. Phys. Chem. Soc., **40**, 860 (1908).
K,-Kelley: J. Am. Chem. Soc., **51**, 779 (1929).
L,-Louguinine: Ann. Chim. Phys., (7) **13**, 289 (1898).
P,-Parks: J. Am. Chem. Soc., **47**, 338 (1925).
R,-Regnault: Mem. de l'Acad., **26**, 262 (1862).
S,-Schüller: Pogg. Ann., Erg V, **116**, 192 (1871).
Su,-Sutherland: Phil. Mag., (5) **26**, 298 (1888).
T,-Timofejew: Dissertation, Kiew (1905).
W-D,-Williams and Daniels: J. Am. Chem. Soc., **46**, 903, 1569 (1924); **47**, 1490 (1925).

TABLE II

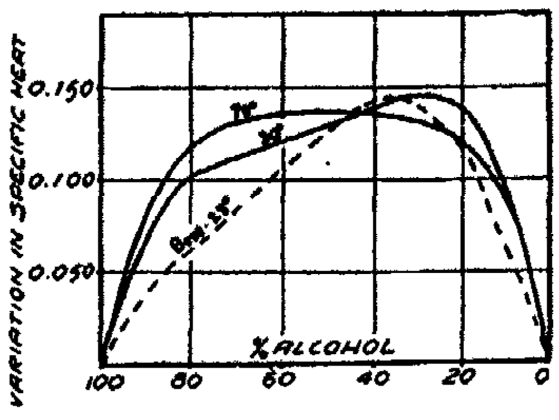
Specific Heats of Ethyl Alcohol-Water Mixtures

Temp.	Per Cent Alcohol 100%	95%	75%	50%	25%
30	0.603	0.668	0.796	0.919	1.051
35	.614	.683	.815	.925	1.053
40	.633	.698	.834	.946	1.055
45	.653	.716	.855	.955	1.060
50	.669	.734	.878	.964	1.062
55	.688	.753	.893	.975	1.065
60	.705	.771	.904	.983	1.066
65	.723	.792	.918	.995	1.066
70	.753	.828	.943	1.008	1.074
75	—	—	—	1.013	1.074



GRAPH 8

Relations of Concentration and Temperature in the Specific Heats of Ethyl Alcohol-Water Mixtures.



GRAPH 9

Variations in the Specific Heats of Ethyl Alcohol-Water Mixtures from the Ideal Mixture Relationship.

At 30°, the maximum variation is found for 30% alcohol. The corresponding mole fractions are alcohol 0.17, water 0.83. As the temperature rises, the maximum moves regularly in the direction of higher alcohol concentration until at 70° it reaches 55% alcohol. For this concentration the mole fractions are alcohol 0.33, water 0.67.

Summary

The specific heats of five pure organic liquids and of ethyl alcohol-water mixtures have been measured over a range of temperatures.

Irregularities in the specific heat of ethyl benzene, and the departure of the specific heats of alcohol-water mixtures from those of ideal mixtures, are discussed.

THE PHASE DIAGRAM OF THE SYSTEM SILVER IODIDE-LEAD IODIDE*

BY FRANK E. E. GERMANN AND CHARLES F. METZ

While working on the conductivity of solid crystalline compounds, Tubandt and Eggert,[1] made a study of the phase diagram of the system silver iodide-lead iodide, and from the results obtained, concluded that these two substances formed a compound having the empirical formula $4AgI,.PbI_2$. From their curve, Fig. 1, it is evident that the point represented by the above formula may be merely a suppressed maximum. Certain authors call such points compounds when the composition is such as can be expressed by a simple formula. There is, however, no justification for this procedure. It appears that Tubandt and Eggert did not determine time cooling curves. The present investigation is devoted to a complete study of the above system by thermal analysis in an attempt to settle definitely the question of the existence or non-existence of a compound between the two iodides

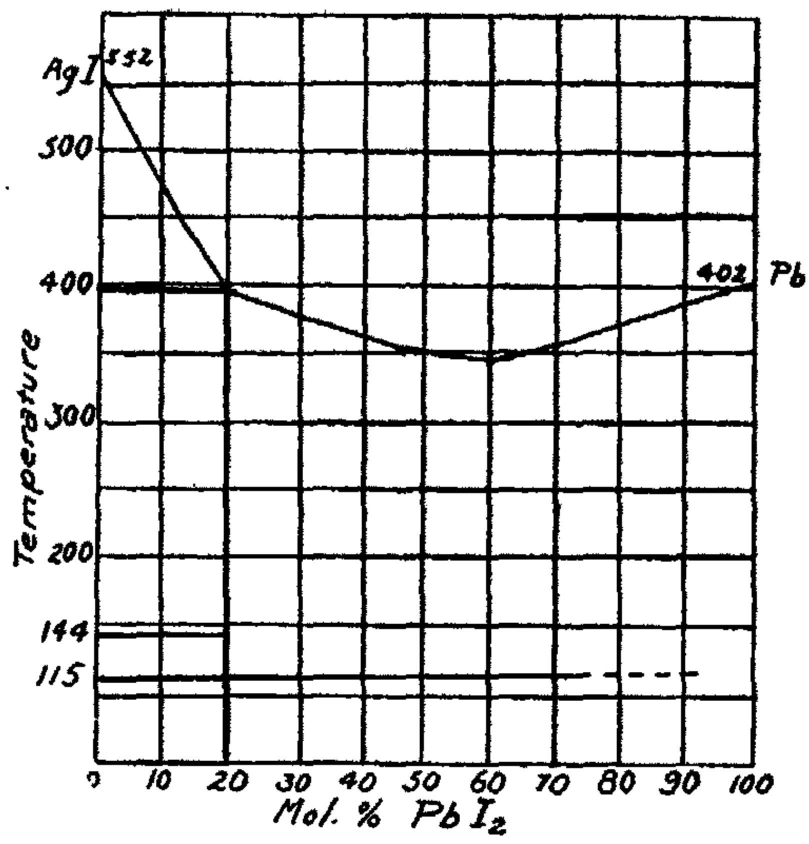


FIG. 1

Theoretical Considerations. The two-component system studied in this work seems to be similar to the system represented by Fig. 2, which may be considered a general case. The exact similarities and differences between the

---

* Contribution from the Department of Chemistry of the University of Colorado.

[1] Tubandt and Eggert: Z. anorg. allgem. Chem., 110, 196 (1920).

general case and the system AgI-PbI_2 are pointed out in the following paragraphs. First, however, the behavior of solutions of different concentrations, in the general case will be discussed.

Suppose a mixture having an initial concentration between point E and pure B of Fig. 2, be heated to the molten condition and allowed to cool slowly. This is represented by dotted line No. 1 in Fig. 2. When the temperature has fallen to the point (l_1) the l-curve is reached and solidification begins. The composition of the crystals which separate will then be given by the point (s_1) of the s-curve which corresponds to the temperature (l_1). Assuming the separating crystals are constantly maintaining a condition of equilibrium with the melt, this melt will have solidified to a conglomerate of mixed crystals all possessing the composition (s′) of the original mixture, by the time the temperature has fallen to (s′). In consequence, the cooling curve of this mixture can show but one interval, namely, one reaching from (l_1) to (s′). This cooling curve is represented graphically in Fig. 3 by curve No. 1, the portion of the curve between (a) and (b) being the crystallization interval.

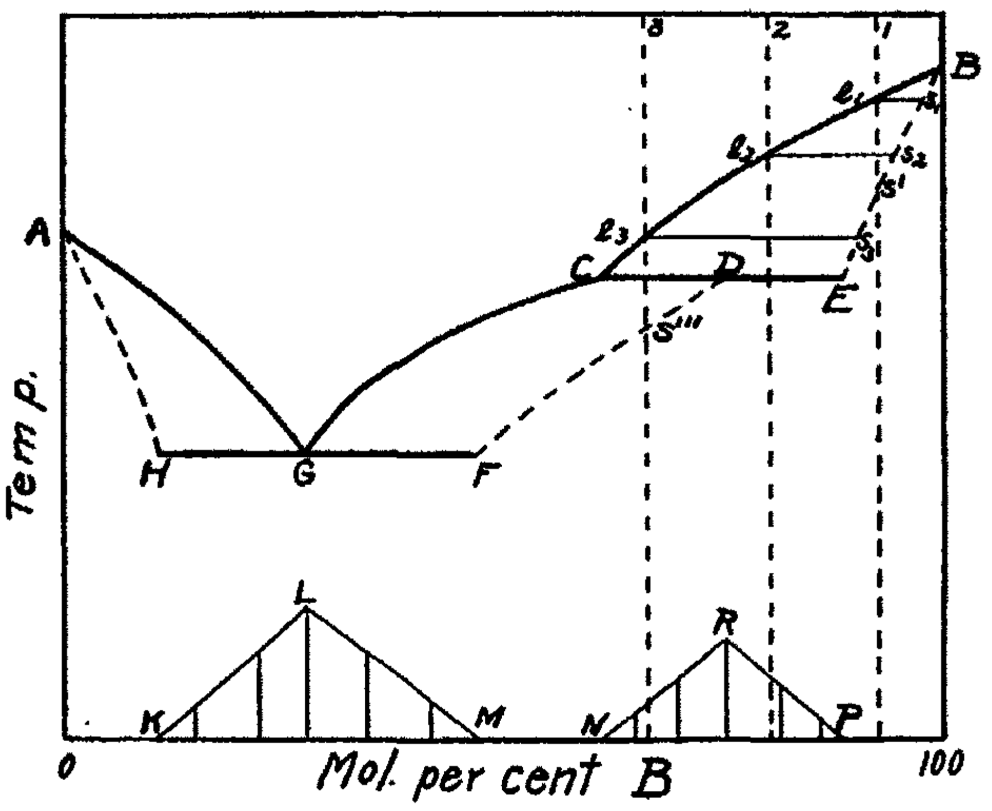


FIG. 2

Suppose now a mixture having an initial concentration represented by dotted line No. 2 be cooled from the molten condition as before. Initial crystallization will begin at a temperature (l_2) on the l-curve, and these crystals will have the composition (s_2). When the temperature has fallen to that of the horizontal CDE the mixture consists of melt of composition C and crystals, which on account of the previously assumed ideal concentration balance, are uniformly of concentration E. If heat is further removed from the system further lowering of the temperature does not at once result. The first thing that occurs is transformation of B-rich saturated mixed crystals E plus melt into saturated mixed crystals having composition D. This reaction persists until the melt is entirely exhausted. This crystallization change is represented graphically in Fig. 3, curve No. 2, by that portion of the curve between (b) and (c). That portion of the curve between (a) and (b) represents the initial crystallization beginning at (l_2) and ending at the temperature of the horizontal CDE. When point c is reached further abstraction of heat causes temperature fall along the lower branch of the cooling curve.

Now, it can readily be seen that the time of duration of this second halt (bc) depends upon the composition of the mixture. When the original composition is that of point D, the duration of this halt will be a maximum, because at this concentration only, will the solid phase, at the close of crystallization, consist only of crystals of concentration D. At the bottom of Fig. 2 is found the length of this halt plotted against composition, and is labeled NRP. This is the only method by which point D can be located by thermal analysis methods.

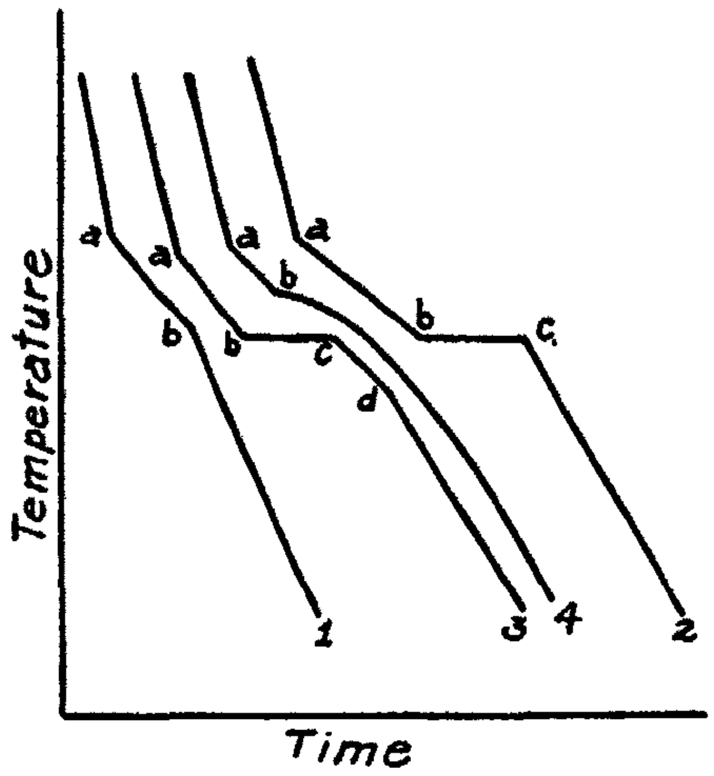


Fig. 3

If a third mixture, represented in composition by dotted line No. 3 is cooled from the molten condition, initial crystallization occurs at the temperature (l_3). These crystals have the composition (s_3). When the temperature has fallen to that of the horizontal CDE, the whole mixture consists of melt C and B-rich crystals of concentration E, as did mixture No. 2 at this temperature. On further abstraction of heat, transformation of these B-rich crystals plus the melt into the crystalline variety D occurs. When this reaction has proceeded to completion, no crystals of concentration E are left, and the mixture consists of crystals of composition D and melt C. Thus far, the time-cooling curve is identical to curve No. 2 of Fig. 3, and is also represented by curve No. 3 of the same figure, down to point (c). Further solidification of the melt C follows along the branch CG of the l-curve, whereby the composition of the crystals with which it is in equilibrium is given by the branch DF. In accordance with our assumption of complete concentration balance between crystals and melt, the latter will have become completely solidified by the time the temperature (s''') is reached, the solid phase consisting of a conglomerate of homogeneous crystals of this composition. This last crystallization is represented by a break in the cooling curve, represented by the (cd) section of curve No. 3, Fig. 3.

In case of sluggish crystallization and in the absence of complete equilibrium between melt and crystals, the (bc) and (cd) portion of curve No. 3, Fig. 3 are not well defined, and there results a cooling curve similar to No. 4. Thus the determination of the maximum length of the crystallization interval at the temperature of the horizontal CDE is rendered practically impossible. The system studied in this work seemed to present these difficulties.

A careful study of Fig. 2 will reveal the fact that the behavior of mixtures having concentrations between C and pure D is not unlike the behavior of a system showing a "suppressed maximum." Thus, in spite of the fact that there has been some controversy over whether a crystal of concentration D should be called a compound, it is believed there can be no serious objection to this, providing the composition at that point can be expressed by a simple formula.

The above theoretical considerations are offered in some detail because it seems that the system studied in this work belongs to a limiting case of the above where point F coincides with G, and point E coincides with pure B, or practically so in each case.

Experimental. The silver iodide was precipitated from a solution of silver nitrate in pure water by means of a solution of potassium iodide. The lead iodide was precipitated from a solution of lead nitrate in pure water by the addition of a solution of potassium iodide. The silver and lead nitrates and the potassium iodide were all Mallinckrodt's C.P. quality.

After precipitation, each precipitate was repeatedly washed by decantation with distilled water, until a portion of the decanted solution would not give a test for nitrates when diphenylamine in concentrated sulfuric acid was used as testing reagent. Both precipitates were then dried on porcelain plates for twenty-four hours at room temperature, and then placed in an oven at 110°C for six hours. They were then pulverized and dried again for six hours at 110°C. Finally they were placed in colored glass desiccators over anhydrous calcium chloride, and kept there until used. The preparation of both iodides was carried on in the absence of daylight due to the fact that AgI is rather easily decomposed by light, while in the moist condition.

In order to obtain good cooling curves, a Hoskins combustion furnace, well insulated to allow slow cooling, was used. This furnace was placed in a vertical position in a straight side iron bucket, with a diameter of twelve inches and a height of fourteen inches. The bucket was filled with fine dry sand. This served as a good heat insulator as well as a heat reservoir. The furnace so insulated against rapid radiation was used in all this work, giving excellent satisfaction.

Because of its high thermoelectric power, an iron-constantan thermocouple was used for obtaining the temperatures. One wire of this couple consisted of iron, analyzing 99.7% having a diameter of 0.320 mm. The other wire was of "constantan" having a composition of 60% copper and 40% nickel, covered with black enamel, and having a diameter of 0.30 mm.

The hot junction was protected by a quartz tube closed at one end, having an outside diameter of 3 mm. and an inside diameter of 2 mm. The length of the tube was 25 cm. A small pyrex glass tube just large enough to slide over the iron wire, and of a length equal to that of the quartz tube, was placed over the iron wire, next to the junction. This was for the purpose of insulating the two wires of the couple. The junction was then slipped into the quartz tube. The cold junction was protected by a pyrex glass tube having approximately the same dimensions as the above. A small pyrex tube was used here also to insulate the two wires of the couple. The cold junction was kept by at 0° C by means of a thermos bottle filled with ice. The protecting tube of this junction occupied a position in the thermos bottle such that it was not immersed in the ice water. In other words, the tube protecting the junction was in contact with only the fine cracked ice.

The couple was compared with a nickel-chromium couple whose temperature-E.M.F. curve was accurately known. The results when plotted gave practically a straight line.

The potentiometer used in this work was a Leeds and Northrup Type K, capable of being read to 0.01 millivolts. The galvanometer used was a Leeds and Northrup wall type, having a resistance of 1150 ohms. An Eppley cell, having an E.M.F. of 1.01889 volts at 26°C was used as a standard. A working E.M.F. of two volts was obtained from one cell of an ordinary three cell, six volt storage battery. The different mixtures were kept in double pyrex test tubes and nitrogen gas was circulated above them for several minutes before heating in order to insure the absence of oxygen. A standardized set of weights and an accurate analytical balance were used in obtaining weights of the two components of the mixtures.

The furnace was previously heated to a temperature of 650° C for twenty-four hours in each case. After the mixtures had attained a temperature of approximately 600°C, the current was decreased by means of a resistance so the furnace would cool uniformly and slowly. Readings were taken every minute and the data tabulated. The rate of cooling in the neighborhood of the freezing points of the different mixtures was between one and two degrees per minute which was thought to be slow enough. Mixture No. 20 was repeated with the rate of cooling about 0.5°C per minute, but the results were no different.

Each mixture while in the molten condition, was a heavy viscous liquid, dark red in color. As it cooled down, it passed through an orange color to a yellow. The mixtures containing a large amount of silver iodide were a pale yellow, but this color changed progressively to a deep yellow, as the silver iodide content decreased.

During the determination of each of these time-cooling curves, the working battery was kept balanced against the standard cell, and the cold junction of the thermocouple was kept at 0°C in the manner previously described.

Results. The freezing points of the various mixtures were tabulated and plotted. Table I shows the results obtained. The centigrade temperatures obtained in Table I were obtained from the calibration curve for the iron-constantan thermocouple. The time-cooling curve for each mixture was plotted and it was found the data obtained gave a very smooth curve. The results given in Table I are plotted in Fig. 4. The ordinates are E.M.F. in millivolts and the abscissae are per cent composition.

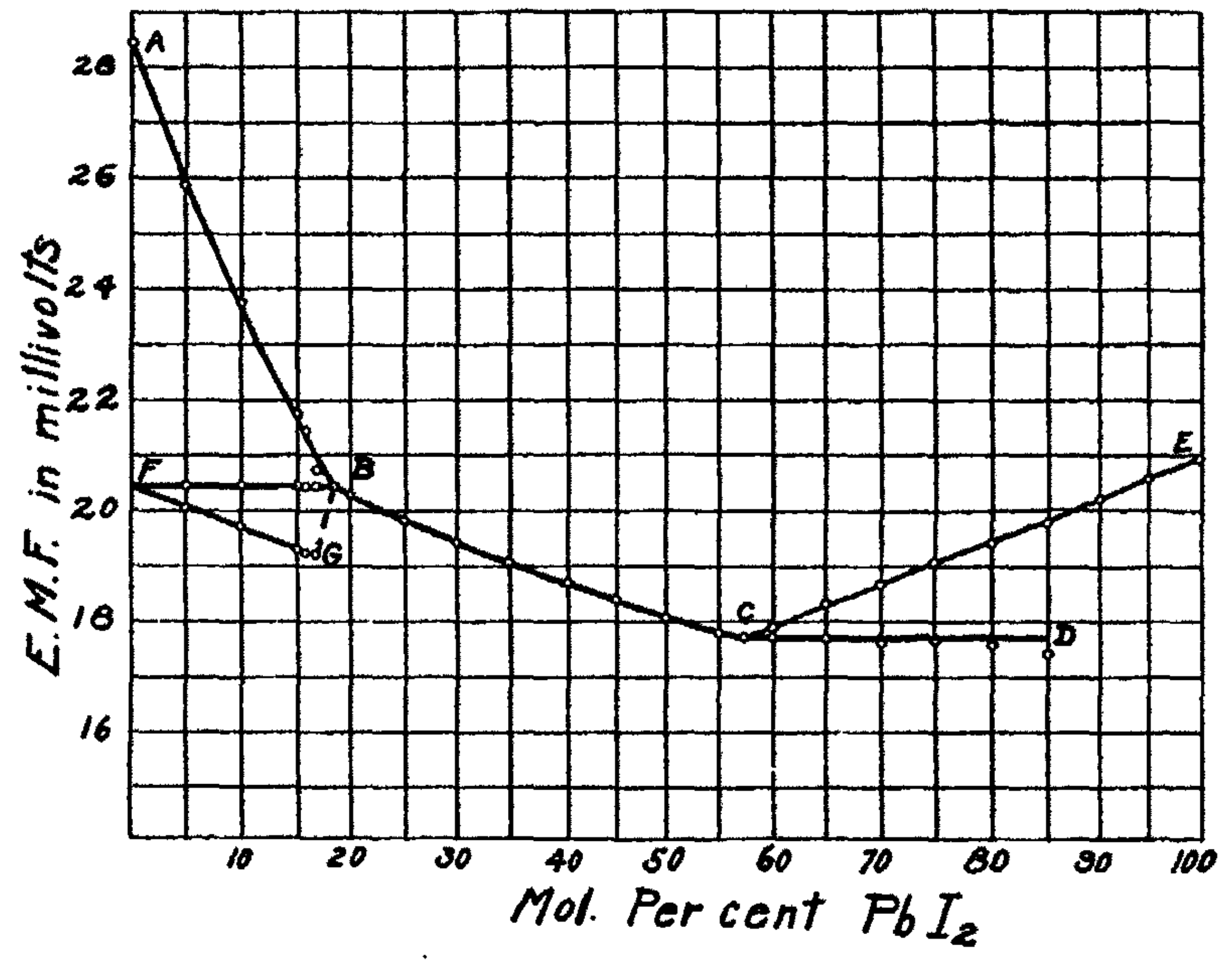


FIG. 4

The following interpretation has been given of the diagram. Between the concentration 18.5 Mol% PbI_2 represented by point B, and 57.5 Mol% PbI_2 represented by point C, we have equilibria between pure AgI and solid solutions of varying composition. Similarly between 85 and 100% PbI_2 we have solid solutions in equilibrium with pure PbI_2. As the temperature falls the solid solution first appearing breaks down. Between the concentrations represented by the points C and D the time-cooling curves showed two halts, the first halt being caused by pure PbI_2 crystallizing from the melt, while the second halt was caused by a solid solution of composition C (57.5 Mol% PbI_2) crystallizing from solution. The length of time of this second halt grew less with increasing concentration of PbI_2, and was scarcely noticeable at a concentration of 85 Mol% PbI_2. Point D then represents the limit of miscibility of AgI in PbI_2. At concentrations greater than 85 Mol% PbI_2, only one halt was obtained on the time-cooling curves of these mixtures.

Point A represents pure AgI, and only one halt was obtained on the time-cooling curve. Silver iodide crystallizes very sluggishly, also having a tendency to supercool. The cooling curve for this substance is far from ideal. Mixtures having an original composition of 5, 10, 15, 15.75, and 16.66 Mol% PbI_2 each showed two intervals of crystallization on their time-cooling curves. The temperature of the second crystallization of these mixtures was identical in each case. The length of time of the second crystallization in each of these mixtures increased with increasing PbI_2 content. However, owing to very sluggish crystallization, the curves were not ideal, making the determination of the length of time of this second crystallization rather inaccurate. In so far as this portion of the diagram has the possibility of a suppressed maximum, the relative lengths of time of the second crystallization in the above mixtures is the only method of determining the composition of the compound. Suppose a compound is formed and has the composition $5AgI.PbI_2$ corresponding to 16.66 Mol% PbI_2, then the mixture having a composition greater than 16.66

TABLE I

Mixture No.	Composition (Conc. PbI_2)	Freezing Point			
		E.M.F. Millivolts		(Degrees Cent.)	
		First	Second	First	Second
1	Pure PbI_2	20.92	—	412	—
2	95 Mol%	20.58	—	405	—
3	90 Mol%	20.20	—	398	—
4	85 Mol%	19.79	17.23	389	342
5	80 Mol%	19.43	17.44	383	344
6	75 Mol%	19.08	17.57	376	346
7	70 Mol%	18.68	17.62	368	348
8	65 Mol%	18.32	17.71	360	350
9	60 Mol%	17.93	17.72	353	350
10	57.50 Mol%	17.75	—	350	—
11	55 Mol%	17.80	—	351	—
12	50 Mol%	18.08	—	356	—
13	45 Mol%	18.40	—	362	—
14	40 Mol%	18.70	—	368	—
15	35 Mol%	19.07	—	375	—
16	30 Mol%	19.44	—	382	—
17	25 Mol%	19.84	—	390	—
18	20 Mol%	20.29	—	399	—
19	18.50 Mol%	20.47	—	402	—
24	16.66 Mol%	20.70	20.48	408	402
25	15.75 Mol%	21.45	20.48	420	402
20	15 Mol%	21.60	20.48	425	402
21	10 Mol%	23.75	20.48	467	402
22	5 Mol%	25.84	20.45	507	402
23	Pure AgI	28.43	—	558	—

Mol% PbI_2 and less than 18.5 Mol% would show two crystallizations on its time-cooling curve, but at the end of the first crystallization (crystallization of the compound itself) there would still be some melt left having a concentration of B. In this case the melt would begin solidifying at the same temperature as the compound, thus increasing the total interval of crystallization. Thus it is impossible to determine the length of the crystallization interval of the compound itself. This particular difficulty is explained by time-cooling curve No. 4 of Fig. 3.

In view of the above we are inclined to believe that if a compound is formed, it probably has the composition $5AgI.PbI_2$, since no other simple formula corresponds to any composition between 16.66 Mol% PbI_2 and including 18.5 Mol% PbI_2 (point B). The results obtained here prove conclusively that the two iodides do not form a compound having the formula $4AgI.PbI_2$, as stated by Tubandt and Eggert.

In Fig. 4, below the horizontal FB, will be found the curve FG, which indicates the time of crystallization at the temperature of FB plotted against composition. As was stated above, the cooling curves obtained were not ideal, making the determination of these intervals rather difficult. However, the curve FG indicates in a general way the relative lengths of time of these halts.

Referring again to Fig. 1, we note a halt on the cooling curves of mixtures having concentrations up to and including 20 Mol% PbI_2, at a temperature of 144°C. In the above region of concentrations, the time-cooling curves were determined in the neighborhood of the above temperature, and it was found that this crystallization was not present in mixtures having concentration greater than 15.75 Mol% PbI_2. Just what significance this fact might have on the interpretation of the above results is not clear. However, it is known that AgI undergoes a polymorphic transformation at this temperature, as well as another change at about 115°C. This being the case it might lead to the conclusion that possibly the formation of a compound at concentration of 16.66 Mol% PbI_2 would prevent or at least slow up this change of the AgI so it would not be noticeable on a time-cooling curve.

The melting point of silver iodide was found to be 558°C, while that of lead iodide was found to be 412°C. These results appear to be higher than any previously reported. From what could be found in the literature, the highest reported value for the melting point of silver iodide was 556°C. The difference between this value and the one found in this work is only two degrees, which is within the limits of experimental error. The highest reported value for the melting point of lead iodide, previous to this time was 402°C. The difference between this value and the one found in this work is ten degrees. It seems hardly possible to attribute this much of a difference to experimental error.

The two sources of error most likely to creep in, in work of this kind are first, impurities in the salt, and second, incorrect calibration of the thermocouple. In view of the fact that an impurity in a substance or compound usually lowers its melting point, it seems possible that this has been one of the chief causes of some of the low results that have been reported in the literature. The salts used in this work were washed by decantation until entirely free from nitrates and it is believed they were as free from impurity as it was possible to make them.

The thermocouple used in this work was calibrated in two different ways and since the results obtained checked very closely, it is believed this couple was accurate to within one degree over the entire range. In view of the foregoing, it is believed the results obtained are accurate to within one degree.

Conclusions. 1. The system $AgI.PbI_2$ may possibly form a compound having the empirical formula 5 $AgI.PbI_2$, but not $4AgI.PbI_2$.

2. The method of thermal analysis ordinarily used in determining the composition of the compound formed in cases of a "suppressed maximum" cannot be used in this case due to a region of formation of solid solutions, and very sluggish crystallization.

3. The system formed a series of solid solutions, the extreme limits of composition being 18.5 Mol% to 57.5 Mol% PbI_2, and 85 to 100% PbI_2.

4. Silver iodide is miscible with lead iodide up to a concentration of approximately 15 Mol% AgI.

5. The melting points of pure lead iodide and pure silver iodide have been redetermined and higher values than any previously reported have been obtained. Since impurities usually tend to lower melting points, it is believed that the new values are more nearly correct than any previously reported. The values suggested for adoption are, silver iodide 558° ± 1°C, and for lead iodide 412° ± 1°C.

6. It appears that Tubandt and Eggert failed to find the region of limited miscibility, and the region of limited formation of solid solutions. From the diagram obtained in this work it is impossible to assume that a compound having the composition $4AgI.PbI_2$ is formed, which is miscible in an excess of PbI_2.

7. It is believed that the phase diagram for this system is the first of its kind to be reported. Although theoretical treatment has been given to this same type of diagram, this seems to be a limiting case. Even though the possibility of a "suppressed maximum" may exist, the composition of the compound cannot be determined by thermal analysis alone.

A CRITICAL STUDY OF PRECISION CRYOSCOPY: THE FREEZING-POINT DEPRESSIONS OF POTASSIUM COBALTICYANIDE AND POTASSIUM FERRICYANIDE*

BY CAMPBELL ROBERTSON ** AND VICTOR K. LA MER

1. Introduction

The modern uses of exact dilute freezing-point data are concerned with the behavior of the freezing-point depression-concentration relation, at molalities so low that the unknown factors which enter at concentrations above 0.05 molal are negligible.

At sufficient dilution, it is possible to calculate activities of the solute by thermodynamic methods, without bringing in extensive simplifying assumptions. The accuracy of this procedure is dependent upon the range of dilution into which we may extend measurements without undue sacrifice of experimental precision.

In addition to the thermodynamic treatment, we may interpret freezing-point measurements by introducing kinetic and electrostatic considerations, and evaluating the osmotic properties of the solute on the basis of a physical picture. This approach is exemplified in the Debye-Hückel theory,[11] and its extensions in the work of Gronwall, LaMer, and Sandved.[13]

At the dilutions necessary, the plot of the observed freezing-point depressions against concentration is so nearly linear as to be of no significance. It is essential to use a divergence function which will be sensitive to deviations of the observed measurements from the ideal behavior. For this purpose Bjerrum introduced the osmotic coefficient, $\phi = \frac{\vartheta}{\nu\lambda m}$, i.e. the van't Hoff "i" divided by ν, the number of ions. His osmotic deviation, $1 - \phi$, is equivalent to the Lewis and Randall "j." In the testing of the Debye theory it is convenient to employ the function $\frac{\theta}{z_1 z_2 K}$, which is proportional to the function $j/m^{\frac{1}{2}}$ used by Randall and his co-workers. In this expression, z_1 and z_2 are the valences of the anions and cations respectively, and $K^2 = \frac{4\pi N\epsilon^2}{DkT} \sum_{1}^{s} z_i^2 m_i$.

We shall not enter into extensive mathematical treatment of these theories. The subsequent discussion will accordingly be confined to a few points of major importance, which are of especial moment in determining the experimental requirements.

---

* Contribution No. 655 from the Chandler Laboratories of the Department of Chemistry, Columbia University, New York, N. Y.

** Dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science of Columbia University by Campbell Robertson, University Fellow for 1929-30.

The developments of the Debye-Hückel theory by Gronwall, LaMer, and Sandved, indicate that the plot of $j/m^{1/2}$ against $m^{1/2}$ (or the analogous plot of the Debye development, $\frac{\theta}{z_1 z_2 K}$ against $m^{1/2}$), should show a definite "hump," at concentrations of the order of 0.001 molal, the exact concentration depending on the valence type of the salt under consideration. The experimental data of Hausrath,[40] and of Randall and Scott,[8] on barium nitrate, may be interpreted on this basis.

The existence and magnitude of the hump are crucial points, and it is unfortunate that it occurs at just about the concentrations at which experimental freezing-point results of sufficient precision are difficult to obtain.

The j-function, as before mentioned, is exceedingly sensitive, and its sensitivity to experimental error increases rapidly as measurements are carried below 0.001 M. An error of temperature measurement of 1×10^{-5} degrees, which represents the extreme limit of precision with present methods, corresponds to a change in j of 4% for a uni-univalent salt at 0.001 M (one of the least extreme cases). For high valence type salts at dilutions where the hump is most manifest, the same temperature error may change j by as much as 10 or 12%.

It is evident from the foregoing that unambiguous interpretation of freezing-point measurements depends upon reducing the sum of the errors to exceedingly small magnitudes in very dilute solution. The present experimental technique is barely adequate for the purpose, and this study will be primarily devoted to investigating the sources of error, and the limits to which precision may be carried.

2. Experimental Aspects of the Problem

The first methods of Raoult[45] and of Beckmann[36] involved the actual freezing of the solution, with appropriate efforts to measure a static quantity in a continuously changing system. With good technique, the method will yield results of moderate accuracy when the concentrations employed are of the order of 0.1 molal, but it can never be considered exact.

Twenty years later, it was recognized that inasmuch as the freezing point of a solution is the point at which the solution is in equilibrium with the solid phase of the pure solvent, it would be more logical procedure to bring a large quantity of the solid solvent into contact with the given solution and attempt to attain a fairly permanent equilibrium state. Richards, [46,47] in 1903, first realized the marked advantages of the equilibrium method. The subsequent history of the problem has involved the further refinement of this technique.

Temperature Measurement

Richards in his 1903 paper emphasized the fact that the Beckmann thermometer had insurmountable limitations and that further refinement depended upon the development of better temperature measuring devices.

There are now two instruments which measure small temperature differences more precisely than the Beckmann thermometer: the multiple junction thermoelement, and the platinum resistance thermometer.

The thermoelement was first used for freezing point work by Hausrath,[40] and by Osaka,[43] both in 1902, and later by Jahn,[41] Dixon,[37] and Flugel.[38] Adams[2] in 1915 greatly improved thermoelement technique, and his refinements have been followed by all the subsequent investigators; namely, Harkins, Randall, and their students,[4,5,6,8,9] Hovorka and Rodebush,[7] Abel, Redlich and v. Lengyel,[1] and Wesöe.[10]

The resistance thermometer was first used by Griffiths[39] in 1891, and later by Barnes, Archibald and McIntosh,[34] Bedford,[3] Elliot,[22] Chadwell,[20] and Getman.[25] Bedford used a differential resistance thermometer, and others a simple single coil. Richards was instrumental in improving the technique of the resistance thermometer, in connection with his calorimetric researches.

At the present time it appears that the thermoelement is the superior instrument for freezing-point work. In general, potential readings present fewer difficulties and errors than resistance readings, particularly at high sensitivities, where contact resistances are a source of error in bridge methods.

It is not a matter of great difficulty to construct a thermoelement, which, with a fairly sensitive galvanometer, will detect temperature differences of less than 1×10^{-5} C., while the two most recent investigators using platinum resistance thermometers, Chadwell in 1927, and Getman in 1929, only claim a reading precision of 5×10^{-4} C. Bedford, it is true, claimed for his differential platinum thermometer a reading precision of 6×10^{-6} C., but since this involved measuring the movement of a sliding contact on a wire to 1/250 mm., it is doubtful whether his contention deserves much weight.

Concentration Measurement

The production of a stable two-phase equilibrium, by using roughly equal quantities of solution and solid solvent, and the measurement of the equilibrium temperature by means of multiple junction thermoelements, solved two of the three major problems in freezing-point determinations. The third is the determination of the concentration of the equilibrium solution.

There are two fundamentally different ways of accomplishing this. Either the solution may be introduced in a roughly known concentration, allowed to attain equilibrium, and a portion of it then removed and analyzed, or the solution may be made up in the beginning to an exact concentration, and brought into contact with the solid solvent at so nearly the final temperature that the concentration change produced by the attainment of equilibrium may be neglected.

Adams[2] took the first course, using the interferometer for the analysis of his dilute solutions. Hall and Harkins[4] made further determinations using Adams' apparatus. Randall and Vanselow,[9] and later Randall and Scott,[8] and Wesoe,[10] employed conductivity measurements as means of analysis. Hovorka and Rodebush[7] introduced the second, or pre-cooling, method.

The precision of the interferometer falls off very rapidly in the dilute range,[17] and cannot compare with that of the conductivity method. The relative merits of the latter and of the pre-cooling method are more closely balanced, and the decision between them hinges on finer points, such as labor involved, expense of construction, and available apparatus. The conductivity method is more expensive and involves more operations during the course of a determination. In this investigation it was found that the method of pre-cooling was more expeditious and fully as precise. Although conductimetric measurements were used to check the efficiency of the pre-cooling, the former is an unnecessary refinement, if the apparatus is suitably designed for the pre-cooling technique.

Secondary Factors influencing Design

The Influence of Dissolved Air. The solubility of air in water at 0°C. is 1.28×10^{-3} mols per liter, hence it is obvious that air constitutes a source of great potential errors in dilute solutions. The use of the thermoelement as a measuring instrument involves the immersion of one of its legs in the mixture of solution and solid solvent, and the other in a mixture of the two phases of the pure solvent alone. Thus as a necessary condition for precise measurements the contents of the two vessels must be identical in all points except for the dissolved substance being measured; either we must have no foreign material, such as air, in either vessel, or, alternatively, we must have it present in the same concentration in each.

At first glance the simplest way of fulfilling the above condition would appear to be the evacuation of both vessels. The experimental difficulties, however, are very great, due to the tendency of dissolved gases to remain supersaturated, and to the difficulty of maintaining an anaerobic condition in the apparatus during the manipulations. Randall and Vanselow's apparatus embodies provision for evacuation, but at the cost of considerable experimental complexity. Even then, they are obliged to release the vacuum during the manipulations.

The other means of attaining identical conditions is to pass air into both vessels and keep them completely saturated. This procedure, first used by Hovorka and Rodebush, possesses the inherent advantage that, although the last traces of air are difficult to remove from solution, the solution process is rapid. The process of solution of air in water has been intensively studied[18,19,23,26] in connection with the purification of water supplies, and it has been definitely established that the solution of the gas in the surface layer of liquid is practically instantaneous, so that only adequate mixing of the liquid is needed for quick and complete total saturation. We have accordingly adopted the method of saturating with air at atmospheric pressure.

Errors of the Air-saturation Technique. The systematic errors of the air saturation method are small and of definitely calculable magnitude. The solubility of the air will be changed by the slightly lower temperature of the vessel which contains the ice and solution, and by the presence of the dissolved salt. These errors give a constant percentage error in the observed freezing-point lowering, since the effects on air solubility are, nearly enough, linear functions of salt concentration.

From the measurements of Fox,[24] summarized by Coste,[21] we may calculate both errors for the case of sodium chloride, and safely assume that they will be of the same order of magnitude for other salts. Dissolved sodium chloride decreases the solubility of the air to the extent of introducing an error of 0.026% in the observed freezing-point depression, while the lower temperature in the solution vessel will tend to increase the solubility to give an error of 0.004% in the other direction.

The pressure of air over the liquid in the two vessels must be equal. A difference in pressure of 2 cm. of water will change the solubility of the air by 2.5×10^{-6} mols per liter, introducing a 0.13% error for the case of a 0.001 molal KCl solution. This percent error will be greater for more dilute and less for stronger solutions.

If the air-stream used for stirring and saturating is not pre-cooled to exactly 0°C, it will melt ice and cause dilution. If it is not saturated with water vapor at 0°C it will evaporate some of the water in the solution vessel as it passes through and thus concentrate the solution. These contingencies are guarded against by passing the air stream through a series of wash bottles filled with ice and water, which simultaneously cool it, and saturate it with water vapor at 0°C. A slight amount of water will be condensed in the solution vessel on account of this treatment, since the solution has a lower vapor pressure. This error, however, is only of the order of 0.002%.

Some ice will be melted in the solution vessel, since the incoming air is warmer than the solution by an amount equal to the freezing-point lowering, but this error is, under the most adverse conditions, less than 0.02%. The calculations for the foregoing error figures are given in detail in the section on errors.

The State of Equilibrium. The term "equilibrium state" describes an ideal, which rarely, if ever, exists in the physical world. It is often approximated to a point beyond the detecting sensitivity of instruments, but in freezing-point work on dilute solutions considerable care is required to bring about even this close an approach to the ideal condition. It is fairly easy to maintain a solid-liquid equilibrium when the two phases have the same composition, but where a solution is in contact with the solid phase of the pure solvent, it is more difficult.

To define the difficulty, let us consider a static system consisting of ice, solution, a containing vessel, and the leg of a thermoelement. Let it be assumed that at some given instant a state of temperature equilibrium exists in this vessel, and that the walls of the vessel are perfect heat insulators, so that the only thermal flow is through the thermoelement.

Since the outer end of the thermoelement is at a slightly higher temperature than this leg, a quantity of heat will be continually flowing in through the wires and the casing. If the element is to indicate the temperature, which has been assumed momentarily to exist, this heat must be absorbed as fast as it leaks in. The only place where it can be absorbed without raising the temperature of the liquid is at the ice-solution interface. However, as soon as a minute quantity of ice melts, a film of water in contact with the ice is formed, and the temperature of equilibrium for this contact is not the freezing-point of the solution, but that of water. Hence, if there is no mixing whatever in the vessel, the presence of a thermoelement will continually tend to destroy the equilibrium temperature it is meant to measure.

Counteracting this tendency we have convection currents due to the slight temperature differences set up, and whatever artificial stirring which may be introduced. It cannot be anticipated that convection effects will be efficient considering the minute temperature differences involved. Hence it is evident that there must be continual and very efficient stirring if we are to successfully measure the temperature equilibrium condition with an instrument which is a conductor of heat.

It is important to minimize the amount of heat conduction along the thermoelement, but unless it is rendered absolutely zero, the stirring cannot be omitted.

The foregoing discussion has been postulated on the perfect heat insulating properties of the containing vessels. Thermal leakage through the vessel walls of course exists, concurrently with that through the thermoelement, but its effect on the stability of the measured equilibrium is less, because in this case the absorption of heat occurs at a relatively remote region of the vessel.

Another consideration, as well as the above, dictates thorough stirring. The pressure coefficient of the freezing-point of water is 0.0075°C. per atmosphere. Therefore if we have a vertical vessel 14 cm. deep, filled with a mixture of ice and water, the equilibrium temperature for the bottom will be 0.0001°C. lower than that for the top. A state of perfect freezing-point equilibrium cannot exist in a vessel of finite size, (unless we have only a plane horizontal contact surface between the phases) and efficient stirring is imperative if we are to approximate the mean temperature to an equal extent in both containers.

It is best to have the temperature of the outside thermostatic bath approximate that of the vessel which contains the ice and the solution. By doing this, a higher thermal head is put on the vessel which contains the ice and water, but here there is not the disability existing where the two phases differ in composition.

3. The Apparatus and Procedure

Outline of Apparatus

The apparatus is illustrated in Figs. 1 and 2. Fig. 1 shows that part of the assembly which is contained within the ice-water thermostat. Fig. 2 shows the electrical system. The assembly consists of the following chief parts:

(1) A double-walled copper tank (Fig. 1,A) of about 100 L. capacity, equipped with air-jet circulators (not shown), which, filled with ice and water, serves as a thermostat.

(2) Two 500 cc silvered Dewar vessels (Fig. 1,B), supported in a brass frame in the thermostat. The vessels are provided with air circulators, and with lead tubes to permit emptying and filling without disturbing the assembly.

(3) A rack holding ten 500 cc bottles, clamped into the bottom of the thermostat. The bottles are each equipped with a lead tube and vent tube opening above the surface of the bath, and contain the series of concentrations on which measurements are being made.

(4) A 48 junction copper-nickel thermoelement (Fig. 1,D) the legs encased in seamless silver tubes, one leg sealed into each Dewar vessel.

(5) An electrical measuring system, (Fig. 2) consisting of a standard 1-ohm coil (A) kept at 25°C., a high sensitivity galvanometer (B), and a special form of potentiometer circuit.

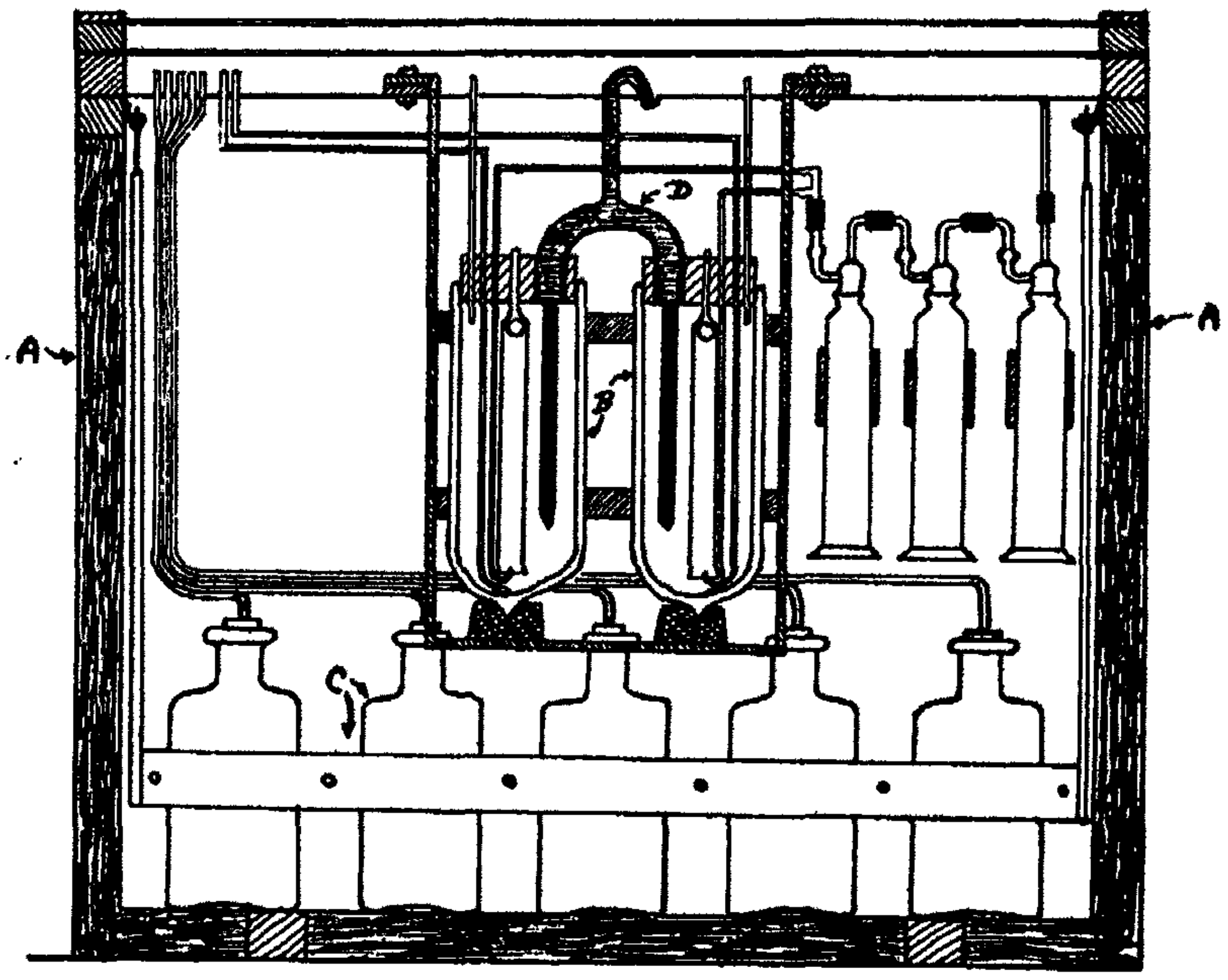


FIG. 1
Freezing-Point Apparatus

Procedure in making Measurements.

As the first step, all glassware was cleaned with chromic acid. It was then steamed out for four hours, and kept in contact with distilled water for 24 hours more to remove adsorbed material from the cleaning mixture.

Dilute solutions of desired concentrations were made up by weight from the dried salt. Usually five concentrations were prepared, and two reservoir bottles filled with each. The bottles were then assembled in the rack, and the latter clamped in place in the bottom of the thermostat tank. The stoppers carrying the tubes leading from the bottles were sealed with "picein" cement as an extra precaution against leaks.

One hundred and fifty pounds of cracked ice were placed in the tank, enough water run in to make a mush, the circulators started, the tank covered, and the assembly left over night to allow the contents of the bottles to reach 0°C. Several measurements of the rate of cooling of these bottles were made, using an auxiliary thermoelement, the average half-time being 18 minutes. On this basis about 4 hours should be sufficient to cool the bottle contents from 25°C. to 0.003°C. In the mornings the auxiliary thermoelement reading was never greater than 0.01 degree and the average was nearer 0.004°C.

At the start of the actual run, the series of three gas-washing bottles, which served to chill the air used for saturating and stirring the contents of the freezing-point vessels, were half-filled with cracked ice and water and put in place inside the thermostat.

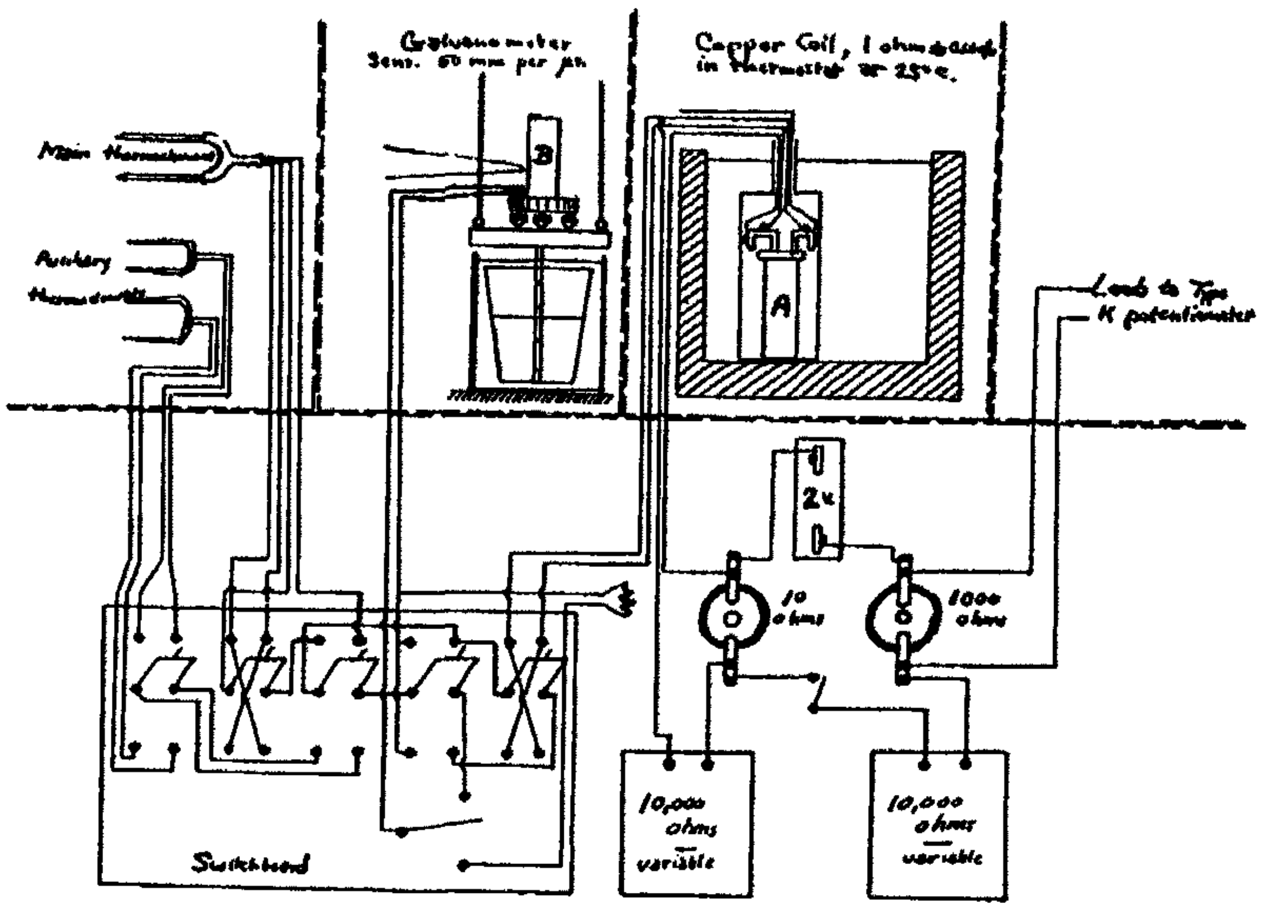


Fig. 2
Electrical System

The two freezing-point vessels were filled with sifted and washed cracked ice, the stoppers, carrying inlet and exit tubes, stirrers, and thermoelement, were inserted, sealed into place with "picein" cement, the seals tested for tightness with compressed air, and the frame carrying the vessels lowered into place in the thermostat tank. The thermoelement lead wires were connected to the potentiometer circuit, the vessels filled with previously chilled distilled water, and a zero thermoelement reading taken.

The procedure in making a measurement for a given concentration was then as follows: the contents of the solution vessel were transferred by suction to a waste container, and the vessel filled from bottle No. 1, by applying air pressure through the vent tube of the bottle.

The small stirrer and saturator inside the vessel was run for three minutes. Then, with the circulator running, this first filling was removed in the same manner as before. The whole operation was then repeated twice more in the same way, except that the third filling was from bottle No. 2 and was circulated for five minutes. The third filling was removed, and the final filling run in from bottle No. 2. The circulator was again started, and at intervals of ten minutes, readings of the thermoelement electromotive forces were taken. If the 20-minute and 30-minute readings agreed to within 5×10^{-6} degree, their mean was then recorded as the reading, and the entire process repeated for the next concentration. If the solution was slow in coming to equilibrium, a reading was taken at the end of 40 minutes.

Detailed Description of the Apparatus

(A) The ice thermostat.

The thermostat consisted of a double-walled copper tank, inside dimensions 80 × 60 × 30 cm, the gross capacity being 95 liters. The 5 cm. space in the hollow walls was filled with ice-box felt, to minimize the heat losses. When the tank was allowed to stand filled with ice without disturbing the cover, the last of the ice did not melt for about four days.

The tank was covered with a frame carrying two sheets of glass about 5 cm apart, allowing inspection of the interior without removal of the cover, and at the same time diminishing the heat losses. To eliminate stratification, four air-jet circulators were placed on the sides of the tank, lifting 36 liters of water per minute from the bottom of the tank, and distributing it over the ice at the top. They were made from pieces of one-inch conduit, about 25 inches long, and extended from the bottom to the top of the tank, the upper end being bent around on a 6 inch radius to a horizontal delivery opening at the level of the liquid in the tank. Large diameter glass tubes are fastened to the backs of the pipes, and at the bottom are bent around in goose-neck shape, terminating in a vertical jet projecting one inch into the bottom orifice. With circulators of the type described, no variations of greater than a few thousandths of a degree were ever observed on auxiliary thermoelements inserted in various parts of the bath.

(B) The freezing-point vessel assembly.

The freezing-point vessels were high-vacuum silvered Dewar flasks with a capacity of about 450 cc. They were rigidly fastened about 3 cm. apart in a frame made of heavy brass. With the frame and flasks in position, the tops of the flasks were 18 cm. below the surface of the bath.

The flasks were closed with large rubber stoppers. From the stoppers were suspended miniature air-jet circulators, similar in principle to those which were found to work well in the outside tank. They were made of glass, the construction being evident from the diagram. These small circulators lifted about 200 cc. per minute, a volume equal to the total liquid contents of each vessel during measurements. The stoppers carried thin glass drain tubes, extending exactly to the center of the rounded bottom of each flask, so that when suction was applied to this tube and the liquid drained, less than 0.3 cc. remained in the bottom. The flasks were also equipped with vent tubes extending about 1½ cm. below the lower surface of the stopper, the extension being long enough so that the contents of the flasks never came in contact with the rubber. The legs of the thermoelement extended to within 5 cm. of the bottoms of the flasks. The thermoelement leads were carried to the top of the bath through an 8 mm glass tube filled with paraffin.

(C) The solution bottle assembly.

The solution bottles were ten 500 cc bottles rigidly held in a frame, the latter carrying two brass rods extending to the top edge of the tank, and there being clamped under projecting lugs, to hold the rack in place as the bottles were gradually drained.

The lead tubes, extending from the bottoms of the bottles, and the vent tubes, extending from the shoulders, were single lengths of small diameter glass tubing. The lead tubes were carried to the center front of the rack, where they were bent up to the top of the tank. The vent tubes were likewise carried above the surface, five at each side. The lead and vent tubes were capped to prevent the accidental ingress of water.

The Design of Sensitive Thermolements

By increasing the number of junctions, the theoretical sensitivity, attainable with a thermoelement, increases almost without limit. In the design of a specific instrument for a given problem, however, there are binding restrictions, and for any set of conditions there is a definite optimum design.

The thermolement is an instrument of low electromotive force and relatively high resistance, so that the greatest degree sensitivity, while nominally a question of electromotive force per degree, is ultimately, where galvanometers are involved, a question of current per degree. The design is also limited by the allowable heat conductivity and by the necessity of having the element of such form and size that all the junctions at each end may be assuredly at the temperature they are meant to measure.

The weight to be assigned to each of these factors varies acccording to the problem in hand, but in general for the type of element where the junctions are bundled together and enclosed in a case, the first and third are the most important. Thus the allowable bulk of the completed instrument is the chief limiting factor and the following development is based on this assumption.

The most desirable metal pair, fulfilling these criteria, is one which has the maximum ratio of thermal electromotive force to total resistance. It is of no value to select a couple of high electromotive force per degree if the resistance is simultaneously increased in like or greater proportion. This governing ratio has been ascertained for a number of combinations which seemed promising.

When the thermoelectric potentials of the various metals are plotted on a linear scale, it is at once seen that most of the common metals lie close together, and since this group includes copper, the others in it may be neglected, as having no advantage, since silver alone has a lower resistance than copper. The available metals away from the central group on the scale, are iron and antimony, on one side, nickel, cobalt, bismuth, and constantan, on the other. Thus there are some ten combinations for which the electromotive force-resistance ratio may profitably be calculated.

The following data are from the International Critical Tables.

Pair	Ratio	Pair	Ratio
Iron-copper	1.39	Iron-nickel	2.18
Antimony-copper	0.81	Iron-constantan	0.90
Bismuth-copper	0.60	Antimony-nickel	1.17
Constantan-copper	0.77	Antimony-constantan	0.83
Nickel-copper	2.47	Antimony-bismuth	0.66

From these ratios, which are the true measure of the relative sensitivity to be obtained from an element of given cross-section, it is evident that the thermal electromotive force alone is not a reliable guide. Several combinations are superior to the copper constantan commonly employed, copper-nickel particularly so, for this type of work.*

Ratio of the Two Metals. For a given pair of metals, there is an optimum ratio of cross-sections which gives the minimum resistance. If A represents the total cross-section of a pair of wires M and R, and ρ is the total resistance of the two,

$$\rho = \rho_M/Ax + \rho_R/A(1-x) \tag{1}$$

where x is the fraction of cross-section represented by M. Solving for the minimum value of ρ in terms of x,

$$\frac{\delta\rho}{\delta x} = -\rho_M/Ax^2 + \rho_R/A(1-x)^2 \tag{2}$$

$$x = \frac{-\rho_M \pm \sqrt{\rho_M \cdot \rho_R}}{\rho_R - \rho_M} \tag{3}$$

The real root gives the optimum fraction of cross-section for M. For copper-nickel elements, this ratio is 1:2.1, which is most nearly satisfied by a difference of three sizes in the B. & S. gauge.

Number of Junctions. The final point of design is the choice of specific sizes and number of junctions, as functions of the metal pair, the allowable cross-section, and the galvanometer characteristics.

Let: D = scale divisions per amp.
A = allowable cross section.
K = res. const. of metal pair.
N = number of junctions
R_g = galv. res. (plus potentiometer res. if appreciable.)
R_j = resistance per junc.
E = e.m.f. per degree per junc.
C = cross sec. per junc.
y = scale divisions per °C.

From these quantities we may obtain the expression for scale divisions per degree, the criterion of sensitivity.

$$y = DNE/(R_g + R_jN), \tag{4}$$

or scale divisions per degree equal scale divisions per microampere times the ratio of total electromotive force to total resistance.

---

*See footnote at bottom of page 1976.

$$\text{But, } N = A/C \text{ and } R_j = K/C \tag{5}$$

Substituting,

$$y = DAEC/(R_gC^2 + AK) \tag{6}$$

Solving for the maximum,

$$dy/dC = DAE(AK - R_gC^2)/(R_gC^2 + AK)^2 \tag{7}$$

Equating the derivative to zero, we get,

$$C_{\text{optimum}} = \sqrt{AK/R_g} \tag{8}$$

Or, from (5),

$$N_{\text{optimum}} = \sqrt{AR_g/K} \tag{9}$$

Thus for any allowable cross-section selected for the element, two wire sizes may be found which will give the maximum sensitivity. To make the numerical calculation from equations (8) and (9), it is necessary to have a value for K. This is obtained from the expression.

$$K = L[(\rho_M/x + \rho_N/(1 - x),] \tag{10}$$

where L is the length of one junction, and x and (1 − x) are the fractions of cross-section of the respective metals. K has the dimensions of ohms × cm^2, and has the value for copper-nickel elements 35 cm. long, of 5.29×10^{-4}.

The condition for greatest sensitivity is that the resistance of the element equal the external resistance. This may be shown by transposing equation (7).

$$R_g = AK/C^2 = R_jN$$

Insulation. When the thermoelement is immersed in the solution, the condition for precision is that the temperatures of the wire junctions and the outside of the casing shall differ only by a negligible amount. The total heat conductivity from the junctions out through the insulating and embedding material, and casing, must be much greater than that along the thermoelement wires and the casing from the outside environment, which is at some differing temperature.

The first obvious requisite is that the bundled thermoelement wires should, as nearly as possible, entirely fill the casing, to obtain the shortest possible heat path from the solution to the tips of the junctions. This requires very thin, but electrically effective, insulation between the junctions.

In the course of this work, several sorts of insulating compound were used. The thin rubber coat, described by Adams[2] and by White[31] was first tried, but with little success, due to the difficulty of getting an even coat of the rubber over the tips. The solution of rubber in carbon disulphide tended to gather into globules over the heavy parts of the junctions and to pull away entirely from the sharper bends of the metal, producing short circuits. Bakelite varnish and a special compound of gutta percha and rosin were tried, but did not prove as satisfactory as shellac. Shellac can be evenly applied with a fine camel's hair brush, dries readily and does not crack or come off unless the wire is bent very sharply.

It is necessary to fill the space between the bundle of wires and the casing with some suitable heat conducting imbedding material. Wood's metal is unsuitable, for although it is not difficult to secure adequate insulation between the bundled thermoelement junctions, it is quite another matter to sufficiently insulate the junctions to allow insertion in a conducting mass without the advent of short circuits.

After several unsuccessful trials, the metal-imbedding idea was abandoned in favor of paraffin. The thermal conductivity of paraffin is considerably greater than that of air, though of course much less than that of any metallic mass. White[31] recommends the use of naphthalene, which has a slightly higher thermal conductivity than paraffin, but the difference was not thought to be of sufficient moment to offset the ease of handling of paraffin.

The thermal properties of elements as ordinarily constructed can be greatly improved by using silver, or other metal, tubes instead of glass. The improvement in the use of silver is not entirely a function of the thermal conductivities, though that of silver is much greater than that of glass. The important point is that the silver tube may be very thin-walled, not over 0.15 mm. in thickness, while a glass tube of such wall-thickness would be too fragile for use.

Construction and Calibration of the Thermoelements.

Two multi-junction thermoelements were constructed. The first, a 25-junction copper-constantan element, enclosed in glass, was used for the first freezing-point measurements, and subsequently as an auxiliary element for ascertaining the stability and attainment of the temperature equilibrium between the ice bath and the solutions in the reservoir bottles. The second, a 48-junction copper-nickel element, enclosed in silver tubes, was used for the freezing-point measurements here reported.

The copper-constantan element was made from No. 30 double cotton copper covered copper wire, and No. 28 double cotton covered constantan wire. The wires were given several coats of shellac, cut to 35 cm. length, and the ends bared for about 7 mm. The thermoelement was assembled on a board 32 cm. in width, along the edges of which were bolted two strips containing grooves on the side in contact with the board. Each strip had more than enough grooves for the entire number of wires in the thermoelement. The wires were inserted through these grooves in the proper order, and the projecting ends twisted together. The junctions were soldered by successive dips into small crucibles of melted rosin and solder, the temperature of the solder being such that only the thinnest of coats remained on the junction.

The enclosure for the first thermoelement consisted of glass tubes of 8 mm. outside diameter. The central portion of the element was enclosed in a semicircular glass tube of 14 mm. diameter, bent to a radius of 70 mm.

After the shellac insulation on the junctions had dried, the wires were bundled together into a U-shape, thrust through the center enclosure, and the two lead wires brought out through a side tube. The glass legs were then poured partly full of paraffin, the bundle of junctions inserted, the legs fastened into the central bend, and the remaining interior poured full of paraffin as a precaution against the intrusion of moisture.

Since this element was not intended to be used for other than a relatively rough instrument, it was calibrated against two Beckmann thermometers, which had previously been compared with each other along the entire length of their scales. The electromotive force of the copper-constantan element as thus obtained was 956 microvolts per degree. Its resistance at 0°C. was 92.5 ohms.

The Copper-Nickel Element. The copper-nickel thermoelement embodied the findings of the previous section as to wire sizes, and the improvement of making the legs of the enclosure of silver instead of glass.

Insulated nickel wire is not an article of commerce, but a quantity of No. 28 high purity nickel wire was specially double silk insulated for us by Driver, Harris & Co., of Newark. The copper wire was No. 32 double silk covered. The methods of assembling, soldering, and insulating the tips, were identical with those previously described, except that on account of the larger number of junctions, the wires were cut in lengths of 33.5, 34.5, 35.5, and 36.5 cm., in order to stagger the junctions and avoid undue bulk at any one point.

The silver tubes were seamless spun of C.P. silver, the dimensions being 15 centimeters length by 8 mm. outside diameter. The average wall thickness was 0.15 mm. There were no appreciable corrosion effects.

For the calibration of the copper-nickel thermoelement, the equation $E = E_0 - aT^n$, first suggested for thermoelements by Rodebush,[16] and subsequently used by Randall and Vanselow,[9] was taken as the calibration function.

One leg of the element was kept at 0°C. in a mush of melting ice, and the other was immersed successively in a mush of redistilled mercury, in melting ice, and in a thermostat at 25°C., the exact temperature of the latter being checked with a Bureau of Standards calibrated thermometer. The results are given in the following table:

	E,	T, °K.
Ice-mercury	−26775	234.2
Ice-ice	0	273.1
Ice-25 C.	−19708	298.1

From these three points on the curve, the values for the constants a and n, in the above equation, were derived. The values were: $a = 0.5887$ $n = 2.1388$

The values for the derivatives at 273.1 K, are:

$$\left(\frac{dE}{dT}\right)_{273.1} = 748.67 \qquad \left(\frac{d^2E}{dT^2}\right)_{273.1} = 3.12$$

The electromotive force of this element at 0°C. is accordingly 748.67 microvolts per degree. The deviation from linearity is only 0.02% for a measured temperature difference of 0.1°C., and the calibration can hence be regarded as linear for the small temperature differences measured in this work.

The Electrical Measuring System

The thermoelectromotive forces measured ranged from two to 100 microvolts, and it was necessary to measure them with a precision of at least 0.1%. Fig. 3 shows an auxiliary circuit, resembling that used by Hovorka and Rodebush,[7] which, when used in conjunction with a Type K potentiometer, allows the rapid measurement of electromotive forces from 0.1 microvolt to 500 microvolts, with a precision limited only by the sensitivity of the galvanometer in the thermoelement circuit.

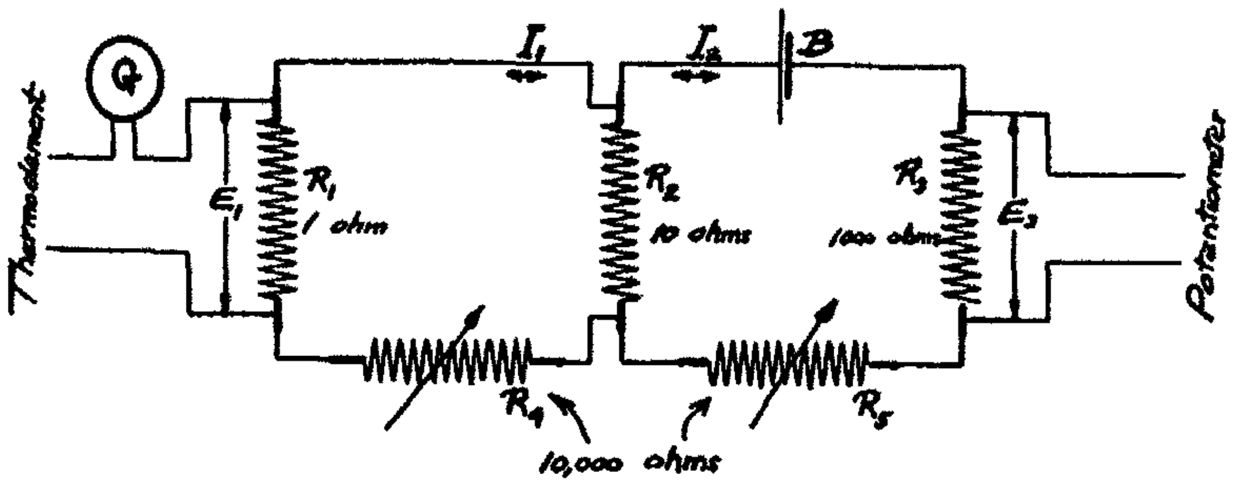


Fig. 3
The Electrical Measuring Circuit

Description. The unknown electromotive force of the thermoelement is balanced against a potential drop produced across a calibrated 1-ohm copper coil R_1, kept in a thermostat at 25°C.

The potential drop E_1 is varied by adjusting the variable resistances R_4 and R_5, until a balance is secured. Its magnitude is then easily calculated from the simple relations of the circuit.

Current from an auxiliary battery B flows through the circuit, and this current I_2 divides itself between the two branches of the circuit containing R_1 and R_2 respectively. The total current I_2 is measured with the Type K potentiometer, in terms of the potential drop across the 1000 ohm coil R_3. This measured electromotive force E_3, is then related to E_1, the electromotive force balanced against the thermoelement, by the following functions:

$$E_1 = I_1R_1$$

$$I_1 = I_2 \times \frac{R_2}{(R_1 + R_2 + R_4)}$$

$$I_2 = \frac{E_3}{R_3}$$

Or, combining,

$$E_1 = E_3 \times \frac{R_1 \times R_2}{(R_1 + R_2 + R_4) \times R_3}$$

Thus E_1 is an exact function of E_3 and a factor made up of the resistance values of the coils employed.

Miscellaneous Observations on the Electrical System

The high sensitivity galvanometer used was a Leeds & Northrup Co., Type HS, having a coil resistance of 14.8 ohms, period 7.1 seconds, external critical damping resistance 20 ohms, and an approximate sensitivity of 50 mm. scale per microvolt at the reading distance of 5 meters.

The galvanometer was supported on a weighted platform, the latter suspended by three heavy ropes from a ceiling beam. From the underside of the platform extended a heavy brass rod, carrying three heavy sheet steel vanes, which dipped into a vessel filled with heavy lubricating oil. The effectiveness of this suspension is evidenced by the fact that the vibrating movement of the reflected beam on the scale was on the average less than 0.2 mm. at five meters scale distance, although when the galvanometer was placed on the stone-topped desk in the same laboratory, the vibration at one-meter scale distance was such as to render reading almost impossible.

It was found that the direction and force of the wind made some difference in the behaviour of the instrument, which was located on the sixth floor of the Chandler laboratories, and on very windy days it was impossible to make precision readings.

The coils and variable resistance boxes indicated on the diagram were connected throughout with No. 18 rubber insulated copper wire. The electrical system was supported entirely on metal, and the parts of the metal supporting system connected, as recommended by White.[30] This procedure eliminates the danger of stray potential differences from the 110 or 220 volt supply mains leaking into the sensitive circuits.

Parasitic Currents. In general, it may be said that there will always be some stray thermoelectric force. A voltage may even be detected between two pieces of copper, due to differences in hardness or surface condition, and a soldered joint may be a grave source of error, if any appreciable thermal gradient exists through the solder. Precision circuits should include only one metal, preferably copper, and if dissimilar metals must be joined, the junction should be lagged, if there is any possibility of its acquiring a thermal gradient.

Fortunately for the operation of thermoelement systems, it is always possible to ascertain and roughly measure the magnitude of the parasitics. If a copper coil of exactly the same resistance be substituted for the thermoelement, the rest of the circuit remaining untouched, the galvanometer will register zero, unless parasitics are present. Where they exist, they are ordinarily fairly constant over periods as long as 10 or 12 hours, and a false zero setting may therefore be used to compensate.

Preparation of Materials.

The potassium cobalticyanide and potassium ferricyanide were C.P. salts, recrystallized three times and dried. The solutions of known concentration were made up directly by weight in quantity sufficient to assure a precision of better than 0.1%.

In the early part of the work, "conductivity water" was prepared after the usual method, but it was subsequently found that the distilled water supply of the Chandler Laboratories was of sufficiently high quality for freezing-point work. (See p. 1979.)

The ice used was commercial ice, sifted to remove small particles, and thoroughly washed with distilled water. Several previous workers[4,9] on freezing-points have noted that clear samples of commercial ice were exceedingly pure, giving when melted a water having a conductivity commensurate with that of carefully distilled "conductivity water." This observation was verified in the present work.

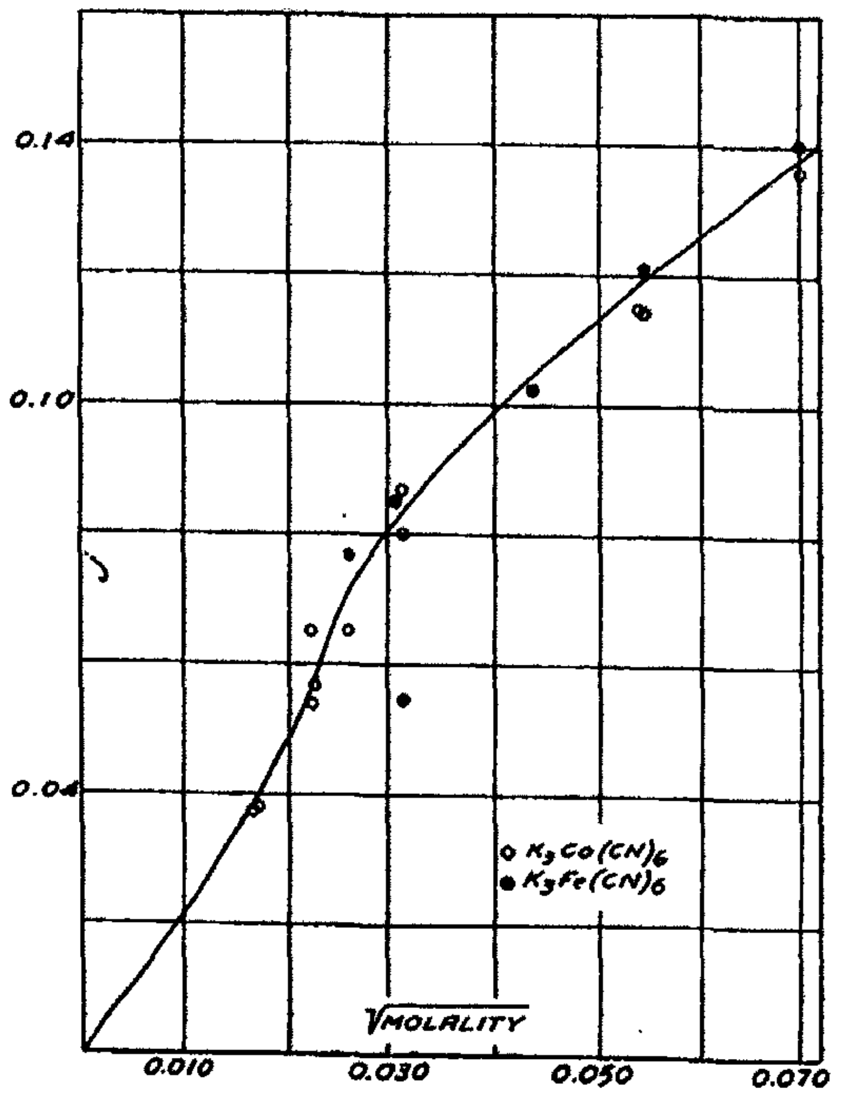


Fig. 4
Freezing-Point Data

The solutions, after being made up, were always used within 18 hours. It was observed that on several occasions when delays arose and precluded prompt use of solutions, that the concentrations appreciably diminished, due to slow adsorption on the vessel walls.

Experimental Results and Errors

Observed Freezing-Point Depressions for Potassium Cobalticyanide and Potassium Ferricyanide

The data obtained for these salts are presented in Tables I and II and Fig. 4. The conductivity measurements given in columns 3 and 4 show that if the proper precautions are observed, the change in concentration of the solution being measured from the time it is made up until the final equilibrium reading is made, cannot be a source of serious error. In a few of the earlier measurements reported, however, a slight change in concentration, detectable by final conductivity measurements, took place, and in these cases it was deemed proper to compute a corrected concentration from the conductivity-concentration relation for the salt in question.

Interpretation of the Results.

The interest attached to these measurements turns upon the value of the limit of $j/m^{\frac{1}{2}}$, as m approaches zero, and on the path by which the limit is approached.

The Value of the Limit. Since experiment can never give the limiting value, without extrapolation, appeal must be made to some theory of which the postulates are reasonable, and which is not inconsistent with experimental data at finite concentrations. Both the original form of the Debye-Hückel theory[11] and the mathematical extension given by Gronwall, LaMer and Sandved,[13] predict the same limiting value for $j/m^{\frac{1}{2}}$; namely 2.76 for 1,3 valence types of salts.

The various theoretical objections to the validity of this theory in finite concentrations, such as local smoothing, fluctuation terms, D in neighborhood of ions, and the assumption of spherical symmetry, which have been raised by such competent authority as R. H. Fowler,[12] admittedly vanish as m approaches zero, so that this limiting value of $j/m^{\frac{1}{2}}$ should not be subject to an error greater than the uncertainty in $D^{-3/2}$, where D is the dielectric constant of water.

The Approach to the Limit. The essential difference between the Debye-Hückel form of the theory and the purely mathematical extension given by Gronwall, LaMer and Sandved, resides in the form of the function produced by the introduction of the parameter "a" representing the ion size, which introduction is inescapable in finite concentrations.

The original theory demanded that $j/m^{\frac{1}{2}}$ approach its limit concavely to the X axis, i.e. $j/m^{\frac{1}{2}}$ was always less than the limiting value, regardless of the value of "a" as long as it remains finite. On the other hand the equations of Gronwall, LaMer and Sandved, predict that whenever "a" is less than about 7Å for 1,3 types of salts, then $j/m^{\frac{1}{2}}$ will exhibit values greater than 2.76 and will approach this limit by passing through a maximum, the characteristics of the maximum being dependent upon the value of "a."

Significance of the Present Measurements. Extrapolation for the evaluation of limits is trustworthy only when experimental data and theory together justify a linear extrapolation. This is certainly not the case for aqueous solutions of electrolytes of valence type higher than (1, −1), and all present day freezing-point measurements, including these reported, are insufficient to verify the *exact* numerical value of the limit for $j/m^{\frac{1}{2}}$.

Consideration of the data as plotted in Fig. 5 for the 3,1 salts studied, would lead us to place the limiting value of $j/m^{\frac{1}{2}}$ at a lower value than 2.76; perhaps 2.4. The allowable weight to be attached to the points, however, decreases decidedly at the dilute end of the curve, and, if we consider only the more accurate points at the four higher concentrations, it is evident

TABLE I

Freezing-Point Data for Potassium Cobalticyanide

Run	m_i, milli-mols	conductivity, r.o. × 10^6 initial/final		m_f, milli-mols	$\mu\nu$, obs. (av.3)	$-\Delta t$, 10^3°C.	j	$m^{1/2}$	$j/m^{1/2}$
15	0.2973	146.5	145.6	0.2973	1.592	2.126	0.0380	0.01724	2.205
15	0.4955	237.3	235.3	0.4920	2.560	3.419	0.0650	0.02218	2.930
15	2.973	1281	1256	2.914	14.36	19.17	0.1148	0.05400	2.127
15	4.955	2043	2031	4.923	23.66	31.61	0.1361	0.07016	1.939
16	0.2973	145.6	141.0	0.2870	1.536	2.052	0.0380	0.01694	2.241
16	0.4955	236.5	237.3	0.4955	2.610	3.486	0.0535	0.02226	2.400
16	0.6937	327.5	327.6	0.6937	3.606	4.819	0.0652	0.02634	2.474
16	2.973	1280	1271	2.948	14.52	19.40	0.1146	0.05430	2.110
21	0.5000	237.8	—	0.5000	2.625	3.506	0.0565	0.02236	2.527
21	1.000	458.9	456.0	0.9938	5.087	6.794	0.0802	0.03152	2.543
21	1.000	458.3	452.3	0.9850	5.013	6.687	0.0866	0.03138	2.760

TABLE II

Freezing-Point Data for Potassium Ferricyanide

Run	m_i, milli-mols	conductivity, r.o. × 10^6 initial/final		m_f, milli-mols	$\mu\nu$, obs. (av.3)	$-\Delta t$, 10^3°C.	j	$m^{1/2}$	$j/m^{1/2}$
14	1.000	465.4	459.9	0.9878	5.190	6.940	0.0546	0.03143	1.738
14	3.000	1297	1284	2.968	14.51	19.39	0.1211	0.05448	2.222
14	5.000	2075	2044	4.916	23.50	31.42	0.1401	0.07011	1.998
17	0.700	331.1	329.8	6.972	3.580	4.785	0.0766	0.02640	2.902
17	1.000	464.3	440.7	0.9470	4.813	6.440	0.0850	0.03077	2.761
17	2.000	890.0	849.6	1.904	9.517	12.71	0.1025	0.04377	2.363

that the limit of 2.76 would be entirely compatible with these points. The final decision, however, as to the correctness of the theoretical limit, on the basis of freezing-point measurements, must be deferred until it is possible to obtain experimental data at even lower concentrations.

On the other hand, the data submitted for potassium cobalticyanide and potassium ferricyanide yield evidence in favor of the correctness of the extension of Gronwall, LaMer and Sandved, as regards the path of approach to the limit, since $j/m^{\frac{1}{2}}$ passes through a maximum value instead of along a concave path.

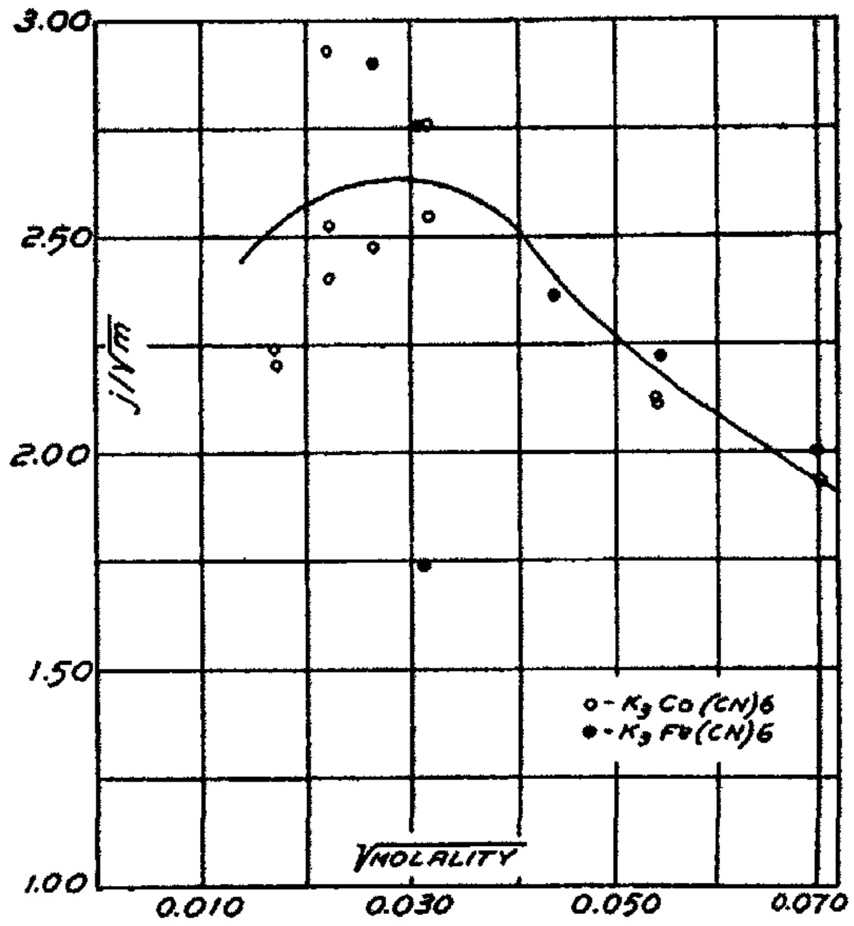


FIG. 5
Freezing-Point Function for (1, −3) Salts

In evaluating the significance of the curve, as determined by these experimental points, the accidental errors may be considered as one group, and the constant and systematic errors in another. The deviation of the points among themselves is a sufficient criterion of the accidental errors to demonstrate that the shape of the curve is not fortuitous. The independent runs indicated by the differently shaped points were made at different times, and indicate that the precision of reading and the errors in making up the solutions were sufficiently low to permit determination of the approximate form of the curve.

Other considerations which must be entertained are the possibilities of systematic or constant errors being of such a nature and magnitude as to bring about the observed juxtaposition of the experimental points. It may be observed from the tabular summary of errors given elsewhere (p. 1974), that most of the constant and systematic errors affect the result by a constant percentage, although some, such as the error in reading the galvanometer, would take the form of a constant fraction of a degree.

In order to check the possibilities of systematic errors, two series of values for $j/m^{\frac{1}{2}}$ were calculated, using values lower by 1×10^{-6}°C than those actually found, as a criterion of the effects of constant degree errors, and values of observed depression uniformly lower by 0.5%, as a criterion of the effect of constant percentage error. The curves obtained by the use of these values still show the "hump" shape, and are illustrated in Fig. 6.

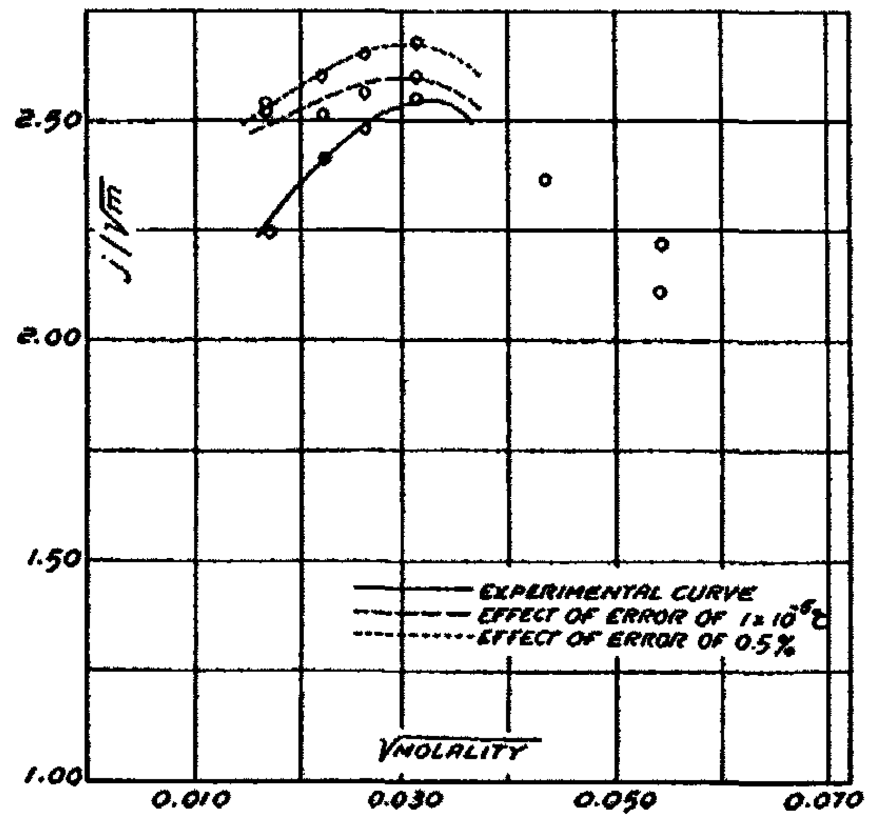


Fig. 6

Effect of errors on the $\frac{j}{m^{\frac{1}{2}}}$ function

It is shown in the section on errors, that the maximum probable errors are distinctly less than these assumed values, and we may therefore conclude that these measurements prove the existence of the shape of curve, at low dilutions, predicted by the extension of the Debye-Hückel theory, as given by Gronwall, LaMer and Sandved.*

Summary of Errors

In order that we may make a significant estimate of the meaning of the results for such sensitive measurements as these, it is necessary to systematically tabulate the possible sources of error, and satisfactorily account for each.

---

*The "hump" appears at higher concentrations in the corresponding curves for the activity coefficient of the solute than for that of the solvent.

The data for the activity coefficient of $CdSO_4$ recently obtained by LaMer and Parks (J. Am. Chem. Soc., 53, June (1931)) using the method of electromotive force and the similar results obtained for $ZnSO_4$ Cowperthwaite and LaMer (J. Am. Chem. Soc., 53, June (1931)) furnish conclusive proof of the validity of the Gronwall, LaMer and Sandved extension of the theory.

The form adopted for this purpose is that of Table III. The errors are grouped first in three principal categories: errors of the thermoelement and electrical measuring system; errors in concentration of solutions; error in the equilibrium state.

Within each of these heads the individual errors are further classified into the usual categories of constant, accidental, and systematic.

In the table each error is named and a figure given as a description of its magnitude. In the pages following the separate errors are discussed and the source of each figure in the table is given.

(*A*) *The Thermoelement and Electrical Measuring System.*

The electrical system consists of means whereby the electromotive force in the thermoelement is balanced against a potential drop produced across a standard 1-ohm copper coil, which electromotive force at balance is taken as that of the thermoelement.

(1.) Electromotive force measurement.

The known electromotive force E_t produced across the 1-ohm copper coil is calculated from the electrical relations of five resistances and the potentiometer readings:

TABLE III

Summary of Possible Errors

Error	Magnitude
Group I. Errors in Thermoelement and Electrical System	
Constant	
(1). Error of standard cell.	
(1a). Error in resistance coil values.	0.022%
(2). Error in calibration of thermoelement	0.05 %
Systematic	
(3). Inhomogeneity of thermoelement metal.	0.01 %
(4). Stray electromotive forces	nil
(5). Parasitic electromotive forces.	5×10^{-6}C.
(6). Peltier or current heating in thermoelement.	0.1 %
Accidental	
(7). Reading error of galvanometer.	1×10^{-6}C.
Group II. Errors in Concentrations.	
Constant	
(7a). Calibration errors. (see under 16).	
(8). Attainment of equilibrium temperature.	0.025%
(9). Effect of dissolved salt and lower temperature on air solubility.	0.02 %

TABLE III (Continued)

Error	Magnitude
Systematic	
(10). Errors of rinsing procedure.	1×10^{-5}°C.
(11). Possible insufficiency of pre-cooling.	0.02 %
(12). Melting by stirring air.	nil
(13). Condensation from stirring air.	nil
Accidental	
(14). Purity of salts.	0.1 %
(15). Purity of water	5×10^{-6}°C.
(16). Error in making solutions.	0.05 %
(17). Contamination by dissolved glass.	0.1 %
(18). Effect of thermal leakage of freezing-point vessels.	0.01 %
Group III. Error in Stability and Homogeneity of Equilibrium	
Systematic	
(19). Effect of imperfections in thermal isolation on the equilibrium temperature attained and recorded.	

$$E_1 = E_3 \frac{R_1 \ R_2}{(R_1 + R_2 + R_4)\, R_3}$$

E_1 is an exact function of E_3, the potentiometer reading, and a factor made up of the resistance values of the various coils employed. Below are tabulated the percentage accuracies of the factors of the above equation, together with notation as to the source of the precision figure.

Factor	Accuracy	Source of Figure
E_3	0.01%	Calibration of type K potentiometer and Bur. of Stand. calibration of std.cell
R_2 & R_3	0.01%	Maker's calibration
R_1	0.01%	Calibration against R_2
$(R_1 + R_2 + R_4)$	0.01%	Calibration of the box R_4 against the std. res. R_3

Lead resistance enters into none of the factors above save $(R_1 + R_2 + R_4)$. In this case the total lead resistance is 0.23 ohm, as measured after the apparatus was set up. Since R_4 is never less than 1000 ohms, neglecting the lead resistance entirely will introduce a maximum error of only 0.02%. The net accuracy, or extent to which the electromotive force is to be taken as the value in volts, then is, by least squares,

$$\text{Error} = \sqrt{5(0.01)^2} = 0.022\%$$

The electrical measuring system thus is of such accuracy that its error may be entirely neglected in any consideration of the accuracy of the final result.

(2.) Calibration of the thermoelement.

The magnitude of the absolute temperatures used as fixed points for the calibration was known to 0.1°C., or less than 0.04%. In consideration of this and of the small second derivative of the calibration curve, it is safe to say that the error in the slope at 0°C. is less than 0.05%.

(3.) Inhomogeneity of the thermoelement wires.

White[31] has pointed out that for constantan wire this may be a serious error. If the composition of the wire is not uniform along its entire length, a slight change in the position of the temperature gradient along the length of the element will produce a difference in the observed electromotive force, even though the ends are maintained at constant temperatures.

The error due to inhomogeneity in the copper-nickel element was checked by varying the position of the 25 degree thermal gradient used for the calibration. No difference in the observed electromotive force was noted, as the position of the gradient was shifted several centimeters. It should be observed that with an element having as many as 48 junctions, the probability is high that small variations will cancel each other.*

(4). Stray voltages.

Since the electromotive force corresponding to a temperature difference of 0.00001°C. is only 9×10^{-9} volts, it is obvious that a very small leak from the 110 volt power line, or from other sources, is capable of introducing serious error. Fortunately the method of equipotential shielding, referred to in the description of the apparatus and first brought out by White,[30] may be depended upon to entirely remove this danger.

(5). Parasitic electromotive forces.

These have been discussed on page 1968 and, as there noted, the only remedy is to keep the entire system at as uniform a temperature as possible, by avoiding temperature changes within the room, and by lagging where necessary. The size and direction of the parasitics may be ascertained by immersing both legs of the thermoelement in pure ice and water. This was always done before and after measurements and the observed parasitic was never greater than 5×10^{-9} volts.

(6). Peltier and current heating in the thermoelement.

The galvanometer draws a finite current from the thermoelement, but the errors thus produced are very small, as the following calculation shows:

Peltier Heat = $-$ EI, and if we assume a temperature difference of 0.01°, and the switch closed for 10 sec., the heat developed is 4.3×10^{-12} cal.

The current heat for the same temperature difference and time would = $I^2R = 2 \times 10^{-7}$ cal.

---

*Since this work was completed, a paper has come to our attention entitled "Thermoelectricity of Nickel Wire" by T. Tsutsui: Tokyo Scientific Papers, Institute of Physical Chemical Research, **11**, 93 (1929), in which it is stated that nickel wire may give serious errors of inhomogeneity, if the wire is bent very often. As above noted, the first copper-nickel element tested as a whole did not display this trouble, but a second one subsequently made in this laboratory was not so satisfactory, and it is possible that nickel is in general an unreliable element for couples.

Since both temperature and time given are much larger than ever used in this work, it is obvious that the error is nil.

(7). Galvanometer sensitivity.

The sensitivity of the galvanometer used as a balancing instrument is such that, when connected with the 48-junction copper-nickel thermoelement, 1 mm. on the illuminated galvanometer reading scale is equal to 0.00004°C. The error in the observation of the position is certainly less than 0.25 mm. and the degree of precision of the reading is equal, conservatively, to 1×10^{-5}C.

Errors in Concentration.

(8). Attainment of equilibrium.

When the solution is introduced, it is at 0°C., and the lowering of the temperature of the contents of the vessel to the freezing point for that concentration will bring about a certain amount of melting, and thus a dilution. A simple calculation, however, will show that at concentrations such as those worked with, this error is negligible. Consider a solution of 0.001 molal potassium ferrocyanide, for which the freezing-point depression is about 0.013 degrees. The flasks contain 200 g of ice, of specific heat 0.5, 250 grams of water, specific heat 1.0, and the water equivalent of the flask is about 25 grams. The total water equivalent is 375 grams, which for 0.013 degrees change requires 4.87 calories. This will melt 0.062 grams of ice, which, for the 250 grams of solution introduces an error of 0.025%. The error is less when the solution is more dilute.

(9). Change in air solubility.

Fox[24] made an extended study both of the solubility of air in pure water at temperatures from 0°C. to 25°C., and of the change in solubility due to the presence of small amounts of sodium chloride.

From his results the following may be calculated:

Solubility of air in pure water at 0° = 1.28×10^{-3}m/l

Change in solubility due to small quantities of dissolved sodium chloride = 5.22×10^{-4} mols/mol NaCl

Change in solubility with temperature = 2.35×10^{-5} mols/degree

The change in solubility of air with salt concentration is linear, within the limits of error, for these small concentrations, and since the error due to the lower temperature of the solution is likewise linear within the limit of residual error, it is a simple matter of division to obtain the result that for NaCl both errors are of constant percentage, and are respectively −0.026% and +0.004% of the observed freezing-point depression.

(10). Errors of rinsing.

Since the solutions of known concentration are brought into equilibrium contact with the ice by a series of rinses, the question arises as to whether this process is effective and accurate. Horvorka and Rodebush,[7] who also used the rinsing method, report that they rinsed three times, using each time only enough solution to fill their vessel about one quarter. Furthermore, this rinse solution was introduced from a fixed delivery tube at about the center of their vessel at the top, and the rinse, as it ran through, would be almost certain to follow a few channels.

The procedure in this work was to completely fill the freezing-point vessel with the solution of known concentration three times, each time allowing the circulators to run for several minutes. In this way the error due to adhering liquid films on the ice surface is eliminated. To test this point, several measurements of freezing-point depression were made using the third rinse as the equilibrium solution, and in every case the difference between this reading and that of the fourth final filling was less than 1.5×10^{-5} degree.

(11). Error in pre-cooling.

The error which would result, if the solution as run in was not exactly at 0°C., was obviated by the overnight standing in the ice-water thermostat. Furthermore, for some weeks of trials a thermoelement was kept in one of the ten bottles in the bath and the difference in temperature frequently noted. It was never more than 0.01 degree and averaged more nearly 0.004°C. By referring to paragraph (8) of this section it may be seen that this source of error is negligible.

(12). Melting by stirring air.

The stream of air may melt ice and thus change the concentration. About 0.5 liter of air per minute was run through each vessel, for a total time previous to the final readings of about 35 minutes. To test the possible error from this source, a Dewar vessel containing water at 0°C. was inserted into the thermostat, and a stream of the same air used for stirring was bubbled through it for two hours. Since this flask contained water only, if the air had been warmer than 0°, the temperature of the contents should have reflected it. No change greater than 0.01 degree, however, could be detected in the two hours. This would not indicate that the air, if at any temperature above 0°C., was not enough so as to melt a significant quantity of ice and appreciably change the concentration.

(13). Condensation from stirring air.

A slight amount of water will be condensed from the stirring air, since this is saturated at 0°C., and the solution, being at a slightly lower temperature, has a lower vapor pressure. This effect, however, due to the small total amounts of air used, and the extremely small difference in vapor pressures at 0°, is of an order of magnitude beyond consideration.

(14). Purity of the salts.

The purification and testing of the salts is described on page 1968. This error is independent of concentration, and may be regarded as negligible, after the three recrystallizations carried out.

(15). Purity of the water.

The table below gives a series of conductance measurements on the distilled water supply extending over several months, including vacation periods and periods of laboratory session when the distilled water was being constantly used.

Conductivity Values—Chandler Laboratories
Distilled Water Supply—25°C.

Dec. 28, 1929 to March 24, 1930			May 30, 1930 to June 6, 1930
1.02 (r.o. × 10^6)		Supply accidentally contaminated and very bad from March 24 to May 30.	0.91
1.65			0.76
1.44			0.75
1.21	1.30		1.12
1.14	1.04		1.14
1.08	1.16		1.06
0.80			.88
1.13			
1.17			
1.07			

The mean value is about 1.10, the highest is 1.65 and the lowest is 0.75.

Kendall,[27] in reviewing the question of purity of water for conductance measurements, summarizes an extended body of data and arrives at the following conclusion. Water, which may be described as "good standard conductivity water," containing dissolved carbon dioxide in equilibrium concentration with that in the atmosphere, has a specific conductance of 0.80 × 10^{-6} reciprocal ohms at 0°C., practically all of which conductance is due to this carbon dioxide

It is thus evident that the distilled water used in the Chandler Laboratories is very nearly the equivalent of standard conductivity water.

The importance of the small additional contamination for this freezing-point work may be further defined from the following data: a large sample of water was drawn and its conductance measured. Then small measured amounts of a 0.03 M KCl solution were added, and the conductances again determined. After subtracting from each reading the original conductance of the water, the additional conductances imparted by the small concentrations of KCl were plotted. The plot of specific conductance against moles per liter from 0.00004 to 0.0006 molar gave a straight line which extrapolated accurately to the origin, the slope being 6.8 mols per reciprocal ohm. From this relation, it is possible to estimate with moderate precision the effect of contamination, as measured by conductance, on the freezing-point depression, the relation holding if the assumption is made that the unknown contaminating substance does not have abnormal ionic mobilities, differing greatly from those of KCl.

If we assume that of the conductance of the Chandler water, 0.80 × 10^{-6} reciprocal ohms, is due to carbon dioxide, then the additional conductance of, say, 0.30 × 10^{-6} should correspond to 2.1 × 10^{-6} mols of dissolved substance, and should affect the freezing-point depression by .756 × 10^{-5}°C. And it is, of course, only a difference in concentration between the liquid in the two freezing-point vessels which will give rise to an error in the results. Consequently the consistent use of the same water supply for making up solutions and for filling the reference flask largely cancels out the above small effects.

(16). Errors in making up the solutions.

It is not difficult to make up solutions with an error of less than 0.05%. Calibrated weights and flasks were used throughout.

(17). Possible solution of glass (Pyrex).

The magnitude of this error was ascertained by measuring the increase of conductance of distilled water after standing in the bottles for several days. The mean of several trials showed an increase of concentration of 0.000018 mol/l., estimated as KCl.

To further diminish the errors due to contact of the solution with the bottles, a uniform technique of cleaning solution, steaming and standing in contact with distilled water for at least 24 hours, was employed for the cleaning of all glass with which the solutions came in contact.

(18 . Thermal leakage.

The thermal leakage modulus of the containing vessels was about 0.7 calorie per minute, per degree thermal head. This will introduce an error proportional to the thermal head. A calculation of its magnitude shows, however, that it is not large. Consider a solution having a freezing-point depression of 0.01°C. The solution is in the vessel for, say, 35 minutes. The total heat leak is $0.7 \times 0.01 \times 35 = .245$ calories. This will melt 0.003 grams of ice, which, in a total solution volume of 250 cc., means an error of only 0.0012%.

Errors due to Deviation from the Equilibrium State.

(19). Shift in equilibrium.

Error from this source may arise from a variety of causes. If the vessels contain insufficient ice, if stirring is not fully adequate, if the pressure on the contents of the vessels varies unequally, the equilibrium will be seriously disturbed. It has been pointed out in an earlier section that it is impossible physically to have an accurate solid-liquid equilibrium state in a vessel of finite size, due to the effect of hydrostatic pressure. Therefore, in each vessel, we have something more or less approaching an average temperature of that which tends to be attained in the different parts of the vessel. It is a mobile system and is sensitive to external influences.

The only way by which the extent of a shift of equilibrium or its stability, may be judged, is by the constancy of the temperature readings attained. The constancy with this apparatus was very good. In one typical run the temperature remained constant to $\pm 4 \times 10^{-6}$°C. for 40 minutes. This is the most reliable criterion of equilibrium, as in the case of inter-comparisons of check runs, all the errors of the entire system enter, and it is difficult to ascribe causes with certainty.

The Design of Improved Freezing-Point Apparatus

The design of apparatus brought out by Adams[2] in 1915, and refined in various ways by subsequent workers, is limited to a precision of about 1×10^{-5}°C. It would be of value for the study of solutions to be able to obtain measurements precise to 1 × 10^{-6}°C., and the subsequent discussion will attempt to demonstrate that this is not only feasible but would not entail great expense.

Shortcomings of the Present Apparatus.

The original design of Adams as exemplified in Fig. 1 has persisted thus far, changed only in minor details. The crux of the problem is to obtain sufficient sensitivity of the thermoelement while retaining a high degree of thermal isolation of the system. High thermoelement sensitivity dictates two vessels very close together, to give a short thermoelement, while good thermal isolation requires that the vessels have much distance and insulation between them. In the present design the necessary compromise results in a construction equally distributed between the conflicting demands.

Thermoelement Sensitivity.

It has been demonstrated in a previous section that, given a certain allowable total thermal conduction of the thermoelement wire itself, the size of wires and number of junctions follow a definite optimum rule. The ultimate limiting factor is the allowable total heat conduction of the thermoelement wires.

In the present design, where the thermoelement wires are bundled together and encased, the extraneous considerations which enter, such as the thermal conduction of the case, and the thermal conduction through the bundle of junctions to the junctions at the center, make it impossible to calculate solely on the basis of conduction of the wire.

The conduction of the thermoelement wires alone, even for a fairly large element, is very small. Therefore it would be possible, if the design of the two containing vessels were suitably changed, to use a thermoelement which would be very short and have perhaps two or three hundred junctions, without introducing a serious thermal leakage between the vessels.

Thermal Isolation of the Equilibrium Mixtures.

The ordinary glass Dewar vessel does not provide the best thermal insulation, because it is necessarily uninsulated at the top. The connecting tubes and stirrers of a type necessary with Dewar vessels also contribute heat leakage paths of relatively large capacity.

A New Design.

It is evident from a study of the Dewar vessel type of apparatus, that the most detrimental feature is the vessel itself, and in the following design a radical change from this type of construction is proposed.

The new design is shown in center section in Fig. 7. It embodies the following features:

(1) The solutions are contained in two solid silver cylinders (A), of about 6 cm. inside diameter, 30 cm. long and about 8 mm. wall thickness, having covers fastened with clamps. The cylinders are supported parallel to each other, about 12 mm. apart, by a framework of micarta, (B), which com-

bines to a remarkable degree low thermal conductivity and high strength. The leakage modulus is made extremely small by constructing the supporting framework to make the heat path between the cylinders and from the outer environment very long. This is easily achieved by using a suitable construction of micarta tubing and rod.

(2) The outsides of the two cylinders are threaded with a pitch of about 10 per cm, (C), and the thermoelement consists of bare wires wrapped around the two cylinders, the threads serving to keep the junctions evenly spaced.

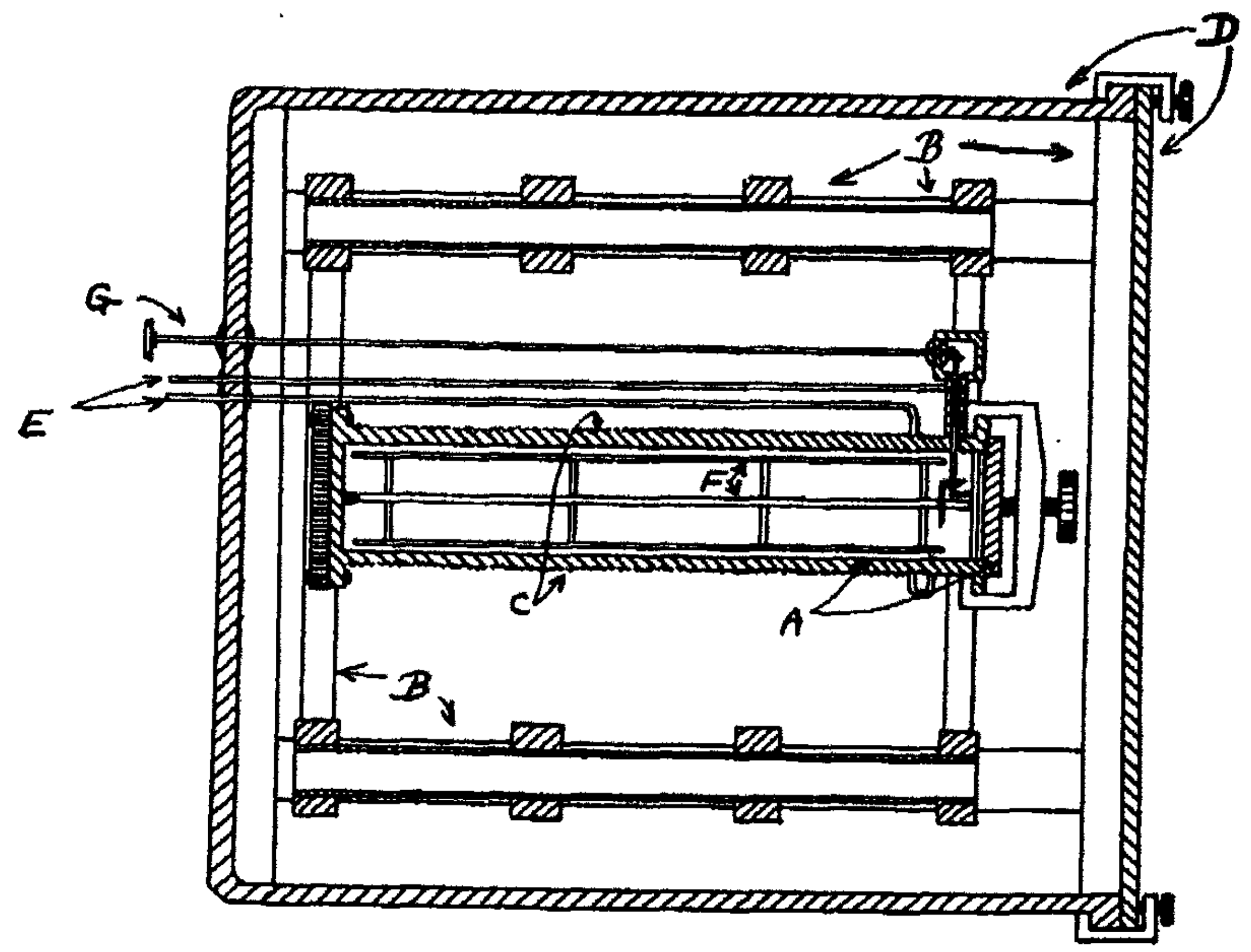


Fig. 7
A Proposed New Design for Precision Freezing-Point Apparatus

Before wrapping on the thermoelement, the cylinders are given a thin coat of bakelite varnish, which is the only insulation necessary. The thermal insulation of the 8 mm. silver wall is considerably less than the insulation of a glass thermoelement case.

(3) The assembly, consisting of the two cylinders, the thermoelement wrapped around them and the supporting micarta, is isolated from the outside environment by being placed entirely within a heavy glass cylinder, (D), with a removable ground-on cover. The large glass container is filled with rice flour, and evacuated to about 0.003 mm. This means of thermal insulation has been found to be far more effective than a vacuum alone. It has been used in research[50] and tested by Professor S. L. Quimby of the Department of Physics of Columbia University, and found more efficient than any other combination of evacuated spaces.

(4) Access to the vessels is supplied by long thin platinum or bakelite tubes, (E), extending through the end of the outer glass container. The heat conduction here introduced may be made infinitesimal.

(5) Stirring is effected by means of a rotating cage of platinum wire, working in pivots within the cylinders, and driven from outside the vessels by a thin bakelite rod, (G).

(6) In operation, both silver cylinders would be packed with ice, the covers clamped on, and the assembly placed in the outer container. Water for the reference vessel, and solution for the other, would be introduced through the tubes. With the isolation here attainable, the thorough agitation of the cage stirrers, and perhaps a 250-junction thermoelement, it should be possible to obtain data precise to 1% at about 5×10^{-5} molal.

Summary and Conclusions

(1). The many sources of error inherent in the determination of freezing-point depressions in highly dilute aqueous solutions have been critically reviewed and numerically evaluated. The past and present means for minimizing these errors are discussed, and conclusions drawn as to their effectiveness.

(2). A freezing-point apparatus precise to 1×10^{-5}C. has been assembled, and the magnitudes of the specific errors of its operation considered in detail.

(3). The apparatus has been used to measure the freezing-point depressions of potassium cobalticyanide and potassium ferricyanide in the concentration range 0.005 M to 0.0003 M.

(4). The experimental data confirm the extension of the theory of Debye and Hückel as given by Gronwall, LaMer, and Sandved, as regards the form of the osmotic deviation function in this region of concentration.

(5). As a result of this study, the design of a radically different form of freezing-point apparatus is submitted, which should overcome many of the difficulties and errors of the present type.

VII. Bibliography

Modern freezing-point measurements.
1. E. Abel, O. Redlich and B. v. Lengyel: Z. physik. Chem., **132**, 189 (1928).
2. L. H. Adams: J. Am. Chem. Soc., **37**, 481 (1915).
3. T. G. Bedford: Proc. Roy. Soc., **83A**, 454 (1910).
4. R. E. Hall and W. D. Harkins: J. Am. Chem. Soc., **38**, 2658 (1916).
5. W. D. Harkins, R. E. Hall and W. A. Roberts: J. Am. Chem. Soc., **38**, 2643 (1916).
6. W. D. Harkins and W. A. Roberts: J. Am. Chem. Soc., **38**, 2676 (1916).
7. F. Hovorka and W. H. Rodebush: J. Am. Chem. Soc., **47**, 1614 (1925).
8. M. Randall and G. N. Scott: J. Am. Chem. Soc., **49**, 647 (1927).
9. M. Randall and A. P. Vanselow: J. Am. Chem. Soc., **46**, 2418 (1924).
10. R. Wesöe: Physik. Z., **30**, 412 (1929).

Theoretical
11. P. Debye and E. Hückel: Physik. Z., **24**, 185 (1923).
12. R. H. Fowler: "Statistical Mechanics," pp. 194-9, 314-325. (1929).
13. T. H. Gronwall, V. K. LaMer and K. Sandved: Physik. Z., **29**, 358, (1928).
14. M. Randall: J. Am. Chem. Soc., **48**, 2512 (1926).
15. W. H. Rodebush: J. Am. Chem. Soc., **40**, 1204 (1918).
16. W. H. Rodebush: J. Phys. Chem., **28**, 1113 (1924).

Experimental

17. L. H. Adams: J. Am. Chem. Soc., **37**. 1181 (1915).
18. W. E. Adeney and H. G. Becker: Phil. Mag., **38**, 317 (1919); **39**, 385 (1920); **42**, 87 (1921).
19. H. G. Becker: J. Ind. Eng. Chem., **16**, 1220 (1924).
20. H. M. Chadwell: J. Am. Chem. Soc., **49**, 2795 (1927).
21. J. H. Coste: Analyst, **48**, 433 (1923).
22. L. D. Elliot: J. Phys. Chem., **28**, 611 (1924).
23. H. W. Foote and G. Leopold: Am. J. Sci., **11**, 42 (1926).
24. C. J. J. Fox: Trans. Faraday Soc., **5**, 68 (1909).
25. F. H. Getman: J. Phys. Chem., **33**, 1781 (1929).
26. Bull. No. 19, Ill. State Water Survey, pub. by Dep't. of Registration & Education, (1924).
27. J. Kendall: J. Am. Chem. Soc., **38**, 2465 (1916).
28. W. P. White: Phys. Rev., **23**, 449, 470, 140 (1906).
29. W. P. White: Phys. Rev., **31**, 135 (1910).
30. W. P. White: J. Am. Chem. Soc., **36**, 1874 (1914).
31. W. P. White: J. Am. Chem. Soc., **36**, 2292 (1914).

Other freezing-point measurements.

32. Abegg: Z. physik. Chem., **20**, 207 (1896).
33. Archibald: Trans. Nova Scotian Inst. Sci., **10**, 44.
34. Barnes, Archibald and McIntosh: J. Am. Chem. Soc., **27**, 47 (1905).
35. Barnes: Trans. Roy. Soc. Canada II, **6**(3), 37 (1900).
36. Beckmann: Z. physik. Chem., **2**, 715 (1888).
37. Dixon: Sci. Proc. Roy. Dublin Soc., **13**, 49 (1911).
38. Flugel: Z. physik. Chem., **79**, 579 (1912).
39. Griffiths: J. Chem. Soc., **60** ii, 251 (1891).
40. Hausrath: Ann. Physik, (4), **9**, 522 (1902).
41. Jahn: Z. physik. Chem., **59**, 37, 129 (1907).
42. Nernst and Abegg: Z. physik. Chem., **15**, 681 (1894).
43. Osaka: Z. physik. Chem., **41**, 560 (1902).
44. Ponsot: Ann. Chim. Phys., (7) **10**, 79 (1897).
45. Raoult: Z. physik. Chem., **1**, 186 (1887).
46. Richards: J. Am. Chem. Soc., **25**, 291 (1903).
47. Richards: Z. physik. Chem., **44**, 563 (1903).
48. Roth: Z. physik. Chem., **79**, 599 (1912).
49. Walker and Robertson: Proc. Roy. Soc. Edinburgh, **24**, 363 (1902).
50. I. C. Tables, **2**, page 315; W. B. Ellwood: Phys. Rev., (2) **36**, 1067 (1930).

REACTION BETWEEN GLUCOSE AND POTASSIUM PERMANGANATE IN ACID SOLUTION*

BY S. LOUISA RIDGWAY

Purpose

The purpose of this investigation has been to work on the reaction between potassium permanganate and glucose in acid solution especially with reference to the following points:—

1. The possible formation of gluconic acid at the pH at which it is formed by bromine. Some unpublished work done in the Cornell laboratory suggested this. If gluconic acid were formed by such oxidation by potassium permanganate, this might be a better method of preparing it than by the use of bromine or silver oxide.

2. The change in the amount or rate of oxidation with change in pH.

3. The possibility of finding conditions at which the reaction products would be stable and the oxidation could be stopped. If such a set of conditions could be found, this would be a convenient method of determining glucose in solutions known to contain no other oxidizable material.

Method

The method used was quite simple. The potassium permanganate solution and the acid (sulphuric unless otherwise specified) were put into distilled water in an Erlenmeyer or a Florence flask and brought to the required temperature. Then the glucose solution was added and the reaction time reckoned from that point. When the reaction had proceeded for the desired length of time, an amount of standard sodium oxalate greater than that needed to react with the permanganate was added. If necessary, enough acid was added to bring the total amount up to 10 cc of 1:1 sulphuric acid and the temperature was brought nearly to the boiling point. Then the excess oxalate was titrated back with permanganate quickly. The first relatively permanent pink (lasting 15 sec.) was taken as the end-point, for of course unused glucose would continue to reduce any permanganate present.

This procedure gave a convenient method for varying concentrations, volume, acidity, temperature, reaction time, etc. The only temperatures used were room temperature and boiling (refluxing, using fine carborundum to prevent bumping). The results obtained were accurate to within about two percent, (Table I).

---

*A thesis presented to the Faculty of the Graduate School of Cornell University for the degree of Master of Arts, 1930.

TABLE I

Time	KMnO$_4$ N/25	Acid	Oxalate	Back KMnO$_4$	KMnO$_4$ for blank
1 hr.	35 cc	10 cc 1:1	40 cc	9.5 cc	5.1 cc
1 hr.	35 cc	10 cc 1:1	35.5 cc	3.6 cc	4.1 cc
1 hr.	35 cc	10 cc 1:1	35.6 cc	5.0 cc	4.5 cc
1 hr.	35 cc	10 cc 1:1	35 cc	4.5 cc	5.0 cc
1 hr.	35 cc	2 cc 1:1	35 cc	1.8 cc	2.3 cc
1 hr	35 cc	2 cc 1:1	35 cc	2.0 cc	2.5 cc
1 hr.	35 cc	4 cc 1:1	35 cc	1.85 cc	2.35 cc
1 hr.	44.3 cc	4 cc 1:1	45 cc	2.5 cc	2.5 cc
73 hr.*	35 cc	10 cc 1:1	41 cc	7.1 cc	1.7 cc
78 hr.*	35 cc	2 cc 1:1	36 cc	.7 cc	0.2 cc
5 min.	35 cc	0.01394 g	40 cc	4.55 cc	0.15 cc
10 min.	35 cc	0.01394 g	36 cc	.6 cc	0.1 cc
1 hr.	35 cc	0.01394 g	36 cc	1.1 cc	0.6 cc
1 hr.	35 cc	0.01394 g	36 cc	1.1 cc	0.6 cc
4¾ hr.	35 cc	0.01394 g	36 cc	1.4 cc	0.9 cc
0 hr.**	None	10 cc 1:1	None		0.1 cc
0 hr.**	None	10 cc 1:1	None		0.15 cc

*Room temperature. All the other runs were made at the boiling-point.
**The volume was 110 cc; 150 cc in all other runs.

Blanks run in the usual way on the reagents gave practically negative results. Blanks on the reagents refluxed for some time gave low positive results. Blanks to which had been added a small amount of oxalate previous to standing long periods of time or refluxing (in order to produce a small amount of manganese sulphate which is known to catalyze oxidation by permanganate and which was present in all experimental flasks) gave quite high positive results. As all ordinary precautions were taken to guarantee the purity of the reacting substances, extreme care would be necessary to reduce the positive value of this blank any considerable amount. The data later presented have been corrected on the basis of these blanks, unless it is otherwise stated.

The solutions used were:—

1. N/25 sodium oxalate made by weighing out the pure reagent.

2. N/25 (approx) potassium permanganate made by dissolving 5 gm in a liter of water, boiling ten minutes, letting stand one day, filtering through a Gooch filter, diluting to 4 liters, and standardizing against oxalate.

3. 1:1 sulphuric acid made up from c. p. acid and distilled water in a graduated cylinder (as slight change in acidity had no effect).

4. 0.2% anhydrous glucose made up by weighing out Baker's C. P. The moisture content was determined by drying at 7 in. of mercury and 60° for two hours, and then at 70° until the weight was constant. This treatment drove off water of crystallization. The value obtained was checked by use of the polarimeter.

5. Solutions of potassium permanaganate, sodium oxalate, and glucose were made up approximately 12 1/2 times as strong as the preceding; and also solutions of potassium permanganate and glucose about 25 times as strong. 0.45 N sodium oxalate is nearly a saturated solution.

The mechanism of the reaction was at first assumed to be

(1) $2KMnO_4 + 5$ glucose $+ 3H_2SO_4 \rightarrow 5$ glucose cxidation product $+ K_2SO_4 + 2MnSO_4 + 3H_2O$.

(2) $2KMnO_4 + 3MnSO_4 + 2H_2O \rightarrow 5MnO_2 + 2H_2SO + K_2SO_4$

for the solutions rapidly became colorless with the precipitation of manganese dioxide. The manganese dioxide thus formed would have the same amount of oxygen to give up as the permanganate and would continue the reaction with the glucose.

(3) $MnO_2 +$ glucose $+ H_2SO_4 \rightarrow MnSO_4 +$ glucose oxidation product $+ H_2O$.

Then as is shown later in this paper, the last 2/5 of the oxygen (corresponding to having all the manganese in the form of manganese dioxide) is given up much less rapidly than the first 3/5 of the oxygen. If manganese dioxide is the oxidizing agent except at the very start, why should there be this difference in speed? It was suggested that first

$$2KMnO_4 + 3 \text{ glucose} + H_2SO_4 \rightarrow 2MnO_2 + K_2SO_4 + H_2O + 3 \text{ glucose oxidation product},$$

and then oxidation was continued more slowly by manganese dioxide. The first equations were finally considered to be the actual ones for these reasons:

1. With oxalic acid[1] and glucose, manganese sulphate is a catalyst and increasingly so up to 3 molecules for 2 of permanganate. The amount of oxidation of 5 cc of 0.2% glucose in 4 hours at room temperature in a total volume of 150 cc with 2 cc of 1:1 sulphuric acid was 0.29 atoms of oxygen per molecule when no manganese sulphate was added, and 3.77 atoms when 3 molecules of manganese sulphate were added.

2. At room temperature with glucose, an initial period is evident before the reaction starts, due presumably to the formation of manganese sulphate. Cf. Figs. 9-11.

3. Manganese sulphate is shown to have an inhibiting effect on oxidation by manganese dioxide, so when it is no longer removed by action with permanganate the reaction slows up. 5 cc of 0.2% glucose in a total volume of neutral solution refluxed one hour with manganese dioxide equivalent to 35 cc N/25 (approx) permanganate was oxidized to the extent of 5.92 atoms of oxygen per molecule, while in the presence of 15 cc N/25 manganese sulphate, it was oxidized only to 4.78 atoms per molecule.

If the action of glucose may be considered analogous to that of oxalic acid, except that it is slower, Skrabal,[2] who assumes the formation of a $Mn^{\cdot\cdot\cdot}$ ion which is instantaneously reduced, would write the equations in this way:—

---

[1] Harcourt and Esson: J. Chem. Soc., **20**, 460 (1867).

[2] Z. anorg. Chem., **42**, 1 (1904).

$$\begin{array}{lll}
(1) & \text{glucose} + KMnO_4 & \rightarrow Mn^{\cdot\cdot\cdot} + \text{oxidation product} \\
 & Mn^{\cdot\cdot\cdot} + \text{glucose} & \rightarrow Mn(OH)_2 + \text{oxidation product} \\
(2) & Mn(OH)_2 + KMnO_4 & \rightarrow Mn^{\cdot\cdot\cdot} \\
 & Mn^{\cdot\cdot\cdot} & \rightarrow Mn(OH)_2 + Mn(OH)_4 \\
(3) & Mn(OH)_2 + Mn(OH)_4 & \rightarrow Mn^{\cdot\cdot\cdot} \\
 & Mn^{\cdot\cdot\cdot} + \text{glucose} & \rightarrow Mn(OH)_2 + \text{oxidation product}
\end{array}$$

Formation of Gluconic Acid

In attempting to oxidize the glucose to gluconic acid by potassium permanganate at the pH at which this oxidation is brought about by bromine, the method of Kiliani and Kleeman,[1] Ruff,[2] and Herzfeld and Lenert[3] was repeated and the calcium gluconate prepared. Measuring the pH of the reaction mixture itself was impossible. The pH was too low for ordinary indicators aside from the fact that the bromine destroyed all those tried and the color of the bromine masked any indicator change. The hydrogen and quinhydrone electrodes can not be used in the presence of free bromine. The next best procedure was to determine the pH of the mixture after the reaction had been completed and the solution freed from bromine by boiling and repeated shaking with carbon tetrachloride. With the quinhydrone electrode, the pH was found to be very nearly 0.0. In other words, the solution was normal in respect to hydrogen ions.

In order to make up a sulphuric acid-permanganate mixture having such a pH, it is necessary to use more than a normal solution of acid as the dissociation is far from complete at such concentrations. Also at these concentrations, a large change in the amount of acid causes a relatively very small change in pH. Sulphuric acid from 5-8 normal or from 1:4 to 1:8 concentration was found to be within the approximate range.

Using 1:8 sulphuric acid and solid reagents—10 gm anhydrous glucose and 4 gm potassium permanganate in 50 cc of acid, the reaction was immediate and violent. The permanganate was in slight excess over that needed to furnish one atom of oxygen per molecule of glucose. Enough extra acid was added to neutralize the KOH formed from the permanganate. A clear colorless solution resulted which became yellow on standing. The sulphate was precipitated by barium hydroxide. A dark brown caramelly smelling liquid was obtained on evaporation. This was precipitated as the phenyl-hydrazine compound. It was recrystallized from alcohol and melted at 198°-200°. This corresponds to gluconic acid phenylhydrazide (195°-200°), but was not the colorless compound described. Besides it could not be converted into calcium gluconate by the method used by Fisher and Passmore.[4] It was not considered to be a derivative of gluconic acid. Another point of evidence in favor of this view was that the reaction between the glucose and permanganate was

---

[1] Ber., 17, 1298 (1884).

[2] Ber., 32, 2273 (1899).

[3] Z. Ver. Zuckerind., 1919, 122.

[4] Ber., 22, 2728 (1889).

TABLE II

Effect of Change of Acidity in Dilute Solutions

Glucose: 5 cc of 0.2%
$KMnO_4$: 35 cc of N/25
Volume: 150 cc
Temp.: Boiling

A/G: Atoms of oxygen used per molecule of glucose
Time: 30 min. for experiments marked with an asterisk; 60 min. for the others

1:1 H_2SO_4 cc	N of H_2SO_4	Oxalate cc	Back $KMnO_4$ cc	$KMnO_4$ used by glucose cc	A/G
0	0	15	.9	22.3	8.89*
0		15	1.2	22.6	9.01
2	0.236	20	4.7	21.6	8.61*
2		16.5	2.65	22.7	9.05
4	0.472	20	5.0	24.1	8.6*
4		16	2.9	25.2	9.0
8	0.946	16	1.15	23.45	8.3*
8		16	2.5	24.5	8.7
10	1.18	15	.85	23.8	8.5*
10		14	1.2	25.1	9.0
14	1.675	15	.7	23.8	8.5*
14		15	2.0	25.1	8.96
16	1.895	15	1.25	23.8	8.68*
16		15	3.3	26.4	9.43
18	2.13	15	2.2	25.3	9.04*
18		15	3.9	27.0	9.64
20	2.37	14	.7	24.6	8.79*
20		13	2.6	27.3	9.75
24	2.84	14	2.8	25.7	9.25*
24		11	2.7	29.0	10.35
28	3.35	13	4.5	29.2	10.43*
28		10	3.6	30.6	10.93
32	3.79	10	1.2	28.25	10.1*
32		10	1.0	28.0	10.0
36	4.26	7	2.15	31.6	11.29*
36		6	2.75	33.0	11.79
40	4.74	6	1.0	31.2	11.14*
40		4	1.4	33.2	11.85

uncorrected

accompanied by a marked evolution of gas which must have been carbon dioxide formed from the more complete oxidation of some of the glucose. Still another point was the fact that all the permanganate was used, although the amount present was in excess of that needed to convert all the glucose to gluconic acid. It is of interest to note here that calcium gluconate will reduce permanganate under the conditions of the experiment. This makes it possible, though it is improbable, that the oxygen available is used to oxidize a part of the glucose more or less completely going through gluconic acid as an intermediate compound.

The result of this experiment was confirmed by the reaction of dilute solutions of permanganate and glucose in a reacting mixture of the same acidity. The glucose was oxidized almost to carbon dioxide and water as shown by the amount of permanganate used. See Table II.

Another method of making gluconic acid was tried. Permanganate and hydrobromic acid were added to a glucose solution. The permanganate of course liberated bromine from the acid. It was hoped that by keeping the hydrobromic acid in excess, so the ordinary reaction of permanganate in acid would not take place, the nascent bromine (though not in as high concentration as in the methods using liquid bromine) would oxidize the glucose to gluconic acid. In quite a number of experiments no gluconic acid was isolated as the calcium compound or the phenylhydrazide. A large amount of the bromine escaped as the free gas and the concentration was always low.

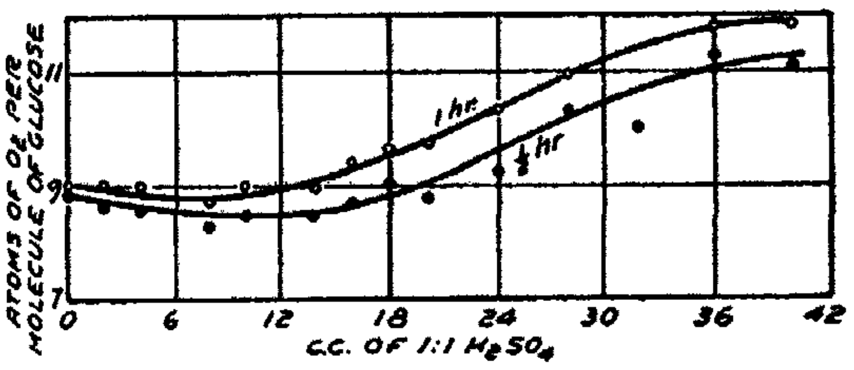


Fig. 1

Effect of Change of Acidity

Reaction Rate Between Glucose and Potassium Permanganate

The study of the change in amount and rate of oxidation with change in pH, and the search for a stable intermediate point in the oxidation of glucose by potassium permanganate was carried on by the titration method outlined above. Table II and Fig. 1 show the effect of change of acid concentration in dilute and Table III and Fig. 2 in concentrated solutions. In dilute solutions, increasing acidity has no accelerating but a slight depressing effect on the oxidation of glucose by permanganate until a normality of about 1.75 is reached. Then the effect is steady increase up to the maximum. In concentrated solutions, the amount of oxidation steadily increases from zero acidity to the highest acidity used. It is suggested that possibly the decrease in pH forces back the enolization and therefore the amount of oxidation,[1] until such high acidity is reached that the products of partial oxidation are themselves rapidly oxidized. Evans found that in the presence of strong acids, oxidation

---

[1] Evans: J. Am. Chem. Soc., 50, 2267 (1928); Chem. Reviews, 6, 281 (1929).

by such a weak reagent as copper acetate practically stops. In the more concentrated solutions the effect of the concentration overbalances this.

However Table IV and Fig. 3 show that by decreasing the volume and thereby increasing the concentration up to three times the original, the oxidation is only slightly if any increased. The change due to concentration must be relatively gradual. This knowledge is of value in interpreting some later results.

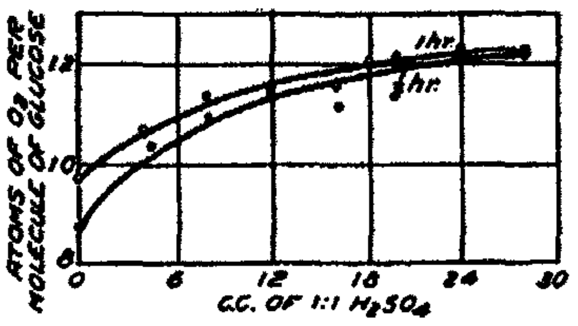


Fig. 2
Concentrated Solutions

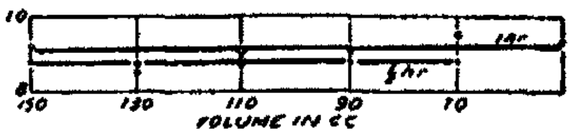


Fig. 3
Effect of Change of Volume. Ordinates are Atoms of Oxygen per Molecule of Glucose.

TABLE III

Effect of Change of Acidity in Concentrated (25x) Solutions

Glucose: 5 cc of 5%
KMnO₄: 35 cc of N
Volume: 150 cc
Temp.: Boiling

A/G: Atoms of oxygen used per molecule of glucose
Time: 30 min. for experiments marked with an asterisk; 60 min. for the others

1:1 H_2SO_4 cc	N of H_2SO_4	Oxalate cc	Back $KMnO_4$ cc	$KMnO_4$ used by glucose cc	A/G
0		100.0	38.5	25.0	8.74*
0		15.6	0.3	27.7	9.69
4.5	0.550	13.05	0.85	29.5	10.38*
4	0.472	11.3	1.1	30.6	10.70
8	0.946	9.2	0.8	31.3	10.96*
8	0.946	6.4	0.6	32.5	11.36
12	1.418	6.0	0.4	32.5	11.36*
12	1.418	5.0	0.25	32.8	11.47
16	1.895	7.0	0.25	31.9	11.15*
16	1.805	5.0	0.4	33.0	11.54
18	2.13	6.0	2.4	34.5	12.06*
18	2.13	4.0	1.2	34.3	12.00
20	2.37	4.0	0.1	33.2	11.96*
20	2.37	1.4	0.5	34.8	12.17
24	2.84	1.0	0.4	34.9	12.20*
24	2.84	0.2	0.1	35.0	12.24
28	3.35	0.1	0.05	35.0	12.24*
28	3.35	0	0.05	35.05	12.25

uncorrected

TABLE IV

Effect of Change of Volume

Glucose: 5 cc of 0.2%
KMnO$_4$: 35 cc N/25
H$_2$SO$_4$: concentration (1:27) or 1.3 N
Temp: Boiling

A/G. Atoms of oxygen used per molecule of glucose
Time. 30 min. for experiments marked with an asterisk; 60 min. for the others

Vol. cc	1:1 H$_2$SO$_4$ cc	Oxalate cc	Back KMnO$_4$ cc	Total KMnO$_4$ used by glucose cc	A/G
150	11	11.0	0.5	24.5	8.8*
150	11	10.0	0.7	25.7	9.2
130	9.5	15.2	0.45	23.5	8.5*
130	9.5	13	0.3	24.1	8.7
110	8	15.2	1.3	24.3	8.7*
110	8	13	1.1	24.9	9.0
90	6.6	14.7	1.2	24.6	8.8*
90	6.6	13	1.5	25.3	9.1
70	5.1	13	.6	24.4	8.8*
70	5.1	13	2.6	26.4	9.5
50	3.7	11.6	.6	21.4	7.7*
50	3.7	13	2.1	25.9	9.3

uncorrected

TABLE V

Effect of increasing Amount of Permanganate relative to that of Glucose

Glucose: 5 cc of 0.2%
H$_2$SO$_4$: 11 cc 1:1 or 1.3 N
Volume: 150 cc
Temp.: Boiling

A/G: Atoms of oxygen used per molecule of glucose
Time: 30 min. for experiments marked with an asterisk; 60 min. for the others

KMnO$_4$ cc N/25	Oxalate cc	Back KMnO$_4$ cc	Total KMnO$_4$ used by glucose cc	A/G
35	11	.5	24.5	8.8*
35	10	.7	25.7	9.2
40	20	2.1	26.35	9.5*
40	20	2.65	26.9	9.7
45	25	1.6	26.9	9.7*
45	23	1.0	27.9	10.0
50	30	2.4	28.8	10.4*
50	27	1.5	30.3	10.9
55	35	2.4	29.8	10.7*
55	32	3.3	33.1	11.9

corrected

TABLE VI

Reaction Velocity in Hot Dilute Solution

Glucose: 5 cc of 0.2%
KMnO$_4$: 35 cc N/25
Volume: 150 cc
Temp.: Boiling

H_2SO_4: 2 cc 1:1
A/G: Atoms of oxygen used per molecule of glucose

Time	Oxalate cc	Back KMnO$_4$ cc	KMnO$_4$ used by glucose cc	A/G
10 min.	32	13.7	19.8	7.90
20 min.	18	2.8	21.5	8.29
30 min.	16	1.4	21.9	8.31
40 min.	15	3.4	25.0	8.39
50 min.	15	1.55	23.0	8.45
60 min.	15	2.05	23.5	8.50
3 hr.	15	4.1	23.5	8.30
5 hr.	10	.7	26.7	9.35
6 hr.	10	2.8	28.8	10.09
8 3/4 hr.	10	3.4	29.4	10.00
11 hr.	10	3.6	29.6	10.00
		corrected		

TABLE VII

Reaction Velocity in Hot Dilute Solution

Glucose: 5 cc of 0.2%
KMnO$_4$: 35 cc N/25
Volume: 150 cc
Temp.: Boiling

H_2SO_4: 4 cc 1:1
A/G: Atoms of oxygen used per molecule of glucose

Time	Oxalate cc	Back KMnO$_4$ cc	KMnO$_4$ used by glucose cc	A/G
5 min.	22.1	5.6	20.6	8.10
10 min.	20.0	5.0	21.9	8.57
20 min.	15.0	.45	21.9	8.42
30 min.	15.0	1.4	22.8	8.61
40 min.	15.0	1.2	22.6	8.39
50 min.	15.0	1.2	22.6	8.25
1 hr.	12.5	2.4	24.7	7.91
2 3/4 hr.	8.0	.4	27.3	8.61
4 1/3 hr.	8.0	.6	27.5	8.53
7 hr.	6.5	.8	29.2	8.82
8 1/2 hr.	6.0	1.5	30.4	9.08
11 hr.	6.0	.7	29.6	9.00
		corrected		

TABLE VIII

Reaction Velocity in Hot Dilute Solution

Glucose: 5 cc of 0.2%
$KMnO_4$: 35 cc N/25
Volume: 150 cc

Temp.: Boiling
H_2SO_4: 10 cc 1:1
A/G: Atoms of oxygen used per molecule of glucose

Time	Oxalate cc	Back $KMnO_4$ cc	$KMnO_4$ used by glucose cc	A/G
5 min.	27.1	10.2	20.7	8.16
10 min.	17.	1.5	21.1	8.17
20 min.	16.	0.7	21.9	8.24
30 min.	16.	1.6	22.1	8.02
40 min.	15.	1.7	23.1	8.11
50 min.	15.	2.3	23.7	8.05
1 hr.	12.	3.35	26.3	7.73
2 hr.	11.	4.25	28.2	8.20
4 hr.	8.	2.90	29.9	8.19
7 hr.	2.	1.3	34.3	9.54
11 hr.	2.	1.0	34.0	9.54
		corrected		

TABLE IX

Reaction Velocity in Hot Dilute Neutral Solution

Glucose: 5 cc of 0.2%
$KMnO_4$: 35 cc N/25
Volume: 150 cc
H_2SO_4: 0.01394 gm

Temp.: Boiling
A/G: Atoms of oxygen used per molecule of glucose

Time	Oxalate cc	Back $KMnO_4$ cc	$KMnO_4$ used by glucose cc	A/G
5 min.	25	11.3	21.7	7.89
10 min.	25	12.5	22.9	8.33
20 min.	15	2.8	23.0	8.36
30 min.	20	7.9	23.2	8.38
40 min.	15	3.3	23.5	8.44
60 min.	15	3.8	23.8	8.48
90 min.	15	4.45	24.65	8.79
120 min.	15.1	4.7	24.8	8.81
3 hr.	15.	4.65	24.85	8.82
4 hr.	16.0	5.9	25.1	8.86
6 hr.	13.0	3.4	25.6	9.01
10 hr.	13.0	3.05	25.25	8.85
		corrected		

Table V and Fig. 4 show the effect of increasing the amount of permanganate relative to that of glucose. There is here a very definite and steady increase in the amount of oxidation. Fig. 3 shows that this is due not to increase in concentration of permanganate (which we have) but to the relative increase compared to glucose.

Because of the fact that over a wide range of acidity in dilute solutions, there is little change in the amount of oxygen used, it was thought that perhaps this might be the stable or at least relatively stable point for which we were looking. Several representative mixtures from this range were further investigated. Tables VI-IX and Figs. 5-8.

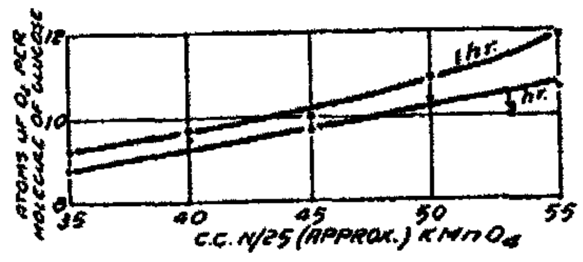


FIG. 4

Effect of increasing $KMnO_4$ relatively to Glucose

TABLE X

Reaction Velocity in Cold Dilute Solution

Glucose: 5 cc of 0.2%
KMnO₂: 35 cc N/25
Volume: 150 cc

H_2SO_4: 2 cc 1:1
A/G: Atoms of oxygen used per molecule of glucose

Time hr.	Oxalate cc	Back $KMnO_4$ cc	$KMnO_4$ used by glucose cc	A/G
2	40	2.2	1.5	0.60
3.75	40	2.1	1.4	0.58
4.25	40	3.2	2.0	0.80
5.25	37	.9	2.4	0.96
7	35	.4	3.7	1.47
9	35	3.0	6.3	2.51
11	35	5.4	8.7	3.46
22.08	30	6.4	14.25	5.67
26	25	3.6	16.0	6.37
30.75	20	3.0	19.9	7.92
35.75	20	2.4	19.3	7.68
46	20	4.6	21.5	8.56
52.5	16	1.3	21.8	8.68
59.6	15	.7	22.1	8.80
70.1	15	1.1	22.5	8.96
75.25	15	.7	22.1	8.80
83	15	1.4	22.8	9.07
97	15	1.6	23.0	9.15

corrections not necessary

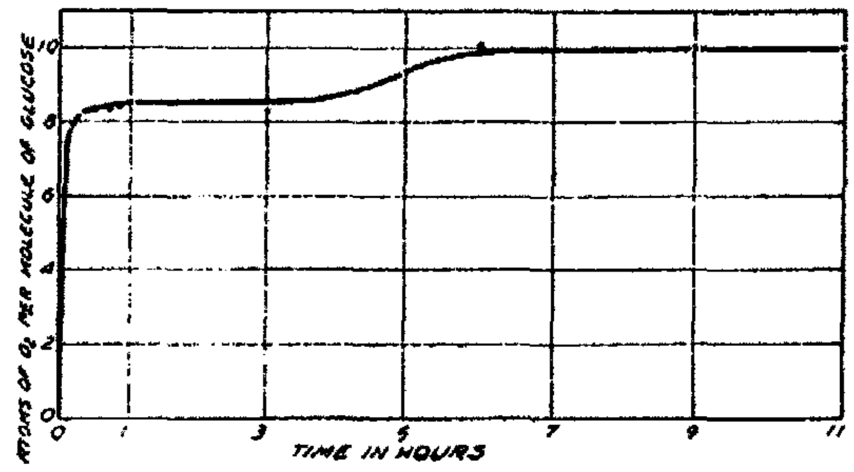


FIG. 5

Reaction Velocity in Hot Dilute Solution 2 cc 1 : 1 H_2SO_4

TABLE XI

Reaction Velocity in Cold Dilute Solution

Glucose: 5 cc of 0.2%
$KMnO_4$: 35 cc N/25
H_2SO_4: 4 cc 1:1
Temp.: Room

Volume: 150 cc
A/G: Atoms of oxygen used per molecule of glucose

Time hr.	Oxalate cc	Back $KMnO_4$ cc	$KMnO_4$ used by glucose cc	A/G
2	40	2.0	1.3	0.52
3.25	40	1.9	1.2	0.48
4.25	40	4.9	3.7	1.47
5.25	35	1.5	4.8	1.91
7	35	2.8	6.1	2.43
9	35	5.5	8.8	3.50
11	30	2.9	10.75	4.28
22	25	3.6	16.0	6.37
26	20	2.0	18.9	7.52
30.75	20	3.1	20.0	7.96
35.75	20	3.15	20.65	8.22
46	20	5.1	22.0	8.76
52.5	17	2.0	21.6	8.60
59.67	15	1.9	23.3	9.27
70	15	1.4	22.8	9.07
75.2	15	1.6	23.0	9.15
83	15	2.3	23.7	9.43
97	15	2.4	23.8	9.47

corrections not necessary

TABLE XII

Reaction Velocity in Cold Dilute Solution

Glucose: 5 cc of 0.2%
$KMnO_4$: 35 cc N/25
Volume: 150 cc
Temp.: Room

H_2SO_4: 10 cc 1:1
A/G: Atoms of oxygen used per molecule of glucose

Time hr.	Oxalate cc	Back $KMnO_4$ cc	$KMnO_4$ used by glucose cc	A/G
0.5	40	1.7	0.5	0.20
1.5	40	1.8	0.6	0.24
3.5	40	3.6	2.4	0.96
5.25	40	7.7	6.5	2.59
7.33	35	7.95	11.3	4.51
9.25	30	7.5	15.4	6.14
11.25	25	6.8	19.2	7.66
13.25	20	1.8	18.7	7.46
14.25	20	2.0	18.9	7.54
24.25	20	4.8	21.7	8.45
26.25	20	5.3	22.2	8.64
28.5	15	1.2	22.6	8.78
31.83	14.7	1.3	23.0	8.92
33.5	15	1.4	22.8	8.82
36.5	15	1.4	22.8	8.79
48.5	15	1.9	23.3	8.80
53	15	2.0	23.4	8.80
63	15	2.35	23.75	8.90
69	15	3.0	24.4	9.11
77	15	2.5	23.9	8.88
87	15	3.4	24.8	9.24
96	15	2.55	23.95	8.90
		corrected		

Since in all of these the curve rises very rapidly at first, an attempt was made to carry on the reaction under conditions which would slow it up. It is common knowledge that permanganate acts more rapidly as the temperature is raised and preliminary experiments had confirmed this very definitely for this reaction. So the same reaction mixtures used above were allowed to react at room temperature with the results shown in Tables X-XII and Fig. 7.

In all these, the reaction proceeds quite rapidly to a certain level and then goes on from there very slowly. In order to test the stability of the products at about 8 1/2 atoms of oxygen per molecule of glucose, more concentrated mixtures (12 1/2 times) were tried at room temperature. Tables XIII-XV and Figs. 8-10. In these last, the reaction is rapid up to that point and slow from there on, but the curve is not as flat as in the other cases.

Another question now presented itself. The stable level is not always exactly at 8 1/2 atoms of oxygen. The amount of permanganate used corresponds about as well to 3/5 of the amount in the reaction mixture. There is the possibility that the reaction between manganese dioxide and glucose is not as rapid as between permanganate, manganese sulphate, and glucose. As all the curves show, the reaction at first proceeds very rapidly and is practically simultaneous with the precipitation of manganese dioxide and the decolorization of the solution. At the point where all the manganese was in the form of manganese dioxide, it would have lost 3/5 of the oxidizing power of the original permanganate. Several experiments and a close check-up on the data already obtained were made to find out whether the flat place in the reaction curve was due to relatively stable oxidation products of glucose or to relatively stable reduction products of potassium permanganate. Table XVI shows the results of using different amounts of glucose and keeping the other factors the same. A small amount of glucose is oxidized more than a larger amount. Another experiment was performed (Table XVII and Fig. 16) using a smaller amount of glucose than usual with the same amount of permanganate and a volume to keep the concentration of glucose equal to that in the previous experiments. It has been already proven that the same amount of permanganate in a smaller volume has little if any different oxidizing power. Cf. Table IV and Fig. 3. There is very clearly greater oxidation per molecule than in the parallel experiment with the usual amount of glucose. Cf. Table IX and Fig. 6.

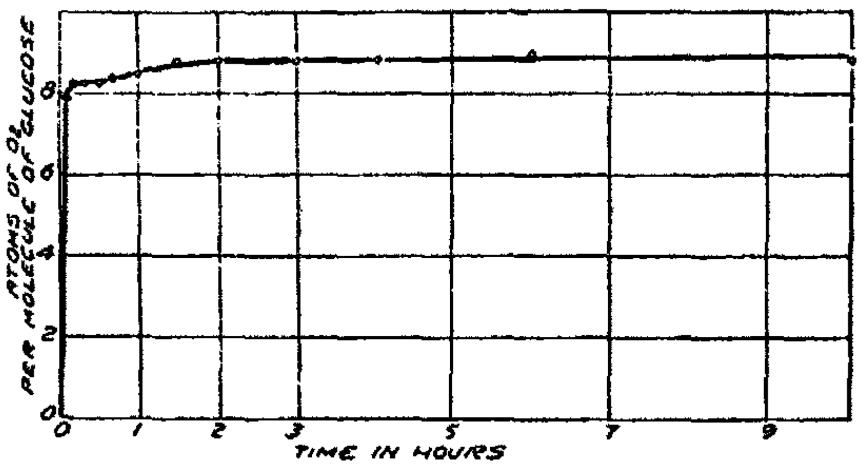


Fig. 6
Reaction Velocity in Hot Dilute Neutral Solution

These and the experiments recorded in Fig. 4, which show increase in the oxidation per molecule with increase in amount of permanganate relative to glucose, prove that the amount and concentration of glucose is not the only factor and that after a certain part of the permanganate has been used its oxidizing power is less in a given time than up to that point. This point is always 3/5 or somewhat more of the original amount of potassium permanganate.

TABLE XIII

Reaction Velocity in Cold Concentrated (12½X) Solution

Glucose: 5 cc of 2.5%
$KMnO_4$: 35 cc N/2
Volume: 150 cc
Temp.: Room

H_2SO_4 : 2 cc 1:1
A/G : Atoms of oxygen used per molecule of glucose

Time hr.	Oxalate cc	Back $KMnO_4$ cc	$KMnO_4$ used by glucose cc	A/G
0.5	35	3.3	4.2	1.47
1	32	5.0	8.9	3.11
2	28	7.95	15.75	5.50
4	20	6.2	21.7	7.58
6	14	2.4	23.8	8.31
9	12	1.4	24.7	8.62
11	11	1.45	25.75	8.99
21	10	2.0	27.3	9.53
23	10	2.4	27.7	9.67
25	7.5	.4	28.1	9.81
29	7	.7	28.9	10.09
32.5	7	1.0	29.2	10.19

uncorrected.

TABLE XIV

Reaction Velocity in Cold Concentrated (12½X) Solution

Glucose: 5 cc of 2.5%
$KMnO_4$: 35 cc N/2
Volume: 150 cc
Temp.: Room

H_2SO_4 : 4 cc 1 : 1
A/G: Atoms of oxygen used per molecule of glucose.

Time hr.	Oxalate cc	Back $KMnO_4$ cc	$KMnO_4$ used by glucose cc	A/G
0.5	35	6.6	7.5	2.62
1	30	5.6	11.4	3.98
2	28	11.3	19.1	6.67
4	15	3.2	23.6	8.24
6	12	.8	24.1	8.41
9	11	1.0	25.3	8.83
11	10	1.4	26.7	9.32
21	9	1.8	28.0	9.77
23	8	1.1	28.3	9.88
25	7	.15	28.35	9.90
29	7	.85	29.05	10.14
32.5	7	1.2	29.4	10.26

uncorrected.

TABLE XV

Reaction Velocity in Cold Concentrated (12½X) Solution

Glucose: 5 cc of 2.5%
$KMnO_4$: 35 cc N/2 40 cc in 1st experiment
Volume: 150 cc

H_2SO_4: 10 cc 1 : 1
Temp.: Room
A/G: Atoms of oxygen used per molecule of glucose.

Time hr.	Oxalate cc	Back $KMmO_4$ cc	$KMnO_4$ used by glucose cc	A/G
0.5	35	4.4	10.3	3.60
1	30	9.6	15.6	5.45
2	25	11.4	22.1	7.71
4	12	.7	24.0	8.38
6	12	2.0	25.3	8.83
9	10	1.0	26.3	9.18
11	9	1.0	27.2	9.50
21	8	1.25	28.45	9.98
23	7	.3	29.1	10.16
25	7	.7	29.2	10.19
29	7	1.45	29.95	10.46
32.5	7	1.95	30.45	10.63

uncorrected.

TABLE XVI

Oxidation of Different Amounts of Glucose using Same Amount of Permanganate

$KMnO_4$: 35 cc N/25
Volume: 150 cc
Temp.: Boiling

Time: 1 hour
A/G: Atoms of oxygen used per molecule of glucose.

2% glucose cc	$KMnO_4$ used by glucose cc	A/G
2	12.7	11.60
2	11.9	10.87
2	10.6	9.71
4	19.35	8.86
4	19.2	8.77
4	17.5	8.00
5	22.9	8.38
5	21.6	8.91
5	21.9	8.00
6	23.5	7.16
10		$KMnO_4$ used up in .5 hr.

corrected.

On the other hand can we consider that the state of the manganese is the sole or predominating factor determining the extent of the reaction? The relatively stable part of the reaction curve is due to one of three possibilities. First there may be relatively stable oxidation products of glucose while the rate of oxidation by potassium permanganate is constant except for concentration effects. Second there may be some relatively stable state of manganese while the glucose, except for change in concentration, is oxidized at a constant rate to carbon dioxide and water. Third there may be somewhat stable

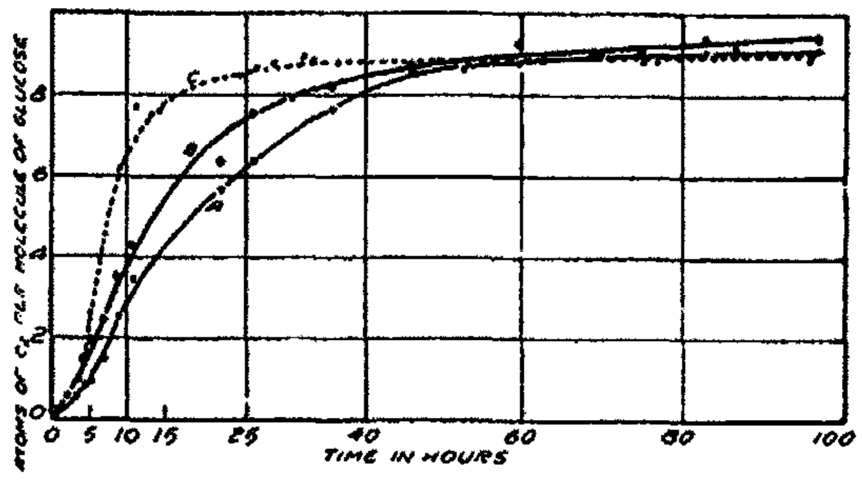


Fig. 7

Reaction Velocity in Cold Dilute Solution
A = 2 cc 1 : 1 H_2SO_4
B = 4 cc 1 : 1 H_2SO_4
C = 10 cc 1 : 1 H_2SO_4

Table XVII

Reaction Velocity in Hot Dilute Neutral Solution (with 4 cc Glucose)

Glucose: 4 cc of 0.2% Temp.: Boiling
$KMnO_4$: 35 cc N/25 A/G: Atoms oxygen used per molecule of glucose
Volume: 120 cc

Time	H_2SO_4 gm.	Oxalate cc	Back $KMnO_4$ cc	$KMnO_4$ used by glucose cc	A/G
5 min.	.01115	20	2.6	17.9	8.13
10 min.	.01115	20	5.9	21.2	9.64
20 min.	.01115	20	7.3	22.6	10.24
40 min.	.01115	15	3.1	23.3	10.45
60 min.	.01394	15	2.9	23.1	10.29
90 min.	.01394	14	2.3	23.5	10.46
2 hrs.	.01394	15	3.1	23.5	10.42
3 hrs.	.01394	15	3.75	24.15	10.71
4 hrs.	.01394	15	4.5	24.7	10.89
7 hrs.	.01394	13	2.45	24.65	10.82
10½ hrs.	.01394	13	2.35	24.55	10.75
13½ hrs.	.01394	13	4.65	26.85	11.80

corrected.

oxidation products of glucose and also a somewhat stable state of manganese, both of which influence the reaction. The preceding paragraphs have disproven the first possibility.

If the second possibility were the true one, the amount of permanganate used would be very nearly proportional to the amount of glucose present (which would be oxidized to carbon dioxide and water) until 3/5 or 21 cc of a 35 cc portion of permanganate had been used and then very little more would be used. If the glucose present required more than 21 cc for oxidation there should be very little difference in the amount used by not too different amounts of glucose. Inspection of Table XVI shows that anywhere from 10.6 to 23.5 cc of 35 cc may be used in an hour according to the amount of glucose present. 4, 5, and 6 cc of glucose all require more than 21 cc to oxidize them completely and 2 cc requires 13.1 cc of permanganate. Even with a large excess of permanganate, the glucose was not completely oxidized showing that in some form the oxidation products must be relatively stable; and even after 3/5 had been used up, the amount of glucose changes the amount of permanganate used. This last might be considered due to change in concentration of the glucose except that in Tables IX and XVII and Figs. 8 and 11, where the concentrations of the glucose have been made exactly alike by decreasing the volume with the smaller amount of glucose, there is a difference in the amount of permanganate used. Also, if this second possibility were true, 2, 4, 5, or 6 cc of glucose instead of using respectively 10.6, 17.5, 21.8, or 23.5 cc corresponding to 9.71, 8.00, 8.00, or 7.13 atoms of oxygen per molecule of glucose would use 13.1, 21.00, 21.00, or 21.00 cc (approximately) corresponding to 12.00, 9.60, 7.68, or 6.40 atoms of oxygen. Quite apparently, the potassium permanganate is not used rapidly up to 3/5 of the amount present, and then slowly irrespective of the amount of glucose present (within reasonable concentration limits). Also the glucose shows some constancy in the amount of oxygen it uses per molecule. The second possibility therefore cannot be true,

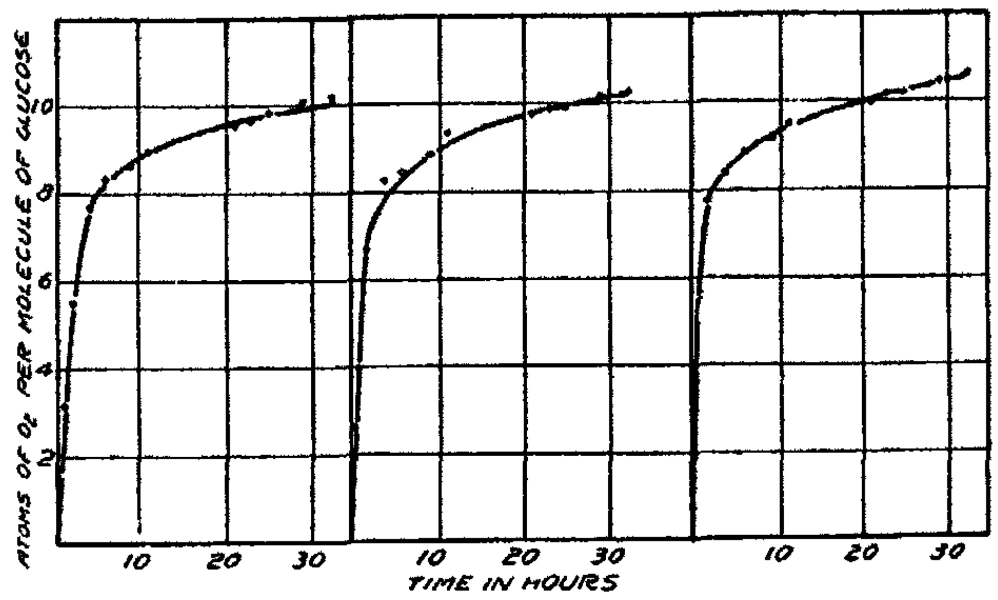


Fig. 8 Fig. 9 Fig. 10

Reaction Velocities in Cold Concentrated (12½ X) Solutions and we are left with the third one that the relatively stable part of the reaction curve is due partly to the relative stability of certain glucose oxidation products and to the relative stability of certain potassium permanganate reduction products. The nature of the permanganate product has been suggested. There are no data on which to base theories of possible products from glucose. As many experiments have shown, a slight change of condition of temperature or relative concentration, a change in absolute concentrations or acidity all change the amount of oxidation. Apparently we must come to the conclusion that everything about this reaction is relative, and that it would be a precarious one to use as a test for glucose.

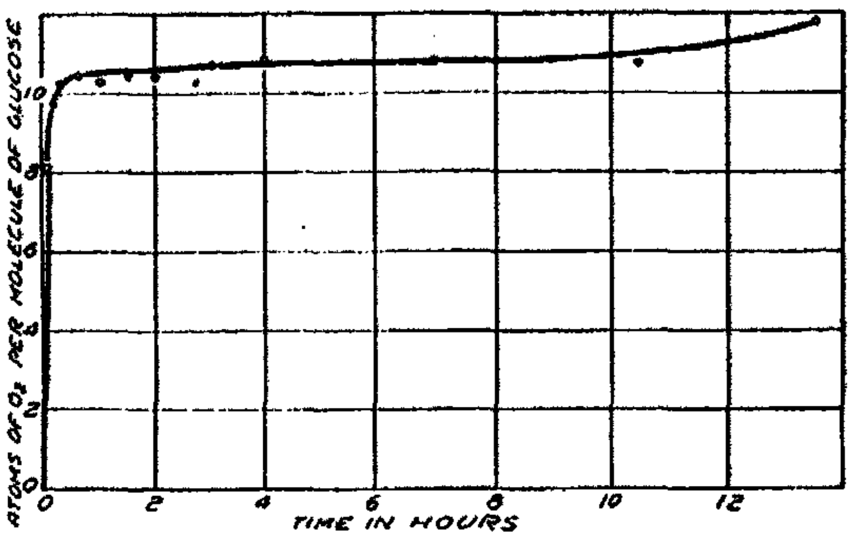


FIG. 11

Reaction Velocity in Hot Dilute Neutral Solution (4 cc Glucose)

Conclusions

1. Gluconic acid could not be isolated as a product of oxidation of glucose by potassium permanganate in acid solution.

2. If gluconic acid is formed, it is oxidized immediately by the acid potassium permanganate.

3. The preparation of gluconic acid by using the nascent bromine liberated from hydrobromic acid by potassium permanganate was not successful.

4. Oxidation of glucose by potassium permanganate in acid solution is increased slowly by increase in concentration. There must be a considerable increase before the change is detectable.

5. Oxidation of glucose by potassium permanganate in acid solution is increased by increase in acid concentration with one important exception—that of acid up to a normality of 1.75 in dilute solutions (N/25).

6. Oxidation of glucose by potassium permanganate in acid solution proceeds much more rapidly at higher temperatures.

7. The reaction proceeds rapidly to a point, which is relatively stable, and very slowly from there.

8. This relatively stable point which varies somewhat in different experiments is determined partly by relatively stable oxidation products of glucose and partly by relatively stable reduction products of potassium permanganate.

9. The relatively stable product of the potassium permanganate is suggested to be the manganese dioxide which is formed and apparently is reduced more slowly than the permanganate itself.

10. The relatively stable products of glucose are not known.

11. This reaction between glucose and potassium permanganate in acid solution is not suitable for determining glucose even in pure solutions.

The author desires to express here her appreciation to Professor Wilder D. Bancroft, who suggested and directed this work. He has always shown a ready interest in the problems which arose; and his many suggestions drawn from his extraordinarily wide knowledge of chemistry have been invaluable in solving them.

Cornell University.

PHENOMENA DUE TO FORCES AT CRYSTAL FACES AS STUDIED BY MUTUAL ORIENTATION*

BY C. ALLEN SLOAT AND ALAN W. C. MENZIES

A. Introduction

A mutual orientation is any regular arrangement of crystals of one substance on a crystal of another. Typical examples are illustrated in Plates 1 and 2. *In general, mutual orientations take place whenever the points in the net planes of two crystals coincide sufficiently in form and dimension to allow a mutual interaction of the crystallizing forces.*

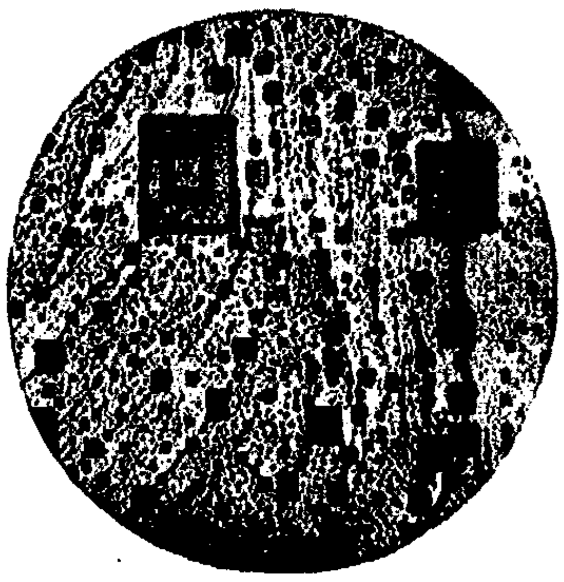


PLATE 1
NaCl on PbS

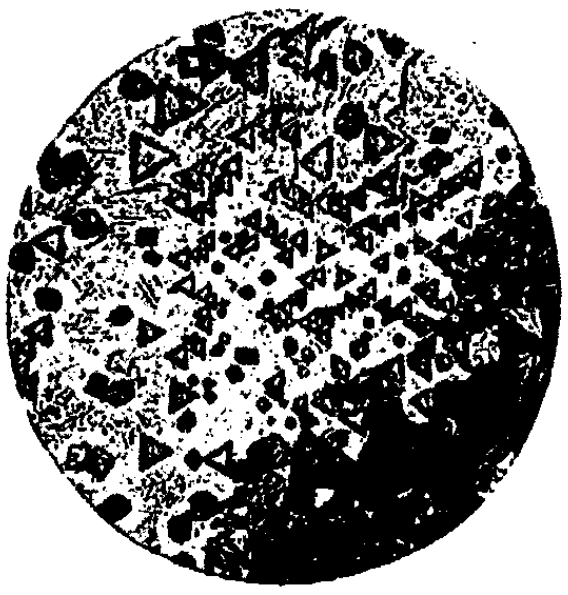


PLATE 2
KI on Mica

The difference between the points in the net planes permissible in the formation of mutual orientations varies. In rare cases, as will be shown later, it reaches as much as thirty percent. At first it is difficult to see how one substance can orientate another under these conditons. Friedel[1] has, however, explained this difficulty by postulating an orientated nucleus. According to Friedel it is only necessary for enough orientated substance to be laid down to form a nucleus. The nucleus then impresses its own orientation on subsequently deposited substance.

The forces in operation in the formation of any mutual orientation may be classified as follows: (1) the mutual attraction between the solute ions and the substrate ions, (2) the mutual attraction between the solute ions and the

---

* *From the thesis of C. Allen Sloat, presented in partial fulfillment of the requirement of the degree of Doctor of Philosophy.*

[1] Friedel: "Leçons de Crystallographie," 527 (1926).

solvent, (3) the mutual orientation between the oppositely charged solute ions, and (4) the mutual attraction between the solvent and substrate. Of these (1) and (3) are the more important. As will be shown later, (2) and (4) are important only when the differences between the parameter of the salt and that of the substrate approaches the limit at which orientation ceases.

Following Lennard-Jones and Dent,[2] force (1) may be further analysed into four parts: (1a) the direct electrostatic attraction of the charge on the ion by the valency charges of the substrate, (1b) the attraction between these ions and the dipole produced by the polarization of the attracted ion by the field near the surface, (1c) the force due to the polarization of the surface ions by the attracted ion, and (1d) the force of attraction known to exist between neutral atoms—conveniently termed the van der Waals' attraction. Contrary to popular belief, the above writers show that the van der Waals' attraction falls off much more slowly with distance than does the electrostatic attraction. At small distances the electrostatic forces are much greater than the van der Waals' attraction. As the distance between the surface and the ion increases, it is the van der Waals' attraction that predominates.

It is thus seen that it is the van der Waals' attraction that acts as the first agent in the adsorption of an ion. When the ion has approached sufficiently close, it is the strong electrostatic force which completes the final capture and fixes the ion in the space lattice.

When cleavage pieces are used as substrates, orientated crystals are usually deposited on the corners and along the edges formed by the step-like layers of the cleavage surface. (See Plate 1) Such depositions may be regarded as definite proof that the more exposed portions of the surface are surrounded by a stronger field of force than the flat portions. Indeed, such depositions are now regarded as independent evidence substantiating the "active spot" theory of the catalytic surface.[3]

The present research is both a study of mutual orientation and an attempt to relate and apply it to the study of specific problems of surface chemistry.

The varied nature of the problems investigated necessitates the division of the paper into sections. The purpose and objectives of each study will be outlined in the appropriate section.

B. Repetition of the Work of Royer on the Orientation of the Alkali Halides on NaCl, KCl, and PbS

The purpose in repeating Royer's work on the orientation limits of the alkali halides on NaCl, KCl, and PbS was, first, to gain a knowledge of the technique involved in performing orientation experiments and, second, to investigate certain differences between the work of Royer and Barker.

Royer[4] arranged the alkali halides of the sodium chloride arrangement in a series according to the lengths of their parameters. He then tried to

---

[2] Lennard-Jones and Dent: Trans. Faraday Soc., 24, 92-108 (1927).

[3] J. W. C. Frazer: Eighth Report of the Committee on Contact Catalysis, J. Phys. Chem., 34, 2134-5 (1930).

[4] Royer: Compt. rend., 29, 2050-2 (1925); See also Friedel: loc. cit. p. 526.

orientate each of these salts in turn upon NaCl, KCl, and PbS as substrates. The results of Royer's experiments are presented graphically in Fig. 1. (See p. 2009). The horizontal lines crossed or touched by the broken arrows indicate the salts found to orientate on each substrate respecitvely.

A study of the existing literature reveals the fact that Barker[5] had previously performed some of the same experiments in using the method of mutual orientations to show that the cubic salts, NH_4Br, NH_4Cl, CsCl, CsBr, and CsI do not belong to the same isostructural series as the other cubic alkali halides.

Royer in his experiments found that all the salts whose parameters lie between and include those of LiCl (5.14 Å) and KCN (6.55 Å) were orientated on NaCl. Of those salts whose parameters exceed that of KCN none were found to orientate. Barker, on the other hand, found a number of salts of parameter greater than that of KCN to orientate on NaCl, but was uncertain about the orientation of some salts Royer found to orientate. A comparison of the results of Royer and Barker in these cases is given in Table I.

TABLE I

Comparison of the Differences in Results obtained by Royer and by Barker in Certain Doubtful Cases of Orientation when using NaCl as a Substrate

Parameter in Å	6.45	6.57	6.60	7.05
Salt	NaI	KBr	RbCl	KI
Barker	M?	M	M?	M
Royer	M	Ir	Ir	Ir

M = mutual orientation
Ir = irregular

In the case of NaI on NaCl Barker was uncertain about orientation because the NaI was so hygroscopic that it took on water and streamed down the sides of the substrate.

The growth of RbCl on NaCl was indeterminate. However, NaCl is orientated by RbCl. Barker, therefore, concluded that RbCl ought to be orientated on NaCl. Both KBr and KI were found by Barker to orientate on NaCl with ease. RbBr was not found to orientate by either worker.

If KI orientates on NaCl, it means that the limiting difference allowable between NaCl and that of the most widely spaced salt found to orientate upon it has been increased half an Ångstrom unit, thus making the total difference between the parameter of the substrate and that of the orientated salt 25.2 instead of 16.35 percent of the parameter of the former.

Preliminary experiments made upon galena were generally unsuccessful until it was discovered that a film of grease upon the surface of the galena had a deleterious effect upon its ability to orientate those salts whose parameters

---

[5] Barker: Mineralog. Mag., **14**, 235-257 (1906); Z. Kryst. Mineral., **45**, 1-67 (1908).

differed very much from its own. The addition of a small amount of the base corresponding to the salt was found to be very helpful in removing the adsorbed grease. A more thorough discussion of the effect of grease on the orientating action of galena will be given in a succeeding section.

Materials.

For NaCl, rock salt was used. This at times contained orientated inclusions, thus making it necessary to inspect carefully all cleavage pieces before using them for substrates.

KCl crystals of sufficient size were grown from saturated solutions of this salt containing just enough formamide to give clear cubes.

The galena came originally from the mines at Joplin, Mo. It contained a great many orientated halite inclusions as shown by the white precipitate obtained with a solution of the orientated substance and $AgNO_3$. These inclusions made it very difficult to get clean, smooth, cleavage pieces.

The salts used were the C.P. grade of commerce or better. Any specimens of unknown purity were purified by repeated crystallization.

Rubidium hydroxide was made by the double decomposition of rubidium sulfate and barium hydroxide.

Procedure.

A drop of an aqueous salt solution, usually saturated, was placed upon a carefully inspected fresh cleavage piece of the substrate and allowed to evaporate. The result was then viewed under a microscope. In the cases where the salts were deliquescent, as were LiCl, LiBr, KF, NaBr, and NaI, the substrate was placed in a small brass box with glass top and bottom. By this means evaporation was secured by passing a stream of dry or warm dry air over the specimen. In the case of the most hygroscopic substances like LiCl and NaI, both the solution and the substrate to which it was applied were heated in order to secure the salt in the form of anhydrous cubes.

Saturated solutions of very soluble salts like KCl and KI sometimes deposit in the form of a thick heavy crust which obscures the orientation underneath. This difficulty was overcome by diluting the solution slightly and applying it in smaller quantity.

In the case of galena a fresh cleavage piece was boiled in a solution of the salt made slightly alkaline with the corresponding base. This served the double purpose of removing traces of grease and securing rapid evaporation.

Results.

NaCl as Substrate. All salts between and including LiCl and KI were found to be orientated from aqueous solution with the exception of RbCl and RbBr.

KCl as Substrate. The limits for the orientation of aqueous salt solutions were found to be the same as those determined by Royer. All salts between and including LiBr and RbBr were readily orientated.

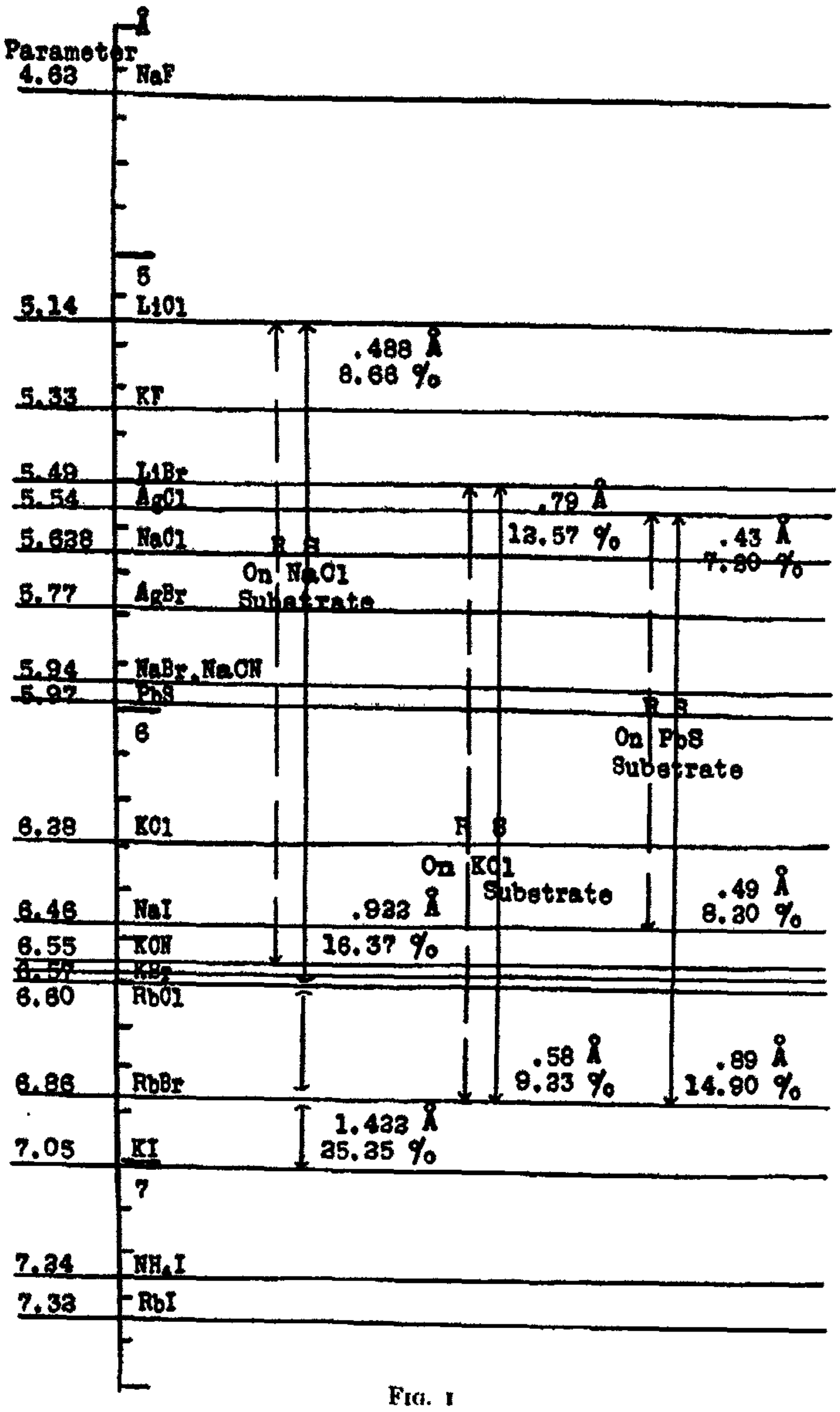


Fig. 1

PbS as Substrate. All salts between and including AgCl and RbBr were found to be orientated from aqueous solution. Of these KCN, KBr, RbCl and RbBr were not obtained as mutual orientations by Royer.

The results obtained for all substrates used are summarized and contrasted with those of Royer in Fig. 1.

The coarse broken line and the continuous black line indicate the orientation limits established by Royer and by ourselves respectively. The sign, $\overset{\downarrow}{\uparrow}$, indicates that the salt was not orientated from aqueous solution. The figures to the right of each arrow head represent the difference in Ångstrom units and in percent between the substrate marked R and S and the first and last salt to be orientated.

Discussion of Results.

From the figure it is seen that there is no difference between the results of Royer and ourselves in the case where KCl was used as the substrate. This is, however not true of the other two substrates, PbS and NaCl.

With PbS as a substrate, it is seen that we have obtained the orientation of four additional salts, KCN, KBr, RbCl, and RbBr, thereby increasing the limiting difference between the parameter of PbS and that of the most widely spaced salt orientated upon it from 0.48 Å to 0.89 Å. This increase may be attributed to the precautions taken to prevent contamination of the galena surface with grease.

The results obtained by us for the orientation of the alkali halides on NaCl agree with those of Royer for all salts whose parameters lie between and include those of LiCl and KCN.

For the salts whose parameters are larger than that of KCN the results can best be represented by Table II in which the results obtained by Royer and by Barker are contrasted with our own.

Table II

Comparison of the Results obtained by Royer and by Barker with our Results.
NaCl as Substrate

Parameter in Å.	6.46	6.57	6.60	7.05
Salt	NaI	KBr	RbCl	KI
Barker	M?	M	M?	M
Royer	M	Ir	Ir	Ir
Sloat and Menzies	M	M	Ir	M

M = mutual orientation Ir = irregular

From Table II it is seen that the results obtained by us on NaCl agree with the results obtained by Barker except in the case of RbCl. In this case we were neither able to orientate RbCl on NaCl nor confirm Barker's observation that NaCl orientates on RbCl. The character of the deposit obtained in each case was very similar.

No really adequate explanation can be given as to the reason Royer did not get KBr and KI to orientate on NaCl. It is quite probable, however, that Royer's method of applying a hot solution to a substrate, especially if the solution were concentrated, would most likely produce a thick heavy crust which would obscure any orientation underneath.

Two other interesting cases which demand an explanation arise from the fact that RbCl (6.60 Å) is not orientated on NaCl (5.628 Å) although it has a parameter only slightly larger than that of KBr (6.57 Å) and from the fact that KI (7.05 Å) is orientated on NaCl while RbCl and RbBr (6.86 Å) are not orientated although their parameters lie closer to that of NaCl than does that of KI.

Simple correlation of the facts observed with the values for the various salts of such quantities as lattice energy, energy of ion hydration or heat of solution in a saturated solution could hardly be anticipated in view of the fact that we are here dealing with the initial stages of formation of a monomolecular layer of one salt upon a different salt. Examination, however, of the available data on the radii of ions as given by Goldschmidt[6] did show that the ratio of the radius of the anion to that of the cation is 1.215 for RbCl, 1.315 for RbBr, 1.473 for KBr, and 1.654 for KI. From these it is seen that the ratios of the two orientated salts are larger than those of the unorientated.

That these ratios do have a significance is further verified by several examples taken from the last-mentioned paper of Barker. This work shows that KCl (a/c = 1.361) does not orientate on KI or RbI although NaBr (a/c = 2.000) does; and that RbCl (a/c = 1.215) does not orientate on NH_4I or RbI although KCN (a/c = 1.457) does. In each of these cases the parameter of the unorientated salt lies closer to that of the substrate than that of the unorientated salt, but in every case the unorientated salt has a lower ratio of the radius of the anion to cation than the orientated salt.

The fact that KI is orientated by NaCl while RbCl and RbBr, although fitting the NaCl lattice more closely, fail to be orientated is thus not an isolated fact. In the analogous cases also, a larger value of the ratio of the radius of the anion to that of the cation is found to be concomitant with greater susceptibility to orientation. Paraphrasing the latter statement, it might be said that the greater the lack of symmetry, or uniformity of field over the surface of a sphere enclosing the ion pair, the better the chance of orientation. An analogy may be drawn from a consideration of the relative temperatures of crystallization of liquids. Whether on not the forces causing crystallization be termed van der Waals' forces, when the external fields of force surrounding the molecule are symmetrical and uniform in azimuth, then, as in the case of sulfur hexafluoride, the freezing point is lower than it is in the general run of substances.

This correlation between dissymetry and ease of orientation serves also to interpret the superiority of NaCl over KCl as a substrate causing orientation.

C. An Apparent Correlation of Mutual Orientation with the Dielectric Constant of the Solvent

Experiment showed that very soluble salts like KCl, LiCl, LiBr, NaBr and NaI could be advantageously deposited from organic solvents such as methyl and ethyl alcohol, acetone, and furfural. These experiments sug-

---

[6] Goldschmidt: Trans. Faraday Soc., 25, 282 (1929).

gested that organic solvents might be used in investigating borderline cases of salts which barely fail to be orientated from aqueous solutions. In such cases the attraction of the solvent for the solute and for the substrate might be expected now to show itself as a factor of greater influence. In the so-called polar liquids, for example, the solute ions are pictured as surrounded by an envelope of solvent which must be squeezed out when the anhydrous salt is laid down upon its substrate. This work of dehydration should be smaller in liquids which are less polar and of lower dielectric constant. The following paragraphs give the experimental facts for various solvents in borderline cases. When the solute is deposited from the vapor phase, the solvent may be regarded as a vacuum.

Materials.

For this purpose, the same series of salts and substrates was used as in the preceding studies, namely the alkali halides on NaCl, KCl and PbS. Since no test can be made unless the salts are not orientated from water, only those salts of larger parameter than that of the most widely spaced salt orientated from water were used, KBr and KI on NaCl excepted.

All the salts used were of the same purity as those of the preceding section. As solvents furfural, ethyl alcohol, methyl alcohol, and acetone were used.

Procedure.

The method used for the deposition of salts from organic solvents was the same as that used for aqueous solutions in section B.

A new procedure is involved, however, in the deposition of ammonium salts from the vapor phase. In order to sublime salts upon a substrate, a flat bottomed test tube inserted through a rubber stopper was placed in another test tube provided with a side arm. The substrate was fastened upon the bottom of the inside tube by a copper wire. After exhausting the apparatus through the side arm the ammonium salt was volatilized by the application of gentle heat to the bottom of the outer tube. The inner tube served as convenient means of regulating the temperature of the substrate where this was necessary.

Results.

The results of these experiments are tabulated in Table III.

From Table III it is seen that the ability of a substrate to orientate those salts whose parameters lie without the limit of those orientated from aqueous solution would seem to be related to the dielectric constant of the solvent, as is not unreasonable. The orientating ability of a given substrate becomes greater as the dielectric constant of the solvent decreases.

The success which characterized the deposition of salts whose parameters lie beyond the orientation limit for water is almost lacking in the case where PbS was used as a substrate. This may be ascribed to the presence of traces of foreign bodies which foul the galena surface by preferential adsorption. NH_4I does not orientate on galena from the vapor phase because the HI vapor attacks the galena surface.

TABLE III

Substrate, NaCl.5.628 Å

Dielectric Constant →		81	39	32	25	21	1
Medium		water	furfural	methyl alcohol	ethyl alcohol	acetone	vapor
6.57 Å	KBr	M	M	M	M	N.S.S.	
6.60	RbCl	Ir	Insol	M	M	N.S.S.	
6.86	RbBr	Ir	M	M	M	N.S.S.	
7.05	KI	M	M	M	M	M	
7.24	NH_4I	Ir	Ir	Ir	Ir	Ir	M
7.32	RbI	Ir	Ir	Ir	Ir	M	
		Substrate, KCl. 6.28 Å					
7.05	KI	Ir	Ir	M	M	M	
7.24	NH_4I	Ir	M	M	M	M	M
7.32	RbI	Ir	M	M	M	M	
		Substrate, PbS. 5.97 Å					
7.05	KI	Ir	Ir	Ir	Ir	M	
7.24	NH_4I	Ir	Ir	Ir	Ir	Ir	Ir
7.32	RbI	Ir	Ir	Ir	Ir	Ir	

M = mutual orientation
Ir = irregular
Insol = insoluble
N.S.S. = not sufficiently soluble for experimentation.

In Fig. 2 the results obtained in this section are added to and contrasted with those obtained by Royer and by ourselves with aqueous solutions. Lines and numbers which occur both in this figure and in Fig. 1 have exactly the same significance as those of Fig. 1. The fine broken lines extending down from the solid arrows represent the increase in the limiting difference between the parameter of the substrate and that of the most widely spaced salt orientated upon it brought about by using solvents of low dielectric constant rather than water.

For the substrate, PbS, this increase is 3.19 percent and for KCl 7.33 percent. It may be said, however, that the orientating limit has not been reached since RbI orientates on KCl from all solvents except water. A much larger limit would probably be found if alkali halides of larger parameter were available for experimentation.

In the case of the substrate, NaCl, the use of organic solvents has increased the limiting difference between the parameter of NaCl and that of the most widely spaced salt orientated upon it 4.81 percent above that obtained by us for aqueous solutions, and 13.69 percent above that obtained by Royer for the same solvent. NaCl is, therefore, shown to have the ability to orientate a salt whose parameter is 30.06 percent larger than its own.

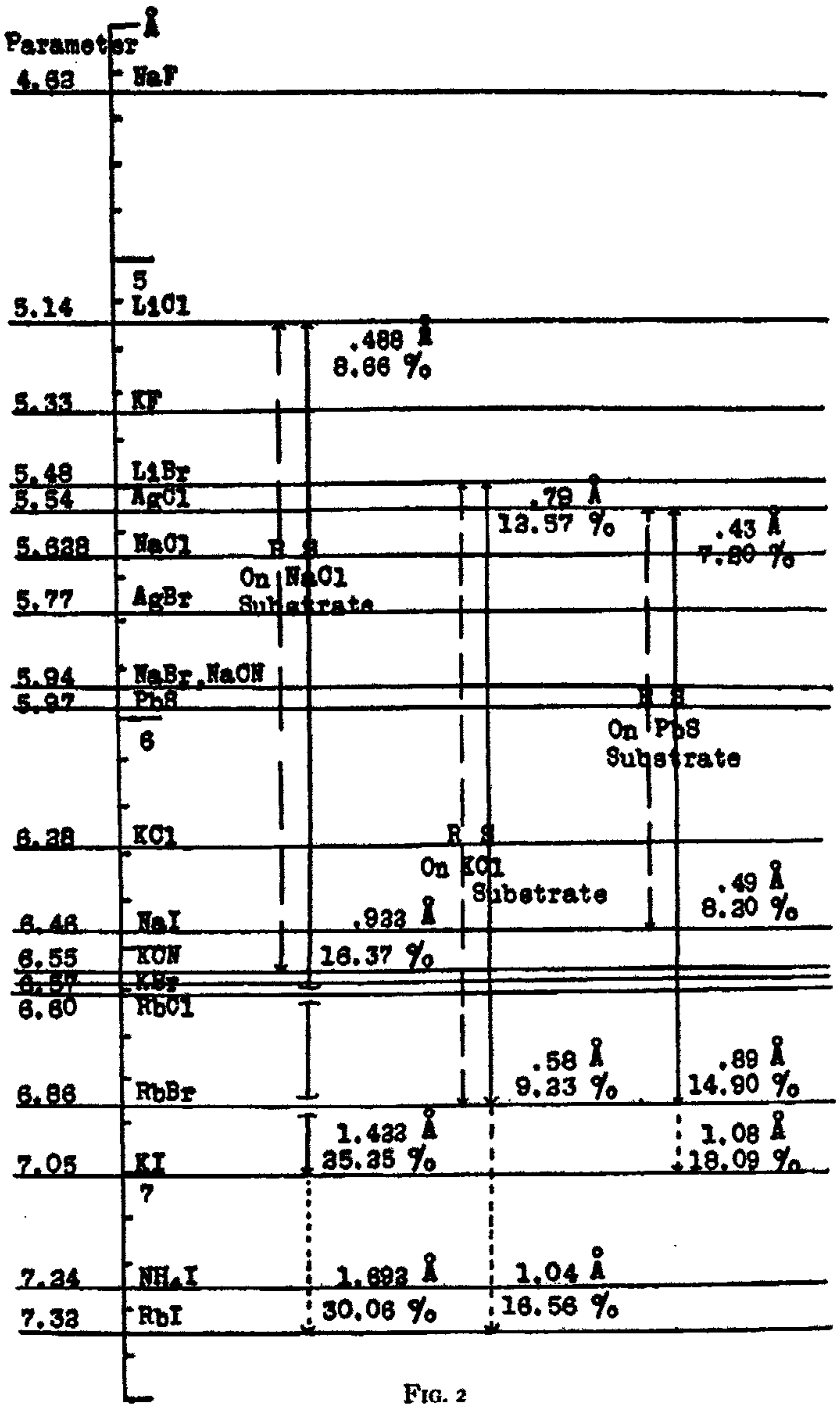


Fig. 2

D. The Effect of Grease on the Orientating Action of Galena
The Hydrophobia of Galena

As previously stated some difficulty was encountered in getting the alkali halides to orientate on galena. When a drop of an aqueous solution of sodium chloride was placed upon a galena substrate, it stood upon the galena very much like mercury on glass. On evaporation of the water the salt was deposited in the form of a miniature crater. Any attempt to remove the excess of the solution simply resulted in the diminution of the area covered by the solution.

Since galena is said to be hydrophobic,[7] it was natural to suppose that the solution did not wet the galena on account of some inherent quality of the galena.

To overcome the tendency of the solution to stand upon the galena in drops an attempt was made to use solvents of lower surface tension such as methyl and ethyl alcohol or part alcohol and water. In this case the solutions spread well enough, but scarcely any orientation resulted. This was probably due to the preferential adsorption of traces of higher alcohols or other foreign bodies in alcohols.

Contrasted with this strange behavior of the sodium chloride and other alkali halides in plain aqueous solution, aqueous ammonia solutions of AgCl and AgBr readily yielded orientations on galena. This together with the fact that Langmuir[8] has found that the angle of contact of galena is increased when the galena surface is contaminated with grease led to the conclusion that orientation was prevented by the presence of grease.

The previous experiment with aqueous sodium chloride solution was then repeated with the addition of a few drops of dilute sodium hydroxide. The substrate was then boiled in this solution, removed, and allowed to cool. On evaporation of the solution a film of closely-spaced perfectly-orientated sodium chloride crystals was deposited. This meant that the negative results previously obtained were most likely due to grease. Accordingly all glassware was carefully cleaned in hot chromic acid solution, rinsed, and placed in covered containers. All handling was done with tongs. Special care was taken to prevent grease films from the fingers from reaching the glass.

Although these precautions were taken to prevent grease contamination of the solutions through the glassware and water, little improvement was seen in the orientation of the sodium chloride or the spreading of the solution.

It was noticed that standing solutions still showed the presence of grease at the liquid-air junction as evidenced by the poor capillary rise. Since all possible sources of contamination had been removed except from the salt itself, it was finally concluded that the contamination was due to grease in the sodium chloride.[9]

The sodium chloride was then heated to fusion to drive off all traces of organic matter. Solutions, neutral to phenolphthalein, were prepared from this salt. These solutions spread well and in nearly all cases crept over the surface of the galena in much the same fashion as water upon clean glass

---

[7] Freundlich: "Colloid and Capillary Chemistry," p. 160.

[8] Langmuir: Trans. Faraday Soc., 15, 62 (1920).

[9] It was later learned that du Noüy had encountered somewhat similar difficulties in attempting to measure the surface tension of rabbit blood serum in a physiological salt solution. Initial surface tension varied from 63 to 74 dynes. This variation was traced to the presence of grease in the "C.P." sodium chloride. du Noüy: "Surface Equilibria of Biological and Organic Colloids," p. 30.

leaving a deposit of small perfectly orientated crystals such as previously shown in Plate 1.

There still remained a few instances in which the grease-free sodium chloride solution did not spread readily. It may be suggested that these were due to a film of adsorbed air since galena left in dry air becomes still more difficult to wet.[10] This explanation is, however, quite unlikely, first because Edser[11] has observed that air is not measurably adsorbed upon galena, blende, or quartz, and second because no difference could be detected in the wetting or orientating properties of such galena when it was cleaved in air or under the sodium chloride solution.

Any grease not yet accounted for must occur with the natural galena. How then can the presence of this grease be explained? Any solution of this problem will have to be sought in the history of the galena and in the manner in which it was deposited.

In the mines around Joplin, Mo., from whence came the galena that was used in this study, the galena is found above the lighter zinc sulfide. The presence of bitumen of petroleum origin has led J. E. Spurr[12] to suggest that the galena was carried to the top by oil flotation. It would be natural to expect that some of the petroleum had remained in the ore in much the same fashion as the sodium chloride that has left the ore full of inclusions. (See p. 2008). Indeed, in view of the strong affinity of the so-called hydrophobic sulfides for greasy bodies, it would not be surprising if some of these were found to have grease built into their space lattice in much the same fashion as certain crystals are found to be colored by dyes.

Additional evidence which shows that the hydrophobia of galena is not an inherent property is found in the authors' observation that pure water spreads readily over lead sulfide prepared by heating lead and sulfur and in the observation of Hall[13] who found that artificially prepared MoS_2 is readily wetted by pure water in spite of the fact that the natural MoS_2 is said to be the most hydrophobic of sulfides.

F. The Orientation of Salts by Single Crystals of Silver

Many theories of the metallic state have been put forward; of these, many have been discarded, and none is universally accepted. We here describe some new experimental facts which bear upon this problem.

Materials.

For this study silver, a non-oxidizing face-centered cubic metal whose parameter is 4.07 Å, was selected as the substrate. For salts the body-centered cubic alkali halides, NH_4Cl (3.866 Å), NH_4Br (4.047 Å), CsCl (4.11 Å), and CsBr (4.29 Å) were selected. Comparison of the space lattice of each type as shown in Figs. 3a and 3b reveals the fact that the (100) face of

---

[10] Edser: Brit. Ass. Adv. Sci., Report on Colloid Chemistry, p. 289 (1922).

[11] Edser: Ibid. p. 277.

[12] Spurr: Eng. Mining J., 123, 204-5 (1927).

[13] Hall: "Master's Thesis" Gettysburg College, (1929).

the silver is very similar in form and dimension to the corresponding face of the ammonium bromide, excepting the extra atom in the face of the silver lattice. It was not thought that this would present any experimental difficulties in view of the wide differences under which mutual orientations have already been shown to occur. There are no face centered cubic salts available which are suitable for this investigation.

Single crystals of silver were grown by suspending a copper wire in a two percent solution of silver nitrate. Crystals grown by this method were not very large. However, patient search revealed a number of good cube faced crystals that could be used as substrates.

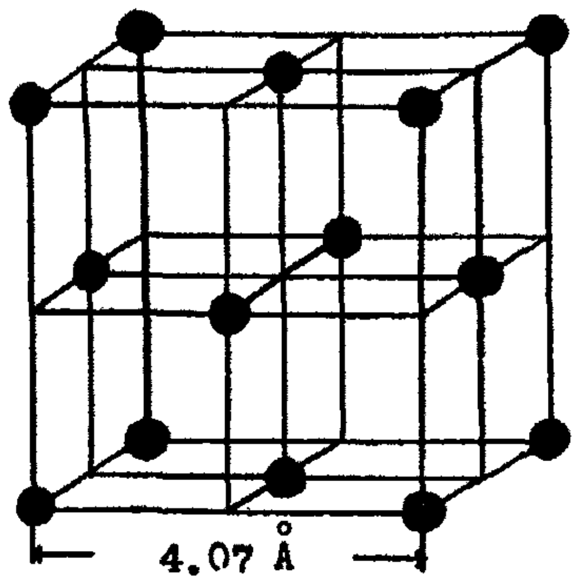


Fig. 3A
● Ag atoms

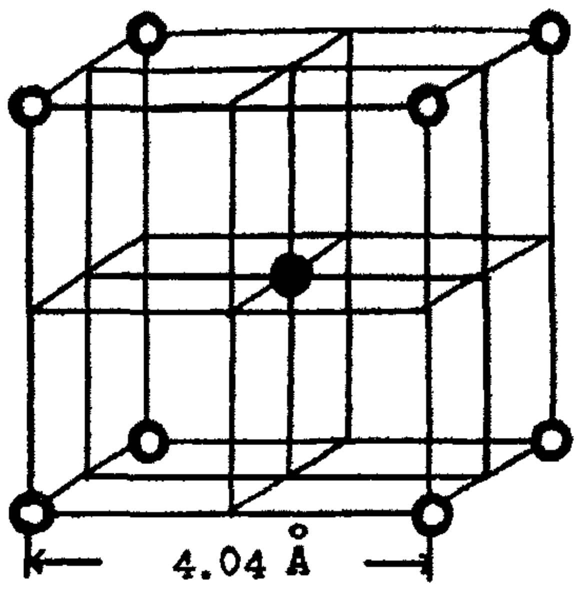


Fig. 3B
● NH_4 ion
○ Br ions

Ethyl alcohol was selected as the preferable solvent, first, because it has been shown that the orientated crystals are deposited more readily from solvents of lower dielectric constant, second, because it is an organic solvent in which all four of the salts are soluble, and third, because it is a solvent in which the bromide ion does not react readily with the silver.

Procedure.

A drop of alcoholic solution of the salt was placed upon a silver crystal, allowed to evaporate, and the result viewed under the microscope.

Results.

NH_4Br and CsCl were orientated on silver. NH_4Cl and CsBr were not. The difference in parameters tolerated by the silver is rather small as compared with that allowed by salts. In the case of NH_4Br it is 0.023 Å or 0.56 percent of the parameter of the silver. For CsCl it is 0.04 Å or 0.98 percent of the parameter of the silver.

This small difference of parameter is in striking contrast to the findings with a salt substrate. It must be remembered that the postulated charges on the ions of the dissimilar net planes, metal and salt respectively, which by their contact determine the orientation are in the present instance all respectively of like charge, a state of affairs that was not encountered in the case of salt upon salt. Again, insoluble contamination on the silver surface would be more prejudicial to orientation than in the case of a soluble salt substrate, in whose case contamination is less likely. Furthermore, salt substrates may be richer than metallic silver in Smekal cracks favorable to orientation.

Because of the observed necessity of such a close coincidence in atomic spacing of salt and silver, it might be plausibly argued that in this case the mutual attraction that directs orientation was attributable entirely to polarization of uncharged silver atoms by approaching charged ions of salt. Again, it is true that innumerable purely covalent compounds crystallize from their melts or from solution, in which process the molecules of solid, containing no charged atoms, are able to orient correctly like molecules from the liquid phase as these approach and settle down to their appropriate regular positions in the growing crystal. This happens for other than the closed-packed arrangements, for which little directive force would be required. In this connection, however, two remarks are pertinent: first, no examples of orientation between crystals of electrovalent and covalent substances have been reported in the literature; second, we were unable to induce NaF or KF to orientate upon carborundum or naphthalene to orientate upon NaCl, KCl, PbS, or $CaCO_3$ (calcite) although there was quite close agreement between the parameters of certain of these substances in at least one dimension.

Since, therefore, the lattice structure of NH_4Br and of CsCl are well established, the simplest interpretation of the observed orientation is to assign to the atoms of the silver crystal positive charges, not necessarily of effectively unit value, which serve to align the negative ions which form net planes in the salts.

F. Crystal Habit and Mutual Orientation

When crystals of barium nitrate are grown from a solution saturated with methylene blue, cubes instead of octahedra are formed.[14] This is caused by the strong adsorption of the dye upon the cube faces of the crystal as is verified by the fact that the cube faces are preferentially colored by the syncrystallization of the dye with the barium nitrate. Since the material modifying the crystal, crystallizes with it, Gaubert[15] believes the change in crystal habit in all such cases is caused by orientated adsorption.

A case exactly the converse of the barium nitrate one is found in the modification of the crystal habit of sodium chloride. When crystals of this salt are grown from a saturated solution containing urea, formamide, glycocoll, or a base, octahedra instead of cubes are formed.

Saylor[16] has shown that both cases of modification are due to the adsorption of anions on the octahedral faces and cations on the cube faces. Since the cube faces of sodium chloride are stable anyhow, modification of this salt takes place only when anions are preferentially adsorbed on the octahedral faces. In the case of barium nitrate the octahedral faces are stable and

---

[14] Gaubert: "Le Facies des Cristaux," p. 13 (1911).

[15] Gaubert: Compt. rend., 180, 378-80 (1925).

[16] Saylor: J. Phys. Chem., 32, 1455 (1928).

modification takes place only when cations are preferentially adsorbed on the cube faces.

Methylene blue is a true basic dye and is, therefore, adsorbed upon the cube face as a true cation. Although urea, formamide, and glycocoll are non-ionizing compounds they are consistently adsorbed as if they were anions.

In view of the fact that a close relation exists between the modification of crystal habit in both of the cases cited above and that Gaubert attributes change in crystal habit by syncrystallization to orientated adsorption, it occurred to us that it might be possible to observe the orientation if it were of the type studied in this paper. It was, therefore, decided to try urea and formamide on the octahedral face of sodium chloride. The adsorbed material, if orientated, should manifest itself in the form of regularly arranged crystals.

Procedure.

Clear octahedral crystals of sodium chloride were grown by allowing an almost saturated solution containing one-tenth its volume of formamide to evaporate slowly in a beaker.

A drop of urea solution applied to the substrate quickly formed a crust which completely obscured the surface of the sodium chloride. To prevent this, as well as to allow the needle-like crystals of urea to grow at an angle to the surface, the substrate was placed in a small glass dish and covered with a saturated solution of urea.

Ethyl and methyl alcohol and aqueous solutions were tried. As formamide is a liquid at ordinary temperatures the substance was applied to the substrate out in the open when the outdoor temperature was below the freezing point of this substance.

Results.

Unorientated crystals of urea were obtained. No crystals were observed in the case of formamide on account of the fact that traces of water lowered its freezing point below the temperature used. With each substance, however, there appeared upon the faces of the substrate a large number of triangular etch figures whose apices pointed toward the base of the octahedral face that contained them.

Etching took place only when urea and formamide were present. None was observed when plain solvent alone was placed upon the substrate.

Discussion of Results.

The results indicate that the change in crystal habit brought about by the presence of the urea or formamide is not due to orientated adsorption. If such adsorption took place, urea grown upon the orientated layer should take the same orientation. This is not borne out by the experiment.

H. Miscellaneous Orientations

$NaCl$, KCl, PbS, and $CaCO_3$ as Substrates.

At ordinary temperatures NH_4Cl (3.86 Å) and NH_4Br (4.04 Å) have the caesium chloride arrangement. Above 184.3° and 137.8° C. they have the sodium chloride arrangement. At 250° the parameter of NH_4Cl is 6.53 Å and that of NH_4Br is 6.90 Å. By suspending a hot substrate in the vapor of these halides by means of the apparatus already described, both were found to orientate on NaCl and KCl. The differences between the parameters of NH_4Cl and NH_4Br and that of NaCl are 15.95 and 22.48 percent and between the same pair and KCl 3.96 and 9.97 percent respectively.

AgCN in aqueous ammonia solution also orientates on both NaCl and KCl. The parameter of AgCN in unknown. Assuming, as is usually the case, that bromide and cyanide ions have the same radius, the parameter of AgCN may be taken as equal to that of AgBr. On this assumption the difference between the parameters is 2.57 percent for NaCl as substrate and 8.1 percent for KCl.

Aqueous solutions of a number of salts were tried upon galena in order to determine if there was any orientation. Of these $KClO_3$ and $KClO_4$ were found to orientate. The crystals of $KClO_3$ (See Plate 3) possess two types of orientation. One form is the mirror image of the other. The orientation of $KClO_4$ is similar to that of $KClO_3$. $KClO_3$ is monoclinic and $KClO_4$ is orthorhombic. The parameters of $KClO_3$ are a, 4.647; b, 5.585; c, 7.085 and of $KClO_4$ a, 8.85; b, 5.66; c, 7.24 Å respectively. The second parameter of each salt is seen to approach most nearly to that of PbS (5.97 Å).

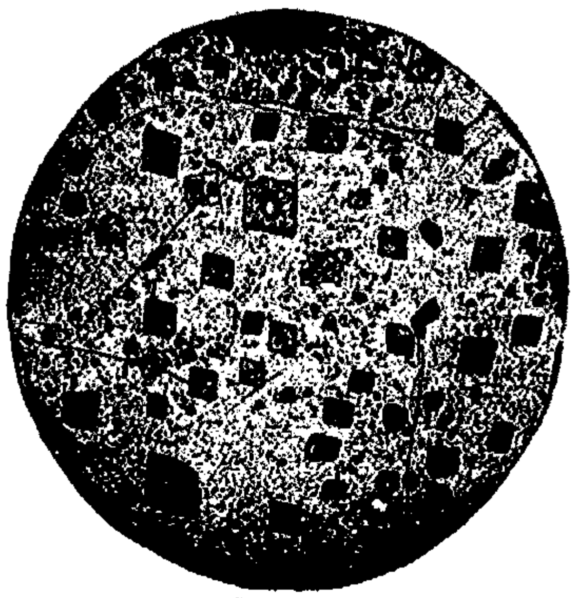


PLATE 3
Orientation of $KClO_3$ on Galena

The cubic salt, $NaClO_3$ (6.55 Å) is not orientated on PbS.

There are no indisputable cases of the orientation of a solid covalent substance on an electrovalent crystal. Orientations between the same type are known. It, therefore, becomes of interest to know whether electrovalent-covalent orientations take place. For this purpose a number of organic compounds were sublimed upon the four substrates mentioned at the beginning of this section and in addition an attempt was made to orientate a number of salts upon the covalent substrate, carborundum.

Calcite is rhombohedral hexagonal. Its parameter is 6.36 Å. The arrangement of the calcium and carbonate ions in the cleavage plane of calcite is very similar to that of the cleavage plane of NaCl. Naphthalene, quinone, and p-dichlorobenzene were sublimed upon NaCl, KCl, PbS, and $CaCO_3$. None were found to orientate although the difference between the b parameter of naphthalene and that of KCl is only 6.28 percent and that between the c parameter of quinone and NaCl is only 0.145 percent.

Carborumdum as a Substrate.

Carborundum is hexagonal. It crystallizes in three types. The a parameter of all of these is given as 3.09 Å while the c parameter is 37.9, 15.17, and 10.10 Å respectively for types I, II, and III. Of the sodium chloride arrangement KBr (6.57 Å), NaCl (5.628 Å), KF (5.33 Å), and NaF (4.62 Å), and of the caesium chloride arrangement NH_4Cl (3.866 Å), and RbF (3.66 Å) were tried, but none were found to orientate.

In view of the above facts, it is extremely doubtful whether orientation takes place between electrovalent and covalent compounds.

Summary

(1). The investigation of the discrepancies between the results of Royer and Barker for the substrate, NaCl, confirms the results of the latter except for the orientation of RbCl on NaCl.

(2). The four salts, KCN, KBr, RbCl, and RbBr, of larger parameter than any found by Royer to be orientated on PbS, were found to be orientated when precautions are taken to prevent the contamination of the galena surface with grease.

(3). The orientating ability of a substrate is correlated with the ratio of the radius of the anion to that of the cation.

(4). The limiting difference between the parameter of NaCl and that of the most widely spaced salt orientated upon it is found to be 25.2 percent of the parameter of NaCl instead of 16.4 percent; for PbS as a substrate it is shown to be 14.9 percent instead of 8.2 percent, as found by Royer.

(5). Mutual orientations are very readily deposited from organic solvents.

(6). Mutual orientations can be obtained from a solvent of lower dielectric constant when a solvent of higher dielectric constant fails to yield an orientation.

(7). Samples of galena were found to contain throughout their mass orientated crystals of halite.

(8). The hydrophobia of galena is not an inherent quality, but is due to the affinity of galena for grease.

(9). NH_4Br and CsCl orientate on metallic silver. The significance of this new type of orientation is discussed.

(10). Change in crystal habit is not due to orientated adsorption.

(11). Certain solutions which are known to cause change in crystal habit are shown to produce characteristic etch figures upon the octahedral faces of sodium chloride.

(12). It has been found possible to deposit mutual orientations from the vapor phase.

(13). High temperature forms of NH_4Cl and NH_4Br were found to orientate from the vapor phase on NaCl and KCl.

(14). Notwithstanding close agreement in atom spacing, no mutual orientation was found between substances one of which was of the electrovalent and the other of the covalent type.

Frick Chemical Laboratory,
Princeton University,
Princeton, N. J.

ADSORPTION OF SOLUTES BY CRYSTALS IN RELATION TO COMPATIBILITY OF SPACE LATTICE*

BY C. ALLEN SLOAT AND ALAN W. C. MENZIES

The forces operating to cause adsorption are similar to those causing mutual orientations.[1] Marc[2] has shown that crystals adsorb those substances which are isomorphous with themselves much more markedly than those which are not. Calcite adsorbs the isomorphous sodium nitrate much more strongly than potassium nitrate. Barium carbonate, isomorphous with aragonite and potassium nitrate, adsorbs potassium nitrate more strongly than sodium nitrate. Since isomorphous salts have closely similar space lattices, Marc's results would seem to indicate that compatibility of space lattices and lattice dimensions might be as important factors in adsorption as they are in mutual orientations. No studies of adsorption seem to have been made where both the adsorbent and the adsorbed salts belong to the same system and arrangement.

It is the purpose of this study to investigate the relation between adsorption and lattice dimensions of the adsorbent and adsorbed substances, using members of the sodium chloride arrangement.

Materials

Some difficulty was encountered in finding a suitable adsorbent with which to conduct the experiment. It is necessary to have an adsorbent which has a parameter close to that of one of the salts to be adsorbed upon it, but the neighboring salt should not have the smallest solubility of the series to be adsorbed because this would not allow any differentiation between the relative importance of solubility and lattice dimensions. Silver bromide (5.77 Å) does not meet these requirements. Silver chloride (5.54 Å) is reasonably close to sodium chloride (5.628 Å), but since the pair form mixed crystals and sodium chloride has a low mol fraction solubility, it is quite likely that the latter would be strongly adsorbed in any case. Moreover, both silver halides are ordinarily sensitive to light. Galena (5.97 Å), near sodium bromide (5.94 Å), seems to meet the requirements of the experiment. Ground galena could not be used because it contained halide inclusions. Furthermore, galena is slowly oxidized to lead sulfate. These difficulties were overcome by using precipitated lead sulfide and making up all solutions with water saturated with lead sulfate and sulfide.

As salts to be adsorbed upon the precipitated lead sulfide, the following alklai bromides were chosen:

---

* From the thesis of C. Allen Sloat, presented in partial fulfillment of the requirement of the degree of Doctor of Philosophy.

[1] See preceding paper. J. Phys. Chem., 35, 2005 (1931).

[2] Marc: Z. physik. Chem., 75, 710 (1910); 81, 641 (1913).

LiBr	2.74Å	KBr	3.285	RbBr	3.43
NaBr	2.97	NH_4Br	3.329	CsBr	3.67

With the exception of the ammonium and caesium bromides which belong to the body-centered cubic arrangement all belong to the face-centered sodium chloride arrangement. The numbers refer to the distances between the centers of the anions and cations in the space lattice. For the sodium chloride arrangement the values are equal to one half the length of the parameter of a unit cube of four molecules. These numbers rather than the parameters are used because they allow a comparison of the body-centered ammonium bromide and caesium bromide with the other halides.

It may be pointed out that sodium bromide crystallizes as the monoclinic dihydrate below 50.7°C. It was not thought that this would affect the validity of the experiment at the dilution used, since Taylor and Close[3] at the same dilution could detect no sudden change in the degree of hydration of calcium chloride in crossing the transition temperature of the tetra- to the dihydrate.

It may also be pointed out that lead sulfide is a bi-valent compound while the alkali halides are uni-univalent compounds. The relationship of these is, however, very similar to that between the calcite and sodium nitrate. Any effect due to the bivalence of the lead sulfide should affect the whole series uniformly.

The alkali halides were carefully purified by recrystallization and tested for impurities. Lead sulfide was prepared by precipitating lead nitrate with hydrogen sulfide. The product was then repeatedly washed with good distilled water containing hydrogen sulfide and dried in a stream of hydrogen.

Procedure

Hundredth molar solutions of the alkali bromides were made up and a small amount of pure lead sulfate and sulfide added. The solutions were then placed in a thermostat at 25°C. to saturate.

Fifteen grams of the dry lead sulfide preparation were placed in a six inch test tube provided with a ground glass stopper. Twenty cubic centimeters of hundredth molar solution were then added, and the test tube sealed by wrapping around the stopper a string dipped in hot de Khotinsky cement. After shaking for ten hours in a thermostat at 25° the tube was placed in an upright position to allow the suspension to settle. A dipping conductivity cell was then inserted into the clear supernatant liquid and the change in concentration produced by the adsorption was then determined by the conductivity method.

A typical conductivity setup was used. It consisted of a Leeds and Northrup "Student Type" combined potentiometer and bridge, a ten thousand ohm four dial resistance box and a microphone hummer. The bridge as used consisted of a 100 ohm slide wire with a 450 ohm coil in series at each end.

---

[3] Taylor and Close: J. Phys. Chem., 29, 1085-98 (1915).

To determine the amount adsorbed twenty cubic centimeters of the original hundredth molar solution were placed in a test tube and the cell inserted. When temperature equilibrium was attained the slide wire contact was set on the midway point and the resistance of the solution exactly balanced by adjusting the resistance box. The solution was then diluted by successive additions of one cubic centimeter of water saturated with lead sulfate and sulfide. By keeping the reading of the resistance box constant and by balancing the resistance of the solution by means of the slidewire, a resistance for each concentration in terms of the slide wire readings was obtained. The slide wire reading was similarly obtained against the constant resistance of the resistance box for the adsorption experiment. The value of this reading in terms of the equilibrium concentration was then determined by plotting the bridge readings against the concentration produced when the hundredth molar solution was diluted with water as described above.

The amount adsorbed was calculated by the following formula:

$$a = \frac{(M_2 - M_1)c}{1000\ w}$$

a = amount of adsorbed salt in moles per gram of lead sulfide.
M_2 = initial molar concentration of the solution.
M_1 = equilibrium molar concentration after adsorption.
c = number of cc. of solution used.
w = weight of lead sulfide used.

Repetition of the experiments shows that the results are reproducible to 0.5 percent.

Results

TABLE I

Variation of Adsorption with Lattice Dimensions

Sum of ionic radii	Salt	Amt. ads. in 10^{-6} moles per gm. PbS.
2.745 Å	LiBr	40.0
2.97	NaBr	43.0
2.985	PbS	
3.285	KBr	126.7
3.329	NH_4Br	62.7
3.43	RbBr	82.7
3.67	CsBr	84.0

Inspection of the results given in Table I shows that the amount adsorbed does not depend upon the ability of the adsorbed material to fit the space lattice of the adsorbent. Sodium bromide which has lattice dimensions nearest those of the lead sulfide is, with the exception of lithium bromide, adsorbed the least. Ammonium bromide which belongs to the body-centered caesium chloride arrangement is adsorbed less than the caesium bromide, although ammonium bromide is capable of assuming the sodium chloride arrangement and is a better fit than caesium bromide.

Neither does the amount adsorbed seem to depend upon the ability of the salt to orientate on PbS, for the amount adsorbed by the three unorientated salts, LiBr, NH_4Br, and CsBr, is of the same order as the amount adsorbed by the other three salts which are known to be orientated.

TABLE II

Variation of Adsorption with Solubility

Mol fraction solubility 25°	Salt	Amt. ads. in 10^{-10} moles per gram of PbS
0.281	LiBr	40.0
0.141	NaBr	43.0
0.127	NH_4Br	62.7
0.111	RbBr	82.7
0.0949	CsBr	84.0
0.0897	KBr	126.7

Table II shows that the amount adsorbed in each case increases as the mol fraction solubilities decrease, thus showing that the solubility is a more important factor in adsorption than lattice dimensions. Broadly speaking, it may be stated that in our dilute solutions the change from solute to solute of the attractive forces between solute and adsorbent are apparently of a lower order of magnitude than the parallel changes in attractive forces between solute and solvent. When a solution is saturated, the latter forces are obviously much weakened, so that the former are enabled to exhibit themselves in producing certain phenomena of mutual orientation.

Summary

(1). The quantities of six different salts adsorbed from aqueous solution of like concentration by crystalline lead sulfide were investigated. Only three of these salts were known to be oriented when deposited on a substrate.

(2). The amount of adsorption was found to be related much less closely, if at all, to relative lattice dimensions of salt and adsorbent than it was to the aqueous solubility of the solute.

Frick Chemical Laboratory.
Princeton University,
Princeton, N. J.

SURFACE LEAKAGE OF PYREX GLASS

BY W. A. YAGER AND S. O. MORGAN

Introduction

The direct current surface leakage of various insulating materials has been studied at a number of humidities by Curtis,[1] but there has been very little study of the alternating current surface leakage. The importance of the problem from the standpoint of telephone insulators, especially those used for the transmission of carrier frequencies has been pointed out by L. T. Wilson.[2] A study was undertaken to determine the effect of relative humidity, frequency, and temperature upon the total conductance, total capacity, surface conductivity, surface capacity, and power factor of various kinds of glasses. This paper gives the results obtained on E. J. Pyrex glass at 25°C. and 50°C. over the range of humidities from 0 to 96% and at frequencies from 1 to 100 K.C. A study is also being made of the effect of composition of the glass upon surface properties and upon the weathering.

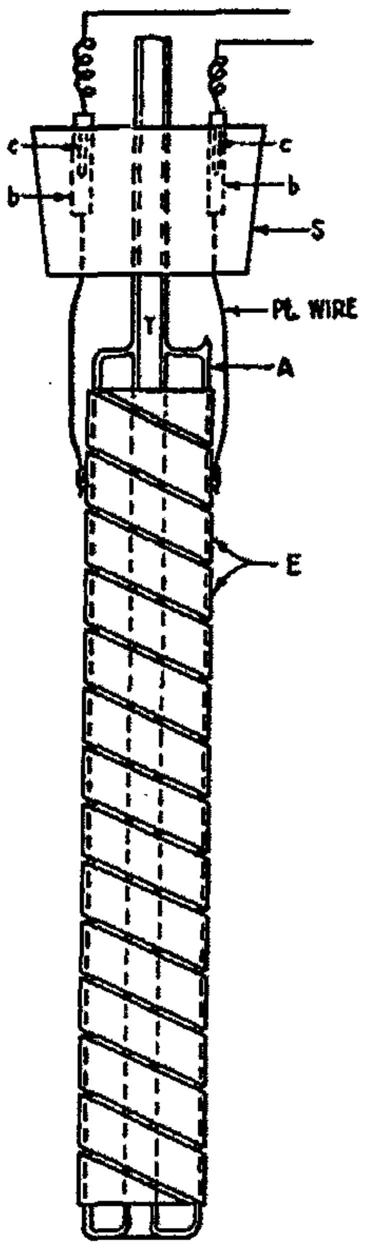


Fig. 1
Pyrex Test Condenser for studying Surface Leakage

Test Condenser

Considerable difficulty was experienced in preparing a satisfactory test condenser, i.e., one which would have a capacitance and conductance which would be easily measurable with the apparatus available. It was necessary in order to measure with sufficient accuracy the lowest conductance to be studied, namely, that at 0% humidity and 1 K.C., to have electrodes 100 cm. long separated by a 0.25 mm. gap. A test condenser of the proper characteristics was obtained by making two adjacent metallic spirals 1/2″ wide on a tube 1-3/8″ in diameter and 8″ long. This test condenser is shown in Fig. 1. The metal electrodes were put on the glass by silvering, the gaps between the electrodes being produced by keeping a fine rubber band wound on the tube during the silvering process. In order to make the coating adhere better, the glass was first sand blasted, the gap being protected by a large rubber band. After silvering, the electrodes were copper-plated and finally gold-plated to reduce the resistance and to prevent tarnishing. Contact with the spiral electrodes E

---

[1] H. L. Curtis: U. S. Bureau of Standards, Scientific Paper No. 234.

[2] L. T. Wilson: J. Am. Inst. El. Eng., 49, 1536-48 (1930).

was made by platinum wires sealed to the glass as indicated in Fig. 1. The short projecting end of the platinum wire insures a good contact with the electrode regardless of the bending of the other end of the wire which occurs in handling. The inner walls of the tube were cleaned and the space sealed off at A under a vacuum to prevent any conduction over this surface. The exhaust vapors passed out of the apparatus through the inner sealed tube T which also served to support the test condenser in a hard rubber stopper S which fitted into the humidity chamber.

Humidity Apparatus

Efficient humidity control was obtained by a dynamic method in which dry air and saturated air were mixed in various proportions to give any desired humidity. A description of this method may be found in a paper by Walker and Ernst.[1] The humid air thus produced enters near the top of the humidity chamber, is forced down past the test condenser and escapes to the atmosphere through the inner supporting tube T. A small capillary was inserted in the outlet to prevent air from diffusing back into the chamber. The highest humidity obtainable with this apparatus was 96%.

The humidity chamber and saturator were maintained at constant temperature in a thermostat and the surrounding temperature was kept slightly higher to prevent condensation of moisture in the "wet" line.

General Considerations

Measurements of total conductance and total capacitance were made at 25°C and 50°C. ± .05° at 1, 3, 10, 30, 50, 75, 100 K.C. and at a number of humidities between 0 and 96% relative humidity. These quantities were measured as equivalent parallel conductance and capacitance on a capacitance and conductance bridge, described by Shackelton and Ferguson.[2] The conductance could be determined to 10^{-9} mhos. above 30 K.C., and to 10^{-10} mhos. below this frequency. The capacitance could be measured accurately to 0.1 mmf. In this paper, G and C are used to indicate conductance and capacitance respectively. The subscripts V, S, and T, are used to denote volume, surface, and total properties respectively.

Curtis studied the effect of humidity upon the volume resistivity of various substances. In the case of glass, the results on one sample indicated a slight change of volume resistivity with humidity, but it was too small to be certain of. In our tests, the conductance of the pyrex test condenser at zero humidity before and after a run checked within the error of measurement. The change of volume conductance with relative humidity is therefore insignificant in comparison to the large change in the surface conductance with relative humidity.

The surface quantities are therefore obtained by subtracting the volume quantities as measured at zero humidity from the total quantities measured

---

[1] A. C. Walker and E. J. Ernst Jr.: Ind. Eng. Chem., Anal. Ed., 2, 134 (1930).

[2] W. J. Shackelton and J. G. Ferguson: Bell System Tech. J., 7, 70-89 (1928).

at any other humidity. It is apparent that the error involved in determining G_s and C_s may be rather large at low humidities where the differences $G_T - G_v$ and $C_T - C_v$ are small.

The surface conductivity is determined by dividing the surface conductance by a constant which is the sum of the ratios of length to width of the two gaps. The values for this constant were 4395 at 25°C, and 4155 at 50° C, the difference being due to the removal of 5.4 cm. of one electrode between runs. The conductance and capacitance at 50° C are consequently about 6% lower than they would otherwise have been. The surface conductivities, γ, are, however, directly comparable.

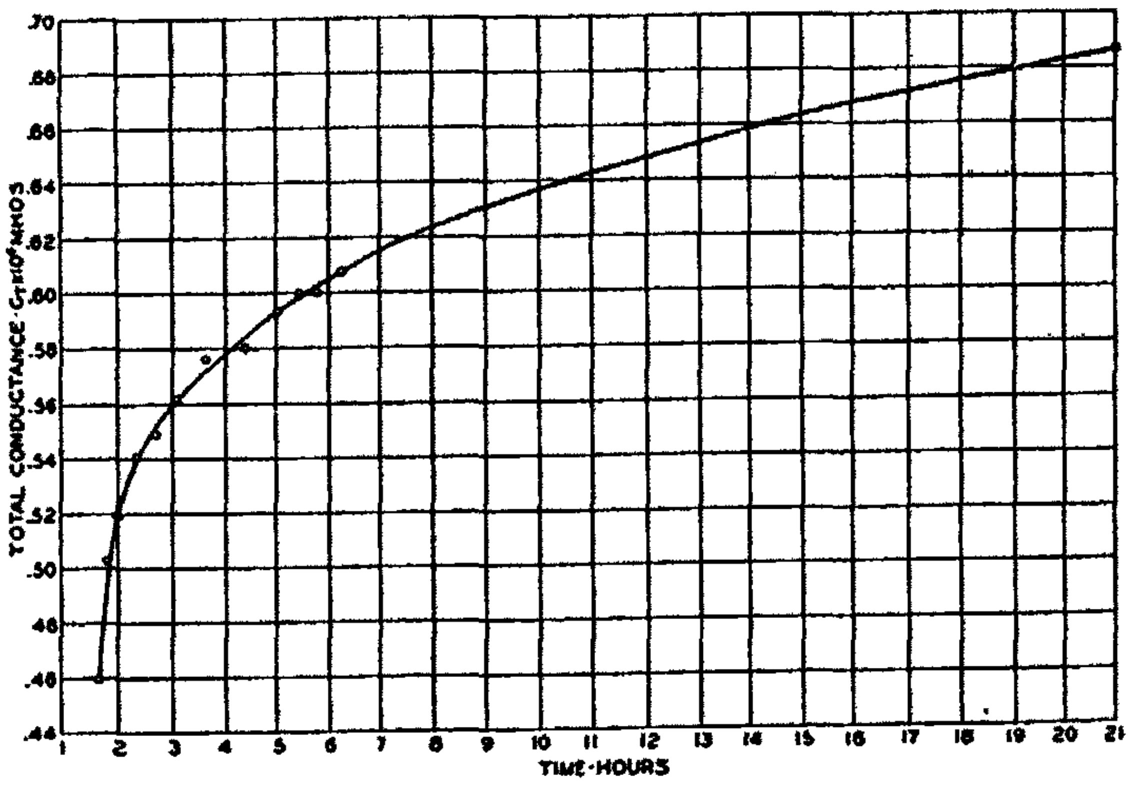


FIG. 2

Equilibrium Curve showing the Change with Time of the Total 30 Kc. Conductance of Pyrex Glass exposed to 96% Relative Humidity at 25°C.

The loss angle, δ, and power factor may be calculated from the conductance and capacitance data and are given by the following equations:

$$\delta = \tan^{-1} \frac{G}{\omega C} \qquad (1)$$

$$\text{power factor} = \cos \Theta = \frac{G}{\sqrt{G^2 + \omega^2 C^2}} \qquad (2)$$

For small values of δ, the tangent of the loss angle is practically equivalent to the power factor.

A constant humidity was usually attained within the chamber in a half-hour, but the surface reactions did not reach equilibrium so rapidly. In order to determine when equilibrium was reached the 30 K.C. conductance was followed with time and when it became constant the conductance and capacitance were measured at the remaining frequencies. At low humidities two hours was usually sufficient, but at high humidities much longer times were necessary. A curve of the 30 K.C. conductance vs. time is shown for 25°C and 96% humidity in Fig. 2 and it is apparent that while a final value is being approached it has not been reached after 20 hours. At 50° and 95% humidity it was impossible to even approach equilibrium, probably because the surface of the glass was being chemically attacked by the water. It is interesting to note that the time required to reach equilibrium at any humidity is different for each frequency, it being shorter for low frequencies than for high. This is probably only apparent due to the fact that the conductance at low frequency, being so much lower than at high frequencies, appears, within the limits of the apparatus, to be constant.

The Nature of Surface Leakage

Surface leakage is the flow of current thru a film of moisture or other conducting material on the surface of the dielectric. The magnitude of this leakage depends upon the thickness and volume conductivity of this surface film in place. The possibility must be considered that the conductivity of the surface film is different from that of the bulk material because of the adsorption forces. It is also possible that instead of considering the adsorbed water as constituting a surface film containing a certain amount of dissolved salts that it should be considered as a solution of the water in the glass forming a surface layer of hydrated glass which has quite different conducting properties from the unhydrated glass.

It has been known for a long time that water vapor is adsorbed on glass and it has been assumed that the formation of surface films on glass was due to a solution in or combination with the alkali of the glass. Reviews of the literature on the adsorption of water vapor by glass may be found in papers by Strömberg[1] and by Frazer, Patrick and Smith.[2]

The thickness of the adsorbed film depends to a large extent upon the nature of the adsorbing surface. Thus Frazer, Patrick, and Smith have shown that apparently there is no adsorption of water vapor upon a virgin glass surface, but they found evidence that when water vapor was condensed on the glass surface it dissolved out some of the soluble constituents of the glass such as sodium hydroxide. A second run with decreasing humidity after the water vapor had been in contact with the glass surface, showed marked evidence of adsorption. These authors did not calculate the thickness of the adsorbed film considering such a calculation absurd in view of the fact that they did not know how much the vapor pressure was reduced by the solutes present or by the capillary action of the amorphous silica. They state that glass is undoubtedly attacked by water and acids. The results of such action must be the removal of alkali and the deposition on the surface of amorphous silica which is most suitably adapted to the adsorption of vapors. Also the molecular planeness is thereby destroyed. Hence they believe that

---

[1] R. Strömberg: Kgl. Svenska Vetenskapsakad. Handl., 6, [2] 1-122 (1928).

[2] Frazer, Patrick and Smith: J. Phys. Chem., 31, 897 (1927).

all results of adsorption measurements on acid-cleaned glass are questionable in so far as the results were interpreted from the standpoint of molecularly plane surfaces.

Since it was necessary to treat the glass test condenser with chromic acid, nitric acid, and distilled water in the process of construction, it seems advisable to compare the conductance with the water adsorption on a glass having received the same treatment. The data of McHaffie and Lenher[1] have been selected for this purpose. These authors used a soft Duroglass, the internal surface of which was cleaned by first washing with organic solvents, then filled with freshly prepared cleaning solution and allowed to stand 24 hours. The cleaning was completed with fuming nitric acid and repeated washings with distilled water. Fig. 3 shows the relation between the number of layers of adsorbed water and the relative humidity. According to McHaffie and Lenher a monomolecular layer is not formed until a relative humidity of 50% is reached. Over the range from 50% to 85%, the thickness increases from 1 to 10 layers, and above 85% the thickness increases very rapidly to 90 layers at 97% relative humidity.

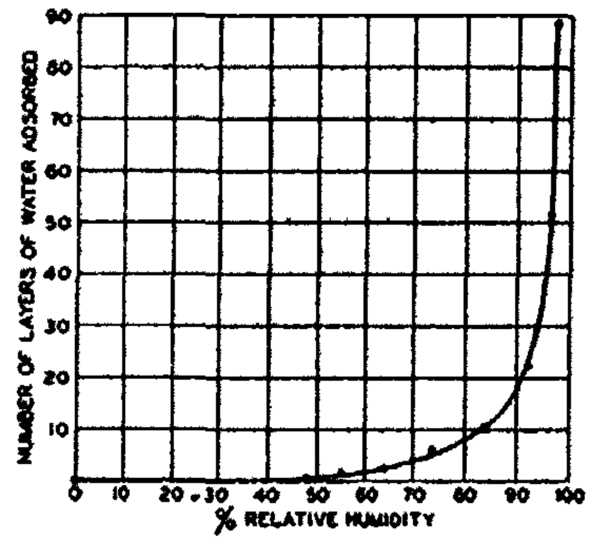


Fig. 3

McHaffie and Lenher's Data showing the Number of Layers of Water adsorbed by a Glass Surface as a Function of Relative Humidity

The other important factor in surface leakage is the volume conductivity of the surface film. It is a well known fact that water in contact with glass surfaces, tends to dissolve out some of its constituents, so that the conductivity of the solution will increase as the concentration of solute increases. Kohlrausch[2] studied the susceptibility of various glasses to attack by water by measuring the conductivity of the solutions formed by the attack. In observations extending over weeks or months, the quantity of electrolytes in solution was found to increase continually though at a diminishing rate,—the conductivity therefore increases with time of exposure. On the other hand, the solution formed by water in contact with such very insoluble substances as gypsum, calcspar and silver chloride soon reaches a constant conductivity. Long contact of glass with water apparently improves its surface. Thus Kohlrausch and Heydweiller[3] found that the conductivity of successive samples of water left in contact with the same glass surface decreased continually and finally approached a constant low value.

Furthermore, the thickness and volume conductivity of the surface film are not independent of one another, but are interrelated since the solution of electrolyte lowers the vapor pressure of the condensed layer which should cause further condensation of water.

---

[1] McHaffie and Lenher: J. Chem. Soc., 127, 1559 (1925).

[2] F. Kohlrausch: Ann. Physik. Chem., 44, 577 (1891).

[3] Kohlrausch and Heydweiller: Ann. Physik. Chem., 53, 209 (1894).

An approximate calculation may be made to estimate the smallest film thickness detectable with the test condenser and measuring apparatus used in this work. Taking the conductivity of water to be 2×10^{-6} mhos. cm.$^{-1}$, and 5×10^{-14} mhos. as the minimum conductivity change measurable, it is seen that the smallest layer that can be detected is 2.5×10^{-8} cm. in thickness, or assuming the diameter of the water molecule to be 2.9×10^{-8} cm., about one molecule deep. If the surface film is not pure water but an electrolyte, its conductivity would be greater than that of pure water. It may not be possible to detect films of less than one molecule thick on account of the discontinuous conducting path. The calculation indicates, however, that it should be possible with this equipment to detect films one molecule thick.

Results

The measured values of conductance and capacitance for the pyrex test condenser at 25°C. and 50°C. for various frequencies at zero humidity, and the corresponding values of the power factor are given in Table I.

TABLE I

Volume Quantities

f	25°C			50°C*		
KC	G_v m.mho.	C_v mmf.	$\cos \theta_v$	G_v m.mho.	C_v mmf.	$\cos \theta_v$
1	.0044	83.80	.00835	.0059	82.91	.01134
3	.0111	83.37	.00705	.0147	82.36	.00954
10	.0331	82.90	.00636	.0411	81.85	.00799
30	.0914	82.68	.00587	.1094	81.43	.00709
50	.1496	82.55	.00577	.1755	81.26	.00685
75	.221	82.40	.00569	.258	81.10	.00666
100	.297	82.33	.00575	.345	80.96	.00658

* These conductance and capacitance data have not been corrected for the change in length of the electrode referred to on page 2028.

The remaining tables give the surface quantities which have been obtained by subtracting the volumes quantities, given in Table I, from the total measured quantities for other humidities. Tables II and III give the surface conductivity at 25°C. and 50°C. at frequencies from 1 to 100 KC and humidities up to 96%. These values were computed from the dimensions of the gap as described above. These data are shown graphically in Fig. 4.

The marked resemblance of these curves to the water adsorption curve of Fig. 3 is very striking. In the previous calculation, it was shown that the first measurable surface leakage should occur on the formation of the first molecular layer which according to the adsorption curve occurs at approximately 50% relative humidity. This was found to be the case,—the first noticeable change in total conductance occurring at approximately 50% relative humidity. Continuing similarly to the increase in film thickness with relative

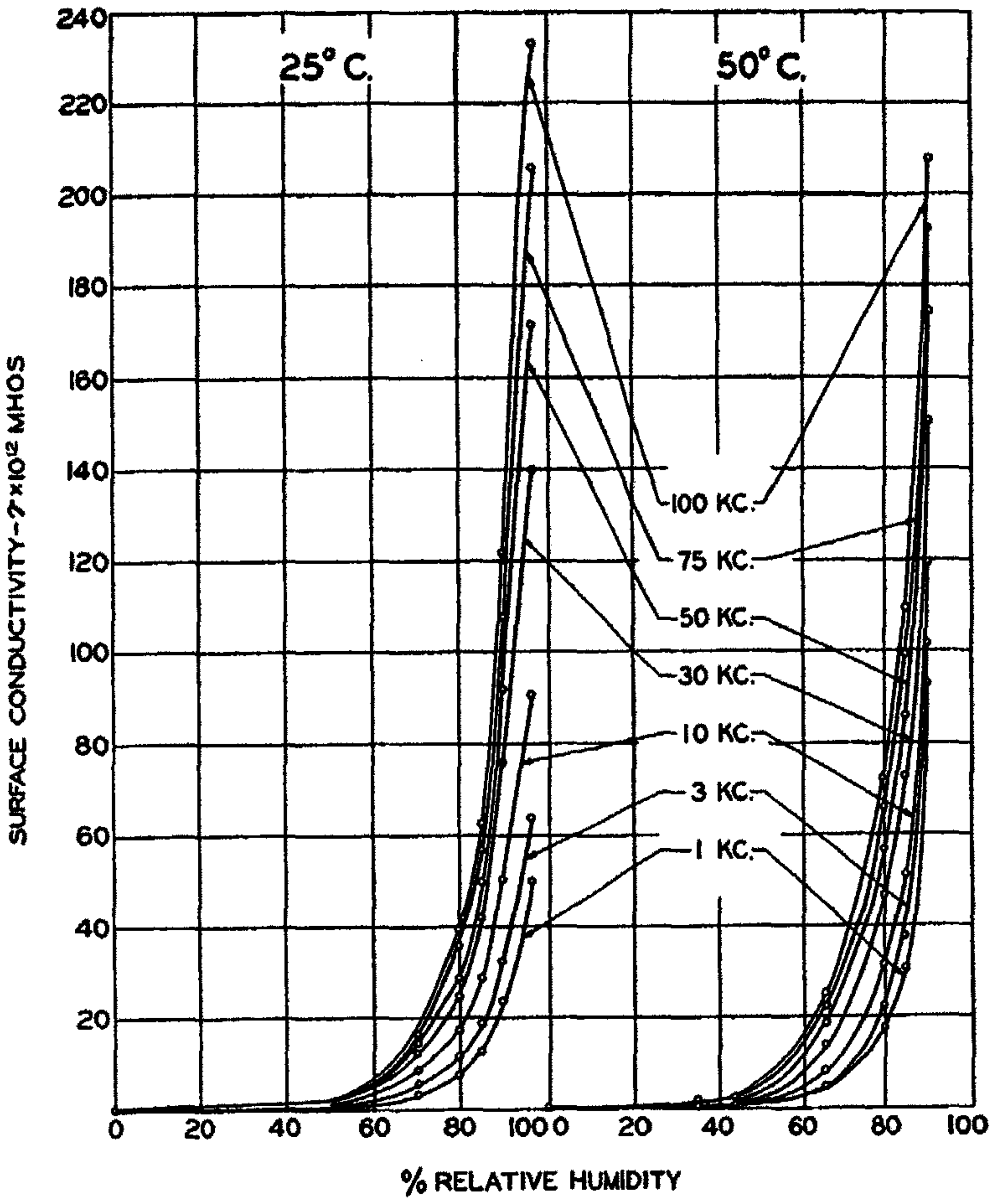


Fig. 4
The Surface Conductivity of Pyrex at 25°C. and 50°C. for various Frequencies as a Function of Relative Humidity

Table II

Surface Conductivity of E. J. Pyrex at 25°C.
$\gamma \times 10^{12}$ mhos.

% R.H.	Frequency K.C. 1	3	10	30	50	75	100
0	0	0	0	0	0	0	0
49.9	.4325	.7281	1.114	1.524	1.728	1.774	.91
70.2	3.412	5.212	8.210	12.28	14.46	16.60	—
79.7	7.375	11.16	17.18	24.77	28.71	35.50	39.40
84.8	12.44	18.55	28.72	42.00	49.84	56.75	62.12
89.8	23.50	32.39	50.15	75.90	91.61	107.6	121.3
96.2	50.00	63.85	90.30	139.5	171.2	205.8	233.0

TABLE III

Surface Conductivity of E. J. Pyrex at 50°C.

$\gamma \times 10^{12}$ mhos.

% R.H.	Frequency K.C.						
	1	3	10	30	50	75	100
0	0	0	0	0	0	0	0
35.2	.2165	.337	.722	1.540	1.69	1.93	1.45
44.0	.313	.626	1.13	1.97	2.53	2.65	2.65
65.4	4.31	4.69	8.20	14.22	18.45	22.40	25.02
80.0	17.46	22.30	31.55	46.58	56.42	65.5	72.2
85.2	31.24	37.85	50.95	72.6	85.6	98.9	109.2
90.3	93.2	101.4	119.1	149.9	174.5	192.5	207.5

humidity, the surface conductivity increases moderately from 50 to 85% humidity and very rapidly above 85%. As pointed out earlier, equilibrium could not be obtained at the very high humidities. At 50°C. the conductivity increased very rapidly with the time and at the high humidities gave no indication of reaching equilibrium for a long time. This behavior is to be expected from the nature of surface leakage.

Measurements of the D.C. surface leakage by Curtis for glass and other insulating materials show somewhat the same shape of curve, i.e., the surface conductance is practically zero at low humidities and then increases very rapidly. At the very high humidities, however, Curtis' curves flatten out and the conductance seems to approach a constant value.

The curves of conductivity vs humidity at 50° show the same general behavior as those at 25°. The surface conductivity is greater at 50° than at 25° at all points but by an amount which is much less than that calculated from the temperature coefficient of conductance of water. From the curves it appears that the surface conductance is measurable at a slightly lower humidity at 50° than at 25°. It is to be expected that at 50° the thickness of the adsorbed layer would be somewhat less than at 25° and hence the increased conductance at 50° must be attributed to the greater conductivity of the water layer at the higher temperature.

The curves just discussed show the variation of surface conductivity with humidity, frequency being the parameter. In order to bring out more clearly the effect of frequency, the same data have been plotted as surface conductivity vs frequency with humidity as the parameter. These curves are shown in Fig. 5. They show a very definite dependence of surface conductivity upon frequency at least as measured in this type of condenser. If the surface conductivity were independent of frequency, the curves in Fig. 5 should all be horizontal, the value of the ordinate depending upon the thickness of the adsorbed film and hence upon the relative humidity. It might be expected that the surface conductivity would be independent of frequency, since over the range of frequencies from 1 to 100 K.C. the conductivity of water and dilute solutions is independent of frequency.

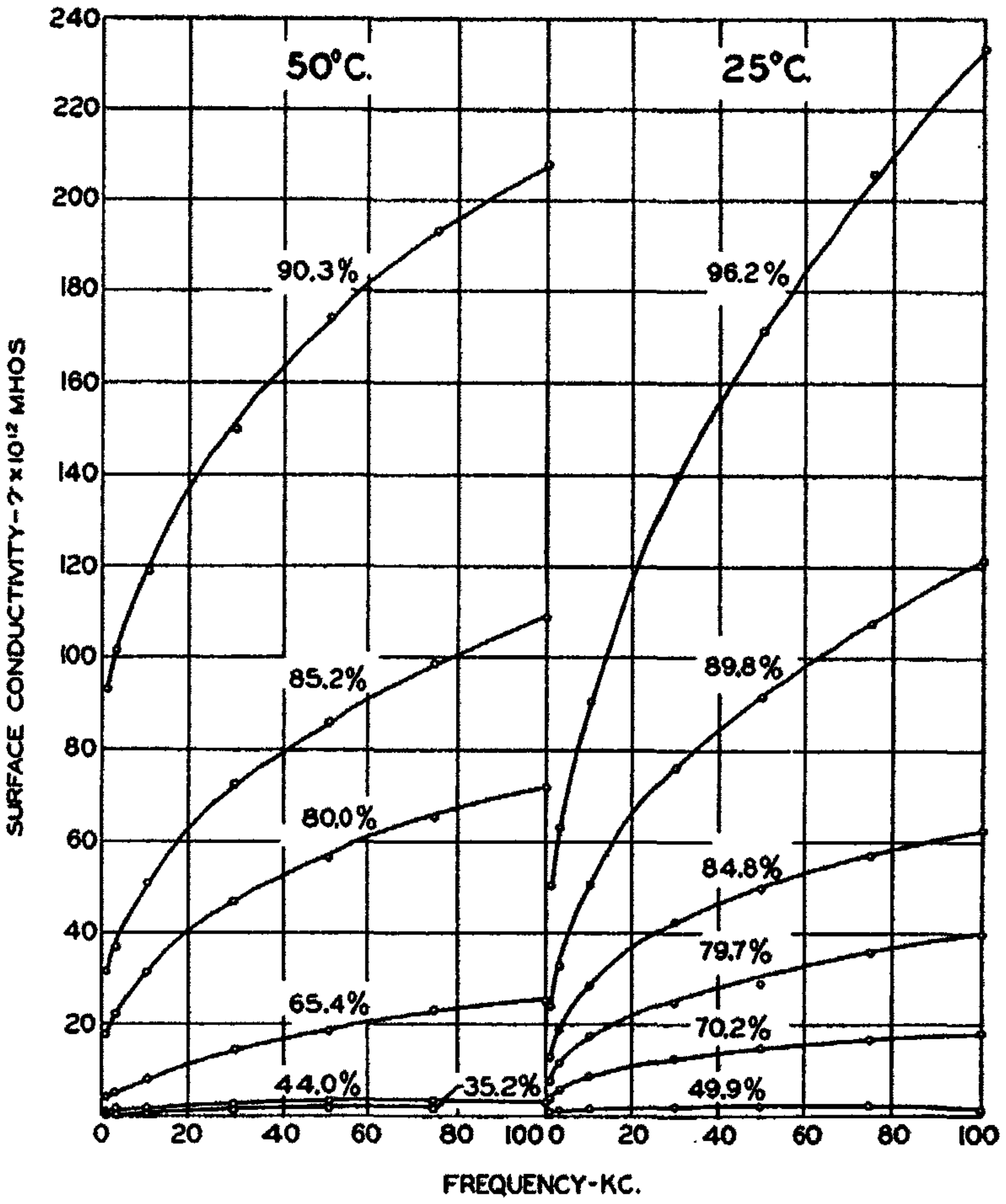


Fig. 5
The Surface Conductivity of Pyrex at 25°C. and 50°C. for Various Relative Humidities as a Function of Frequency

There are several mechanisms which might be proposed to account for the frequency dependence of conductivity observed. In an adsorbed film of water the molecules near the surface of the glass are undoubtedly orientated by the surface forces of the glass and hence may show a change of conductivity with frequency due to the different relaxation times of the various adsorbed layers of water molecules. Murphy and Lowry,[1] have postulated a mechanism to explain the dependence of the conductance of certain dielectrics upon frequency which may explain the results obtained in this work. It assumes that there are layers of adsorbed ions capable of a restricted motion in the field thus producing a form of dielectric polarization, which because of the different

---

[1] Murphy and Lowry: J. Phys. Chem., 34, 598 (1930).

adsorption forces for different layers have different times of relaxation coming within the range of frequencies studied and hence show a frequency dependence of conductance. Still another possible explanation, and perhaps the most probable, is electrode polarization. This may be due to chemical reactions at the electrodes or to a difference between the rate of discharge of ions at the electrode surface and the rate at which they come up to the surface. A review of the literature on electrode polarization may be found in a paper by E. J. Murphy[1] in which he discusses the alternating current conduction in fibrous dielectrics showing that the major portion of the capacity of this type of dielectric is accounted for in amount and characteristics by the electrolytic polarization capacity of the cell formed by the absorbed water and the electrodes. It would be expected that this explanation could also be extended to glass since electrolytic polarization is an electrode effect and therefore does not depend on whether the water through which conduction takes place is adsorbed on the external surface, as in glass or on internal surfaces as in the fibrous dielectrics. In the test condenser used the voltage gradient was about 200 volts per cm. Measurements on the volume conductance of water in a gold-plated condenser where the voltage gradient was 80 volts per cm. showed an increase of conductance with increasing frequency and a very large decrease in capacity which effects were undoubtedly due to electrode polarization. These results raise the question as to whether the surface conductivity as determined by the dimensions of the gap is really an absolute value. If there is electrode polarization present, then the measured surface conductivity would depend upon the electrode separation. The surface conductivities cited are subject to that restriction.

Although the non-D.C. components of the surface conductance and volume conductance do not change very much with rising temperature, the D.C. components increase markedly, the D.C. conductance of the surface film increasing more rapidly than that of the glass. Consequently the surface conductance constitutes a larger fraction of the total conductance at a given humidity and frequency as the temperature rises.

The values of surface capacity are given in Tables IV and V and are shown plotted against relative humidity for 25° in Fig. 6. With a condenser of the type used, the determination of a capacity which may correctly be called the surface capacity involves considerable uncertainty. However, the difference between the capacity values when humidity is the only variable should be significant. The curves of surface capacity vs relative humidity have the same general form as the corresponding conductance curves. The low frequency curves here are, however, higher than the high frequency curves. This similarity, is to be expected by virtue of the fact that both surface conductance and capacitance bear the same relation to the thickness of the adsorbed film.

---

[1] E. J. Murphy: J. Phys. Chem., 33, 200-215 (1929).

It is worth noting that above 30 K.C. the constant frequency curves of Fig. 6 are bunched much more than below this frequency. In Fig. 7 the capacity data have been plotted against frequency. The capacity decreases rapidly with increasing frequency at low frequencies and approaches a constant value, the geometric capacity, at high frequencies. The volume capacity, i.e., of the glass, decreases only slightly with increasing frequency, but the surface capacity decreases by a large factor.

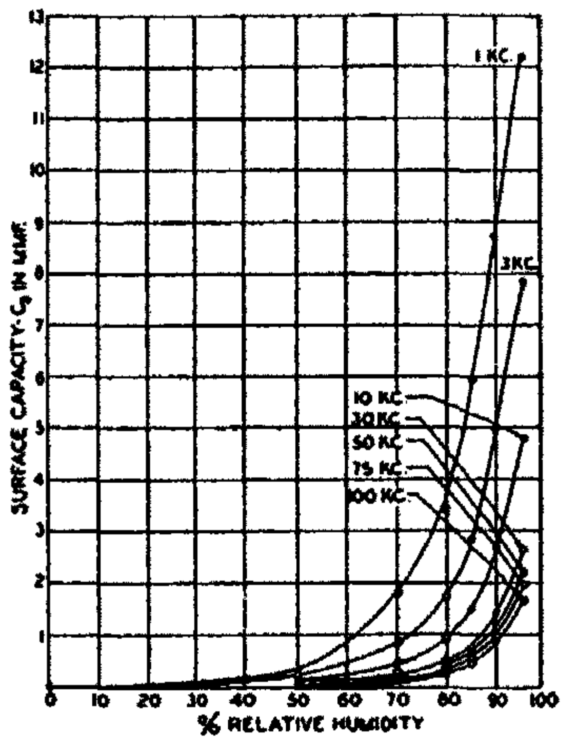


FIG. 6
The Surface Capacity of Pyrex at 25°C. for Various Frequencies as a Function of Relative Humidity

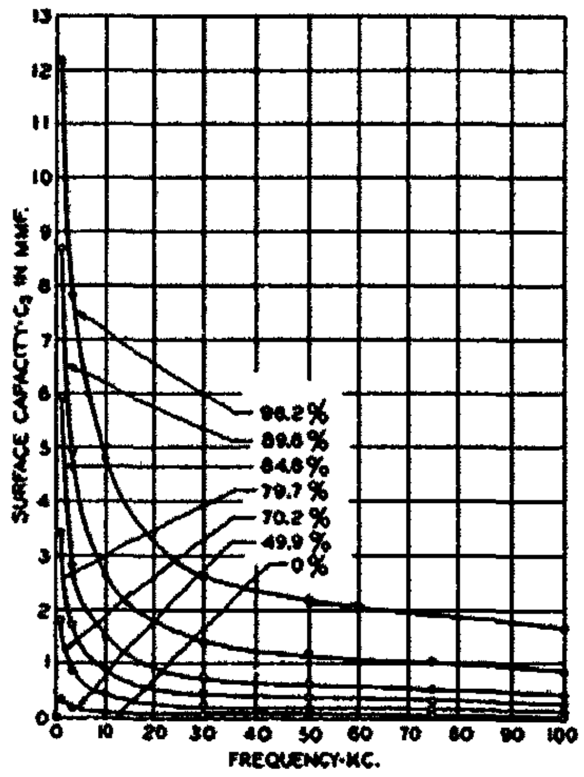


FIG. 7
Surface Capacity of Pyrex at 25°C. for Various Relative Humidities, as a Function of Frequency

TABLE IV

Surface Capacity of E. J. Pyrex Test Condenser at 25°C

C_S M.M.F.

%	Frequency K.C.						
R.H.	1	3	10	30	50	75	100
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00
49.9	0.36	0.20	0.10	0.02	0.02	0.02	0.00
70.2	1.82	0.88	0.45	0.22	0.20	0.18	0.11
79.7	3.43	1.73	0.91	0.47	0.40	0.33	0.27
84.8	5.95	2.82	1.50	0.77	0.65	0.55	0.43
89.8	8.70	4.98	2.66	1.42	1.20	1.05	0.87
96.2	12.20	7.84	4.80	2.64	2.20	1.98	1.67

The capacity of the surface film appears to be consistently higher at 50° than at 25°, but the differences are not large. This increase in capacity with temperature, however, is what would be expected if it were due to electrode polarization.

TABLE V*

Surface Capacity of E. J. Pyrex Test Condenser at 50°C

C_S M.M.F.

%	Frequency K.C.						
R.H.	1	3	10	30	50	75	100
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00
35.2	—	—	—	—	—	—	—
44.0	0.35	0.30	0.07	0.06	0.03	0.03	0.01
65.4	1.70	0.97	0.45	0.26	0.23	0.20	0.19
80.0	4.17	2.38	1.37	0.81	0.68	0.61	0.51
85.2	6.15	3.34	1.95	1.23	1.02	0.87	0.79
90.3	9.56	5.64	3.35	2.17	1.84	1.63	1.51

* See footnote in Table I.

The values of the tangent of the loss angle and the power factor calculated by means of Equations 1 and 2 are given in Tables VI and VII and the data at 25°C. are shown plotted against relative humidity and frequency in Figs. 8 and 9. These data are for the total power factor, i.e., glass plus surface film. The values of the tangent of the loss angle are identical with those of power factor above the stepped lines of the tables while below the lines the values of the power factor are somewhat the smaller. The power factor vs humidity curves are similar to those of capacity vs humidity and show that at a given humidity the power factor is lowest at the high frequencies. This is especially evident at the very high humidities. The curves in Fig. 9 show very clearly that the change of power factor with frequency is very small at frequencies above 30 kc. The ratios of the total power factor to the power factor of the glass alone are given in Table VIII and show the very much larger effect of the surface film in increasing the power factor at low frequencies.

TABLE VI

Total Power Factor of Pyrex Test Condenser at 25°C

Cos Θ_T

%	Frequency K.C.						
R.H.	1	3	10	30	50	75	100
0	.00835	.00705	.00636	.00587	.00577	.00569	.00575
49.9	.01192	.00909	.00728	.00630	.00605	.00589	.00582
70.2	.03606	.02140	.01323	.00931	.00820	.00755	—
79.7	.06700	.03754	.02061	.01280	.01058	.00968	.00906
84.8	.1043	.0569	.0301	.01754	.01410	.01204	.01096
89.8	.1824	.0919	.0471	.02680	.02010	.01766	.01589
96.2	.3483	.1613	.0779	.0438	.0339	.0283	.0250

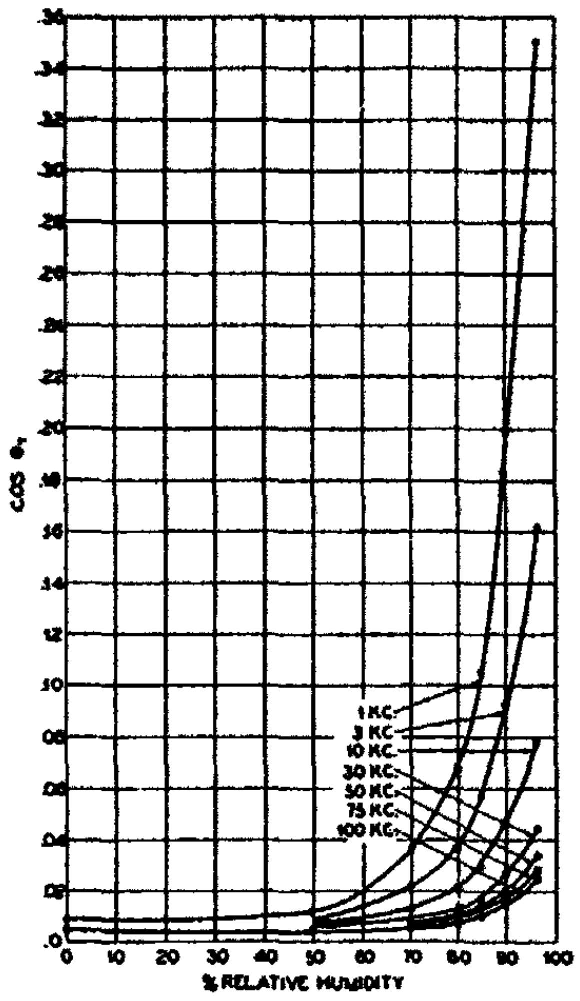


Fig. 8
The Total Power Factor at 25°C. for Various Frequencies at a Function of Relative Humidity

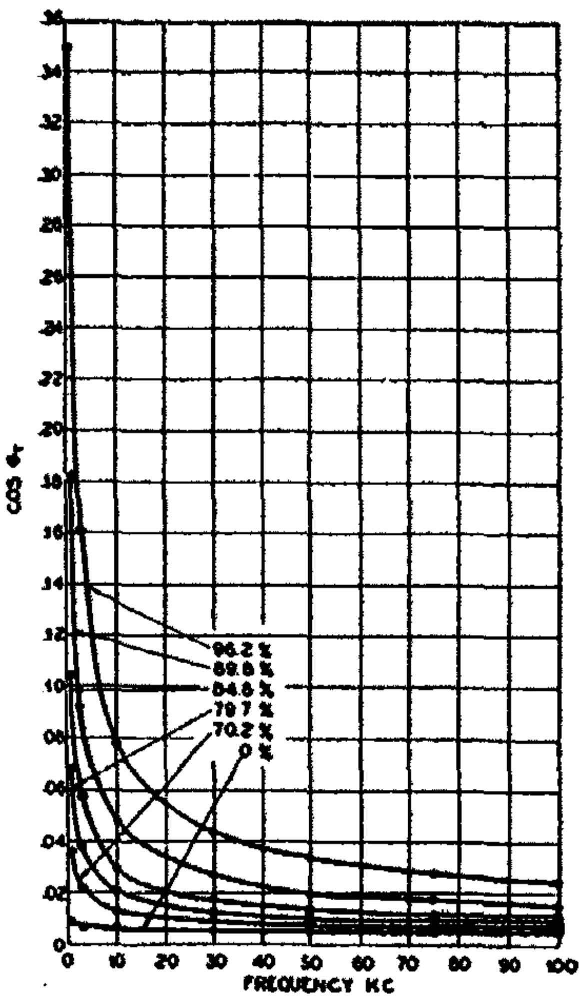


Fig. 9
The Total Power Factor at 25°C. for Various Relative Humidities as a Function of Frequency

Table VII

Total Power Factor of Pyrex Test Condenser at 50°C.

Cos θ_T

% R.H.	Frequency K.C. 1	3	10	30	50	75	100
0	.01134	.00954	.00799	.00709	.00685	.00666	.00658
35.2	—	—	—	—	—	—	—
44.0	.01376	.01110	.00890	.00766	.00728	.00704	.00701
65.4	.04465	.02176	.01455	.0109	.00985	.00916	.00882
80.0	.1419	.0671	.0329	.01956	.01595	.01375	.01260
85.2	.2361	.1059	.04805	.02638	.02056	.01731	.01556
90.3	.5603	.2543	.0996	.04646	.03450	.02718	.02330

Table VIII

Ratio of Total Power Factor to Power Factor of Pyrex

Freq.	% Relative Humidity 25°C.				50°C.		
K.C.	50	80	90	96	44	80	90
1	1.43	8.03	21.82	41.73	1.21	12.51	49.40
30	1.07	2.18	4.57	7.46	1.08	2.76	6.55
100	1.01	1.58	2.76	4.35	1.07	1.92	3.54

The effect of temperature is to increase the total power factor at any given frequency and humidity. The rate of increase with relative humidity at constant frequency likewise increases because the power factor of the surface film increases more rapidly than that of the glass.

Dielectric Loss of Pyrex Glass

The data on the volume properties of pyrex were found to fit von Schweidler's equations[1] which show the relation between dielectric loss and dielectric absorption. They may be expressed as follows:

$$G = G_0 + \omega C_0 B \qquad (3)$$

$$C = C_0 (1 + A) \qquad (4)$$

where $A = \omega^{n-1} \beta \Gamma (1-n) \cos [(1-n) \pi/2]$

and $B = \omega^{n-1} \beta \dfrac{\pi}{2\Gamma (n) \cos [(1-n) \pi/2]}$.

G and C are the apparent conductance and capacitance; G_0, the D.C. component of the conductance; C_0, the geometric capacity; and ω is 2π times the frequency. n and β are constants of the material. The geometric capacity is usually defined as the capacity at very high frequency, but there is some question as to what is meant by high frequency. It may be defined as the capacity at that frequency at which, as the frequency is increased, the capacity, after decreasing with increasing frequency, first becomes constant.

For simplicity equations 3 and 4 may be written:

$$G = G_0 + \alpha f^n \qquad (5)$$

and

$$C = C_0 + \mu f^{n-1} \qquad (6)$$

where

$$\alpha = \frac{2^{(n-1)} \pi^{(n+1)} C_0 \beta}{\Gamma (n) \cos [(1-n) \pi/2]}$$

and

$$\mu = (2\pi)^{(n-1)} \beta C_0 \Gamma(1-n) \cos [(1-n) \pi/2]$$

These equations may now be written in the forms:

$$\ln (G-G_0) = \ln \alpha + n \ln f \qquad (7A)$$

$$\ln (C-C_0) = \ln \mu + (n-1) \ln f \qquad (7B)$$

Straight lines should result from the curves;

$$\ln (G-G_0) \text{ vs } \ln f$$

and

$$\ln (C-C_0) \text{ vs } \ln f$$

The slope in the first case is n, while that in the second case is $n-1$. Fig. 10 shows the data on pyrex obtained at zero per cent humidity at 25°C, and 50°C. plotted in this manner. G_0 and C_0 were obtained by successive approxima-

---

[1] Von Schweidler: Ann. Physik, 24, 711 (1907).

tions. At 25°C., the values of n were found to be .957 from the conductance curve and .948 from the capacity curve. At 50°C. the values were .924 and .931 respectively. The data fit the curves very well.

Equations 5 and 6 may be combined to give:

$$G - G_0 = \frac{\alpha}{\mu}(C - C_0)f = \frac{\alpha}{\mu}C_x f \tag{8}$$

or since

$$\omega = 2\pi f,$$

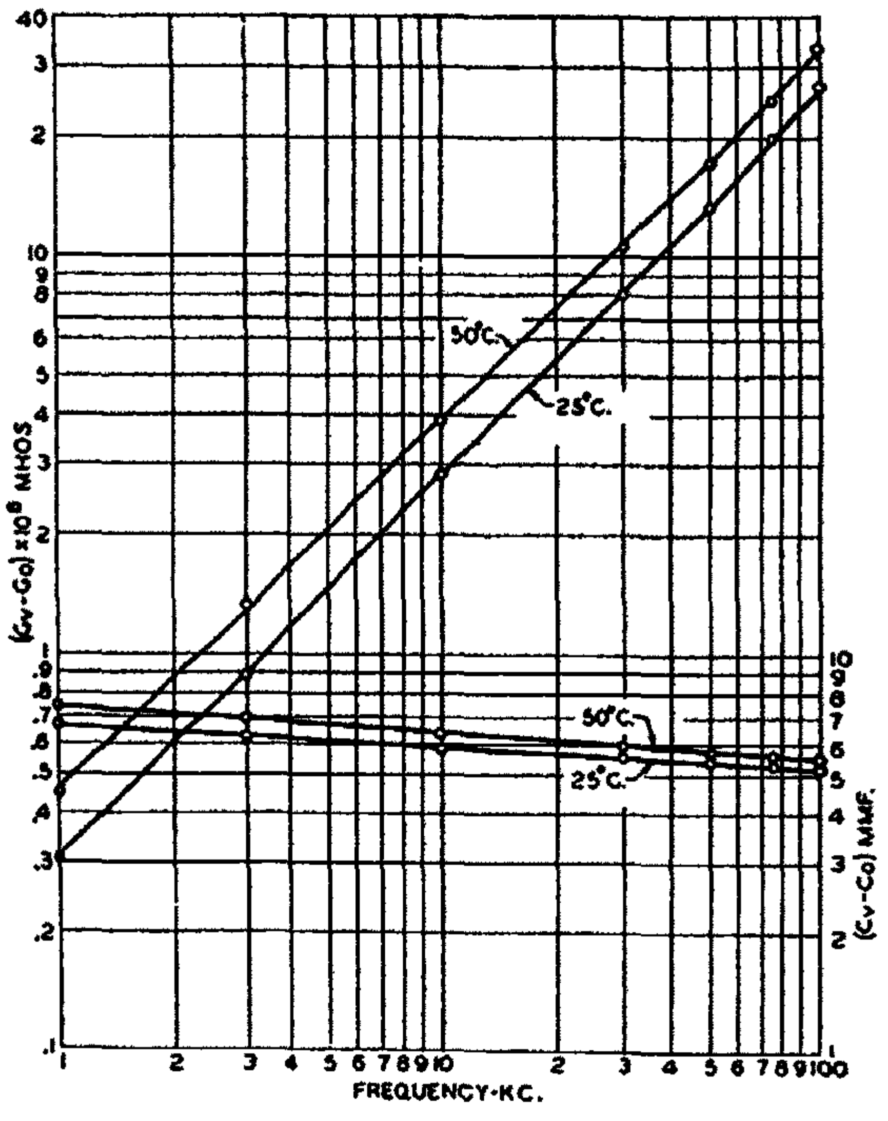


Fig. 10

The Volume Conductance and Capacitance of Pyrex at 25°C. and 50°C.

$$\frac{\overline{G}}{\omega} = \frac{\alpha}{2\pi\mu}(C - C_0) = \frac{\alpha}{2\pi\mu}C_x \tag{9}$$

where $\overline{G}$ represents the non-D.C. component of the conductance and C_x is the increase in capacity over the geometric capacity. If $\overline{\gamma}$ is the non-D.C. conductivity and K, the dielectric constant, then:

$$\frac{\overline{\gamma}}{\omega} = \frac{\alpha k}{2\pi\mu}(K - K_0) = \frac{\alpha k}{2\pi\mu}K_x.$$

This equation shows that the term $\overline{\gamma}/\omega$ which may be regarded as a damping coefficient is directly proportional to the change in dielectric constant with frequency.

Equation 9 may also be written:

$$\bar{G}/\omega C_x = \alpha/2\pi\mu \qquad (10)$$

If the left hand member of Equation 10 represents a loss angle, tan Φ, then

$$\bar{G}/\omega C_x = \tan \Phi = \alpha/2\pi\mu \qquad (11)$$

All of the terms on the right hand side being constants, Equation 11 indicates that in any dielectric for which von Schweidler's equations are valid, there is a constant loss angle, Φ, independent of frequency.

The total loss angle as determined by the relation:

$$\tan \delta = G/\omega C \qquad (12)$$

is, however, a function of the frequency. For pyrex, Φ was found to be about 9° at room temperature, whereas δ was less than 1°. The constant loss angle Φ is associated with the non-D.C. component of conductance. The vector diagram in Fig. 11 is given to show the relation between this constant loss angle and the total loss angle. I_R is the resultant current, I_C is the normal charge or discharge current, while I_A is the anomalous current. The significance of Equation 11 is evident from the diagram. Equating 11 and 12:

$$\bar{G}/\omega = C_x \tan \Phi = C \tan \delta - G_0/\omega \qquad (13)$$

so that

$$\tan \delta = C_x/C \tan \Phi + G_0/\omega C \qquad (14)$$

Equation 14 gives a more complete picture of the factors which may cause dielectric loss. Thus the loss angle depends upon the ratio C_x/C, upon the constant loss angle Φ and upon the D.C. component $G_0/\omega C$.

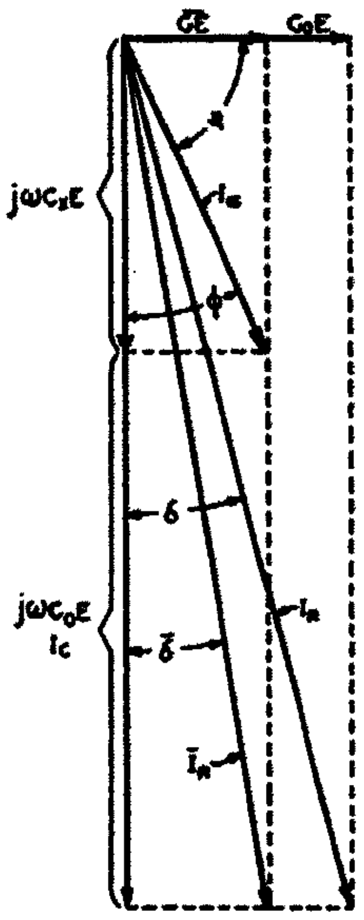


Fig. 11

Vector Diagram showing the Relation between the Constant Loss Angle Φ and the Total Loss Angle δ

McDowell[1] cites the work of Snow who treated von Schweidler's equations mathematically and obtained the equation

$$C_x = (\tan n\,\pi/2)\, C \tan \delta \qquad (15)$$

If Equations 14 and 15 are equated, neglecting the term $G_0/\omega C$ in Equation 14 since Snow did so in his work, then

$$C_x/C \tan \Phi = \frac{C_x}{C \tan n\pi/2}\,. \qquad (16)$$

From this it is seen that

$$\tan \Phi = \frac{1}{\tan n\pi/2} = \cot n\pi/2$$

---

[1] McDowell and Begeman: Phys. Rev., (2) 33, 55-65 (1929).

or since

$$\tan \Phi = \cot (\pi/2 - \Phi)$$

$$n = \frac{\pi/2 - \Phi}{\pi/2} = \frac{\Psi}{\pi/2} \qquad (17)$$

where Ψ represents the constant phase angle of the anomalous current. The n appearing in the above equations is consequently the ratio of the phase angle of the anomalous current to 90°, the phase angle of an ideal condenser.

For an ideal condenser, $\tan \delta = 0$. For equation 14 to satisfy this condition, Φ must equal zero; that is, n must equal 1, and G_0 must also be zero. n is sometimes taken as a measure of the quality of a dielectric but Equation 14, which may be expressed in the following form:

$$\tan \delta = C_x/C \cot n\pi/2 + G_0/\omega C$$

shows that n alone is not a sufficient criterion of the quality of a dielectric but that the ratio C_x/C and G_0 are also determining factors. MacLeod[1] found that for a certain glass the loss was 24 times as great as that for paraffin and yet the corresponding values of n were .86 and .85 respectively. The great difference is due to the fact that for glass the percentage change of capacity with frequency is much greater than for paraffin.

Summary

A method of measuring surface leakage of glass at various humidities is described.

The nature of surface leakage of glass is discussed.

The surface conductivity, surface capacity, and power factor all depend upon the thickness of the surface film, which in turn depends upon the relative humidity. The surface conductivity and power factor further depend upon the volume conductivity of the surface film. The surface quantities as well as the power factor increase with relative humidity in much the same manner as the adsorption of water vapor on glass as observed by McHaffie and Lenher.

The conductance was found to increase with increasing frequency whereas the capacity and power factor decrease. The increase in power factor with relative humidity is least at high frequencies.

The surface conductivity and capacity were found to depend upon frequency. Several mechanisms have been proposed to account for this dependence of which electrode polarization is the most probable.

The data for the dielectric loss and absorption in Pyrex glass were found to fit von Schweidler's equations. The constant n appearing in these equations was shown to be the ratio of the phase angle of the anomalous current to 90°, the phase angle of an ideal dielectric.

Acknowledgment is made to Dr. Homer H. Lowry for suggesting this study and to Mr. E. J. Murphy for helpful suggestions in interpreting the results.

Bell Telephone Laboratories,
New York, N. Y.

---

[1] MacLeod: Phys. Rev., (2) 21, 53 (1923).

IRON AND CERIUM COMPOUNDS AND INSULIN AS INDUCTORS IN OXIDATION REACTIONS AND THE MECHANISM OF INDUCED REACTIONS

BY N. R. DHAR

Iron and Cerium Compounds as Inductors and the Mechanism of Induced Oxidations

In several publications the author[1] has emphasised the wide applicability of induced reactions and numerous reducing agents have been used as inductors. But ferrous and cerous salts and sodium sulphite are the inductors, which have been largely investigated. Numerous organic compounds and several food materials, nickelous hydroxide, sodium arsenite, etc., have been oxidised simply by passing air at the ordinary temperature through solutions or suspensions of the substances in contact with freshly precipitated ferrous hydroxide, which plays the part of an inductor. Similar results have been obtained with cerous hydroxide and sodium sulphite as inductors. Goard and Rideal[2] have oxidised several sugars and potassium arsenite in the presence cerous hydroxide. Spoehr[3] *has oxidised sugars, glycerol etc.,* by passing air through solutions of the substances containing an excess of sodium pyrophosphate and ferrous or ferric salt. In those cases, where the inductor is sparingly soluble, the oxidation is more rapid, because of the surface of the inductor. Spoehr as well as Dhar and coworkers have found that ferrous salts are more active than ferric salts, as these induced oxidations are caused by the simultaneous oxidation of the ferrous salts.

In order to explain the mechanism of these induced oxidations in the presence of ferrous and cerous salts, the formation of higher oxides like FeO_2 (Manchot[4]) and Ce_2O_5 (Job[5]) has been assumed; and these higher oxides oxidise the difficultly oxidisable substances like the food materials.

In the oxidation of organic substances by hydrogen peroxide and ferrous salts, the formation of the oxides Fe_2O_5 (Manchot[6]) and FeO_3 (Hale[7]) has been assumed. The experimental results of Palit and Dhar[8] on the oxidation of sodium formate by air in the presence of ferrous and cerous hydroxides lend support to the hypothesis of the intermediate formation of the higher oxides

---

[1] Dhar: J. Chem. Soc. **111**, 697 (1917); Proc. Akad. Wet. Amsterdam, **29**, 1023 (1921); Mittra and Dhar: Z. anorg. Chem., **122**, 146 (1922); J. Phys. Chem., **29**, 376; Palit and Dhar: 799 (1925); **30**, 939 (1926); **32**, 1663 (1928); **34**, 711 (1930).

[2] Proc. Roy. Soc., **105A**, 148 (1924).

[3] J. Am. Chem. Soc., **46**, 1494 (1924).

[4] Ann., **314**, 177 (1899); **325**, 93 (1902); **460**, 179 (1927).

[5] Job: Ann. Chim. Phys., (7) **20**, 207 (1900).

[6] loc. cit.

[7] J. Phys. Chem., **33**, 1633 (1929).

[8] J. Phys. Chem., **34**, 711 (1930).

Fe_2O_5 and Ce_2O_5. This hypothesis of the formation of higher oxides is based on the determinations of the induction factor; but Dhar and coworkers and Hale have shown that the induction factor changes with the concentrations of the inductor and the acceptor as well as with the pH value of the medium.[1] Goard and Rideal and Manchot have utilised the oxidation-reduction potentials in determining the true nature of the intermediate peroxide compounds. But these results have to be accepted with a good deal of caution, in view of the results obtained by Ihle,[2] who found that the potential of nitric acid is lowered by the addition of a trace of nitrous acid, although this treatment increases the oxidative activity of nitric acid.

Dhar[3] has given out the view that the primary reaction in all induced oxidations consists in the oxidation of the inductor, and that this is exothermic e.g. oxidation of phosphorus, sodium sulphite, ferrous salt, etc. The energy of this exothermal chemical change may be partly given out in the form of ions and electrons, which will activate the molecules of the acceptor or actor or both and thus the induced reaction takes place. Dhar[4] has shown that by passing air through water in which a mixture of phosphorus and sulphur is suspended, considerable amount of sulphuric acid is formed, and it is well known that ions are generated in the oxidation of phosphorus. This hypothesis easily explains the observed variation of the induction factor, under different experimental conditions, whereas according to the peroxide hypothesis, the induction factor should have a definite unchangeable value. With changing experimental conditions, the ions generated in the primary reaction may be dissipated before they can activate the molecules of the acceptor or the actor. Mittra and Dhar[5] found that increasing the concentration of the acceptor (sodium arsenite) while keeping the concentration of the inductor the same (sodium sulphite) increases the inductor factor. Similar results are obtained by Dhar[6] in the induced reaction between oxalic acid and mercuric chloride in presence of potassium permanganate as inductor. These results can be explained as follows:—

Ions are generated in the primary exothermal oxidation of the inductor; these ions have a greater chance of being dissipated in dilute solutions of the acceptor than in the stronger solutions.

From the experimental results of Palit and Dhar on the induced oxidation of glucose by air in presence of ferrous and cerous hydroxides, it will be seen that the induction factor (i.e.) the ratio of the amount of oxygen taken up by glucose to the amount of oxygen taken up by the inductor is as high as 8 or 9. Similar results are obtained by the above authors with other reactions. From Spoehr's results on the induced oxidation of glucose by air in presence of sodium ferropyrophosphate, it will be seen that induction factor has a value 15. It

---

[1] Compare Gire: Compt. rend., 171, 174 (1920) and Spoehr: loc. cit.

[2] Z. physik. Chem., 19, 577 (1896).

[3] J. Phys. Chem., 28, 948 (1924); Z. anorg. Chem., 159, 103 (1926).

[4] Z. anorg. Chem., 146, 307 (1925).

[5] J. Phys. Chem., 29, 376 (1925).

[6] J. Chem. Soc., 111, 697 (1917).

therefore appears that the oxidised form of the inductor (Fe_2O_3 or CeO_2, etc.) is also capable of oxidising the acceptor, thereby regenerating the original inductor. Hence these induced reactions appear to be partly catalytic in nature, but in as much as the rate at which the original inductor is regenerated is small compared with the rate of its oxidation, these reactions belong more to the induced type rather than the catalytic one. Moreover Palit and Dhar have shown by analysis that the residual cerium oxide is mostly CeO_2 in the induced oxidation of carbohydrates by air in presence of cerous hydroxide.

These high values of the induction factors can be satisfactorily explained from the point of view of the generation of ions in the primary exothermal reaction. Suppose a small quantity of the inductor is oxidised; some ions will be generated in this exothermal reaction, and the ions will activate some molecules of the acceptor or the actor or both. These then react. This reaction being exothermal will, in its turn, give rise to more ions, which will activate some more molecules of the reactants and so on. Thus the oxidation of a small quantity of the inductor brings about the oxidation of a large quantity of the acceptor. This appears to be a sort of chain reaction.

In a subsequent communication the mechanism of other induced reactions will be considered.

Recently Chakrabarti and Dhar[1] have shown that when not only fats, but carbohydrates and nitrogenous substances are oxidised with hydrogen peroxide and a ferric salt at 37°, volatile aldehydic or ketonic products are formed. In this connection it must be emphasised that the oxidising power of hydrogen peroxide is greatly increased not only by ferrous salts but by ferric salts as well.

Palit and Dhar,[2] however, have conclusively proved in a systematic manner that fats, carbohydrates, nitrogenous and other organic substances can be completely oxidised into their main products, carbon dioxide and water by air with the help of an inductor (ferrous or cerous hydroxide) or in presence of light at the ordinary temperature and we have thus been able to imitate successfully the physiological processes of oxidation on which animal life depends. It appears, therefore, that the intermediate iron peroxide obtained in the case of hydrogen peroxide and ferric or ferrous salts must be different from that formed with ferrous compounds and oxygen, because the products of oxidation are different in the two cases.

Body Fluids as Indicators in Biological Oxidations

Some years ago in a publication[3] from this laboratory it was suggested that insulin and allied substances are good reducing agents and are readily oxidised by atmospheric oxygen and the oxidation of these substances induces the oxidation of sugar in the body. We have now been able to substantiate this view by oxidation experiments on insulin and glucose. A definite volume

---

[1] J. Indian Chem. Soc., 6, 617 (1929).

[2] J. Phys. Chem., 34, 711 (1930).

[3] Mittra and Dhar: J. Phys. Chem., 29, 376 (1925).

of air freed from carbon dioxide was passed through an aqueous solution of insulin (British Drug House) kept at 25° and the amount of carbon dioxide obtained by the oxidation of insulin was absorbed by a standard barium hydroxide solution. When glucose is added to the insulin solution and the same volume of air is passed through the mixture, glucose is slowly oxidised and this can be shown by estimation of the glucose by Fehling's solution, which, however, cannot be reduced by the insulin used in our experiments.

It was shown by the author[1] in 1921 that the addition of sodium arsenite, which can be oxidised by air only in presence of sodium sulphite, to sodium sulphite leads to a marked retardation in the velocity of the oxidation of sodium sulphite by air. Similar results are obtained with other cases of negative catalysis in oxidation reactions, where the negative catalysis is due to the induced oxidation of the retarder, which acts an acceptor. In the experiments with insulin and glucose the oxidation of insulin, which seems to be readily oxidised by air at the ordinary temperature, leads to the oxidation of glucose by air.

In this case, the acceptor glucose acts as a negative catalyst in the oxidation of insulin by air and although the glucose itself is undergoing oxidation to carbon dioxide along with insulin, the amount of carbon dioxide formed in a unit of time is less than the amount formed from the insulin solution in absence of glucose, because the velocity of the oxidation of insulin by air is greatly retarded by the addition of glucose, which, however, is slowly oxidised by air at the ordinary temperature in presence of insulin. Experimental results show that the addition of disodium hydrogen phosphate leads to an increase in the induced oxidation of glucose by air in presence of insulin.

In several publications, the author has emphasised the importance of induced oxidations in understanding the phenomenon of animal metabolism. It has been stated that the readily oxidisable substances like glutathione and other substances present in muscle and in other parts of the body, are first oxidised by the inhaled oxygen and these oxidations induce the oxidation of food materials. Insulin and other internal secretions also appear to be readily oxidised in the body and these lead to the oxidation of carbohydrates, fats and proteins. It is now well known that in the treatment of acute diabetes, repeated doses of insulin have to be injected in order to obtain satisfactory results. Our experiments on the oxidation of insulin by air show that it is used up by oxidation in the body and thus repeated doses are necessary. Moreover, this oxidation of insulin leads to the oxidation of glucose in the body and this explains the decrease of glucose in the diabetic blood and urine on injection of insulin. It is interesting to note that biochemists are coming to the view that plant and animal peroxidases also act like inductors in oxidation reactions.

From quantitative experiments on the oxidation of carbohydrates, glycerol, proteins and fats by air in presence of freshly precipitated ferrous and cerous hydroxides and sodium sulphite as inductors, Palit and Dhar[2] have shown

---

[1] Dhar: Proc. Akad. Wet. Amsterdam, 29, 1023 (1921).

[2] J. Phys. Chem., 34, 711 (1930); Z. anorg. allgem. Chem., 191, 150 (1930).

that the amount of carbon dioxide obtained in these slow oxidations is practically the same as is expected from the point of view that the carbohydrates, glycerol, fats and nitogenous substances are completely oxidised into carbon dioxide and water by passing air at the ordinary temperature.[1] Similarly Spoehr[2] has obtained considerable amounts of carbon dioxide from the induced oxidation of carbohydrates by air in presence of sodium ferrous and ferric pyrophosphate. I am of the opinion that these results are of importance, because these oxidations are of the same type as those taking place in the animal body.

Dakin[2] has shown that ammonium butyrate on being oxidised with hydrogen peroxide and a ferrous salt, forms acetone, acetoacetic acid, acetaldehyde etc. Chakrabarti and Dhar have shown that volatile aldehydic or ketonic products are formed when carbohydrates, fats and nitrogenous substances are oxidised with hydrogen peroxide and a ferric salt at 37°. The author has emphasized that in normal health the food materials taken in the body are completely oxidised into carbon dioxide and water without the formation intermediate compounds, just as food materials are oxidised completely to carbon dioxide and water, when air is passed through their solutions or suspensions in presence of inductors. Intermediate compounds are only formed in the diseased condition of the animal body.[3]

Summary

(1) From the experimental results on the induced oxidation of sodium formate by air at the ordinary temperature in presence of ferrous and cerous hydroxides, it appears that Fe_2O_5 and Ce_2O_5 are formed as intermediate peroxides.

(2) The induction factor, that is, the ratio of the amount of oxygen taken up by glucose to the amount of oxygen absorbed by ferrous or cerous hydroxide is as high as 8 or 9. Similar results have been obtained with other carbohydrates. The induction factor in the oxidation of glucose by air in presence of sodium ferropyrophosphate is about 15.

(3) These high values of the induction factor and its increase with the concentration of the acceptor can be satisfactorily explained from the view point of the generation of ions in the primary exothermal reaction. The ions activate the molecules of the acceptor or the actor and a sort of reaction chain is set up.

(4) It has been observed that volatile aldehydic or ketonic products are formed when carbohydrates, fats and nitrogenous substances are oxidized by hydrogen peroxide and an iron salt at 37°, whilst carbon dioxide and water are obtained and there is complete oxidation when the above substances are oxidized by air in presence of ferrous hydroxide as inductor. It appears, therefore, that the intermediate iron peroxide obtained in the case of hydrogen

---

[1] J. Am. Chem. Soc., 46, 1494 (1924).

[2] J. Biol. Chem., 4, 77 (1908).

[3] Compare Dhar: "New Conceptions in Biochemistry" (1931).

peroxide and an iron compound must be different from that formed with ferrous compounds and oxygen, because the products of oxidation are different in the two cases.

(5) Insulin can be readily oxidized and carbon dioxide obtained by passing air at the ordinary temperature through an aqueous solution of insulin. When glucose solution is added to it, the glucose is oxidized to carbon dioxide and this is a case of induced oxidation. The velocity of the oxidation of insulin by air is retarded by glucose, which undergoes oxidation by air at the ordinary temperature in presence of insulin acting as an inductor. These results explain the decrease of sugar in diabetic blood and urine by the injection of insulin. Addition of phosphate increases the induced oxidation of glucose in presence of insulin. It appears that in normal health, the food materials are completely oxidized to carbon dioxide and water. Intermediate compounds are formed in the diseased condition of the animal body.

Chemical Laboratory,
Allahabad University,
Allahabad, India,
January 29, 1929.

CONCERNING THE PHYSICAL PROPERTIES OF SOLUTIONS OF CERTAIN PHENYL-SUBSTITUTED ACIDS IN RELATION TO THEIR BACTERICIDAL POWER[*]

T. C. DANIELS[1] WITH R. E. LYONS

Introduction

Attempts have been made to establish relationships between chemical constitution and biological action on a basis of chemical structure, and this has led to the discovery of a large number of facts which for the most part cannot be correlated. Physiological action must in general be dependent on chemical structure, and that it is also greatly modified by differences in physical properties is well known. The importance of the role of such physical properties as adsorption, solubility, partition coefficient (between oil and water), viscosity, hydrogen ion concentration and surface tension has been recognized, yet it has not been possible to establish the relationship between the variation of such properties and their influence on biological action.

Duggan[2] has shown that in the fatty acid series with increasing length of chain there is a decrease in the antiseptic action. Using bacillus subtilis as the test organism it was found that seven per cent of formic acid was required to restrain the growth of this organism while acetic and propionic acid required nine and twelve per cent respectively. These percentages correspond very closely to the relative molecular weights of the acids, while their relative strength falls in the inverse ratio. This might indicate that the undissociated molecules of these acids are the active portion in the disinfection process. Ishiwara,[3] also Halvarson and Cade[4] have shown a similar relationship in connection with the disinfection action of acids. Levine, Peterson and Buchanan[5] have presented evidence that the undissociated molecules of: sodium hydroxide, sodium carbonate and trisodium phosphate are the active agents in disinfection by these substances.

Parry Laws,[6] for a series of phenyl substituted acids, determined the effect on the bactericidal action produced by changing the length of the side chain. He found that the converse of Duggan's results held for this type of acid. The antiseptic action increased markedly as the carbon chain was lengthened: thus, phenyl acetic acid showed a bactericidal action more than twice as strong as phenol: β-phenyl propionic acid, three times that of phenol; and γ-phenyl butyric, five times that of phenol.

---

[*] Contribution from the laboratory of organic chemistry of Indiana University.

[1] This communication is based upon a portion of a thesis submitted by the first named author, in partial fulfillment of the requirements for the degree Ph.D. in Chemistry at Indiana University.

[2] T. R. Duggan: Compt. rend. des séances de la soc. de biol., 1886, 614.

[3] Fusao Ishiwara: Z. Immunitäts., 40, 429-52 (1924).

[4] Halvarson and Cade: Prac. Soc. Exptl. Biol. Med., 25, 506-9 (1928).

[5] Levine, Peterson and Buchanan: Ind. Eng. Chem., 20, 633-5 (1928).

[6] Parry Laws: J. Physiol., 17, 360 (1894-5).

Stanley, Jay and Adams[1] have recently demonstrated that a ring structure is not necessary for certain higher organic acids to have a bactericidal action.

If Laws' results are correct, the reasons for the differences in bactericidal action should be shown by making a study of the physical properties of the solutions of these acids. It is well known that increasing the length of a side chain produces certain rather definite changes in the physical properties of the solution; thus, boiling point increases, solubility decreases, there is generally a distinct lowering of the surface tension, the viscosity gradually increases as the chain increases in length and the hydrogen ion concentration tends to decrease. We are concerned with the problem of determining in what way such changes influence the action on the organism. In order to make a study of this possible relation between bactericidal power and each of several physical properties presented by an homologous series of compounds, it was decided to obtain or prepare the following acids; benzoic, phenyl acetic, β-phenyl propionic, γ-phenyl butyric, δ-phenyl valeric and ε-phenyl caproic.

Experimental

Preparation of Acids.

The first acid of the series (benzoic) was obtained from the Bureau of Standards. It was an exceptionally pure quality of acid, prepared for use in calorimetric determinations, and no effort was made to further purify it. It melted at 121+°C. The next two members of the series (phenyl acetic and β-phenyl propionic) were obtained from the Eastman Kodak Co., listed as c.p. The phenyl acetic was further purified by twice recrystallizing from hot distilled water and finally drying over sulfuric acid in a vacuum. The purified acid melted at 76.5°C. The β-phenyl propionic acid (hydrocinnamic) was further purified by recrystallizing several times from low boiling petroleum ether and finally drying over sulfuric acid in a vacuum. The purified acid melted at 49°C.

The last three members of the series were prepared by means of the malonic ester synthesis and purified according to the method indicated under each acid. The preparation of γ-phenyl butyric acid will illustrate the method employed.

Preparation of γ-Phenyl Butyric Acid.

The apparatus consisted of: A five hundred cc. three neck, round bottom flask, fitted with rubber stoppers holding a reflux condenser, a separatory funnel and a mercury seal mechanical stirrer.

In the flask was placed 250 cc. of absolute alcohol (distilled over sodium), to this 11.5 grams (1/2 mole) of freshly cut sodium was gradually added. The solution was stirred and cooled to about 50°C., then 85 grams of freshly distilled malonic ester added. To this solution 92.5 grams (1/2 mole) of phenyl ethyl bromide was gradually added. The reaction mixture was re-

---

[1] Stanley, Jay and Adams: J. Am. Chem. Soc., 51, 1261 (1929).

fluxed until neutral to moist litmus after which the excess alcohol was removed by distillation over a steam-bath. The residue was then treated with 200 cc. of water. The ester was separated and dried over anhydrous sodium sulfate. It was distilled and that portion coming over at 178–182°C., 16 mm. pressure, collected. After recrystallizing several times from low boiling petroleum ether and drying over sulfuric acid in a vacuum, the acid melted at 50.5°C.

Fisher and Schmitz,[1] have also prepared this acid making use of the malonic ester synthesis.

Preparation of δ-Phenyl Valeric Acid.

Braun and Kruber,[2] prepared this acid by means of the malonic ester synthesis.

1-phenyl 3-bromo-propane was prepared from hydro-cinnamyl alcohol according to the method of Rupe and Burgin,[3] which consists of treating the alcohol with phosphorus tribromide.

The fraction boiling at 109–111°C., 12 mm. pressure was collected and reacted with sodium di-ethyl malonate, employing the method described under the preparation of γ-phenyl butyric acid.

The acid was purified by recrystallizing several times from low boiling petroleum ether and after drying over sulfuric acid in a vacuum, melts at 59.5–60°C.

Preparation of ε-Phenyl Caproic Acid.

δ-phenyl butyl alcohol was prepared from 1-phenyl 3-bromo-propane, using the method employed by Braun,[4] who also prepared this acid from ε-phenyl caproic acid nitrile. The method makes use of the Grignard reagent and paraformaldehyde. The paraformaldehyde was previously dried for forty eight hours over phosphorus pentoxide in a vacuum desiccator, as recommended by Adams and Noller.[5] The method of Gilman and Schulze[6] was employed to determine when the reaction was completed.

The Grignard compound was decomposed with ice, and a sufficient quantity of 30% sulfuric acid added to dissolve the magnesium hydroxide. The cooled mixture was extracted with ether and dried with anhydrous sodium sulfate. After evaporation of the ether the alcohol was distilled and that portion coming over at 143–148°C., 19 mm. pressure collected.

The δ-phenyl butyl bromide was prepared from the alcohol employing the same method as was used in the preparation of γ-phenyl propyl bromide. The product distils at 121–123°C., at 12 mm.

The ε-phenyl caproic acid resulting from the malonic ester synthesis was distilled and that fraction boiling between 175–190°C., at 15 mm. pressure, collected. There was slight decomposition accompanying the distilla-

---

[1] Fisher and Schmitz: Ber., 39, 2211 (1906).

[2] Braun and Kruber: Ber., 45, 384-91 (1912).

[3] Rupe and Burgin: Ber., 43, 178 (1910).

[4] Braun: Ber., 44, 2872-73 (1911).

[5] Adams and Noller: Org. Syn., 6, 22.

[6] Gilman and Schulze: J. Am. Chem. Soc., 47, 2002 (1925).

tion. The distillate was further purified by repeated crystallizations from low boiling petroleum ether. In order to facilitate, it was necessary to crystallize at a temperature of near freezing. The acid thus purified melts at 16°C. At room temperature it is a clear colorless oil.

Solubilities of the Acids.

The solubilities of the acids were determined as follows: A constant temperature bath capable of temperature control to within one-tenth degree centigrade, was equipped with a rotating wheel, similar to that described by Noyes.[1] The apparatus carried four sixty cubic centimeter salt mouth bottles, fitted with rubber stoppers. Rotation was accomplished by means of an electric motor fitted with a standard gear-reducer. Fifty cubic centimeters of distilled water were added to each bottle together with an excess of the acid, the solubility of which was to be determined. The solutions were rotated from four to six hours at the desired temperature, then placed in an upright position and allowed to stand for several minutes in the bath, to permit clarification. A portion was then transferred to a specific gravity bottle which was

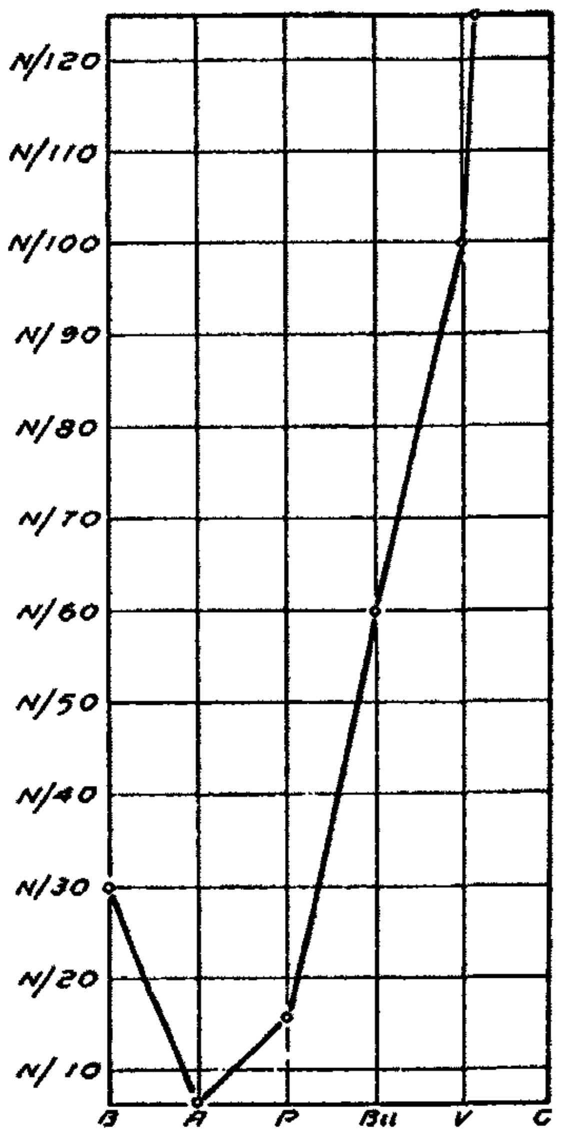


FIG. 1
Solubilities in Terms of Normalities
at 30°C.

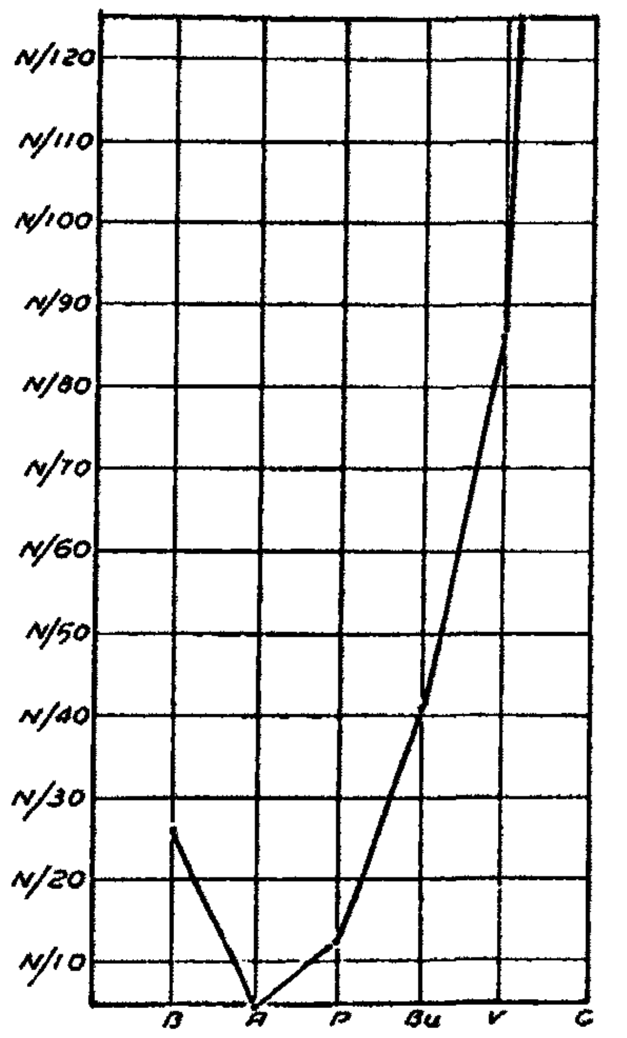


FIG. 2
Solubilities in Terms of Normalities
at 40°C.

---

[1] Noyes: Z. physik. Chem., 9, 606 (1892).

kept immersed in the constant temperature bath. This transfer was accomplished by means of a constant temperature pipette, prepared from a glass tube (12 mm. in diameter), covered with a large water jacket, which was filled and kept immersed in the water bath. A small bulb was attached at the end, which carried a cotton plug for filtration.

The filled specific gravity bottles were removed from the bath and allowed to come to room temperature, after which they were weighed. The solutions were then transferred to an Erlenmeyer flask and titrated with one hundredth normal sodium hydroxide, using phenolphthalein as the indicator. Purified nitrogen was used to displace the carbon dioxide from the solutions and several minutes time allowed for this to occur before completing the titration.[1] The solubilities were determined at thirty and forty degrees centigrade. Duplicate determinations were made in each case. See Table I, and Figs. 1 and 2 for data and curves.[2]

TABLE I

Solubilities of acids expressed in grams of acid dissolved in one hundred grams of water

	30°C	40°C
Benzoic	.407	.556
Phenyl acetic	2.015	2.962
β-phenyl propionic	.934	1.165
γ-phenyl butyric	.273	.530
δ-phenyl valeric	.178	.207
ε-phenyl caproic	.048	.077

Distribution between Oil and Water.

The distribution coefficient between oil and water was determined in the following manner. Solutions of two-hundredth normal acids were prepared,[3] and twenty-five cubic centimeters of solutions of each acid were placed in sixty cubic centimeter wide mouth bottles, fitted with rubber stoppers. To each bottle there was added twenty-five cubic centimeters of a good quality cottonseed oil, the acid value of which had previously been determined. The bottles were placed in a rotating apparatus and agitated at room temperature, for eighteen hours. The bottles were then removed from the apparatus and allowed to stand in an upright position until complete separation of the oil and water was obtained. Twenty cubic centimeters of the water layer were pipetted and transferred to an Erlenmeyer flask, the acid value was then determined by titrating with one-hundredth normal sodium hy-

---

[1] All titrations referred to in this paper were made with a calibrated burette, measuring accurately to .05 cc.

[2] The following abbreviations were used in the preparation of all graphs throughout this study:

B = Benzoic
A = Phenyl acetic
P = β-phenyl propionic
Bu = γ-phenyl butyric
V = δ-phenyl valeric
C = ε-phenyl caproic

[3] Because of limiting solubility, it was necessary to use a five-hundredth normal solution of the phenyl caproic acid. This, however, should not change the distribution coefficient.

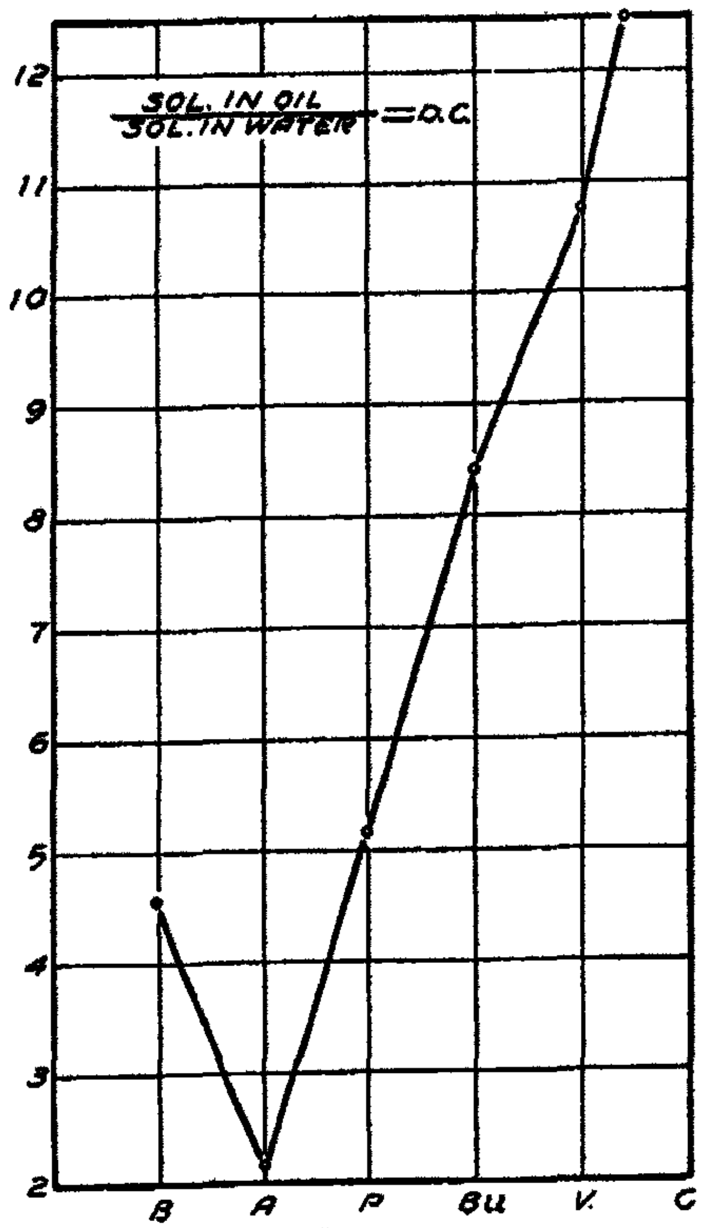


FIG. 3
Distribution Coefficients

droxide, using phenolphthalein as the indicator, and again employing nitrogen to displace carbon dioxide. The relationship of solubility in oil to solubility in water, $\left(\frac{\text{sol. in oil}}{\text{sol. in H}_2\text{O}} = x\right)$ is shown in Table II, and Fig. 3.

TABLE II

	Distribution Coefficient
Benzoic	4.53
Phenyl acetic	2.24
β-phenyl propionic	5.26
γ-phenyl butyric	8.40
δ-phenyl valeric	10.75
ε-phenyl caproic	17.80

Adsorption on Activated Charcoal.

The relative adsorption of the acids on activated charcoal was determined using one hundredth normal solutions of the acids (phenyl caproic excepted because of limiting solubility), as the starting concentration. Four dilutions were made from these solutions in the following manner:

(1) twenty cubic centimeters of one-hundredth normal acid diluted to twenty-five cubic centimeters of water;

(2) fifteen cubic centimeters of one-hundredth normal acid diluted to twenty-five cubic centimeters;

(3) ten cubic centimeters of one-hundredth normal acid diluted to twenty-five cubic centimeters;

(4) five cubic centimeters of one-hundredth normal acid diluted to twenty-five cubic centimeters. One-tenth gram of activated charcoal was added to twenty-five cubic centimeters of the diluted acid solutions and the solutions were agitated thoroughly at five minute intervals during twenty minutes. At the end of this time, the solutions were filtered through a small filter and ten cubic centimeters of the filtrate titrated with one hundredth normal sodium hydroxide using phenolphthalein as the indicator. The phenyl caproic acid, because of limiting solubility, cannot be compared with the other members of the series except in the last dilution. It is to be seen that as the dilutions reach a concentration of approximately N/250 the curve straightens out and the values for all of the acids are quite closely the same. See Table III, and Fig. 4 for data and curves.

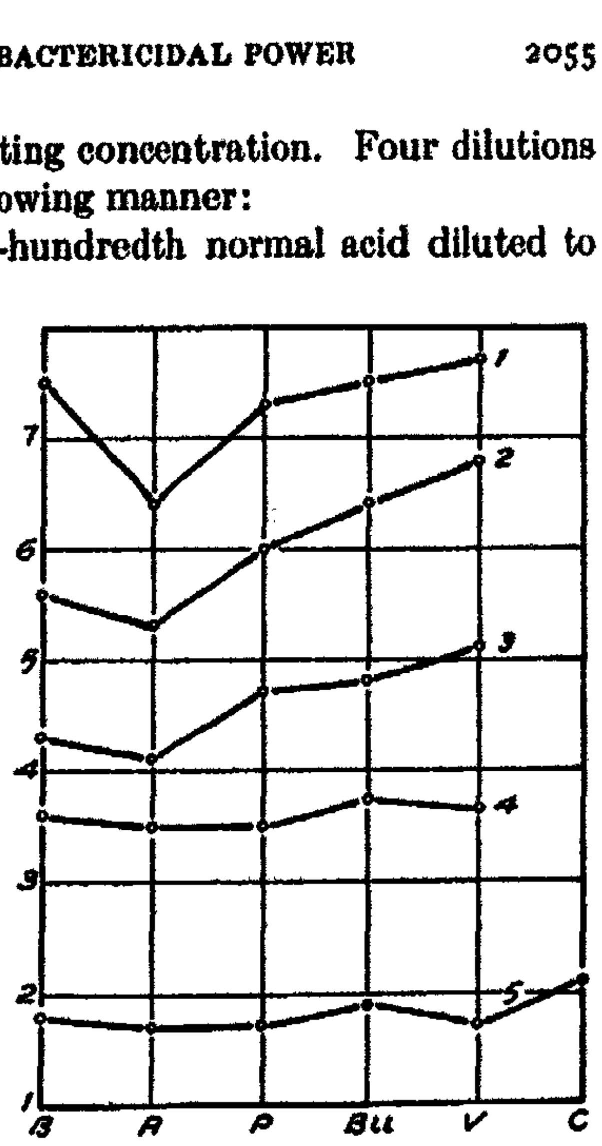


Fig. 4

Adsorption on activated charcoal expressed in mils of N/100 sodium hydroxide corresponding to the amount of acid adsorbed.

1 represents adsorption from N/100 acids
2 " " " N/125 "
3 " " " N/166 "
4 " " " N/250 "
5 " " " N/500 "

TABLE III

Adsorption on activated charcoal expressed in cubic centimeters of N/100 sodium hydroxide

Dilution	N/100	N/125	N/166	N/250	N/500
Benzoic	7.5	5.6	4.3	3.6	1.8
P. Acetic	6.4	5.3	4.1	3.5	1.7
P. Propionic	7.3	6.0	4.7	3.5	1.7
P. Butyric	7.5	6.4	4.8	3.75	1.9
P. Valeric	7.7	6.8	5.1	3.6	1.7
P. Caproic	—	—	—	—	2.1

Relative Viscosities of N/300 Acids at 35°C.

The viscosities were determined by means of an Ostwald-Drucker type pipette. The temperature control was sensitive to a temperature change of

.1°C. An average of several readings was taken for each solution. Because of the slight solubility of phenyl caproic acid it was dropped from the series as it would have necessitated working with five hundredth normal dilutions. The table shows the relative increase of viscosity for the series. The difference is so slight that the time relationship only is given. See Table VI.

TABLE IV

Relative Viscosity of N/300 acids at 35°C.

Benzoic	74.4 seconds
Phenyl acetic	74.8 seconds
β-phenyl propionic	75.0 seconds
γ-phenyl butyric	75.2 seconds
δ-phenyl valeric	75.4 seconds

The water used for preparing the acid solutions gave a reading of 74.2 seconds at 35°C.

Surface Tension.

Surface tension measurements of the solutions were made with a du Noüys Tensiometer. The instrument was calibrated in absolute units and readings were made on, one-hundredth, two-hundredth and three-hundredth normal solutions, of the acids. The glass vessels used in these measurements were carefully cleaned and subjected to prolonged heating in a solution of chromic acid. The water gave a surface tension reading of 72.5 dynes, at 26°C. The hundredth normal solutions consisted of only the first four acids, the two-hundredth normal solutions consisted of the first five acids and the five-hundredth normal solutions included all of the series. See Table V, and Figs. 5 and 6 for the data and curves.

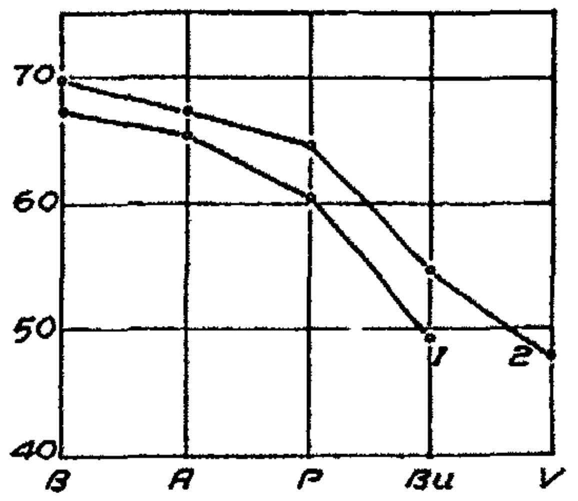


FIG. 5

Surface tension of N/100 and N/200 solutions in dynes/cm. at 26°C. The water used in the preparation of the solutions gave a reading of 72.5 dynes. No. 1 represents N/100 acids. No. 2 represents N/200 acids.

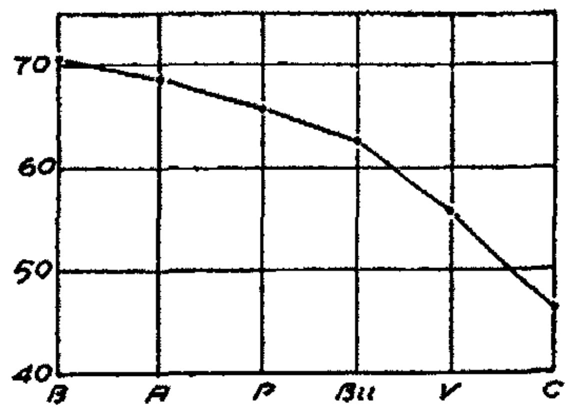


FIG. 6

Surface tension of N/500 solutions at 27°C.

The water used in the preparation of the solutions gave a reading of 72.3 dynes at the same temperature.

TABLE V

Surface Tension in dynes per centimeter at 26°C., for N/100 and N/200 acids; 27°C. for the N/500 acids.

	N/100	N/200	N/500
Benzoic	67.3	69.6	70.6
Phenyl acetic	65.4	67.3	68.6
β-phenyl propionic	60.4	64.4	65.8
γ-phenyl butyric	49.1	54.5	62.7
δ-phenyl valeric	—	48.0	55.6
ε-phenyl caproic	—	—	46.4

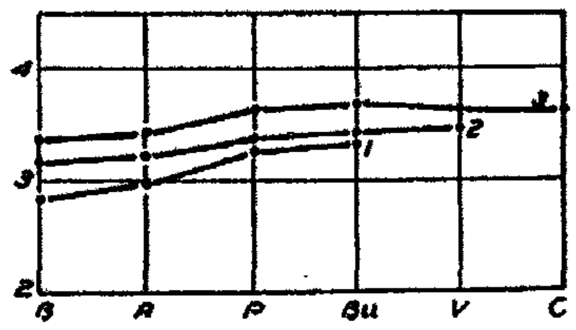


FIG. 7

Hydrogen ion concentrations of N/100, N/200, and N/500 solutions.

1 represents the N/100 solutions
2 " " N/200 "
3 " " N/500 "

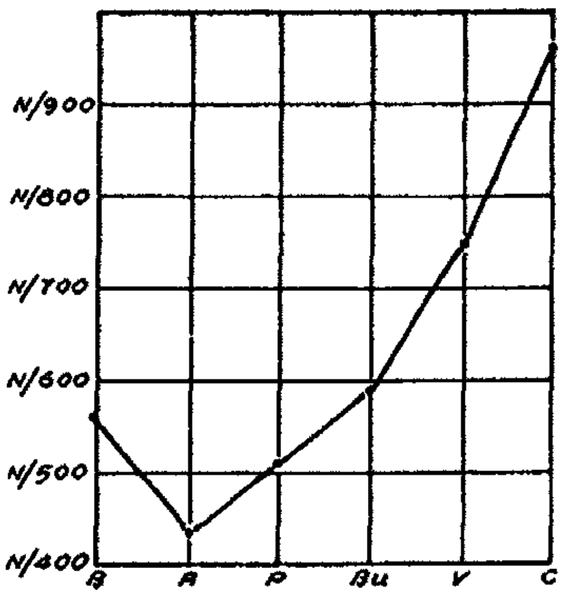


FIG. 8

Bactericidal value of acids in terms of normality.

Hydrogen Ion Concentration of the Acids.

The hydrogen ion concentration of the acid solutions was determined by means of the standard Leeds and Northrup potentiometer, equipped with a Hildebrand type calomel electrode. Determinations were made on, one-hundredth, two-hundredth and five-hundredth normal solutions of the acids. Because of limiting solubility, phenyl caproic acid does not appear in the first two dilutions and phenyl valeric does not appear in the first. See Table VI, and Fig. 7 for the data and curves.

TABLE VI

Hydrogen Ion Concentration of N/100, N/200 and N/500 Solutions of the Acids

	N/100 Sol.	N/200 Sol.	N/500 Sol.
Benzoic	2.83	3.17	3.36
Phenyl acetic	2.97	3.23	3.42
β-phenyl propionic	3.26	3.37	3.64
γ-phenyl butyric	3.31	3.43	3.68
δ-phenyl valeric	—	3.44	3.62
ε-phenyl caproic	—	—	3.62

TABLE VII

Bactericidal Values expressed in Parts per Hundred

Dilutions	Phenol	Benzoic	Phenyl Acetic	β-Phenyl Propionic	γ-Phenyl Butyric	δ-Phenyl Valeric	ε-Phenyl Caproic
1–100	—						
1–200	—						
1–300	/						
1–400	/						
1–500	/						
1–1000	/						
1–1500		—	—	—	—	—	—
1–2000		—	—	—	—	—	—
1–2500		—	—	—	—	—	—
1–3000		—	—	—	—	—	—
1–3100		—	—	—	—	—	—
1–3200		—	—	—	—	—	—
1–3300		—	/	—	—	—	—
1–3400		—	/	—	—	—	—
1–3500		—	/	/	—	—	—
1–3600		—	/	/	—	—	—
1–3700		—	/	/	/	—	—
1–3800		—	/	/	/	—	—
1–3900		—	/		/	—	—
1–4000		—			/	—	—
1–4100		—				—	—
1–4200		—				—	—
1–4300		—				/	—
1–4400		—				/	—
1–4500		—				/	—
1–4600		—				/	—
1–4700		/					—
1–4800		/					—
1–4900		/					—
1–5000		/					—
1–5100		/					/
1–5200							/
1–5300							/
1–5400							/
1–5500							/

Bactericidal Value of the Acids.

The bactericidal determinations were carried out by Dr. F. G. Jones, bacteriologist for the Eli Lilly and Company of Indianapolis. The method used consisted of making proper dilutions of the acids from relatively concentrated solutions. To five cubic centimeters of the diluted acid there was added one-tenth cubic centimeter of a suspension of coli bacillus, which had previously been diluted, one to ten. The organism was allowed to remain in the acid solution for one hour at a temperature of 37.5°C., and was then inoculated into suitable nutrient media. The relative bactericidal power obtained by Jones on B. Coli has further been confirmed by Dr. T. B. Rice and Dr. C. G. Culbertson, of Indiana University School of Medicine, using Hopkins strain B. Typhosus. Table VII gives the bactericidal value of the acids in parts per hundred. See also Fig. 8.

Discussion

The work of Laws[1] indicates a marked increase in the antiseptic action with increasing length of the side chain of certain phenyl substituted acids. Benzoic acid however, was not included in his work and the erroneous conclusion was reached that antiseptic power increases with increase in molecular weight, for this type compound. A study of benzoic acid along with the other acids included in the study would have demonstrated this. It appears that this difference in antiseptic value may readily be accounted for by taking into account the differences in physical properties of the water solutions of the acids. Thus we find the type of curve presented by the distribution coefficients, adsorption on activated charcoal, and solubilities of the acids quite closely parallels the curve presented by the bactericidal value. It is also to be noted that the surface tension is lowered rather constantly with increase in the length of the side chain. This does not account for the difference in the behaviour of phenyl acetic acid. While it is likely true that surface activity is one of the important factors in disinfection by chemical means, it is also clear that other physical properties may so modify the antiseptic action that the surface tension reducing power may only be of secondary importance. Leonard and Feirer[2] have pointed out that under the same conditions a germicide which depresses the surface tension of water is more efficient than one which does not bring about this depression. This is explained on a basis of increased adsorption of the active substance on the bacteria and is also said to be due to the greater penetrating power of "microscopic inequalities of surface," together with greater diffusion through the cell membrane.

The hydrogen ion concentration is a factor to be considered in the disinfection process but it has not been possible to find any definite relation in this series of compounds. There is a gradual fall in the hydrogen ion concentra-

---

[1] Parry Laws: J. Physiol., 17, 360 (1894-5).

[2] Leonard and Feirer: Bulletin of the Johns Hopkins Hospital, 41, No. 1, pp. 21-35 (1927)

tion as the series is ascended, but the variation is not pronounced. Kuroda[1] has found that the antiseptic action of certain phenols is strongest in an acid range below pH4.5 and in an alkaline range above pH10. There is considerable evidence indicating that the undissociated acid molecule is the active portion in disinfection by means of acids, in which case the antiseptic action would be inversely proportional to the hydrogen ion concentration. Waterman and Kuiper[2] have found that the antiseptic action of sodium benzoate and sodium salicylate is much weaker than the free acids. Also, that the addition of free hydrochloric acid increases the antiseptic action of both these acids. This may be due to the diminution of the dissociation, thereby increasing the concentration of the undissociated molecules of the acids. Cooper and Cheeseworth[3] have shown that "trans" acids are stronger than the isomeric "cis" forms, although they are weaker acids.

While viscosity is a factor to be considered in the disinfection process, in an homologous series such as is presented here, there is relatively little difference in the viscosities of the solutions and it is not possible to show any relation of this physical property to bactericidal action.

Summary

1. Bactericidal action in the phenyl substituted acids closely parallels their distribution between oil and water, and their adsorption on activated charcoal. The curve presented for their surafce tension reducing power does not account for the anomalous behavior of phenyl acetic acid.

2. The acids have been carefully purified and accurate determinations of their solubilities in water at 30°C. and 40°C., made.

3. The melting point of ϵ-phenyl caproic acid is given for the first time.

4. Determinations of several physical properties of the acids in water solutions have been carried out.

Acknowledgment

The writers are grateful to Dr. F. G. Jones, of Eli Lilly and Company, also, to Dr. T. B. Rice and Dr. C. G. Culbertson, of the Indiana University School of Medicine, for their cooperation in determining the bactericidal value of the acids.

---

[1] Biochem. Z., 169, 281-91 (1926).

[2] Waterman and Kuiper: Rec. Trav. chim., 43, 323-5 (1924).

[3] E. A. Cooper and H. D. Cheeseworth: J. Phys. Chem., 33, 720-728 (1929).

92 - 89

THE STRUCTURE OF SILICA GEL*

(X-Ray Study)

BY LAURA KREJCI AND EMIL OTT

It has been demonstrated by a series of authors[1] employing different means of investigation that pure precipitated silica will be transformed at least partially into the crystalline state in the form of cristobalite when heated at temperatures between 1000°C. and 1710°C. but that it will remain amorphous at any lower temperature.

In particular X-ray studies by Kyropoulos[2] showed that precipitated silica, which had been heated to about 1300°C for 2 hours gave a powder pattern showing identical diffraction lines as the one obtained from cristobalite. However the former pattern was not as clear and gave evidence of the presence of unchanged amorphous silica. The cristobalite was obtained by melting water-glass with sodium phosphate.

Patrick, Frazer and Ruch[3] reported on some X-ray diagrams which had been made for them showing a non-crystalline pattern for a very pure silica gel, which has been heated at 1100°C for 2 hours. The same gel heated for 3 days at the same temperature yielded a diagram showing the presence of a fair amount of crystalline material.

These experiments were essentially repeated by using Cu-radiation and a Debye-Scherrer camera of 57.7 mm. effective diameter.

Very pure silica gel, which had been heated at 1150°C for 5 hours, gave the very clear powder diagram represented in Fig. 1, whereas cristobalite prepared by fusing water-glass and sodium phosphate, gave the pattern Fig. 2. It can easily be seen that the structures are identical. Furthermore the heated silica gel is evidently free from amorphous material, which is rather remarkable when the comparatively moderate heating is taken into account. The pattern of the cristobalite is less distinct, due to the non-uniform particle size. The presence of extremely small crystals (colloidal) is indicated by the broadening of the lines whereas the existence of Laue Spots in the diagram proves the simultaneous presence of relatively large particles.

Furthermore, contrary to previous concepts, we are able to show the presence of crystal nuclei in a series of silica gels, which have never been subjected to temperatures approaching 1000°C, in particular in one case in which the gel has never been heated above 100°C. As is to be expected the particles are of extremely small colloidal dimensions, causing thus a strong broadening of the interference lines. However it is beyond doubt that definite

---

[*] Contribution from the Department of Chemistry, The Johns Hopkins University.

[1] Compare Sosman: "The Properties of Silica," p. 171 (1927).

[2] Z. anorg. Chem., 99, 197 (1917).

[3] J. Phys. Chem., 31, 1511 (1927).

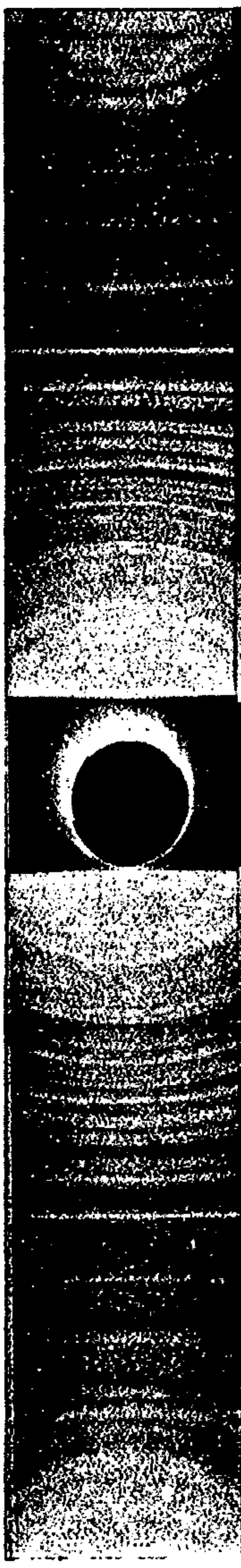


FIG. 1

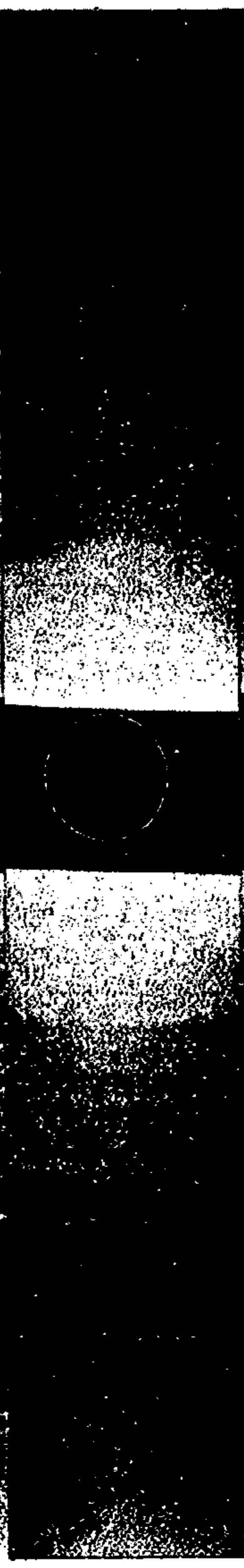


FIG. 2

FIG. 3

FIG. 4

lines such as are characteristic for crystalline bodies are present on the films. The times of exposure were approximately double those used for the cases above.

At first a series of silica gels were investigated which were obtained from a commercial gel of the Silica Gel Corporation of Baltimore. This gel had been activated during the manufacturing process at a fairly high temperature (not exceeding 500°C) but had again become de-activated when this work was begun.

The products used were:

a) The commercial, impure, gel.

b) A pure gel obtained from sample (a) by refluxing with concentrated nitric acid, washing thoroughly with distilled water and drying at 110°C.

c) A purified gel as given under (b), which was dried additionally over phosphorus pentoxide in oil-pump vacuum for 3 days.

All the X-ray photographs obtained are identical. The diagram obtained from sample (b) is reproduced in Fig. 4. The crystalline pattern can evidently not be attributed to the impurities in the cases where such are present. The reactivated gel gave no evidence for progressing crystallization which leads at once to the conclusion that the heating during the preparation of the gel cannot be the actual cause of the presence of crystalline nuclei. These must have been formed in the first stages of the preparation of the precipitated silica.

To prove this point further, a gel was freshly prepared, washed at 80°C and dried at 100°C. No further purification was used, since the previous results had shown that the small amounts of foreign substances present do not change the X-ray diagram in any way for the conditions employed.

The pattern obtained (Fig. 3) is identical with those of the other gels.

It is therefore proved that crystalline centers of colloidal dimensions are formed in freshly prepared silica gel at ordinary temperatures.

Various theories have been proposed to explain the formation of crystalline nuclei in silica gel and other "amorphous" bodies, when the products are heated to temperatures sufficiently high, but not approaching the melting point of the material.

Since the crystalline centers are already present at low temperatures, these hypotheses become superfluous.

The process of crystallization of silica gel appears thus to occur in the following fashion. When the gel is first obtained by interaction of sodium silicate and acid, the solution is of relatively low viscosity thus permitting a sufficiently free movement of the molecules. Now, due to the oversaturation, crystallization begins throughout leading to the formation of colloidal crystals. The presence of these particles increases the viscosity, and thereby slows down the further crystallization. Heating of the dried gel to temperatures below 1000°C does not impart sufficient mobility to the atoms or molecules to continue the interrupted crystallization to a marked extent; only at temperatures above 1000°C does this effect become apparent.

The broadness of the lines in the diagrams of the gels not heated above 500°C makes a comparison with the other modifications of silica somewhat uncertain. Yet the comparison shows a very strong resemblance with the photograph of cristobalite. There is certainly no analogy with the diagrams obtained from low-quartz, the stable modification at any temperature below 573°C.

Tridymite also appears unlikely. This becomes quite certain if it is considered, that if tridymite were present at low temperature there is no conceivable reason why cristobalite[1] should be formed at the temperatures used, exceeding 1000°C. "Under conditions of constant and uniform temperature and pressure, tridymite cannot be converted into any other form of silica if the temperature is between 870 and 1470°C and the pressure is low."

It seems thus to be entirely justified, to consider the crystals formed in silica gel in the first stages of formation, as the cristobalite modification.

Once cristobalite is formed it is quite capable of existence below its stability range. Below 870° quartz becomes stable and cristobalite should be transformed into this modification; however no authenticated case of this is known for cristobalite in the pure dry state. Also the transformation to tridymite at temperatures between 870 and 1470°C is extremely sluggish.

The formation of cristobalite from an aqueous solution at low temperatures outside its stability range provides no difficulties. It is a well established fact that the formation of a given modification outside its stability range may readily be obtained by proper experimental conditions, the constitution of the solution being an especially important factor in this regard.

Summary

Pure precipitated silica has been shown to be entirely transformed into the crystallized state by heating to 1150°C for 5 hours. The crystals obtained are of the cristobalite modification.

Precipitated silica samples which have never been heated above 500°C show distinctly the presence of crystalline centers of colloidal dimensions. The same is true for a freshly prepared sample which has at no time been heated above 100°C. The X-ray patterns of these silica gels are apparently identical and indicate the crystals to be of the cristobalite type.

---

[1] Sosman: loc. cit., p. 52.

ELECTROKINETIC PROPERTIES OF PROTEINS*

I. Isoelectric Point and Solubility of Wheat Proteins in Aqueous Solutions of Ethanol

BY W. M. MARTIN**

Introduction

This investigation was undertaken with the object of obtaining some information concerning the proteins extracted from wheat gluten by ethanol solutions of various concentrations. Solubility has long served as a differentiating property in the isolation and purification of the proteins. They are prepared, according to the prevailing methods, by extracting plant and animal substances with reagents in which they are soluble. Specific reagents are designated as solvents for the various proteins. The composition and concentration of the latter are fixed arbitrarily, and it is usually assumed that the preparations obtained by reprecipitation from such reagents are chemically pure compounds. Chemical entities. The fallacy of our methodology in this regard has been clearly indicated by the experimental studies of Gortner, Hoffman and Sinclair[1] in which they have shown that the percentages of protein extracted from wheat flour with normal solutions of KF, KCl KBr and KI were 13, 23, 37 and 63, respectively. Gortner[2] and his coworkers[1] were the first to emphasize the unsatisfactory state of our present methods involving the solubility properties of the proteins when they ask: "*What salts and what concentrations?*" Obviously the quantity and the nature of the protein extracted are dependent upon the composition, concentration and the temperature of the solvent used as an extractive. This view is also supported by the data of Bailey and Blish,[3] Blish and Sandstedt,[4] Hoffman and Gortner,[5] Haugaard and Johnson[6] and by a number of other workers who have been interested in this phase of the problem.

Apparently no attempt has been made to define or name the proteinaceous material obtained when the concentration of the reagent designated as the solvent for a given protein is altered slightly from that arbitrarily stated. Would a different protein be obtained for each different concentration of

---

* Contribution from the Chemistry Department, University of Montana, Agricultural Experiment Station, Bozeman. Paper No. 3, Journal Series.

** Assistant Professor, Chemistry Department, University of Montana, Agricultural Experiment Station, Bozeman.

[1] R. A. Gortner, W. F. Hoffman, and W. B. Sinclair: Colloid Symposium Monograph, 5, pp. 179-198, (1928).

[2] R. A. Gortner: "Outlines of Biochemistry" (1929).

[3] C. H. Bailey and M. J. Blish: J. Biol. Chem., **23**, 345-357 (1915).

[4] M. J. Blish and R. M. Sandstedt: Cereal Chem., **6**, 494-503 (1929).

[5] W. F. Hoffman and R. A. Gortner: Cereal Chem., **4**, 221-229 (1927).

[6] G. Haugaard and A. H. Johnson: Comptes-rendus des travaux du Laboratoire Carlsberg, **18** (2), 1-138 (1930).

reagent used in its preparation? What are the effects of composition and concentration of solvent on the properties of the protein extracted? In other words, can the proteinaceous materials isolated on the basis of their differences in solubility in arbitrary reagents be logically regarded as chemical compounds? Perhaps they are fragments of the compounds as they existed in nature; or they may be polymers, or condensation products of the undenatured proteins. The effect of different solvents on the physical properties of molecules is well known. Many of the simple and relatively stable compounds are monomolecular in one solvent and di- or polymolecular in others. Associated molecules are commonly known to exist under certain conditions with respect to temperature and chemical character of solvent. The complex nature of the proteins and their extreme lability might be expected to render them even more sensitive to the influence of external forces. Much of the confusion in protein research may undoubtedly be attributed to the tendency, on the part of many workers in this field, to look upon proteins as static bodies, and not as dynamic structures whose properties are inseparably related to the environmental forces acting upon them.

In their ultracentrifugal studies Svedberg[7] and his coworkers have shown that the state of aggregation of protein particles is determined by the chemical properties of the liquids in which they are dispersed. Although a constant value was obtained for the apparent molecular weight of each protein in a given reagent, it was found to vary with changes in the chemical composition of the latter. Recent studies have indicated that protein sols which were hitherto regarded as homogeneous systems, are probably mixtures of two or more components in equilibrium. That is, the dispersed particles are not all in the same state of aggregation. Sörensen[8] has expressed the view that these components do not exist as a simple mixture, but as a system whose equilibrium is influenced by environmental forces due to the temperature, composition and concentration of the suspensions medium. Recent work at the Carlsberg Laboratories, more especially that of Haugaard and Johnson[9] on the fractionation of gliadin, further confirms this view.

Since it is not possible to apply the usual analytical method of study to the proteins on account of their instability toward chemical reagents, it is proposed to introduce a new angle of attack on the problem through studies on their electrokinetic properties by streaming-potential methods. By the latter, the intermolecular force relations of protein systems may be studied in the absence of the influence of reagents. The advantages are obvious.

---

[7] The Svedberg and Bertil Sjogren: J. Am. Chem. Soc., 52, 279-287 (1930); 52, 2855-63 (1930); 51, 3594-604 (1929); 50, 3318-32 (1928); Bertil, Sjogren, and The Svedberg: 52, 3279-83 (1930); 52, 3650-54 (1930); F. Krishnamurti and The Svedberg: 52, 2897-906 (1930); Bertil, Sjogren, and Romauld Spycholski: 52, 4400-04 (1930); The Svedberg, L. M. Carpenter, and D. C. Carpenter: 52, 241-52 (1930); 52, 701-10 (1930); The Svedberg and A. J. Stamm: 51, 2170-85 (1929); The Svedberg, and N. B. Lewis: 50, 525-36 (1928); The Svedberg and Eugen Chirnoaga: Bul. chim. soc. ramona stiinte, 31, No. 1-3, 23-52 (1929); J. Am. Chem. Soc., 51, 1399-411 (1928); The Svedberg and J. B. Nichols: 49, 2920-34 (1929); 48, 3081-92 (1926); 45, 2910-17 (1923); The Svedberg and Robin Fahreus: 48, 430-38 (1926); The Svedberg and Herman Rind: 46, 2677-93 (1924).

[8] S. P. L. Sörensen: *Comptes-rendus du Laboratoire Carlsberg*, 15, No. 11 (1923); 16, No. 8 (1926).

The Problem

As a basis for subsequent studies on the physical and chemical aspects of protein solubility, the initial work has been devoted very largely to the development of apparatus and methods for determining the ζ-potential of protein-liquid interfaces. The methods developed have been applied in determining the ζ-potential, and incidentally the isoelectric point, of the alcohol-soluble proteins extracted from wheat gluten by aqueous solutions of ethanol of various concentrations. The alcohol-soluble proteins (prolamines) were chosen for these experimental studies in order to avoid, as far as possible, the complicating influence of chemical reactions with the solvent.

In his classical work on the vegetable proteins Osborne[9] observed that the solubility properties of the prolamines varied according to the source from which they were derived. In general they are considered to be relatively insoluble in solutions containing less than fifty per cent, or more than ninety per cent of alcohol. Zein is an exception in that it is quite soluble in an alcohol solution of ninety-three per cent by volume. Although ethyl alcohol is usually designated as a solvent for the prolamines, it is an interesting fact that some of them, at least, are also soluble in methyl, propyl and benzyl alcohols, as well as in phenol and paracresol. Apparently the alcohol radical is in some way associated with the solubility of this group of proteins.

Gliadin was probably the first of the alcohol-soluble proteins to be prepared. It was isolated from wheat by Einhof[10] in 1805, and since that time its physical properties as well as the chemical composition of its cleavage products have been extensively studied by numerous investigators. The solubility properties of gliadin are especially interesting. It is relatively soluble in an aqueous solution of alcohol, but quite insoluble in either pure water or absolute alcohol. It shows a maximum solubility in solutions containing from fifty to seventy per cent of alcohol by volume. Although this maximum has been variously stated by different investigators, it is probably in the neighborhood of sixty per cent. Obviously, solubility is influenced by experimental conditions with respect to temperature, quantity of solvent used in the extraction process, and the method of treatment.

Osborne[9] and his coworkers, through rather extensive investigations, were convinced that wheat contained only one alcohol-soluble protein, and in consequence their views have been quite generally accepted. Since different quantities of gliadin are obtained by repeatedly extracting wheat gluten with alcohol solutions of various concentrations, the question arises as to the chemical identity of the protein fractions having different solubility properties. An attempt is being made in this investigation to answer this question by determining the isoelectric point of the proteins extracted from wheat gluten in solutions containing various proportions of alcohol and water. The isoelectric point can be used as a criterion in differentiating between proteins only when they differ with respect to this property. Different proteins may

---

[9] T. B. Osborne: Carnegie Institution of Washington, Publication No. 84 (1907).

[10] H. Einhof: Neues allgem. Jb. Chem., 5, 131-153 (1805).

possess the same isoelectric point, but the latter is obviously a constant for each protein. It follows, therefore, that a different isoelectric point indicates a different protein.

Experimental

The Method.—In the preliminary experiments an attempt was made to determine the ζ-potential and, incidentally, the isoelectric point of the alcohol-soluble proteins of wheat gluten in very dilute unbuffered solutions of hydrochloric acid and sodium hydroxide. The proteins were adsorbed on the surface of quartz particles in diaphragms and their streaming potential determined in accordance with the method developed by Briggs.[11] Apparatus similar to that used by Martin and Gortner[12] was employed in the streaming potential determinations. Notwithstanding the fact that the apparatus was designed to exclude carbon dioxide from the system, it was found to be impossible to prepare a dilute unbuffered solution of acid or alkali and transfer it to the streaming cell without its hydrogen-ion concentration being appreciably altered. It was decided, therefore, to avoid this error by designing a new streaming cell which would facilitate the changing from one solution to the other without exposure to the carbon dioxide of the air. While carrying on some of the initial experiments in this connection, it seemed desirable to simplify the experimental technique as much as possible, particularly the preparation of the quartz diaphragms. In the interests of simplicity and the desirability of a standard type of streaming cell, capillary tubes of pyrex glass were tried experimentally, but the electromotive force developed was too feeble to be measured satisfactorily. This difficulty was finally overcome by using the porous bottom of filter crucibles as diaphragms. The electromotive force developed by streaming liquids through the latter was of such a magnitude that it could be measured even more easily than that developed with the quartz-protein diaphragms used in the initial experiments. Further studies showed that the filter crucible diaphragms adsorbed the proteins quite readily. They were also easily and conveniently freed from the protein by washing with hot nitric acid and then igniting at a red heat for ten minutes.

Apparatus.—The streaming cell and the apparatus used for preparing CO_2-free standard solutions are shown in diagram A and B respectively, in Fig. 1. The arrangement of the apparatus used in making the various measurements is shown in detail in Fig. 2, the description of the parts being as follows: (A) two 45-volt radio "B" batteries (90 volts), (B) storage battery as source of electromotive force for potentiometer, (C) streaming cell consisting of a size No. 1, set-in porous bottom crucible of fine porosity (Akatos A1) with a platinum electrode on each side of diaphragm, closed at top with a two-hole No. 7, rubber stopper and attached to receptacle with a band of Gooch tubing, (D) pinchcock closing aspiration tube in volumetric flask, (E) quadrant electrometer (Dolezalek type), (F) two-liter flask, (G) galvanometer

---

[11] D. R. Briggs: J. Phys. Chem., 32, 641-675 (1928); 32, 1646-62 (1928); J. Am. Chem. Soc., 50, 2358-2361 (1928).

[12] W. M. Martin and R. A. Gortner: J. Phys. Chem., 34, 1509-1539 (1930).

of moderate sensitivity used in balancing potentiometer, (H) reversing switch which permits a reversal of the poles of the streaming cell, (I) double switch for throwing the streaming cell in circuit with either the conductivity apparatus or potentiometer, (J) reversing switch which permits a reversal of the quadrants of the electrometer, (K) wheatstone bridge, (L) lamp with housing and projection lenses which supplies beam of light for quadrant electrometer, (M) two-metre water manometer indicating reduced pressure in mm. of water (2000 mm. = 147.7 mm. Hg), (N) one-metre mercury manometer used when reduced pressure is greater than 147.7 mm., (O) soda-lime trap through which air passes to displace standard solution as it is drawn from volumetric flask through streaming cell, (P) potentiometer (L. and N. Type K), (Q) three-way stopcock in reduced pressure line permitting use of one or both of the manometers, (R) resistance units used in conductivity measurements (magnitude of resistance range from 1 to 1,000,000 ohms), (S) shielding of sheet copper protecting the ungrounded side of circuit against induced currents, (T) traps for catching contents of manometers in case of accidents, (U) Weston standard cell against which potentiometer is balanced, (V) 250 ml. volumetric flask, (W) mercury wells for making connections between switch system and the streaming cell, potentiometer and wheatstone bridge, (X) needle valve for regulating the reduced pressure and incidentally the velocity of the liquid streaming through the cell, (Y) scale showing distance of liquid level below end of discharge tube in evacuated flask (This difference in level in terms of mm. of Hg is subtracted from the pressure indicated by the manometers), (Z) scale upon which light beam from quadrant electrometer is

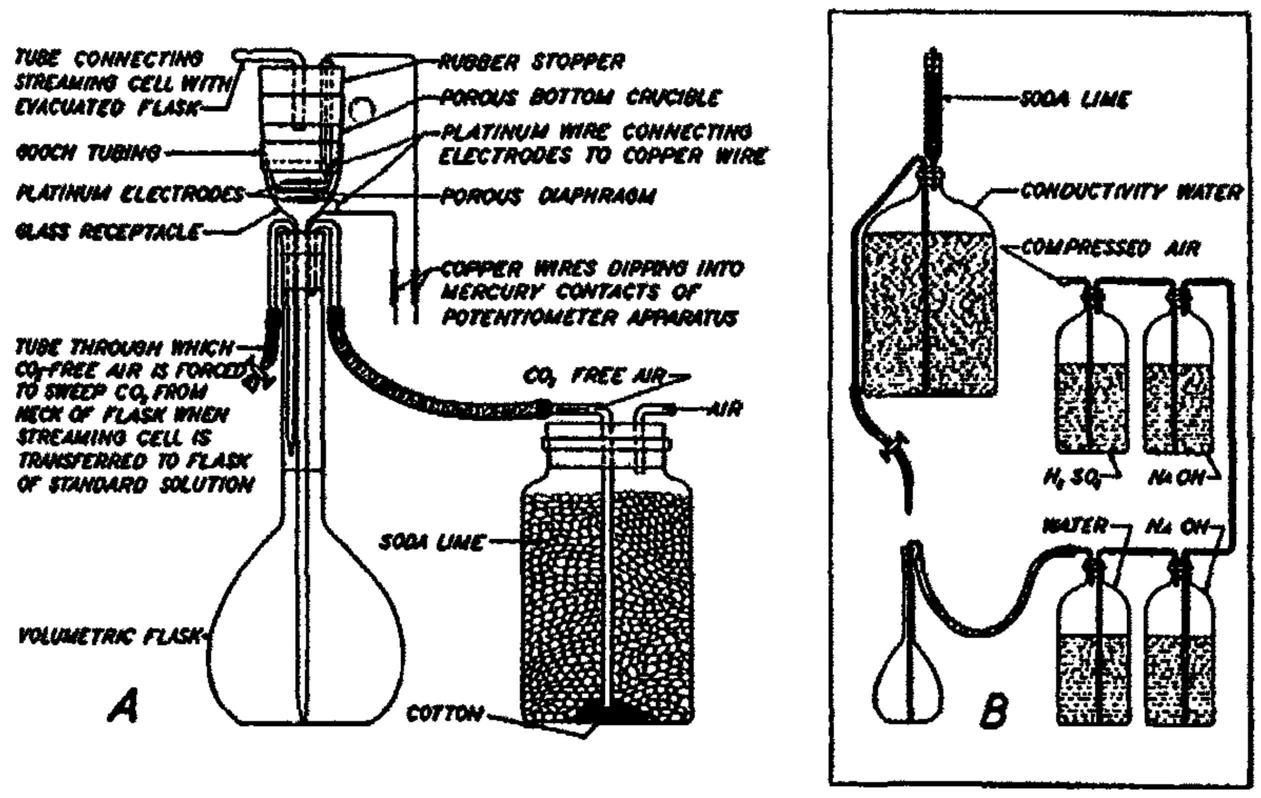


FIG. 1

Streaming-potential cell

A. = Streaming-cell with 250 ml. volumetric flask and soda-lime trap.

B. = Apparatus for preparing CO_2-free standard solutions.

projected, (Θ) stopcock in reduced pressure line used to stop flow of liquid, or when removing volumetric flask with streaming cell to transfer the latter to another flask of standard solution.

In assembling the apparatus as shown in Fig. 2 the electrometer (E) is carefully leveled, and with the circuit closed its needle adjusted so as to be equally divided by the two pairs of quadrants. The positive terminal of the 90-volt battery (A) is then connected to the binding post from which the needle is suspended and the negative terminal to the binding post of one pair of quadrants. If the instrument is in proper adjustment, the two pairs of quadrants will divide the needle equally when it comes to rest. The position of the beam of light reflected from the mirror of the electrometer on the scale (Z) may now be taken as the null-point. The potentiometer (P), having been connected in accordance with the marks on its various binding posts, is adjusted by balancing the source of electromotive force (B) against that of the standard cell (U), using the galvanometer (G) as a null-instrument.

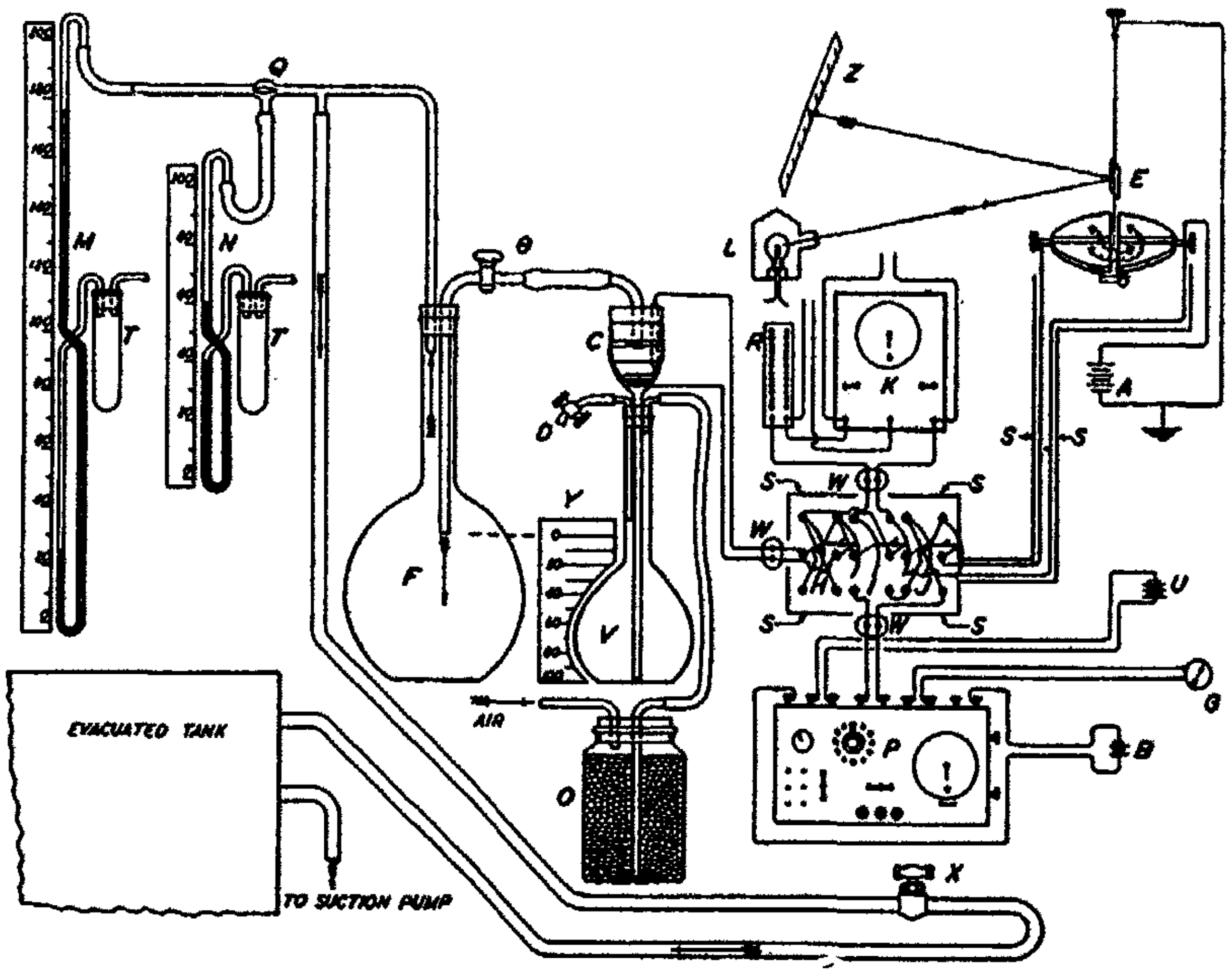


FIG. 2
Streaming-potential apparatus

Preparation and Care of Porous Diaphragms.—The porous diaphragms of the filter crucibles were cleaned by passing hot nitric acid through them under suction followed by a thorough washing with distilled water, then dried by heating gradually and finally ignited at a red heat for ten minutes. The drying and ignition were accomplished very conveniently in a miniature electric furnace constructed from an electric Kjeldahl digestion unit, a rheostat, and a piece of asbestos. To obtain the high temperature necessary for ignition the two outer strands of heating element were removed from the Kjeldahl unit and its opening closed with a piece of heavy asbestos in which a hole was made to receive the crucible. By means of the rheostat the heating element was maintained at a low temperature until the diaphragm of the crucible was thoroughly dry, after which it was raised to a temperature of 900 to 1,000°C. for ten minutes. Following ignition, the crucibles were cooled in a desiccator where they were stored until used. It seemed advisable to protect the porous diaphragms against the absorption of laboratory fumes at all times. ·

Determination of Streaming-Potential.—A porous bottom crucible, having been cleaned, ignited and cooled as described above, is placed in a fifty ml. beaker containing about ten ml. of the protein sol, the streaming-potential of which is to be determined. After the porous diaphragm has been immersed in the sol for ten minutes, it is washed with conductivity water and assembled in the streaming cell as shown in diagram A, Fig. 1. Tube (D) of the cell is then connected with the source of CO_2-free air shown in diagram B and transferred to a flask of standard solution prepared as described in the following section. The current of CO_2-free air is allowed to flow through the system until the last trace of CO_2 is swept out through the soda-lime trap. The assembled cell, flask of standard solution and soda-lime trap are then disconnected from the source of CO_2-free air and connected with the potentiometric apparatus as shown in Fig. 2. Upon opening the stopcock (Θ) and needle valve (X) the liquid is caused to flow from (V) to (F) through the diaphragm of the streaming cell (C). The velocity of the streaming liquid, and incidentally the difference in hydrostatic pressure on the two sides of the diaphragm, is regulated by the needle valve (X). The reduced pressure of the system is indicated by the water manometer (M), or the mercury manometer (N); the former being used for low and the latter for high pressures. Since hydrostatic pressure on the two sides of the diaphragm in (C) in influenced by the level of the liquid in (V), the latter is observed on scale (Y), and its equivalent in terms of mercury subtracted from pressure indicated by the manometers. This gives the true value for the hydrostatic pressure under which the liquid streams through the diaphragm.

The difference in potential on the two sides of the diaphragm produced by the streaming liquid is measured by balancing it against a known electromotive force delivered by the potentiometer (P), the null-point being indicated by the electrometer (E). This is accomplished by closing the switches (H), (I) and (J), and opening the switch connecting the two pairs of quadrants of the electrometer. The potentiometer is then adjusted to deliver an electromotive force which just balances that produced by the streaming cell, the null-point being indicated by the light beam reflected from the electrometer onto scale (Z). When so balanced the streaming-potential is equal to the potentiometer reading. Replicate determinations are made by streaming the liquid through the diaphragm at different hydrostatic pressures.

Determination of Specific Electrical Conductivity across Diaphragm.—The streaming-cell is disconnected from the potentiometric apparatus and thrown into circuit with Wheatstone bridge and standard resistance units by reversing the switch (I). The resistance across the diaphragm is then measured with the liquid streaming through it under a hydrostatic pressure of fifty mm. of mercury. To obtain the diaphragm constant (cell constant) the liquid is displaced from the diaphragm by a standard Kohlrausch solution[13] containing 1,000.0 g. water and 7.4931 g. potassium chloride. The specific electrical conductivity across the diaphragm is, of course, calculated from the observed resistance and the diaphragm constant.

Calculation of ζ-Potential.—The numerical value for ζ-potential in electrostatic units is calculated from the formula, $\zeta = \frac{4\pi\eta HK_s}{P\epsilon}$, by converting all of the values into c.g.s. units. Since one c.g.s. electrostatic unit is equal to 299.86 absolute volts, or 9×10^{11} absolute ohm-centimeters, and the density of mercury is 13.6, and the force of gravity is 981 dynes; the constants in the above formula are evaluated to give the simplified expression:

$$\zeta = 847{,}648{,}450 \times \frac{\eta}{\epsilon} \cdot \frac{H\,K_s}{P},$$

Where, η = the coefficient of viscosity of the liquid,
ϵ = the dielectric constant of the liquid
H = the observed difference in electrical potential across the diaphragm in volts.
K_s = the specific electrical conductivity across the diaphragm in ohms^{-1}
P = the difference in hydrostatic pressure on the two sides of the diaphragm in centimeters of mercury

In calculating the value for ζ in the present investigations the coefficient of viscosity η, and the dielectric constant ϵ were taken as 0.01 and 81.0 respectively. These are the approximate values for water at ordinary laboratory temperatures. Although the liquids used in the streaming-potential experiments were very dilute solutions of hydrochloric acid and sodium hydroxide containing 0.001 g. of protein per liter, their viscosity and dielectric properties were probably not very different of those of pure water.

Preparation of Experimental Materials.—(a) *Conductivity Water.*—Redistilled water collected from a condenser at a temperature not lower than 74°C. was aerated for twenty-four hours with a stream of CO_2-free air. The latter was supplied from an absorption tower specially constructed for the purpose. The air was first bubbled through a solution of sulphuric acid, then through a bead tower containing a twenty-five per cent solution of sodium hydroxide, and finally through pure water. The conductivity water used in all experiments, having been redistilled and aerated the day previous, was

---

[13] International Critical Tables, 6, p. 230 (1929).

stored in ten litre bottles provided with a syphon tube and soda-lime trap as shown in diagram B, Fig. 1. Its specific electrical conductivity in the porous diaphragms was from 0.5 to 1 × 10^{-6} ohms^{-1}

(b) *Absolute Ethanol.*—Commercial ninety-five per cent ethyl alcohol was refluxed with an excess of calcium oxide for twenty-four hours, distilled over and collected in the absence of atmospheric moisture.

(c) *Standard Solutions of Hydrochloric Acid and Sodium Hydroxide.*—Since it was desired to study the electrokinetic properties of the proteins in as simple chemical environments as possible, extremely dilute unbuffered solutions of hydrochloric acid and sodium hydroxide were used in determining the isoelectric point of the proteins adsorbed on the porous diaphragms. The unbuffered solutions offered some difficulties in this connection. The preliminary experiments showed that conductivity water absorbs CO_2 from the air with great avidity. The streaming-potential of an unproteinized porous diaphragm, for example, was changed as much as 900 millivolts by the CO_2 absorbed in filling a 250 ml. flask.

This difficulty was finally overcome by excluding CO_2 from the apparatus and by preparing the standard solutions in a current of CO_2-free air. By use of the apparatus shown in diagram B, Fig. 1, the 250 ml. volumetric flask is swept free from CO_2 by a current of CO_2-free compressed air. About 200 ml. of conductivity water is then run into the flask from the storage bottle above. With the CO_2-free air still bubbling through the water in the flask a volume of protein sol containing 0.00025 g. of protein and a sufficient 0.001 N. HCl or 0.001 N. NaOH to make a standard solution of the desired concentration are added and the solution made up to volume. Throughout these operations the flask is kept free from CO_2 by a current of CO_2-free air. Similar precautions are taken when transferring the streaming-cell from one flask to another. Tube (D) in Fig. 2 is connected to the source of CO_2-free compressed air, and any traces of CO_2 which may have diffused into the neck of the flask in transferring the streaming-cell is swept back through the soda-lime trap (O). Tube (D) is closed before detaching from source of CO_2-free air.

Several attempts were made to determine the hydrogen-ion concentration of the standard solutions after completing the streaming-potential measurements, but consistent results could not be obtained on account of CO_2 absorbed in transferring them from the apparatus to the hydrogen-electrode vessels.

(d) *Extraction of Protein from Wheat Gluten with Aqueous Solutions of Ethanol.*—Approximately two kilograms of patent flour were made into a pliable dough and allowed to stand under water for an hour. The starch was then removed from the gluten by washing in a stream of tap water, tests being made at intervals for the presence of starch in water squeezed from the gluten mass. When free from starch as indicated by the iodine test, the gluten was washed for another thirty minutes in a small stream of distilled water to remove as far as practicable any remaining traces of starch or other dispersable substances. The gluten was then squeezed as dry as possible and three samples of approximately twenty grams each weighed onto watch glasses and placed in a vacuum oven at 96°C. for moisture determinations. The remaining gluten was then weighed out into twenty-five gram portions, torn into small fragments and dropped into 250 ml. of the solvent to be used as an extractive. Water and aqueous solutions of ethanol of various concentrations were used as solvents. As soon as the gluten was added to the liquid the centrifuge bottle was tightly stoppered and placed in a motor-driven shaking machine. Each preparation was shaken for three hours at room temperature (24.5°C), centrifuged for ten minutes, and the supernatant liquid decanted into 100 ml. flasks. The nitrogen content of each extract was determined by the usual Kjeldahl method and its protein concentration calculated, using 5.66 as the nitrogen factor. From the protein content, the volume of each extract to be used in preparing standard acid and alkali solutions containing 0.001 g. protein per litre was calculated.

Data

(a) *Solubility of Gluten Proteins in Aqueous Solutions of Ethanol of Various Concentrations.*—The protein content and concentrations of ethanol in the sols prepared as described above are given in Table I, and presented graphically in Fig. 4. In the second column of the table is given the concentration of the ethanol solution to which the wet gluten was added. The gluten contained 65.2 per cent of moisture, hence 16.3 g. of water was con-

TABLE I

Protein extracted from Wheat Gluten by Aqueous Solutions of Ethanol of Various Concentrations

(25.0 g. wet gluten and 100.0 ml. ethanol solution)

Sample Number	Concentration of ethanol solution before adding wet gluten	Concentration of ethanol solution after adding wet gluten*	Nitrogen per litre of extract	Protein per litre of extract (N × 5.66)
	per cent	per cent	grams	grams
1	0.00	0.00	0.221	1.251
2	10.00	8.60	0.255	1.443
3	20.00	17.20	0.270	1.528
4	30.00	25.79	0.336	1.902
5	40.00	34.39	1.019	5.767
6	50.00	42.99	1.596	9.033
7	60.00	51.59	1.909	10.805
8	70.00	60.19	1.923	10.887
9	80.00	68.79	1.627	9.209
10	90.00	77.39	0.379	2.145
11	99.96	85.98	0.097	0.549

* Values based on assumption that the water contained in the wet gluten fragments was in equilibrium with the solution bathing them.

tained in the 25.0 g. portions of wet gluten added to each 100 ml. of solvent. Assuming that the water contained in the wet gluten fragments was in equilibrium with the solution bathing them during the extraction process, the true concentrations of the various protein sols are as given in the third column of the table. It is not known, of course, how closely the system approached equilibrium in the three-hour extraction period; however, the values given are probably fairly close to the true concentrations.

(b) *Adsorption of Protein on Porous Diaphragm of Filter Crucibles.*—The method of determining the ζ-potential and isoelectric point of proteins is based upon the assumption that the porous diaphragm of a filter crucible adsorbs protein from solution and thus behaves as though it were composed of the protein. To test the validity of this assumption, streaming-potential measurements were made on the same diaphragm using standard solutions of various hydrogen-ion concentration both with and without protein. The ζ-potential and isoelectric point of the unproteinized diaphragm are given in Table II, while corresponding values for the same diaphragm with an adsorbed film of protein are given in Table III and shown graphically in Fig.3. In Table IV is given the isoelectric point of the proteins extracted from wheat

TABLE II

Isoelectric Point and ζ-Potential of the Solid-Liquid Interface of Porous Diaphragm A in Relation to Hydrogen-Ion Concentration

Solution streamed through diaphragm	pH	Pressure in mm. Hg.	E.M.F. in millivolts	$K \times 10^{-6}$ in ohms^{-1}	ζ-Potential in millvolts
Water	—	209	−1586.0	1.3325	−10.58
0.000004N. HCl	5.40	208	−1476.3	1.6315	−12.12
0.000008N. HCl	5.10	208	− 399.1	2.5529	− 5.13
0.000012N. HCl	4.93	208	+ 84.7	4.1763	+ 1.78
0.000016N. HCl	4.80	208	+ 212.3	5.8885	+ 6.29
0.000020N. HCl	4.71	208	+ 218.9	7.6686	+ 8.44
0.000024N. HCl	4.63	208	+ 192.6	9.7968	+ 9.49
0.000032N. HCl	4.50	208	+ 170.8	13.2506	+11.39
0.000040N. HCl	4.41	208	+ 134.3	18.1295	+12.25
0.000004N. NaOH	8.60	209	− 746.7	1.6806	− 6.28
0.000008N. NaOH	8.90	209	− 520.8	2.3144	− 6.03
0.000012N. NaOH	9.07	209	− 363.9	3.1470	− 5.73
0.000016N. NaOH	9.20	209	− 299.7	4.2019	− 6.33
0.000020N. NaOH	9.29	209	− 249.8	5.0911	− 6.37
0.000024N. NaOH	9.37	209	− 188.4	6.2645	− 5.91
0.000032N. NaOH	9.50	209	− 146.4	8.2878	− 6.11
0.000040N. NaOH	9.59	209	− 99.7	10.5065	− 5.24

Isoelectric Point of Porous Diaphragm A = C_H 0.1084 × 10^{-4} = pH 4.9648

TABLE III

Isoelectric Point and ζ-Potential of Protein-Liquid Interface in Relation to Hydrogen-Ion Concentration. Protein extracted from Wheat Gluten with an Aqueous Solution of 60.19 per cent Ethanol adsorbed on Diaphragm A.

Solution* streamed through diaphragm	$C_H \times 10^{-6}$	pH	Pressure in mm. Hg.	E.M.F. in millivolts	$K \times 10^{-6}$ in ohms^{-1}	ζ-Potential in millivolts
0.0000004N. HCl	0.4946	6.31	138.3	−1598.2	0.8345	−10.09
"	"	"	128.1	−1490.1	"	−10.16
"	"	"	118.9	−1373.7	"	−10.09
					Average =	−10.11
0.0000008N. HCl	0.8832	6.05	186.3	−1581.0	0.8715	−7.74
"	"	"	176.1	−1490.8	"	−7.72
"	"	"	165.8	−1391.8	"	−7.66
					Average =	−7.71
0.0000012N. HCl	1.225	5.89	244.4	−1608.8	0.8905	−6.13
"	"	"	234.4	−1540.3	"	−6.12
"	"	"	224.3	−1479.9	"	−6.15
					Average =	−6.13
0.0000016N. HCl	1.666	5.78	282.3	−1427.7	0.9097	−4.81
"	"	"	272.2	−1375.1	"	−4.81
"	"	"	262.1	−1323.0	"	−4.80
					Average =	−4.81
0.0000020N. HCl	2.058	5.69	302.8	−1041.6	0.9293	−3.34
"	"	"	292.7	−1010.1	"	−3.36
"	"	"	283.6	− 976.4	"	−3.35
					Average =	−3.35
0.0000030N. HCl	3.037	5.52	303.0	− 137.1	1.0320	−0.49
"	"	"	292.8	− 132.8	"	−0.49
"	"	"	283.7	− 128.0	"	−0.49
					Average =	−0.49

TABLE III (Continued)

Solution* streamed through diaphragm	$C_H \times 10^{-6}$	pH	Pressure in mm. Hg.	E.M.F. in millivolts	$K \times 10^{-6}$ in ohms^{-1}	ζ-Potential in millivolts
0.0000040N. HCl	4.016	5.40	303.4	+ 494.7	1.1673	+1.99
" "	"	"	293.2	+ 475.8	"	+1.98
" "	"	"	284.1	+ 460.7	"	+1.98
					Average =	+1.98
0.0000050N. HCl	4.995	5.30	303.2	+ 891.0	1.3020	+4.00
" "	"	"	293.1	+ 869.1	"	+4.04
" "	"	"	283.8	+ 835.0	"	+4.01
					Average =	+4.02
0.0000060N. HCl	5.974	5.22	303.5	+1034.3	1.4862	+5.30
" "	"	"	293.4	+1001.0	"	+5.31
" "	"	"	284.2	+ 971.2	"	+5.31
					Average =	+5.31
0.0000070N. HCl	6.953	5.16	303.2	+1039.3	1.7518	+6.28
" "	"	"	293.1	+1005.2	"	+6.29
" "	"	"	284.0	+ 973.1	"	+6.28
					Average =	+6.28
0.0000080N. HCl	7.932	5.10	303.4	+1048.3	2.1165	+7.65
" "	"	"	293.3	+1012.7	"	+7.65
" "	"	"	284.1	+ 972.5	"	+7.58
					Average =	+7.62
0.0000100N. HCl	9.890	5.00	303.1	+1052.1	2.7934	+10.15
" "	"	"	293.1	+1020.5	"	+10.18
" "	"	"	284.0	+ 992.7	"	+10.22
					Average =	+10.18

Isoelectric point of protein adsorbed on diaphragm

$A = C_H\ 0.3231 \times 10^{-5} = \text{pH}\ 5.4907$

* 0.09 ml. of protein extact (0.001 g. protein and 0.0542 ml. ethanol) was contained in each litre of solution streamed through diaphragm.

TABLE IV

Isoelectric Point of Porous Diaphragm and of Eight Different Samples of Protein adsorbed on the Same Diaphragm

Sample Number	Concentration of ethanol used in extracting protein	Isoelectric Point	
		$C_H \times 10^{-6}$	pH
	per cent		
Porous Diaphragm A		10.84000	4.96
Protein adsorbed on Diaphragm A			
1	0.00 (water)	0.01811	7.74
2	8.60	0.02572	7.59
5	34.39	1.85400	5.73
6	42.99	3.18900	5.50
7	51.59	2.52300	5.60
8	60.19	3.23100	5.49
9	68.79	4.57800	5.34
9	68.79	4.47300	5.35

gluten with eight different concentrations of ethanol, the same diaphragm being used in each determination.

(c) *Relative Accuracy of Method as indicated by adsorbing Protein on Different Diaphragms.*—To determine the relative accuracy of the method and thereby ascertain the magnitude of significant difference in the results obtained, replicate experiments were carried out at different times during the progress of the investigation. The results obtained in these experiments are presented in Table V to VIII inclusive. In Table V, VI and VIII are given the results of duplicate determinations on three protein fractions, each of the latter being adsorbed on two different diaphragms. The data presented in Table VII were obtained by adsorbing the same protein on five different diaphragms. While these data show that the ζ-potential of a given protein adsorbed on different diaphragms varies considerably with changes in hydrogen-ion concentrations, the replicate values for the isoelectric point of the different protein fractions agree very satisfactorily.

(d) *Relation of Velocity of Streaming Liquid through Diaphragm to the ζ-Potential of Protein-Liquid Interface.*—It is assumed in the expression, $\zeta = \frac{4\pi\eta\, HK_s}{P\,\epsilon}$, that the electromotive force H is a linear function of the hydrostatic pressure P; and that the value for ζ is independent of the velocity with which the liquid is caused to stream through the capillaries of the diaphragm under the influence of different hydrostatic pressures. To test the validity of this assumption the values for ζ were determined by using pressures of from 10 to 200 mm. Hg. The results are given in Table IX. These data show that, within experimental error, the ζ-potential of a protein-liquid interface is independent of the hydrostatic pressure used in its determination by the streaming-potential method.

TABLE V

Isoelectric Point and ζ-Potential of Protein-Liquid Interface as determined by adsorbing Protein from the Same Sample on Two Different Diaphragms. Protein extracted from Wheat Gluten with an Aqueous Solution of 34.39 per cent Ethanol.

Solution* streamed through diaphragm	pH	Pressure in mm. Hg.	E.M.F. in millivolts	$K \times 10^{-7}$ in ohms^{-1}	ζ-Potential in millivolts
			Diaphragm "A"		
0.0000012N. HCl	5.89	253.7	−1250.5	7.6075	−3.93
0.0000016N. HCl	5.78	292.3	− 747.2	7.7680	−2.08
0.0000020N. HCl	5.69	292.3	+ 658.6	8.0971	+1.91
0.0000030N. HCl	5.52	254.6	+1532.7	8.7525	+5.51

Isoelectric point of protein adsorbed on diaphragm

$$A = C_H\ 0.1854 \times 10^{-6} = \text{pH } 5.7319$$

Solution* streamed through diaphragm	pH	Pressure in mm. Hg.	E.M.F. in millivolts	$K \times 10^{-7}$ in ohms^{-1}	ζ-Potential in millivolts
			Diaphragm "B"		
0.0000012N. HCl	5.89	252.3	−1548.0	7.0178	−4.50
0.0000016N. HCl	5.78	291.3	− 569.5	7.4185	−1.52
0.0000020N. HCl	5.69	291.3	+ 360.2	7.9225	+1.02
0.0000030N. HCl	5.52	194.3	+1513.8	9.1956	+7.49

Isoelectric point of protein adsorbed on diaphragm

$$B = C_H\ 0.1900 \times 10^{-6} = \text{pH } 5.7212$$

* 0.17 ml. of protein extract (0.001 g. protein and 0.0596 ml. ethanol) was contained in each litre of solution streamed through diaphragm.

TABLE VI

Isoelectric Point and ζ-Potential of Protein-Liquid Interface as determined by adsorbing Protein from the Same Sample on Two Different Diaphragms. Protein extracted from Wheat Gluten with an Aqueous Solution of 51.59 per cent Ethanol.

Solution* streamed through diaphragm	pH	Pressure in mm. Hg.	E.M.F. in millivolts	$K \times 10^{-6}$ in ohm^{-1}	ζ-Potential in millivolts
			Diaphragm "A"		
0.0000016N. HCl	5.78	293.3	−1300.6	1.0660	−4.95
0.0000020N. HCl	5.69	292.3	− 514.4	1.1106	−2.04
0.0000030N. HCl	5.52	292.3	+ 556.1	1.1334	+2.25
0.0000040N. HCl	5.40	292.3	+1394.2	1.1804	+5.88

Isoelectric point of protein adsorbed on diaphragm

$$A = C_H\ 0.2523 \times 10^{-6} = \text{pH } 5.5980$$

Solution* streamed through diaphragm	pH	Pressure in mm. Hg.	E.M.F. in millivolts	$K \times 10^{-6}$ in ohm^{-1}	ζ-Potential in millivolts
			Diaphragm "C"		
0.0000016N. HCl	5.78	292.3	−1096.3	0.6744	−2.64
0.0000020N. HCl	5.69	292.3	− 675.4	0.7288	−1.76
0.0000030N. HCl	5.52	293.3	+ 496.8	0.7949	+1.41
0.0000040N. HCl	5.40	174.3	+1413.3	0.8654	+7.34

Isoelectric point of protein adsorbed on diaphragm

$$C = C_H\ 0.2601 \times 10^{-6} = \text{pH } 5.5849$$

* 0.09 ml. of protein extract (0.001 g. protein and 0.0477 ml. ethanol) was contained in each litre of solution streamed through diaphragm.

TABLE VII

Isoelectric Point and ζ-Potential of Protein-Liquid Interface as determined by adsorbing Protein from the Same Sample on Five Different Diaphragms. Protein extracted from Wheat Gluten with an Aqueous Solution of 60.19 per cent Ethanol.

Solution* streamed through diaphragm	pH	Pressure in mm. Hg.	E.M.F. in millivolts	$K \times 10^{-6}$ in ohms^{-1}	ζ-Potential in millivolts
Diaphragm "D"					
0.000002N. HCl	5.69	292.3	−1445.4	0.9411	−4.87
0.000003N. HCl	5.52	291.3	− 233.3	1.0683	−0.89
0.000004N. HCl	5.40	291.3	+ 729.5	1.2088	+3.17
0.000005N. HCl	5.30	292.3	+1233.0	1.3650	+6.02
Isoelectric point of protein adsorbed on diaphragm D = C_H 0.3252 × 10^{-6} = pH 5.4878					
Diaphragm "E"					
0.000002N. HCl	5.69	292.3	−1274.5	0.9441	−4.31
0.000003N. HCl	5.52	292.3	− 227.9	1.0717	−0.87
0.000004N. HCl	5.40	293.0	+ 812.7	1.2127	+3.52
0.000005N. HCl	5.30	291.3	+1454.6	1.3694	+7.16
Isoelectric point of protein adsorbed on diaphragm E = C_H 0.3231 × 10^{-6} = pH 5.4907					
Diaphragm "B"					
0.000002N. HCl	5.69	292.0	−1439.5	0.8892	−4.58
0.000003N. HCl	5.52	291.3	− 284.1	1.0313	−1.05
0.000004N. HCl	5.40	291.3	+ 834.2	1.1670	+3.50
0.000005N. HCl	5.30	292.3	+1367.3	1.3446	+6.58
Isoelectric point of protein adsorbed on diaphragm B = C_H 0.3263 × 10^{-6} = pH 5.4864					
Diaphragm "A"					
0.000002N. HCl	5.69	293.0	−1009.4	0.9293	−3.35
0.000003N. HCl	5.52	293.2	− 132.6	1.0320	−0.49
0.000004N. HCl	5.40	293.6	+ 477.1	1.1673	+1.98
0.000005N. HCl	5.30	293.4	+ 865.0	1.3020	+4.02
Isoelectric point of protein adsorbed on diaphragm A = C_H 0.3231 × 10^{-6} = pH 5.4907					
Diaphragm "F"					
0.000002N. HCl	5.69	292.3	− 952.1	1.1185	−3.81
0.000003N. HCl	5.52	293.0	− 426.2	1.2136	−1.85
0.000004N. HCl	5.40	293.3	+ 149.6	1.3158	+0.70
0.000005N. HCl	5.30	292.0	+ 965.9	1.3975	+4.84
Isoelectric point of protein adsorbed on diaphragm F = C_H 0.3747 × 10^{-6} = pH 5.4263					

* 0.09 ml. of protein extract (0.001 g. protein and 0.0542 ml. ethanol) was contained in each litre of solution streamed through diaphragm.

TABLE VIII

Isoelectric Point and ζ-Potential of Protein-Liquid Interface as determined by adsorbing the Same Sample of Protein on Two Different Diaphragms. Protein extracted from Wheat Gluten with an Aqueous Solution of 68.79 per cent Ethanol.

Solution* streamed through diaphragm	pH	Pressure in mm. Hg.	E.M.F. in millivolts	$K \times 10^{-6}$ in ohm^{-1}	ζ-Potential in millivolts
Diaphragm "A"					
0.000003N. HCl	5.52	294.3	−1294.1	1.0656	−4.90
0.000004N. HCl	5.40	295.3	− 584.5	1.1345	−2.35
0.000005N. HCl	5.30	295.3	+ 406.1	1.2069	+1.74
0.000006N. HCl	5.22	294.3	+ 776.8	1.3915	+3.84
Isoelectric point of protein adsorbed on diaphragm A = C_H 0.4578 × 10^{-5} = pH 5.3393					
Diaphragm "A"					
0.000002N. HCl	5.69	292.3	−1262.2	0.8606	−3.89
0.000003N. HCl	5.52	292.6	− 751.5	0.9361	−2.51
0.000004N. HCl	5.40	292.3	− 288.0	1.0378	−1.07
0.000005N. HCl	5.30	292.0	+ 290.8	1.1722	+1.22
0.000006N. HCl	5.22	293.3	+ 582.5	1.3223	+2.75
Isoelectric point of protein adsorbed on diaphragm A = C_H 0.4473 × 10^{-6} = pH 5.3494					
Diaphragm "B"					
0.000003N. HCl	5.52	293.3	−1547.8	1.1977	−6.61
0.000004N. HCl	5.40	293.3	− 677.0	1.2751	−3.08
0.000005N. HCl	5.30	294.3	+ 249.3	1.3846	+1.23
0.000006N. HCl	5.22	294.3	+ 739.4	1.5639	+4.11
Isoelectric point of protein adsorbed on diaphragm B = C_H 0.4716 × 10^{-5} = pH. 5.3264					

* 0.11 ml. of protein extract (0.001 g. protein and 0.0757 ml. ethanol) was contained in each litre of solution streamed through diaphragm.

(e) *Isoelectric Point of Proteins extracted from Wheat Gluten in Aqueous Solutions of Ethanol of Various Concentrations.*—The isoelectric point of each of the protein fractions extracted from wheat gluten was determined by the streaming-potential method. Standard solutions of hydrochloric acid and sodium hydroxide, whose hydrogen-ion concentrations were within the range of the isoelectric point of the different protein preparations, were used as the streaming liquid. Triplicate measurements were made at different

TABLE IX

Relation of Velocity of Streaming Liquid* through Diaphragm to ζ-Potential. Protein extracted from Wheat Gluten with 68.79 per cent Ethanol adsorbed on Diaphragm B.**

Pressure in mm. Hg.	E.M.F. in millivolts	ζ-Potential in millivolts
9.9	− 89.3	−6.98
16.9	− 132.1	−6.04
24.0	− 198.3	−6.39
31.2	− 251.0	−6.22
38.2	− 295.7	−5.99
45.2	− 351.9	−6.02
52.3	− 414.7	−6.13
66.6	− 522.8	−6.07
80.7	− 632.5	−6.06
94.8	− 739.9	−6.04
108.9	− 851.7	−6.05
123.1	− 964.0	−6.06
137.0	−1075.1	−6.07
151.9	−1188.2	−6.05
170.8	−1344.7	−6.09
189.5	−1490.3	−6.08
199.4	−1567.2	−6.08

* 0.0000012N. HCl containing 0.001 g. protein per litre streamed through diaphragm.

** $K_{\text{Diaphragm B}} = 7.390734 \times 10^{-7}$.

hydrostatic pressures, the average values of which are given in Table X. The quantities of protein extract added to the standard solutions in making them up to contain 0.001 g. protein per litre are given at the end of the table. Obviously, all of the solutions, excepting those used in the measurements on the proteins extracted with water, contain small amounts of ethanol. The quantity of the latter added in the protein sol varied from 0.06 ml. for that of the 8.60 per cent ethanol sol to 1.56 ml. for the 85.98 per cent sol. The influence of these small quantities of ethanol was investigated experimentally and was found to be negligible. The isoelectric point of the proteins extracted from wheat gluten with water and with aqueous solutions of ethanol of various concentrations are summarized in Table XI.

Discussion

That the porous diaphragms of filter crucibles adsorb proteins from solution and thus take on their properties is indicated by the experimental data given in Tables II, III and IV and in Fig. 3. In these studies, the isoelectric point of an unproteinized diaphragm was pH 4.96. When allowed to adsorb different proteins its isoelectric point varied from pH 5.34 for the fraction extracted from wheat gluten with 68.79 per cent ethanol to pH 7.74 for that extracted with water. Biuret tests also indicated the presence of a protein

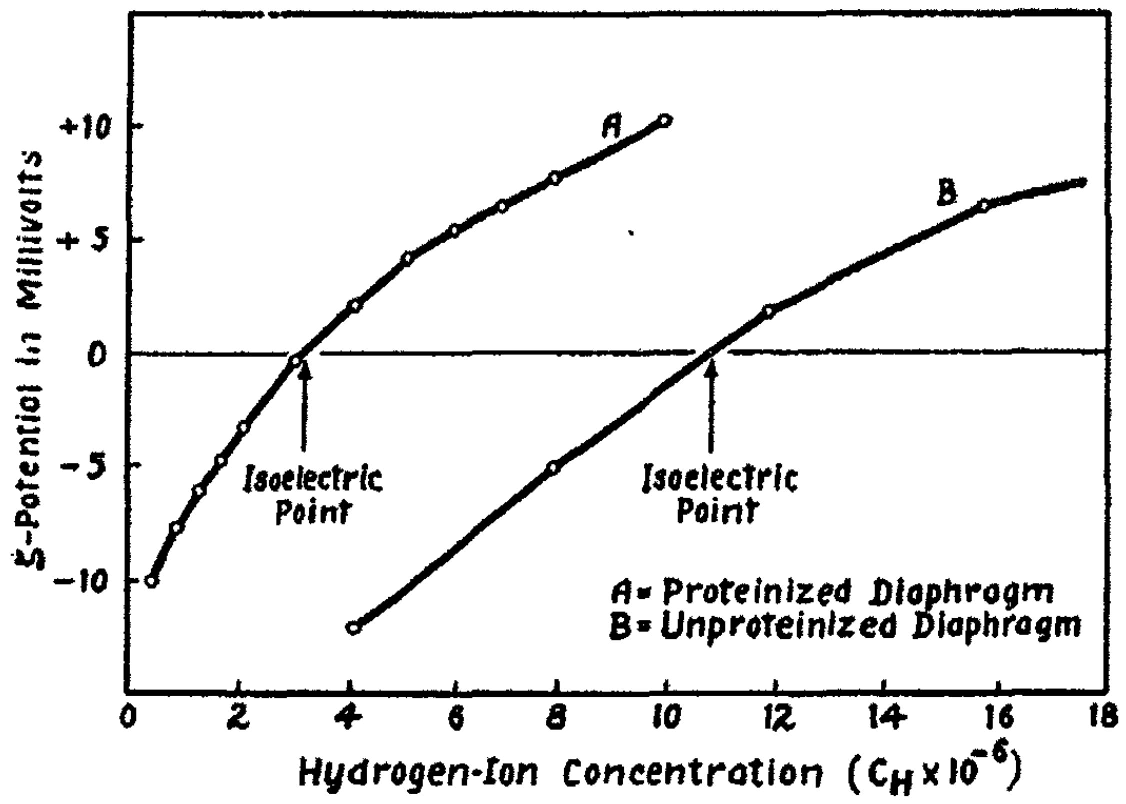


FIG. 3

Showing effect of adsorbed protein on the isoelectric point of porous diaphragm of filter crucible

TABLE X

Isoelectric Point and ζ-Potential of Proteins extracted from Wheat Gluten with Aqueous Solutions of Ethanol of Various Concentrations

Solution* streamed through diaphragm	pH	Pressure in mm. Hg.	E.M.F. in millivolts	$K \times 10^{-6}$ in ohms^{-1}	ζ-Potential in millivolts
Protein extracted with Water,[1] Diaphragm "A"					
0.0000004N. HCl	6.31	234.0	+1551.5	0.749291	+5.20
0.0000002N. HCl	6.53	292.3	+1559.8	0.716854	+4.00
0.0000002N. NaOH	7.47	292.3	+ 481.3	0.716854	+1.23
0.0000004N. NaOH	7.69	292.7	+ 139.2	0.749291	+0.37
0.0000006N. NaOH	7.84	293.3	− 222.1	0.782741	−0.62
0.0000008N. NaOH	7.95	292.3	− 636.5	0.799861	−1.82
0.0000012N. NaOH	8.07	274.3	−1548.2	0.834924	−4.93

Isoelectric point of protein adsorbed on diaphragm

$A = C_H\,0.1811 \times 10^{-7} = \text{pH } 7.7421$

TABLE X (Continued)

Solution* streamed through diaphragm	pH	Pressure in mm. Hg.	E.M.F. in millivolts	$K \times 10^{-6}$ in ohms^{-1}	ζ-Potential in millivolts
Protein extracted with 8.60 per cent Ethanol,[2] Diaphragm "A"					
0.0000002N. HCl	6.53	292.3	+1402.5	0.808347	+4.06
0.0000002N. NaOH	7.47	292.3	+ 212.1	0.826371	+0.63
0.0000004N. NaOH	7.69	291.3	− 142.7	0.844673	−0.43
0.0000006N. NaOH	7.84	293.3	− 515.0	0.863262	−1.59
0.0000008N. NaOH	7.95	291.3	− 970.1	0.882144	−3.07
Isoelectric point of protein adsorbed on diaphragm A = C_H 0.2572 × 10^{-7} = pH 7.5897					
Protein extracted with 17.20 per cent Ethanol,[3] Diaphragm "C"					
0.00000040N. HCl	6.31	292.3	+1447.9	0.846692	+4.39
0.00000020N. HCl	6.53	291.3	+ 751.4	0.828345	+2.23
0.00000012N. HCl	6.66	292.3	+ 422.5	0.810279	+1.22
0.00000012N. NaOH	7.34	292.3	+ 178.5	0.810279	+0.52
0.00000020N. NaOH	7.47	291.3	− 599.4	0.828345	−1.78
0.00000040N. NaOH	7.69	292.0	−1460.9	0.846692	−4.43
Isoelectric point of protein adsorbed on diaphragm C = C_H 0.4296 × 10^{-7} = pH 7.3069					
Protein extracted with 25.79 per cent Ethanol,[4] Diaphragm "B"					
0.00000040N. HCl	6.31	292.6	+ 865.8	0.846607	+2.62
0.00000030N. HCl	6.40	292.3	+ 465.5	0.828262	+1.38
0.00000020N. HCl	6.53	293.3	+ 180.9	0.810198	+0.52
0.00000012N. HCl	6.66	292.3	− 46.5	0.799491	−0.13
0.00000012N. NaOH	7.34	293.3	− 667.3	0.810198	−1.93
Isoelectric point of protein adsorbed on diaphragm B = C_H 0.2336 × 10^{-6} = pH 6.6315					
Protein extracted with 34.39 per cent Ethanol,[5] Diaphragm "B"					
0.0000012N. HCl	5.89	252.3	−1548.0	0.701778	−4.50
0.0000016N. HCl	5.78	291.3	− 569.5	0.741854	−1.52
0.0000020N. HCl	5.69	291.3	+ 360.2	0.792252	+1.02
0.0000030N. HCl	5.52	194.3	+1513.8	0.919565	+7.49
Isoelectric point of protein adsorbed on diaphragm B = C_H 0.1900 × 10^{-5} = pH 5.7212					

TABLE X (Continued)

Solution* streamed through diaphragm	pH	Pressure in mm. Hg.	E.M.F. in millivolts	K × 10^{-6} in ohms^{-1}	ζ-Potential in millivolts
Protein extracted with 42.99 per cent Ethanol,[6] Diaphragm "A"					
0.0000016N. HCl	5.78	215.0	−1459.3	0.894328	−6.35
0.0000020N. HCl	5.69	292.0	−1556.7	0.932548	−5.20
0.0000030N. HCl	5.52	292.3	− 259.3	1.050744	−0.98
0.0000040N. HCl	5.40	291.3	+1220.0	1.215798	+5.33
0.0000050N. HCl	5.30	215.0	+1484.0	1.343966	+9.71
Isoelectric point of protein adsorbed on diaphragm $A = C_H\ 0.3189 \times 10^{-5} = \text{pH } 5.4963$					
Protein extracted with 51.59 per cent Ethanol,[7] Diaphragm "C"					
0.0000016N. HCl	5.78	292.3	−1096.3	0.674411	−2.64
0.0000020N. HCl	5.69	292.3	− 675.4	0.728820	−1.76
0.0000030N. HCl	5.52	293.3	+ 496.8	0.794926	+1.41
0.0000040N. HCl	5.40	174.3	+1413.3	0.865367	+7.34
Isoelectric point of protein adsorbed on diaphragm $C = C_H\ 0.2601 \times 10^{-5} = \text{pH } 5.5849$					
Protein extracted with 60.19 per cent Ethanol,[8] Diaphragm "E"					
0.0000020N. HCl	5.69	292.3	−1274.5	0.944117	−4.31
0.0000030N. HCl	5.52	292.3	− 227.9	1.071700	−0.87
0.0000040N. HCl	5.40	293.0	+ 812.7	1.212713	+3.52
0.0000050N. HCl	5.30	291.3	+1454.6	1.369394	+7.16
Isoelectric point of protein adsorbed on diaphragm $E = C_H\ 0.3231 \times 10^{-5} = \text{pH } 5.4907$					
Protein extracted with 68.79 per cent Ethanol,[9] Diaphragm "A"					
0.0000030N. HCl	5.52	294.3	−1294.1	1.065596	−4.90
0.0000040N. HCl	5.40	295.3	− 584.5	1.134478	−2.35
0.0000050N. HCl	5.30	295.3	+ 406.1	1.206922	+1.74
0.0000060N. HCl	5.22	294.3	+ 776.8	1.391467	+3.84
Isoelectric point of protein adsorbed on diaphragm $A = C_H\ 0.4578 \times 10^{-5} = \text{pH } 5.3393$					
Protein extracted with 77.39 per cent Ethanol,[10] Diaphragm "B"					
0.0000020N. HCl	5.69	255.0	−1453.7	1.111247	−6.63
0.0000040N. HCl	5.40	293.3	− 842.1	1.288844	−3.87
0.0000060N. HCl	5.22	294.3	− 258.3	1.458429	−1.35
0.0000070N. HCl	5.16	294.3	− 95.1	1.614012	−0.54
0.0000080N. HCl	5.10	295.3	− 30.7	1.820649	−0.20
0.0000090N. HCl	5.05	295.3	+ 29.8	2.043168	+0.21
0.0000100N. HCl	5.00	295.3	+ 135.8	2.353292	+1.14
Isoelectric point of protein adsorbed on diaphragm $B = C_H\ 0.8379 \times 10^{-5} = \text{pH } 5.0768$					

TABLE X (Continued)

Solution* streamed through diaphragm	pH	Pressure in mm. Hg.	E.M.F. in millivolts	$K \times 10^{-4}$ in ohms^{-1}	ζ-Potential in millivolts
Protein extracted with 85.98 per cent Ethanol,[11] Diaphragm "C"					
0.0000080N. HCl	5.10	293.3	− 580.8	2.187717	−4.53
0.0000090N. HCl	5.05	293.3	− 298.9	2.597914	−2.77
0.0000100N. HCl	5.00	293.3	− 144.2	2.946888	−1.51
0.0000110N. HCl	4.96	293.3	− 102.2	3.210431	−1.17
0.0000120N. HCl	4.92	294.5	− 58.5	3.778785	−0.78
0.0000160N. HCl	4.80	295.3	− 13.1	5.336257	−0.25
0.0000180N. HCl	4.75	295.3	− 1.9	6.122217	−0.04
0.0000200N. HCl	4.71	295.3	+ 7.4	7.051482	+0.19
0.0000240N. HCl	4.63	295.3	+ 18.2	7.905565	+0.51

Isoelectric point of protein adsorbed on diaphragm

$$C = C_H\ 0.1806 \times 10^{-4} = \text{pH } 4.7433$$

* Sufficient protein extract was added to the solutions streamed through diaphragm to give a concentration of 0.001 g. protein per litre. The volume of protein extract and ethanol per litre of streaming liquid were as follows:

[1] 0.80 ml. protein extract containing 0.001 g. protein and no ethanol.

[2] 0.69 ml. protein extract containing 0.001 g. protein and 0.0593 ml. ethanol.

[3] 0.65 ml. protein extract containing 0.001 g. protein and 0.1118 ml. ethanol.

[4] 0.52 ml. protein extract containing 0.001 g. protein and 0.1341 ml. ethanol.

[5] 0.17 ml. protein extract containing 0.001 g. protein and 0.0596 ml. ethanol.

[6] 0.11 ml. protein extract containing 0.001 g. protein and 0.0473 ml. ethanol.

[7] 0.09 ml. protein extract containing 0.001 g. protein and 0.0477 ml. ethanol.

[8] 0.09 ml. protein extract containing 0.001 g. protein and 0.0542 ml. ethanol.

[9] 0.11 ml. protein extract containing 0.001 g. protein and 0.0757 ml. ethanol.

[10] 0.47 ml. protein extract containing 0.001 g. protein and 0.3637 ml. ethanol.

[11] 1.82 ml. protein extract containing 0.001 g. protein and 1.5648 ml. ethanol.

film on the diaphragms. Gentle heating caused charring, further indicating that the latter had adsorbed appreciable quantities of organic matter. While this experimental evidence supports the assumption that the porous diaphragms of filter crucibles adsorb proteins from solution and thus behave as though they were composed of protein, it does not preclude the possibility of different proteins being preferentially adsorbed. Obviously, if two or more proteins were present in the solutions used, the one reducing the interfacial tension most would be preferentially adsorbed at the diaphragm-liquid interface. If the sols studied in these experiments were mixtures of proteins differing from each other with respect to this property, the ζ-potential values obtained represent only the specific proteins adsorbed on the diaphragms, and not those of the entire sol. From this viewpoint the isoelectric values of the adsorbed proteins are representative of the entire sol only if the latter is chemically pure; or if composed of a mixture, the proteins are adsorbed on the diaphragm in the same proportions as they occurred in the sol. In the present work, the protein sols studied were probably heterogeneous mixtures of different proteins; or perhaps the same protein in different states in equilibrium. Inasmuch as the various fractions differed very widely in their properties under the same environmental conditions, they may be regarded as different compounds.

The relative accuracy of the method is indicated by the replicate values obtained for the isoelectric point of four different protein fractions given in Tables V to VIII inclusive, and summarized in Table XI. With the exception of two out of a total of eleven determinations, the values agreed to within pH 0.013, the variations between the values for the two exceptions being 0.023 and 0.065.

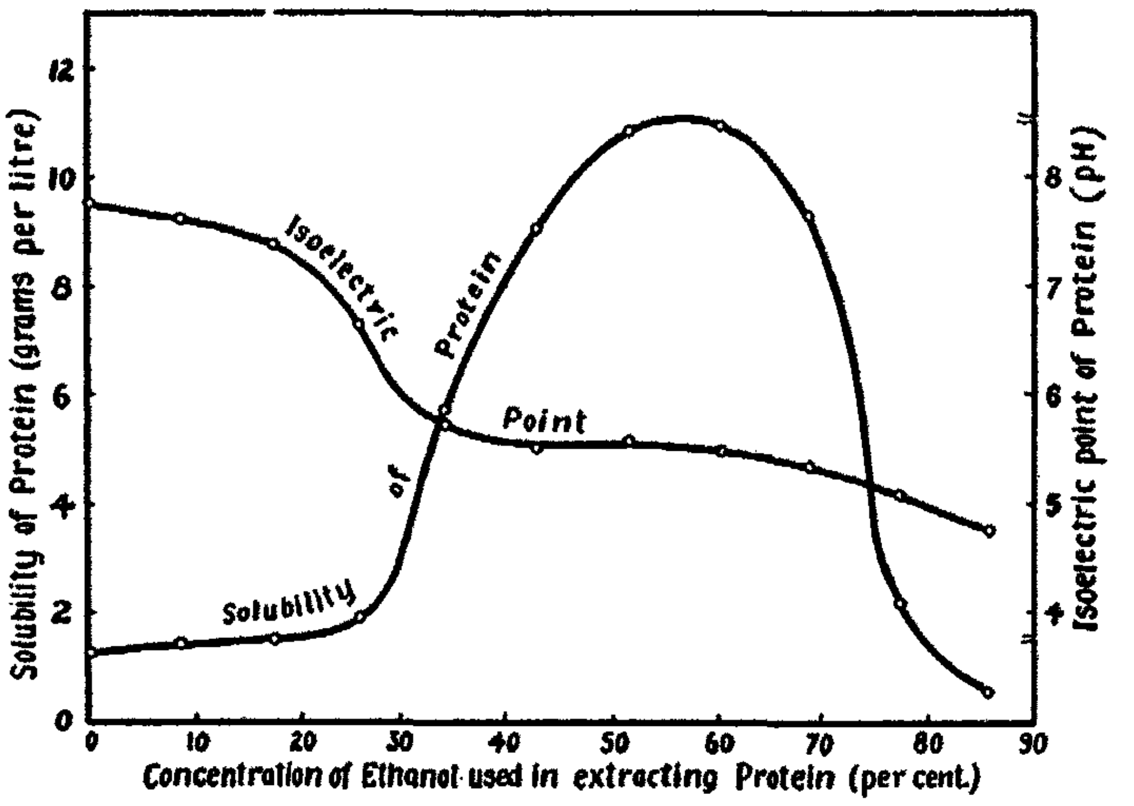


FIG. 4

Showing the quantity and the relative isoelectric point of the proteins extracted from wheat gluten in ethanol solutions of various concentrations.

The quantities of proteins extracted from wheat gluten in ethanol solutions of various concentrations with their corresponding isoelectric values are summarized in Table XII and Fig. 4. These data show that the relative isoelectric point of the alcohol-soluble proteins of wheat varies with the concentration of the solvent used in their extraction. It is fairly constant, being approximately pH 5.5 for those fractions extracted with solutions containing from forty to seventy per cent ethanol by volume. The relative isoelectric point was on the alkaline side of neutrality for the protein fractions extracted with solutions containing less than twenty per cent of ethanol, while it was decidedly more acid than pH 5.5 for those soluble in solutions more concentrated than seventy per cent of ethanol by volume.

TABLE XI

Summary of Values for the Isoelectric Point of Protein extracted with Aqueous Solutions of Ethanol

Sample Number	Concentration of ethanol used in extracting protein	Diaphragm	Isoelectric Point	
			$C_H \times 10^{-6}$	pH
	per cent			
1	0.00	A	0.01811	7.742
2	8.60	A	0.02572	7.590
3	17.20	C	0.04296	7.367
4	25.79	B	0.23360	6.631
5	34.39	A	1.85400	5.732
5	34.39	B	1.90000	5.722
		Average =	1.87700	5.726
6	42.99	A	3.18900	5.496
7	51.59	A	2.52300	5.598
7	51.59	C	2.60100	5.585
		Average =	2.56200	5.591
8	60.19	D	3.25200	5.488
8	60.19	E	3.23100	5.491
8	60.19	B	3.26300	5.486
8	60.19	A	3.23100	5.491
8	60.19	F	3.74700	5.426
		Average =	3.34500	5.476
9	68.79	A	4.57800	5.339
9	68.79	A	4.47300	5.349
9	68.79	B	4.71600	5.326
		Average =	4.58900	5.338
10	77.39	B	8.37900	5.077
11	85.98	C	18.06000	4.743

TABLE XII

Relation of Isoelectric Point to Solubility of Protein
in Aqueous Solutions of Ethanol

Sample Number	Concentration of ethanol used in extracting protein	Protein in solution	Isoelectric Point	
			$C_H \times 10^{-6}$	pH
	per cent	g. per l.		
1	0.00	1.251	0.01811	7.74
2	8.60	1.443	0.02572	7.59
3	17.20	1.528	0.04296	7.37
4	25.79	1.902	0.23360	6.63
5	34.39	5.767	1.87700	5.73
6	42.99	9.033	3.18900	5.50
7	51.59	10.805	2.56200	5.59
8	60.19	10.887	3.34500	5.48
9	68.79	9.209	4.58900	5.34
10	77.39	2.145	8.37900	5.08
11	85.98	0.549	18.06000	4.74

Sinice each litre of standard solution used in the streaming-potential determinatons contained 0.001 g. protein, which was in chemical equilibrium with the ions of acid or alkali present, the actual hydrogen-ion concentrations were not as represented by the normality values. In reality the pH values were greater for the acid and less for the alkaline solutions. The isoelectric points for the various proteins fractions given in the foregoing tables are, therefore, to be regarded as relative and not as absolute values. With these facts in mind, the data may be interpreted as showing that either the various protein fractions possessed different isoelectric points; or, that they differed in their acid and base binding capacities. In either case the data obtained show that the properties of the alcohol-soluble proteins of wheat gluten vary with the concentration of the solvent used in their extraction.

Summary

A practical streaming-potential method has been devised for determining the ζ-potential of a protein-liquid interface in unbuffered solutions by adsorbing the protein on the porous diaphragms of filter crucibles. The data support the following conclusions:

1. Proteins are readily adsorbed by the porous diaphragms of filter crucibles, thus giving to the latter their electrokinetic properties.

2. The results obtained by adsorbing the same protein on five different diaphragms showed that comparable values could be obtained with different diaphragms.

3. That the ζ-potential of a protein-liquid interface is independent of hydrostatic pressure was shown by streaming-potential measurements, using pressures from 10 to 200 mm. Hg.

4. The alcohol-soluble proteins of wheat gluten showed a maximum solubility in solutions containing approximately fifty-seven per cent of ethanol by volume. The values obtained were for the sols in equilibrium with the gluten and do not represent complete extraction.

5. The *relative* isoelectric point of the proteinaceous material extracted from wheat gluten in aqueous solutions of ethanol varies with the concentration of the latter. A fairly constant value was obtained for the isoelectric point for the proteins extracted in solutions containing from fifty to seventy per cent of ethanol by volume.

Acknowledgment

The writer wishes to express his hearty appreciation to Professor Edmund Burke, Head of the Department of Chemistry, University of Montana, Agricultural Experiment Station, for his unfailing interest and encouragement during the progress of these studies.

STUDIES ON GLASS

VI. Some Specific Heat Data on Boron Trioxide

BY S. BENSON THOMAS[1] AND GEORGE S. PARKS

In previous publications[2] heat-capacity data over a range of temperatures have been presented for a number of organic materials in both the glassy and liquid states. In these studies the specific heat curves for the glass and liquid were found to differ greatly. Moreover, between the two states there invariably existed a characteristic transition interval of 8° to 25°, depending upon the complexity of the glass-forming material. Within this interval the specific heat in every case underwent a rapid increase of 60% to 100%, altho the general character of the change and its sharpness, as measured on the temperature scale, were found to depend to some extent upon the previous heat treatment of the glass-forming material as well as upon the rapidity with which this transition interval was transversed in the course of the measurements.

The question then arises as to whether inorganic glasses also exhibit these phenomena. The purely qualitative observations of Tool and Valasek[3] indicate that they do. Also certain results of White[4] for silicate glasses might be interpreted as consistent with these phenomena, altho White's data, obtained over intervals of 100° by the "dropping method," are in themselves hardly sufficient for the drawing of definite conclusions. Accordingly the present study of the specific heats of boron trioxide was undertaken in order to throw further light upon this question.

Boron trioxide was chosen for several reasons. In the first place, as a glass-forming material it possesses a very simple empirical formula and is readily obtained in a state of purity. Then again it forms an extremely stable glass, which shows practically no tendency to crystallize. Equally important is the fact that this glass "softens" between 200° and 300° C.; hence specific heat measurements need not be carried to as high temperatures as with most silicate glasses.

Method and Apparatus

The problem of finding a suitable method and apparatus for the present study at first presented some difficulties. The method of mixtures, commonly employed for the measurement of specific heats at such temperatures (i.e., 30° to 400° C.), was obviously undesirable here, since it does not permit of a

---

[1] Holder of a fellowship on the Charles S. Coffin Foundation during the scholastic year 1929-1930; holder of the Shell Research Fellowship at Stanford during the scholastic year 1930-1931. We hereby wish to acknowledge the generous aid afforded by these fellowships in the present investigation.

[2] Parks and Huffman: J. Phys. Chem., 31, 1842 (1927); Parks, Huffman and Cattoir: 32, 1366 (1928); Parks, Thomas and Gilkey: 34, 2028 (1930); and Huffman, Parks and Thomas: J. Am. Chem. Soc., 52, 3241 (1930).

[3] Tool and Valasek: Bur. Standards Sci. Paper, 15, 537 (1919).

[4] White: Am. J. Sci., 47, 1 (1919).

series of determinations carried out on the same sample in a continuous manner. Moreover, it is not readily adaptable to the determination of a rapidly changing and irregular specific heat curve. On the other hand, the Nernst method, involving the measurement of "true" or instantaneous specific heats with an aneroid calorimeter, had proved extremely satisfactory in the preceding studies on organic materials at lower temperatures; and accordingly we finally developed a modification of it for use in the present investigation.

The two chief objections to the use of the Nernst method at these higher temperatures are (1) the difficulty encountered in insulating the heating coil which must be in good thermal contact with the aneroid calorimeter and (2) the inconveniently large cooling and heating corrections due to the large heat exchanges between the jacket and calorimeter at temperatures much above that of the room. In the present case we really took advantage of this second point to avoid the first difficulty. In brief, we utilized the large rate of heat exchange between calorimeter and jacket as a means of heating (or cooling, as the case might be) our calorimeter and thus dispensed with electrical heating. The apparatus as finally developed might be termed a "radiation calorimeter." In its development we profited greatly by the paper of Steiner and Johnston,[1] altho our apparatus differs considerably from theirs.

The principle of our calorimetric method is very simple. If a calorimeter is suspended in air within a jacket maintained at a small, constant, temperature difference with respect to the calorimeter, the rate of heat exchange between the calorimeter and its surrounding jacket at any instant is a function of the two temperatures involved. Thus according to Newton's law of cooling,

$$q = K_T(T_J - T_C) \qquad (1)$$

where q is the number of calories flowing to the calorimeter from the jacket per minute, T_J and T_C are the respective temperatures of the jacket and calorimeter and K_T is the constant for Newton's law of cooling. It should be noted here that K_T, while a constant at any particular temperature, increases considerably with increase in temperature. We may also write the equation,

$$q = C_p \frac{dT_C}{dt} \qquad (2)$$

where C_p is the heat capacity of the calorimeter and contents, and dT_C/dt is the rate of change of the calorimeter temperature per minute. Combining equations 1 and 2, we then obtain

$$C_p \frac{dT_C}{dt} = K_T\,(T_J - T_C) \qquad (3)$$

If now the rate dT_C/dt is first measured when the calorimeter is filled with a material of known heat capacity (in this case metallic copper), the constant K_T may be readily evaluated for a range of calorimeter temperatures. Then, in turn, the heat capacity of the calorimeter and a second substance (in this

---

[1] Steiner and Johnston: J. Phys. Chem., 32, 912 (1928). In this connection the reader is also referred to White's paper on "Calorimetry in Furnaces," J. Phys. Chem., 34, 1121 (1930) which appeared after the present method was developed.

case boron trioxide) may be determined by measuring the corresponding value of dT_C/dt, when the calorimeter is filled with this substance. As the heat capacity of the calorimeter itself is known, the specific heat of the second substance can be easily calculated. Heats of fusion and of transition also may be determined by this method by simply multiplying the time required for their completion by the predetermined rate of heat transfer for the temperature involved. Thus,

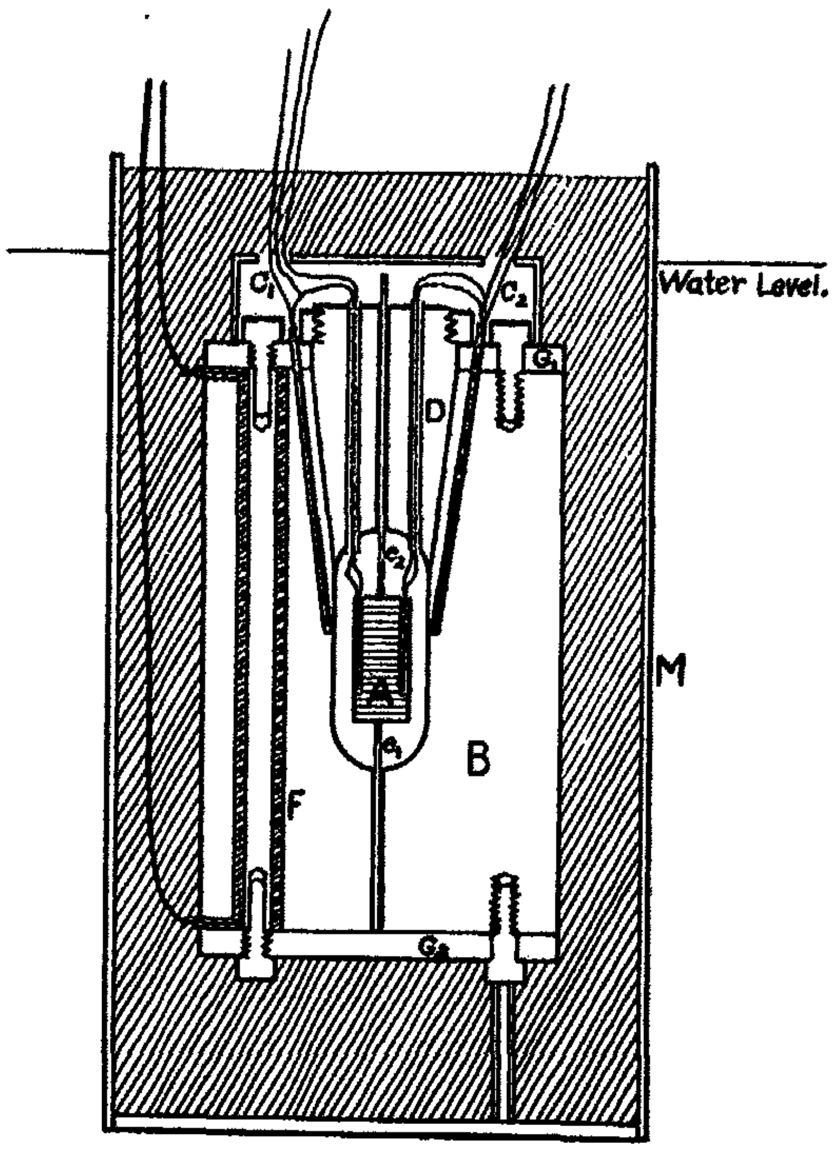


Fig. 1
A Cross-section of the "Radiation" Calorimeter System.

$$\Delta H = K_T (T_J - T_C)t \tag{4},$$

where ΔH is the heat of fusion, or of transition, of the amount of substance in the calorimeter and t is the time required for the completion of the melting or transition process.

A cross section of our apparatus designed to operate on the principles outlined in the preceding paragraphs is shown in Fig. 1. A calorimeter, A, is centrally suspended within a heavy copper block, B, by means of two small glass tubes, e_1 and e_2. The calorimeter (capacity about 15 cc) is constructed of silver tubing, 2.2 cm outside diameter and 4.4. cm. long, having a wall thickness of 0.05 cm. The ends are also of silver 0.05 cm. in thickness. In the measurements on poor thermal conductors, such as boron trioxide, twelve to fifteen perforated silver disks 0.02 cm. in thickness are equally spaced within the tube to promote thermal equilibrium throughout the calorimeter. Two light nickel tubes of 0.24 cm. inside diameter, placed in direct contact with the side wall and sealed into the top, serve as thermocouple wells. The chromel-alumel thermocouple, C_2, with one junction imbedded in the first tube and the other junction in the copper jacket, is used for temperature control (to be described later), while the platinum-platinrhodium thermocouple, C_1, in the second tube is used for measuring the temperature (T_C) of the calorimeter and the thermal head ($T_J - T_C$). The exterior of the calorimeter is polished and the interior cavity of the copper block is heavily silver-plated so as to preserve a constant surface and cut down radiation to a minimum, since it is desirable to effect the heat transfer largely by conduction thru the air space because radiant heat transfer varies considerably with the temperature.

The copper block, B, was made from a piece of 3½ inch rolled copper rod 22 inches long, which was hammered to approximately the final dimensions. The hammered copper was then turned to a diameter of 12.7 cm. and a length of 20.3 cm. The cavity containing the calorimeter was machined out of the block. It has a diameter of 3.5 cm. and a total length of 8.6 cm. This chamber is closed by a copper plug, D, ground to fit the block. The plug is drilled to accommodate the glass support, c_2, and four small alundum tubes thru which the thermocouple wires are led. Imbedded in the copper block are nine alundum, threaded furnace cores, F, each wound with 3.8 meter of No. 25 nichrome IV resistance wire and plastered over with alundum cement. The heating coils are connected together in series of three, the three groups being connected in parallel. Copper rods are cemented in the center of the heating coils in order to further improve the heat transfer. Copper plates, G_1 and G_2, cover both ends of the block and provide for heat transfer between the rods and the block.

The copper block is mounted within a heavy brass can, M, 20 cm. in diameter and 35 cm. high. The intervening space is packed with silocel insulating powder. The various electrical lead wires are led out of the can thru 1.6 cm. copper tubes. The can is immersed in a 120-liter water bath in order to keep its temperature approximately constant.

In order to maintain a given temperature difference between the calorimeter and its surrounding block, use was made of a photoelectric system similar to that employed by Southard and Andrews[1] for the regulation of a low temperature thermostat. The regulation of the temperature difference depends upon maintaining a constant electromotive force in the differential thermocouple, C_2, one junction of which is in contact with the wall of the calorimeter and the second is imbedded in the copper block. This electromotive force is balanced across a potentiometer set to correspond to the desired temperature difference. The thermocouple and potentiometer are

---

[1] Southard and Andrews: J. Franklin Inst., 207, 323 (1929). For further information concerning the use of photoelectric cells the reader is referred to the following papers: Styer and Vedder: Ind. Eng. Chem., 22, 1062; McMaster: 1070 (1930).

connected in series with a high sensitivity Leeds and Northrup galvanometer. When the temperature difference varies from that corresponding to the electromotive force set on the potentiometer, the galvanometer is deflected. This deflection of the galvanometer mirror causes an image of a projection-lantern lamp with concentrated filament to be reflected off from a General Electric PJ-23 photoelectric cell, placed 2 meters from the galvanometer. The operation of this cell then causes relays to actuate which appropriately change the resistance in series with the heating coils and so bring the temperature of the block back to its proper relationship with respect to the calorimeter. The sensitivity of the galvanometer is such that a difference of one degree causes a deflection of 50 cm. at a distance of two meters. With this arrangement the maximum deviation from a definite, predetermined difference is always less than 0.02° under actual operating conditions. The various electrical circuits used in controlling the temperature of the block are schematically shown in Fig. 2.

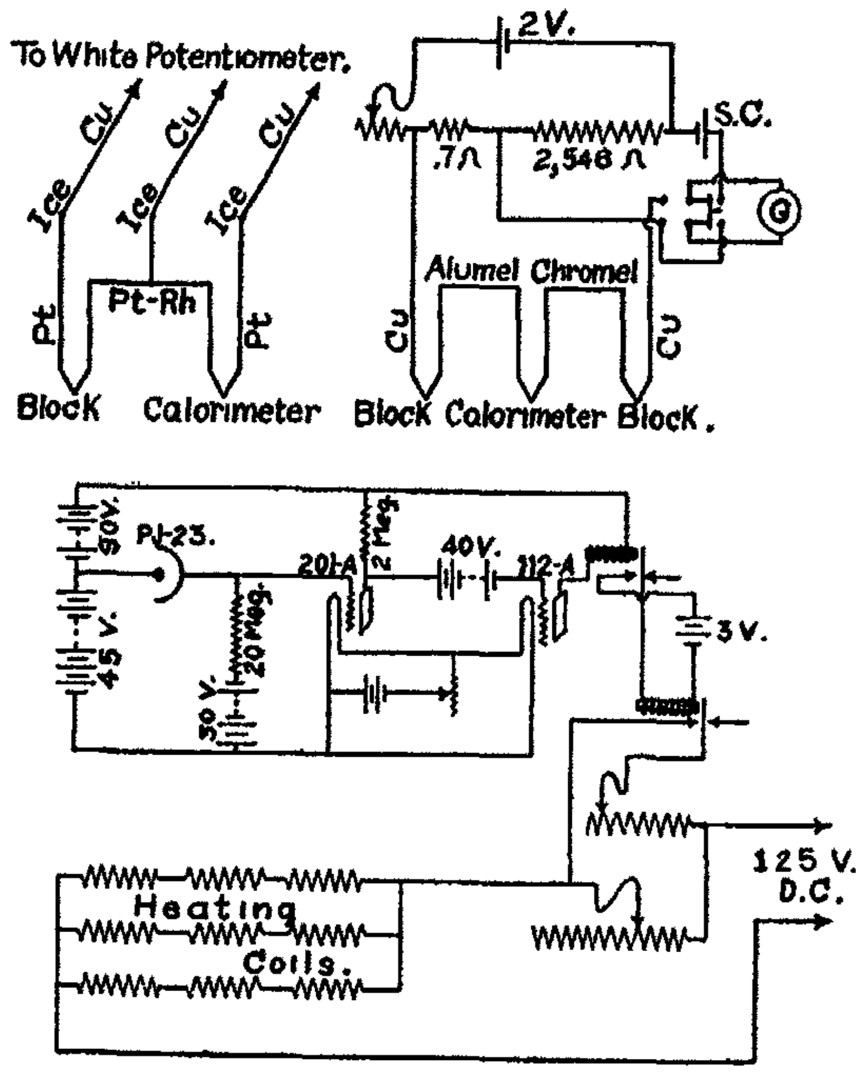


FIG. 2
Temperature-Control Circuits

Tho this photoelectric system serves admirably in maintaining a temperature difference which is almost constant throughout a moderate temperature range, small variations due to thermoelectric inequalities in the chromel-alumel thermocouple are encountered when working over a range of several hundred degrees. The repeated "setting up" of the calorimeter causes further variations in the thermocouple e.m.f. due to unavoidable bending of the wires. For these reasons the actual temperature measurements are made by the platinum-platinrhodium thermocouple system (diagramed in the upper left-hand section of Fig. 2) in conjunction with a White double potentiometer and a sensitive galvanometer, since the platinum-platinrhodium couple has been found to remain more constant thermoelectrically than the chromel-alumel couple. By this noble-metal system[1] the temperature of the calorimeter (T_C), the temperature difference ($T_J - T_C$) and the temperature of the jacket (T_J) may be readily measured at regular time intervals. Also from these readings the values of dT_C/dt may be easily computed. During our studies these two platinum-platinrhodium thermocouples were frequently checked against each other. The method of checking consisted of measuring the electromotive forces of the two thermocouples when the calorimeter and jacket are at the same temperature, this condition being determined by observing the point at which the temperature of the calorimeter remained constant.

The empty calorimeter when fitted with 14 silver disks, as in the measurements on the boron trioxide, weighed 23.6 gm. Its heat capacity was readily calculated from the specific heat values of silver and nickel as given in the International Critical Tables,[2] and varied from 1.61 cal. at 0° to 1.84 cal. at 400°C. In the evaluation of the constant K_T of equation 3, these disks were removed and a copper cylinder (weight, 96.3 gms.), machined to fit within the calorimeter, was inserted in their stead. The heat capacity of this copper cylinder was calculated by use of the following equation, suggested by Maier,[3] for the atomic heat of copper as a function of the Centigrade temperature:

$$C_p = 4.89 + 0.00336T - 0.00000067T^2$$

As calculated in this manner the total heat capacity of the silver calorimeter and copper cylinder varied from about 10.0 cal. at 0° to 11.9 cal. at 400° C. In obtaining the results for boron trioxide, which are given in the next section, a 18.05 gm. sample was sealed into the calorimeter. Under these conditions the total heat capacity of the calorimeter and contents was found to be 6.1 cal. at 100° and 9.7 cal. at 350°C.

With the apparatus as described we were usually able to obtain specific heat values reproducible to 0.5% or better. Such a degree of concordance is very satisfactory and, we feel, serves to indicate the possibilities in applying this "radiation" calorimeter to measurements at moderately high temperatures. However, there are several possible sources of systematic errors in our measurements and these reduce the reliability of our results in an absolute sense. As a rather conservative estimate, we judge the absolute errors in our specific heats to be within 2% at 100° and 4% at 350°.

---

[1] The temperature scale used is that given in the "International Critical Tables," **1**, 57. Suitable percentage corrections (about 0.25% for our couple) are employed to correct this scale to directly calibrated points.

[2] International Critical Tables, **5**, pp. 92 and 93.

[3] Maier: Reports of Investigations, U. S. Bureau of Mines, Serial 2926, April, 1929.

Heat-Capacity Data

In all we have completed four independent groups of specific heat measurements on boron trioxide. The first two groups each included several series of determinations with a copper calorimeter (instead of the silver calorimeter described in the preceding section) and with a chromel-alumel thermocouple system for measuring the calorimeter temperatures and the thermal head. In the third group this copper calorimeter was then replaced by the silver one, which provided a surface less subject to oxidation and to a consequent change in its emissivity. On the whole these first three groups of measurements must be considered as rather preliminary in character, since the results of successive series of determinations showed more or less of a trend with time, which was finally traced to changes in the thermoelectric value of the chromel-alumel thermocouples employed to measure T_C and the quantity T_J-T_C. However, the general character of these results was such as to indicate in an unmistakable fashion the nature of the curve for the boron trioxide glass and liquid, leaving possibly an uncertainty of 4 to 8% in the absolute magnitude of the specific heat values.

In the fourth group of determinations the chromel-alumel thermocouples were replaced by the platinum-platinrhodium thermocouple system mentioned before, whereupon the trend in the results disappeared. In this group we carried out three entirely distinct and rather complete series of determinations, as well as a number of partial series, which were designed to satisfy us regarding the reproducibility of the values obtained. Accordingly, the results of this last group constitute our final and, we think, our most reliable values. For this reason we shall omit all data obtained in the preceding three groups, since these are merely confirmatory.

The material studied was Merck's C. P. anhydrous boron trioxide, with impurities guaranteed to be less than 0.01%. A sample of this was heated in a platinum crucible for eight hours at about 900° C. in order to drive off the last traces of water. The molten oxide was then poured directly into the silver calorimeter which was maintained at a temperature around 500°. The calorimeter cover was immediately put into place and the contents of the calorimeter were cooled to about 50° C. within a period of half an hour.

The heat capacity of the glass formed by this comparatively rapid cooling process was then measured in a continuous series of determinations, starting at 33° and going up to 345° C. In covering this temperature range the heating process required 14 hours. The experimental values so obtained are given in Table I, where Column 1 shows the mean temperature of each determination, Column 2 the corresponding specific heat in 15°-calories per gram of the boron trioxide and Column 3 the heat capacity at constant pressure per mean gram atom.

As the oxide is really a very viscous liquid above 275°, this sample was next cooled very slowly and regularly down to room temperature in order that we might determine the differences between a glass sample formed by slow cooling and one formed by rapid cooling. This slow cooling process required

TABLE I

The Heat Capacities of Boron Trioxide Glass and Liquid

(Determinations made while heating after the formation of the glass by very rapid cooling)

Temp., °C	C_p per gram	C_p per gram atom	Temp., °C	C_p per gram	C_p per gram atom
33.6	0.214 cal.	2.98 cal.	225.6	0.263 cal.	3.66 cal.
46.3	0.220	3.07	235.5	0.281	3.92
58.6	0.225	3.14	244.3	0.320	4.46
72.3	0.231	3.22	252.3	0.385	5.37
84.0	0.238	3.32	260.5	0.448	6.24
104.9	0.245	3.41	266.4	0.451	6.28
120.9	0.248	3.46	272.2	0.440	6.13
129.5	0.251	3.05	281.1	0.439	6.12
142.9	0.254	3.54	294.5	0.436	6.07
159.3	0.256	3.57	309.2	0.438	6.10
176.1	0.256	3.57	324.5	0.436	6.08
191.1	0.255	3.56	338.1	0.437	6.09
210.4	0.257	3.58	345.3	0.436	6.08
217.1	0.257	3.58			

TABLE II

The Heat Capacities of Boron Trioxide Liquid and Glass

(Determinations made while cooling from the liquid condition)

Temp., °C	C_p per gram	C_p per gram atom	Temp., °C	C_p per gram	C_p per gram atom
332.4	0.437 cal.	6.09 cal.	227.8	0.344 cal.	4.79 cal.
318.5	0.438	6.10	221.0	0.333	4.64
303.3	0.439	6.12	207.6	0.314	4.38
285.2	0.437	6.09	200.8	0.304	4.24
278.3	0.434	6.05	190.4	0.293	4.08
271.4	0.430	5.99	177.4	0.285	3.97
261.4	0.424	5.91	161.8	0.274	3.82
255.3	0.413	5.75	153.9	0.271	3.78
248.9	0.398	5.54	135.0	0.261	3.64
242.6	0.383	5.34	124.8	0.255	3.55
234.3	0.360	5.02	112.6	0.251	3.50

about 18 hours and during it a series of heat capacity determinations was made upon the material by keeping the jacket temperature below the calorimeter temperature by a regulated amount and measuring the rate of cooling of the calorimeter. This procedure illustrates one of the great advantages of our "radiation" calorimeter over one which employs electric heating as in the Nernst method: it is possible to study the heat capacity of a substance during cooling as well as during heating. The heat capacity values obtained in this cooling procedure are given in Table II.

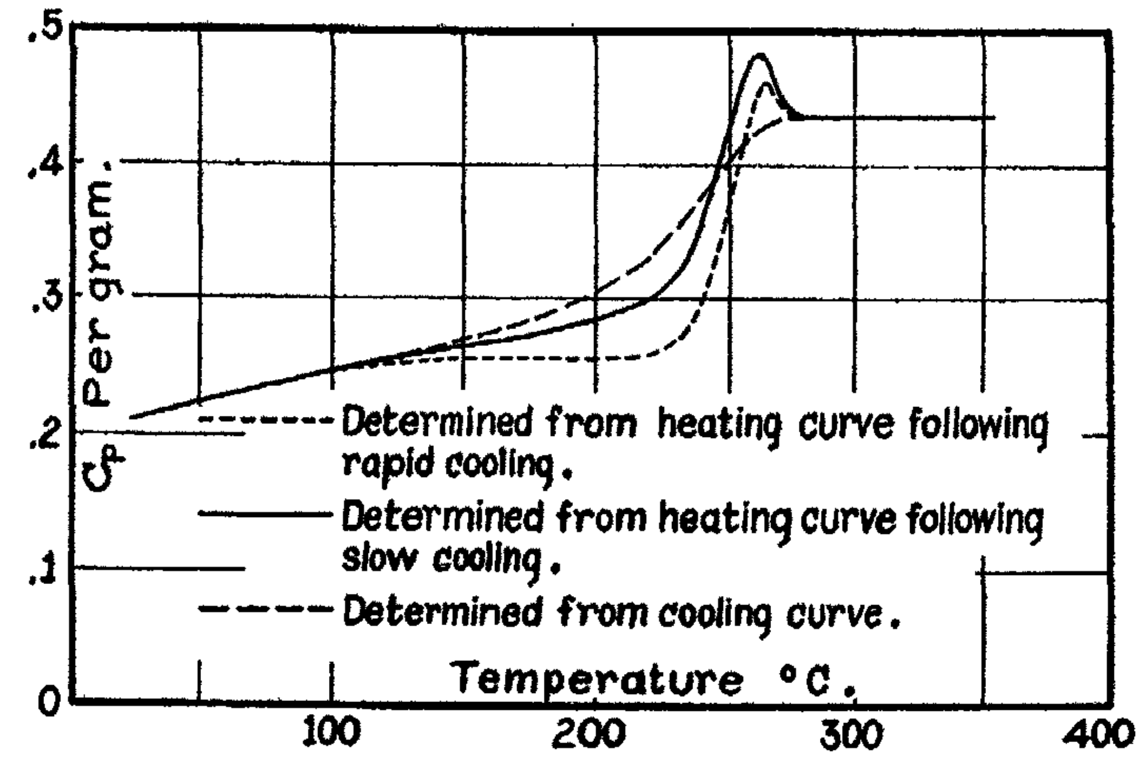


Fig. 3
The Heat-capacity Curves for Boron-trioxide Glass and Liquid.

Table III
The Heat Capacities of Boron Trioxide Glass and Liquid
(Determinations made while heating after the formation of the glass by slow cooling)

Temp., °C	Cp per gram	Cp pergram atom	Temp., °C	Cp per gram	Cp per gram atom
35.3	0.215 cal.	3.00 cal.	223.6	0.308 cal.	4.29 cal.
46.5	0.221	3.08	230.8	0.318	4.43
61.8	0.228	3.18	237.7	0.341	4.75
75.5	0.234	3.26	246.4	0.397	5.53
87.2	0.240	3.35	252.3	0.448	6.24
118.6	0.254	3.54	258.6	0.479	6.67
130.8	0.259	3.61	265.3	0.466	6.49
143.6	0.262	3.65	271.0	0.447	6.23
159.5	0.267	3.72	276.0	0.438	6.10
175.6	0.273	3.80	283.4	0.436	6.07
190.3	0.279	3.89	295.9	0.436	6.07
199.7	0.285	3.97	310.6	0.435	6.06
207.1	0.289	4.03	323.1	0.434	6.05
214.3	0.294	4.10			

A third complete series of determinations (given in Table III) was then made upon this newly formed glass by heating it up gradually from 35° to 325° C. These particular results might, perhaps, be considered as the normal or standard values for a carefully annealed boron trioxide glass.

The three series of determinations are represented graphically in Fig. 3, where the heat capacity (at constant pressure) per gram of boron trioxide has been plotted against the Centigrade temperature. Below 100° and above

280° the three curves practically coincide. On the other hand, in the intervening range they show marked differences, which were also found in the three preliminary groups of determinations.

For comparison with our experimental results the literature[1] contains very few values. Regnault has reported a specific heat value of 0.237 cal. per gram at a mean temperature of 57°; this lies about 4.3% above our curve. Russell by the method of mixtures has obtained a series of three interval specific heats covering the temperature range, $-135°$ to $+40°$. His highest point, 0.217 cal. per gram at a mean temperature of 40° C., falls within 0.1% of our curve. Considering the differences in the experimental methods, these agreements are really very satisfactory. On the other hand, Samsoen and Monval[2] from the results of a discontinuous series of determinations by the method of mixtures believe that the transition between the glassy and liquid states takes place at 218° C. with a heat of transition of 2.3 cal. per gram. They report 0.302 cal. per gram for the specific heat of the glass below 218° and 0.344 cal. per gram for that of the liquid above this point. Our data indicate that this transition is spread over the temperature interval from 220° to 275° and that the specific heat of the glass is steadily increasing with temperature while that of the liquid is practically constant at 0.435 cal. per gram. Thus there are several points of discrepancy between our investigation and that of Samsoen and Monval. We feel, however, that our method, which gives a continuous series of values on the same sample, is far more reliable than theirs.

Discussion of the Curves

In their general form the two heating curves, especially the one made with the annealed boron trioxide glass, are remarkably similar to those which were obtained previously in the studies upon organic glass-forming materials. Thus it is quite evident that the organic and inorganic glasses are essentially the same in character, the former merely showing softening, or the transition into the liquid condition, at a considerably lower temperature.

As suggested in previous papers,[3] the rather sudden increase in heat capacity on changing from the glass to the liquid condition may be explained on the assumption of a great decrease in the magnitude of the interatomic constraints or attractive forces within the material. If we may suppose that these constraints are fairly large within the glass, the resulting mean atomic heat capacity, according to the Einstein or Debye functions, should be much below the limiting value of 3R (i.e. 5.96 calories) at moderate temperatures, as in the present case, altho it should exhibit a marked increase with rising temperatures. On the other hand, a relatively large decrease in these internal constraints throws us at once into the region where Cv approaches

---

[1] Landolt-Börnstein-Roth-Scheel: "Tabellen" 5th Ed., p. 1252 (1923).

[2] Samsoen and Monval: Compt. rend., **182**, 968 (1926).

[3] Huffman, Parks and Thomas: J. Am. Chem. Soc., **52**, 3246 (1930); Parks, Thomas and Gilkey: J. Phys. Chem., **34**, 2032 (1930).

5.96 calories and where Cp, of course, is somewhat larger.[1] In this region (above 280° C in the present case) the heat capacity should exhibit little or no change over rather wide intervals of temperature.

The actual process of loosening up the interatomic constraints[2] within the glass should require energy; and in our opinion this requirement accounts for the very marked maximum or "hump" in the heat capacity curve (corresponding to the data in Table III) of the annealed glass around 260 °C. The excess energy represented by this "hump" thus serves to some extent the same function as the latent heat of fusion in the transformation of a crystalline solid into the liquid state. However, its magnitude is much less than the heat of fusion of a crystalline solid, indicating that probably the strong interatomic constraints in a glass are far less numerous.

In the specific heat curve obtained during the slow cooling process we find evidence of a thermal hysteresis effect. In this case no "hump" appears, altho the energy given up during cooling is clearly equal to that represented in the subsequent heating curve with its hump. Evidently we have here a temperature lag or undercooling effect in the process of tightening up the interatomic constraints, i.e. in the vitrifaction process. This situation is again analogous to the undercooling so frequently observed in a liquid prior to crystallization.

The heating curve for the glass formed initially by very rapid cooling also presents some interesting features. If we are permitted to apply the adjective *stable* to the annealed glass, this particular glass might properly be described as *metastable*. Apparently its formation has been so rapid that the interatomic constraints within it show a wide variety of magnitudes and those of great strength are perhaps much less numerous than in the well annealed product. Accordingly, on heating up this metastable glass to 140° C., marked internal readjustments take place. Strains are to some extent relieved, probably with the evolution of some energy and the production of a larger number of rather strong constraints. These, however, are much less numerous than in the well annealed glass, as evidenced by the relative sizes of the two "humps" involved. In short, the behavior of this metastable glass may well be likened to that of an incompletely crystallized solid. Frequently the latter, on heating up, reaches a temperature at which further crystallization proceeds with the evolution of heat and, possibly, with an apparent decrease in the specific heat. Moreover, if the melting point is reached before crystallization is complete, the heat of fusion (or fusion hump) is found to be less than for a completely crystallized sample of the same substance.

---

[1] We are here assuming that the motions of the component atoms in liquid boron trioxide are primarily vibrational in character as in a crystalline solid. While these vibrations are undoubtedly more or less anharmonic, becoming more so at higher temperatures, the Einstein or Debye heat capacity formulas can probably be applied here as first approximations.

[2] Rosenhain calls this "the rupture of interatomic bonds." We here have borrowed quite freely from the picture and ideas presented by this author in his splendid article on "The Structure and Constitution of Glass," Trans. Soc. Glass Technology, 11, 77 (1927).

Summary

1. A fairly accurate "radiation" calorimeter has been developed for use between room temperature and 500° C.

2. With this apparatus the heat capacities of boron trioxide glass and liquid have been measured between 35° and 350° C. with a probable absolute error of less than 4% and with a reproducibility for comparative purposes of about 0.5%.

3. The heat capacity curves obtained (a) by heating a "metastable" glass, (b) by heating a well annealed glass and (c) by slowly cooling the liquid to produce the annealed glass have been compared and discussed.

Department of Chemistry,
Stanford University, California,
February 2, 1931.

STUDIES ON GLASS

VII. The Conductivities and Dielectric Constants of Glucose and Boron Trioxide Glasses[1]

BY S. BENSON THOMAS[2]

In the preceding papers of this series[3] considerable data have been presented on the physical properties of a number of substances in both the liquid and glassy states. A number of properties, such as specific heat, coefficient of thermal expansion, and dielectric constant, indicate that glasses more closely resemble the crystalline state than the liquid state, from which they are formed by cooling. However, when the logarithm of the viscosity is plotted against temperature a smooth curve showing no evidence of discontinuity between the glassy and liquid states is obtained.[4]

The present investigation is essentially a continuation of previous studies, and was undertaken with the hope that it might serve to extend our knowledge of the glassy state.

Conductivity Measurements

The purpose of this study was to measure the changing conductivity of a number of substances as they are cooled from a temperature at which they are definitely liquids to a temperature at which they are hard glasses. Due to the wide range through which the conductivities vary, it was necessary to use two methods of measurement. The usual A. C. bridge method served for measuring resistances up to about two megohms, but at higher resistances the condenser component of the current was so high that a satisfactory balance could not be obtained and a D. C. ammeter-voltmeter method was employed. By using a high-sensitivity Leeds and Northrup galvanometer as the ammeter, this method was made very satisfactory, since the small current required, 10^{-7} amperes, caused no appreciable polarization if reversed every 20 or 30 seconds.

In measuring high resistances by means of the bridge method an increased sensitivity is obtained by using a bridge of considerable resistance. For this reason a Leeds and Northrup student potentiometer having a slide wire resistance of 100 ohms was used in preference to the usual Kohlrausch bridge of but one ohm resistance. The alternating E. M. F. was supplied by a

---

[1] These studies on glass are being carried on in the Chemical Laboratory of Stanford University under the direction of Professor George S. Parks.

[2] Holder of the Shell Fellowship at Stanford, 1930-31.

[3] Parks and Huffman: J. Phys. Chem., 31, 1842 (1927); Parks, Huffman and Cattoir: J. Phys. Chem., 32, 1366 (1928); Cattoir and Parks: J. Phys. Chem., 33, 879 (1929); Parks and Gilkey: J. Phys. Chem., 33, 1428 (1929); Parks, Thomas and Gilkey: J. Phys. Chem., 34, 2028 (1930); Thomas and Parks: J. Phys. Chem., 35, 2091 (1931).

[4] An extensive, but as yet unpublished, investigation of the viscosity of liquid and glassy glucose has recently been completed in this laboratory. See Master's Theses of Miss Lois Barton, Monroe Spaght, and Wilfred Richardson.

microphone hummer. As standard resistances Leeds and Northrup resistance boxes and calibrated grid leaks were used. Since they are entirely free from inductance and capacity, the latter were found more satisfactory for resistances above 500,000 ohms. The capacity of the cell was balanced out with a variable condenser across the standard resistance units. Three stages of transformer-coupled audio-frequency amplification were used in the output circuit.

The cell used in measuring the conductivities of boron trioxide and sodium borate glasses consisted of two concentric platinum crucibles, the smaller of which had the bottom removed and was suspended within the larger. The suspension was by means of platinum wires attached to alundum rods, the rods being set in notches in the edge of the outer crucible. The cell was mounted in a large iron block lined with alundum cement. This block was equipped with a heating coil and imbedded in silocel so that it served as a rough thermostat. The temperature of the cell was determined by a chromel alumel thermocouple in conjunction with a Leeds and Northrup thermocouple potentiometer. Since the relative positions of the crucible electrodes were subject to small changes, an accurate evaluation of the cell constant was not attempted. The value, however, is constant during each set of determinations and the total variations are probably not over 10%. Therefore, the results are expressed in terms of specific resistances, and are of the correct order of magnitude.

TABLE I

Resistance of a Sodium Borate-Boron Trioxide System Containing 2.4% Sodium Borate

Results obtained using A. C. bridge method

Temp., °C	Specific Resistance	Temp., °C	Specific Resistance
674	3.92×10^4	477	5.92×10^6
660	5.01×10^4	467	8.63×10^6
571	3.16×10^5	448	1.96×10^7
548	5.54×10^5	441	2.83×10^7
522	1.24×10^6	439	3.1×10^7
500	2.39×10^6	408	1.5×10^8
484	4.40×10^6	405	1.7×10^8

Results obtained using D. C. ammeter-voltmeter method

Temp., °C	Specific Resistance	Temp., °C	Specific Resistance
365	2.2×10^9	320	2.9×10^{10}
360	2.8×10^9	311	5.9×10^{10}
352	4.9×10^9	301	9.2×10^{10}
341	9.9×10^9	298	1.1×10^{10}
334	1.7×10^{10}		

The several boron trioxide-sodium borate solutions were formed by heating the mixture in a platinum crucible for several hours at the full heat of a blast lamp. A considerable amount of water was liberated during the first hour of heating but during the latter stages the formation of bubbles in the melt was very slow, indicating that the water had been almost entirely removed.

Table I presents the data obtained for a solution of 2.4% of anhydrous sodium borate in boron trioxide. In Fig. 1 the logarithms of the specific resistances of a number of boron trioxide-sodium borate solutions are plotted against the corresponding temperatures. At the higher temperatures these mixtures are clear, viscous liquids. At the lower temperatures, they are hard, transparent glasses. It is thus evident that insofar as conductivity is concerned the transition between the liquid and what we choose to call the glassy state is gradual and continuous.

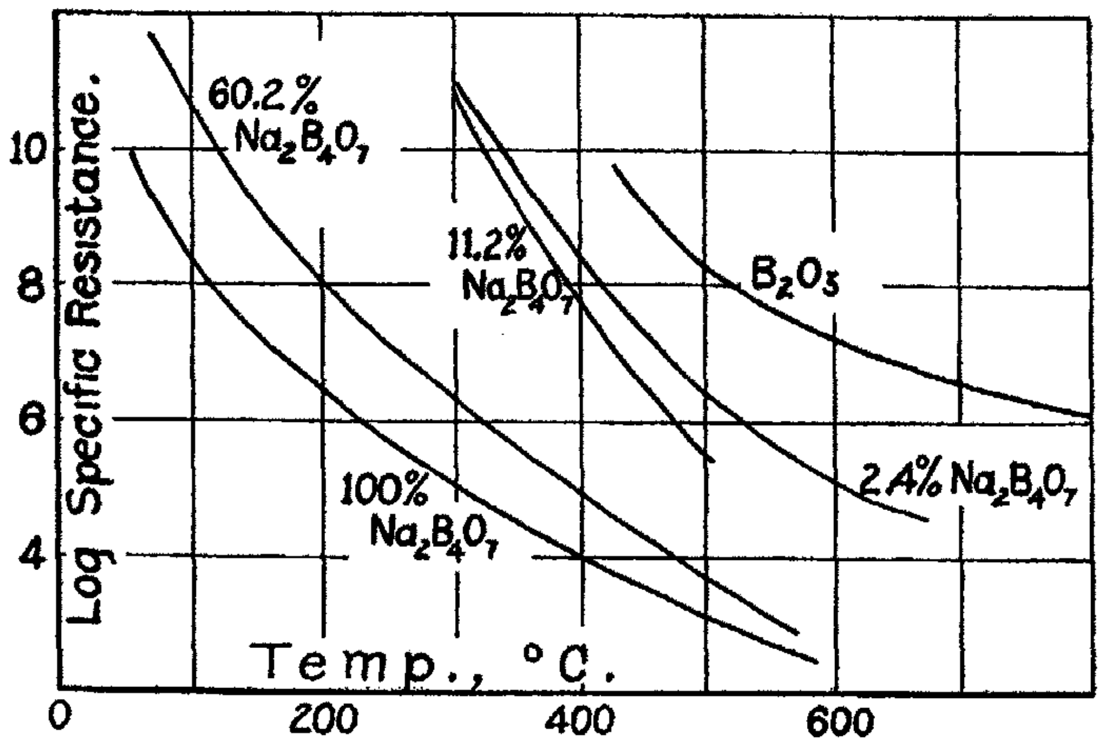


Fig. 1

The Specific Resistances of Several Boron Trioxide-Sodium Borate Systems.

The conductivities of glassy and liquid glucose were measured using the cell previously employed by Cattoir and Parks in measuring the dielectric constants of the same material. The cell consisted of two coaxial copper cylinders hanging vertically in a large pyrex test-tube. The outer copper cylinder had an internal diameter of 2.1 cm. and the inner cylinder an outside diameter of 1.6 cm.; they were both 4.5 cm. in length. The relative positions of these two cylinders were maintained by three small tightly-fitting glass rods placed in the space between them. The cell was introduced into a three-liter Dewar jar filled with transformer oil. Equipped with a stirrer, thermometer and electrical heating coil, it served as a small adjustable thermostat.

Measurements of the resistances of pure glucose and a 1% solution of anhydrous sodium iodide in glucose were made by using the methods previously described. The sodium iodide increases the conductivity considerably above 50° C., but possibly goes out of solution below this temperature, altho there is no visible evidence of such an occurrence. When the logarithm of the resistance is plotted against temperature, a smooth curve is obtained similar to that shown by the boron trioxide and sodium borate glasses, thus supporting the previous statement that electrical conductivity shows only a gradual and uniform transition between the glassy and liquid states.

A marked resemblance is to be noted between the curves obtained by plotting the logarithm of resistance against temperature and the logarithm of viscosity against temperature. If the logarithm of resistance is plotted against the logarithm of viscosity, a curve is obtained that approaches very nearly to straight lines within the temperature intervals 70° C. to 145° C, and 30° C. to 45° C. The gradual change in slope occurring between 45° C. and 70° C. might be ascribed to variations in the dielectric constant which changes rapidly in this region. However, as will be shown later, the dielectric constant is by no means a well defined quantity and an attempt to take it into consideration would appear to be largely empirical.

TABLE II

Resistance of Liquid and Glassy Glucose

Results obtained using A. C. bridge method		Results obtained using D. C. ammeter-voltmeter method	
Temp. °C	Specific Resistance	Temp. °C	Specific Resistance
132	4.2×10^5	78.5	8.7×10^7
129	5.3×10^5	63.7	7.4×10^8
123	5.6×10^5	52.2	8.1×10^9
117	1.23×10^6	42.2	9.0×10^{10}
110	2.03×10^5	32.9	5.8×10^{11}
101.6	4.2×10^6	23.3	3.8×10^{12}
94.3	8.5×10^6		
80.8	4.5×10^7		

Resistance of Liquid and Glassy Glucose containing 1%
Anhydrous Sodium Iodide

Results obtained using A. C. bridge method		Results obtained using D. C. ammeter-voltmeter method	
Temp. °C	Specific Resistance	Temp. °C	Specific Resistance
117	6.3×10^4	68.3	6.8×10^7
111	8.5×10^4	61.8	2.1×10^8
99.0	2.51×10^5	52.5	1.8×10^9
97.0	4.2×10^5	40.0	8.5×10^{10}
86.2	2.00×10^6	38.0	1.4×10^{11}
83.2	3.5×10^6	33.5	4.5×10^{11}
73.0	1.95×10^7	32.7	6.1×10^{11}
68.4	4.4×10^7	26.1	2.4×10^{12}
62.0	1.07×10^8		

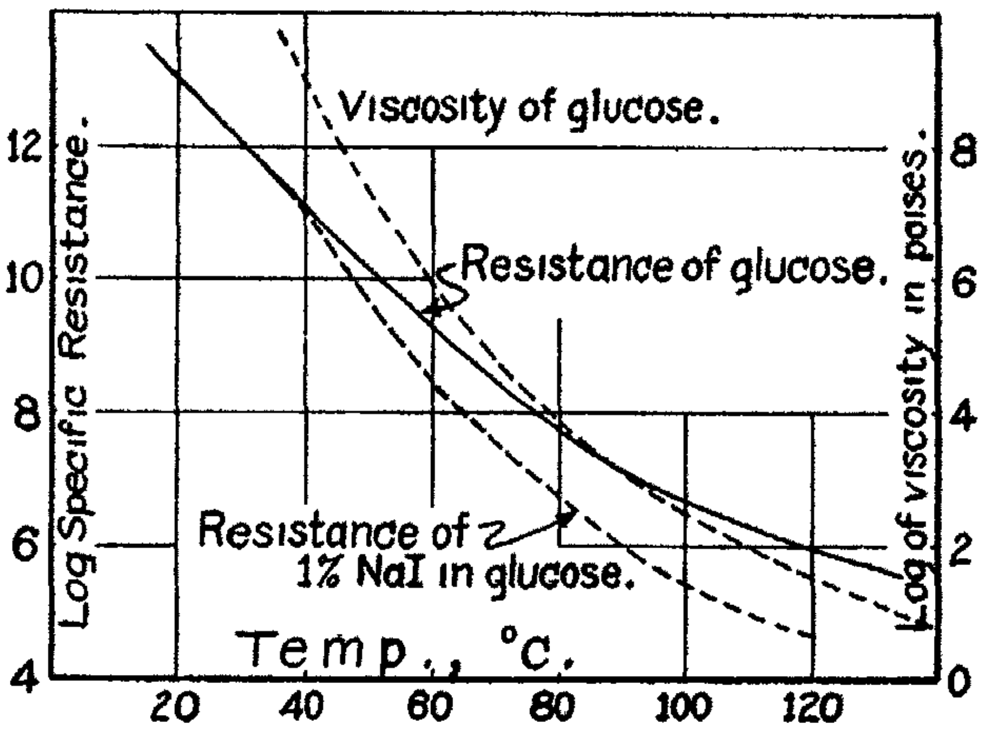


FIG. 2
The Specific Resistance of Liquid and Glassy Glucose, and a 1% Solution of Anhydrous Sodium Iodide in Glucose

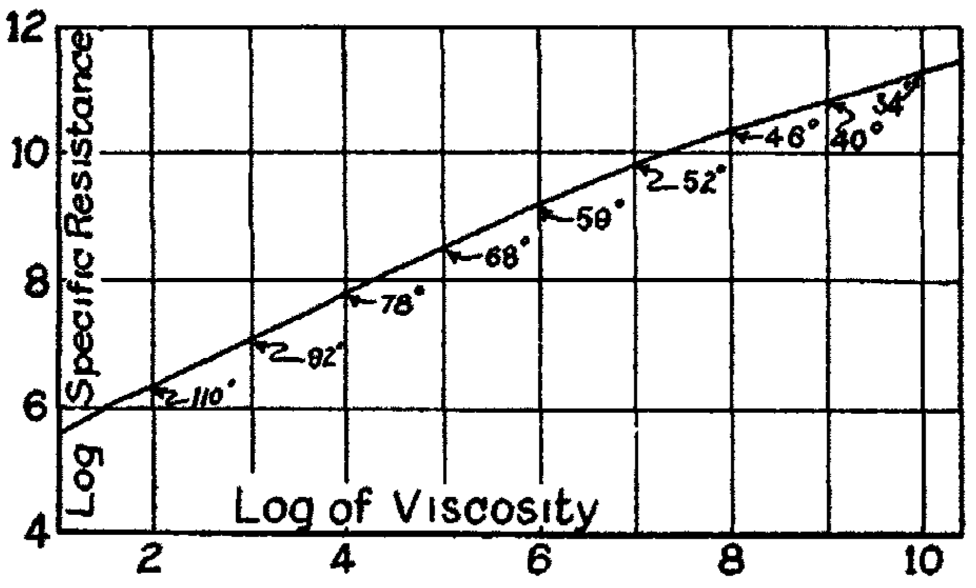


FIG. 3
Relation between the Electrical Resistance and the Viscosity of Liquid and Glassy Glucose.

Dielectric Constants

Cattoir and Parks[1] measured the dielectric constants of glassy and liquid glucose for the temperature range 200° K to 370° K at a frequency of 1000 kilocycles per second. The dielectric constants for glassy glucose were found to vary uniformly from 3.8 at 200° K to 5.4 at 290° K. Between 290° K and 378° K the constant increased rapidly to a value of 23.9, after which it decreased to a value of 21.0 at 423° K. It has been shown by Mizushima[2] and others that this sudden change of dielectric constant is a property of polar

---

[1] Cattoir and Parks: J. Phys. Chem., **33**, 879 (1929).

[2] Mizushima: Institute of Physical and Chemical Research, Tokio, **9**, 209 (1928); Kitchen and Müller: Phys. Rev., (2) **32**, 929 (1928); Bock: Z. Physik, **31**, 534 (1925); Graffunder: Ann. Physik, **70**, 225 (1923).

liquids in general and that the temperature interval in which it occurs is dependent upon the frequency at which the measurements are made. A further investigation of the dielectric constants of glassy and liquid glucose therefore seemed desirable.

An electrical resonance method was used for the determination of the dielectric constants. Two Hartley oscillators were employed as shown in Fig. 4. The construction of these oscillators was such that the inductances were readily replaceable, thus permitting measurements to be made at a number of different frequencies within a few minutes time. Circuit I contains in parallel with the usual inductance and variable capacity a calibrated variable resistance, R, and the dielectric cell, C_x. The cell was used the same as that described in connection with the resistance measurements presented in the first part of this paper. The apparatus was calibrated using liquids of known dielectric constant and quoted as standards in the International Critical Tables.[1] The various frequencies of the oscillators were calculated from the respective values of inductance and capacity, and were checked by comparison with a General Radio wave meter.

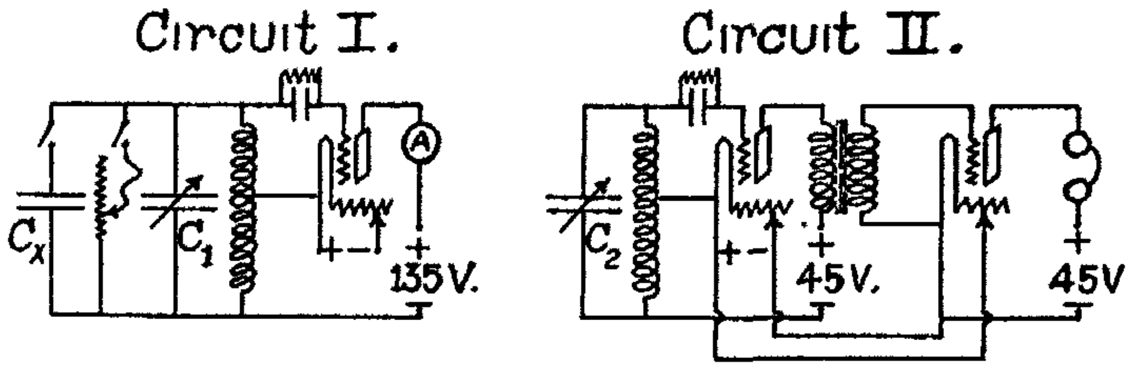


Fig. 4
Schematic Diagram of Oscillator Circuits

The procedure used in making measurements was as follows:

1. The sample was maintained at constant temperature for about fifteen minutes in order to insure thermal equilibrium.

2. The dielectric cell, C_x, being connected and the resistance, R, disconnected, circuit II was tuned to approximately the desired frequency, and circuit I was tuned to resonance. The plate current was then read and recorded.

3. The dielectric cell was disconnected and oscillator I adjusted to an initial setting that was always the same. The resistance, R, was then varied until the plate current was the same as in 2. A final small adjustment of oscillator II was usually necessary to bring it to exact resonance with oscillator I.

4. The resistance, R, was then disconnected and the dielectric cell connected; circuit I was turned to resonance with circuit II and the plate current checked.

5. Matched inductances of a different value were inserted in the oscillators and the process was repeated at the new frequency.

---

[1] International Critical Tables, 6, 82.

Using the last setting of the variable condenser C_1, the dielectric constant of the material may be read directly from the calibration curve. These results are given in Table III and Fig. 5.

Since the plate current of an oscillating vacuum tube is determined by the losses in the oscillating circuit, the resistance, R, must be equivalent to the losses in the dielectric cell. These losses occur as conductivity (which is negligible except at the higher temperatures) and dielectric hysteresis which is due to a lag in the molecular dipole orientation. The latter loss may be regarded as equivalent to a power loss in a resistance, R_x, in parallel with the condenser. Then,

$$\frac{1}{R_X} = \frac{1}{R} - \frac{1}{R_{DC}}$$

where R_{DC} is the direct current resistance of the cell. The conductivity of the hypothetical resistance, R_x, is equal to the dielectric losses of the condenser per unit of applied voltage. The dielectric losses occurring in liquid and glassy glucose at frequencies of 1,300 kilocycles and 2,600 kilocycles have been calculated in terms of specific conductivities which would produce equal losses.

TABLE III

Dielectric Constants of Glassy and Liquid Glucose

Temp. °C	Dielectric Constant			
	2,600 kilocycles	815 kilocycles	160 kilocycles	92 kilocycles
9.0°	5.3	5.3	5.4	5.6
32.2	6.1	6.2	6.7	6.8
50.0	8.3	8.6	9.3	9.5
64.0	11.4	11.8	13.3	14.2
76.0	15.3	16.2	20.1	22.2
84.0	—	19.5	23.5	24.3
97.0	23.0	23.4	24.2	24.2
110.0	—	23.6	23.7	23.9
123.0	—	23.3	23.3	23.5
140.0	—	22.5	—	—

The dielectric constants of abietic acid and boron trioxide were found to have the low values of 3.0 and 3.5, respectively. The values changed but slightly with temperature and frequency. The more polar sodium borate showed effects similar to those shown by glucose but the comparatively high conductivity prevented the complete investigation of this material with the present apparatus.

The Debye theory[1] explains the anomalous effects exhibited by the dielectric constants of polar molecules by assuming that the dielectric properties of a polar molecule depend upon:

1. An electric moment formed by the shifting of the electrons relative to the positive nucleus due to the influence of an external electric field.

---

[1] Debye: "Handbuch der Radiologie," 6, p. 597 (1925).

2. The ability of the polar molecule to orient itself when under the influence of an electric field.

Assuming the dipole moment to be constant, the ability of the molecule to orient itself will be determined by the restricting forces of other molecules, the frequency of the applied field, and the thermal agitation of the molecule which tends to break down any orientation produced.

Considering only liquid or glassy materials it may be assumed that the restricting forces acting on the molecule are a function of the viscosity. At low temperatures where the viscosity is high the molecular orientation is negligible and the dielectric properties are due almost entirely to the electron displacements. Since the natural vibration periods of the electrons are extremely high, they readily shift with the applied field and the dielectric constant is independent of temperature and of all ordinary frequencies. As the temperature is raised a region is reached in which the molecular orientation is rapidly developed. Within this critical region the orientation of the molecular dipole lags behind the changes in the applied field and does not reach its normal or static value for the voltage applied. The higher the frequency the greater this lag becomes. Since the dielectric constant is, in part, a function of the orientation produced per unit of field strength, it may be expected to decrease with increasing frequency as has been shown to be the case. A further effect of the orientation lag is to create a condition whereby the current is no longer displaced 90° from the voltage, and power is consequently absorbed by the condenser. The variations of this power absorption are illustrated in Fig. 5.

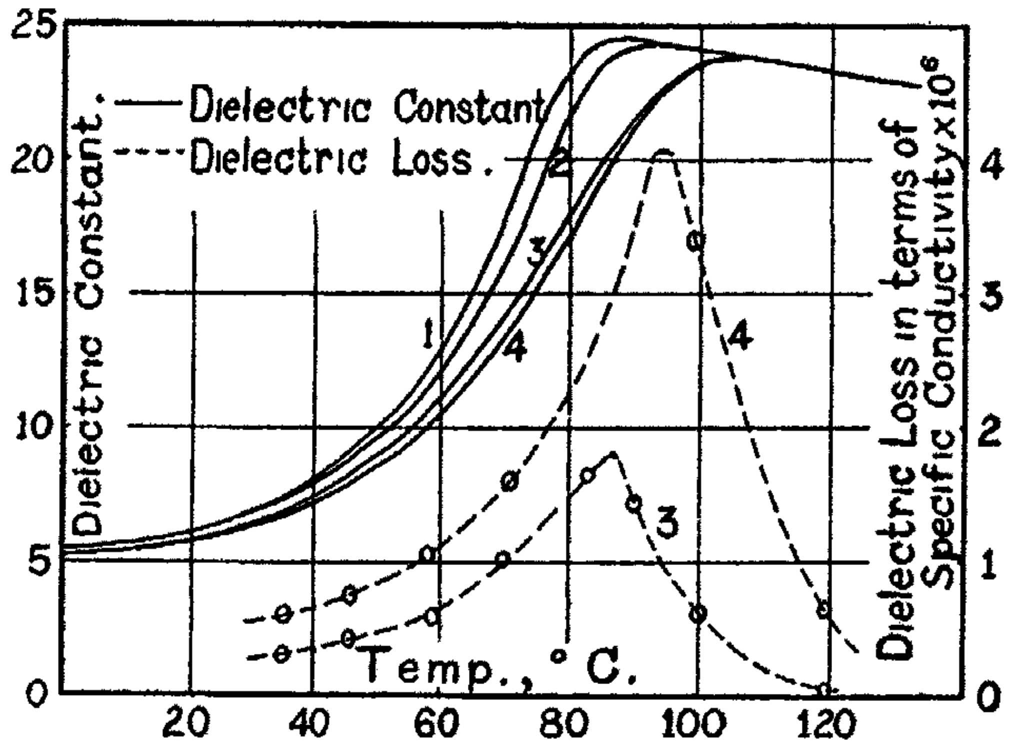


Fig. 5

The Dielectric Constants and Dielectric Losses of Liquid and Glassy Glucose.

Curve I. Measurements made at frequency of 92 Kilocycles
Curve II. " " " " " 160 "
Curve III. " " " " " 815 "
Curve IV. " " " " " 2600 "

As we proceed toward still lower viscosities the greater freedom of the molecules permits them to eventually become completely oriented, insofar as this is permitted by thermal agitation. Consequently a region is reached above which the dielectric constant again becomes independent of frequency and the power loss becomes negligible. Due to increasing thermal agitation the dielectric constants decrease slowly with increasing temperature after having reached their maximum values.

Mizushima has had considerable success in applying the theoretical equations of Debye to the anomalous dispersion of electric waves. An attempt to apply the equations to the data obtained for glucose leads to impossible results. On the other hand, the results may be explained by assuming the glucose molecules to be highly associated as Mizushima has done in explaining the abnormalities observed in the case of glycerine.

Summary

The electrical conductivity and dielectric constant curves of glucose have been determined throughout the temperature interval in which this material changes from a viscous liquid to a hard glass. The results obtained indicate that both electrical conductivities and dielectric constants are functions of the viscosity, and that there is no discontinuity in these properties between the liquid and glassy states. Measurements of the conductivities and dielectric constants of a series of boron trioxide-sodium borate solutions support the conclusions arrived at in the case of glucose.

SOLUBILITY AS A COMPLICATING FACTOR IN ADSORPTION MEASUREMENTS AT GAS-SOLID INTERFACES

BY E. W. R. STEACIE

In adsorption experiments with gas-solid systems complications frequently arise on account of slow and sometimes irreversible effects which are superimposed upon the ordinary rapid process of adsorption. In a recent paper, Taylor[1] postulates the existence of an activation energy in adsorption processes. This leads to the conclusion that, in certain cases, a high activation energy may be necessary, and adsorption will thus take place slowly. More than one kind of adsorption is therefore possible, and each type of adsorption process will proceed at a rate depending upon its necessary activation energy. On this basis Taylor explains the slow and irreversible effects which often accompany the usual rapid adsorption.

In the present communication no attempt will be made to question the postulates of Taylor's theory, or the possibility that it may be true in certain cases. On the other hand, an attempt will be made to show that Taylor's hypothesis is not of general applicability, and that in most cases the slow and irreversible effects which accompany adsorption measurements must be explained on the basis of the known tendency of gases to dissolve in solids. This discussion will be mainly confined to the re-examination of the experimental evidence cited by Taylor in support of his hypothesis of an activation energy.

The Solubility of Gases in Solids

It seems to be the prevailing and erroneous opinion that the amount of a gas dissolved by a solid is invariably exceedingly small. Taylor, for example, states that in many of the cases which he discusses "the quantities of gas involved (in adsorption measurements) are of several orders higher magnitude than the known solubility of the gas in the substance concerned". It will be shown in a later section, however, that in almost all the cases cited by Taylor the solubility is quite large enough to account for the observed facts. We will therefore examine in detail the effects which would be produced in an experimental system if the adsorption equilibrium were complicated by the occurrence of solubility.

The Rates of Adsorption and Solution

The generally accepted view is that adsorption in a gas-solid system is a rapid process, equilibrium always being established within a few minutes. Solution, however, is usually a slow process since its rate is governed by the diffusion of the gas into the solid, and this is a slow process.[2] The actual rate

---

[1] J. Am. Chem. Soc., 53, 578 (1931).

[2] See for example, Johnson and Larose: J. Am. Chem. Soc., 46, 1377 (1924); 49, 312 (1927); Lombard: Compt. rend., 177, 116 (1923); Richardson, Nicol, and Parnell: Phil. Mag. (6), 8, 1 (1904); Deeming and Hendricks: J. Am. Chem. Soc., 45, 2857 (1923).

of solution of a gas in a solid has been measured in only a few cases. The system oxygen-silver has been thoroughly investigated,[1] however, and will be treated as a typical system for purposes of discussion.

At high temperatures in the neighbourhood of 800°C. equilibrium is attained instantly, but at 200°C. several days are required for equilibrium. At low temperatures where the extent to which oxygen is adsorbed is appreciable, the rate of solution is thus extremely small. When oxygen is brought into contact with silver at low temperatures there is thus a rapid drop in pressure due to adsorption, followed by a slow solution of the gas in the metal. This would seem to be the obvious explanation of results such as those obtained by Benton and Elgin[2] with oxygen and silver catalysts. In their experiments at 110°C. about 4/5 of the gas was taken up rapidly, while the remainder required about 24 hours for equilibrium. Benton and Elgin ruled out the possibility of solution on the grounds that Sieverts[3] found no measurable solubility of oxygen in silver below 400°C. This, however, has been disproved by Johnson[4] and the author. The solubility of oxygen in silver at 200°C. is about 0.15 c.c. at N.T.P. per 10 grams of silver. This is about 5% of the total amount taken up in Benton and Elgin's measurements at 110°C.. From the form of the solubility temperature curve, the solubility should be much greater at 110° than at 200°. It would therefore appear that practically all the gas which was taken up slowly can be accounted for on the basis of solubility, and that the assumption of an activation energy and a second type of adsorption is not necessary in this case. Slow effects can similarly be explained in other systems cited by Taylor where it has been definitely established that the gas is appreciably soluble in the solid concerned. Such cases include the systems, palladium-hydrogen,[5] platinum-hydrogen,[6] copper-carbon monoxide, and nickel-carbon monoxide.[7] There is but one known case in which slow complicated adsorption effects have been observed with nitrogen, namely in the system nitrogen-iron.[8] It is highly significant that a large number of investigators have shown that iron is the only metal which will dissolve nitrogen[9] to an appreciable extent.

Rate of Solution and Extent of Surface

It may be objected that at the temperatures at which many catalysts are used, say 100° to 200°, the rate of solution of the gas in the solid is much

---

[1] Steacie and Johnson: Proc. Roy. Soc., **112A**, 542 (1926).

[2] J. Am. Chem. Soc., **48**, 3027 (1926).

[3] Z. physik. Chem., **60**, 179 (1907).

[4] Proc. Roy. Soc., **112A**, 542 (1926).

[5] Neumann and Streintz: Wied. Ann., **46**, 431 (1892); Hoitsema: Z. physik. Chem., **17**, 1 (1885); Holt, Edgar, and Firth: **82**, 513 (1913); Sieverts: **88**, 105 (1914); Holt: Proc. Roy. Soc., **90A**, 226 (1914).

[6] Neumann and Streintz: Wied Ann., **46**, 431 (1892); Mond, Ramsay, and Shields: Phil. Trans., **186A**, 657 (1895); Sieverts: Z. physik. Chem., **60**, 129 (1908); Gutbier and Maisch: Ber., **52**, 1368 (1919).

[7] Sieverts and Krumbhaar: Ber., **43**, 893 (1910).

[8] Frankenburger and Mayrhofer: Z. Elektrochemie, **35**, 590 (1929).

[9] Graham: Proc. Roy. Soc., **15**, 502 (1866); Neumann: Stahl und Eisen, **34**, 252; Jurisch: Doktorarbeit, Leipsig (1912).

slower than the observed slow "adsorption" effect. The rate of solution of a gas in a solid plate is, however, inversely proportional to the thickness of the plate. The rate of solution in finely divided catalysts, while still slow, will be great enough to account for the observed effects.

At very low temperatures it is probable that solubility equilibrium will never be attained. The *amount* of gas dissolved in any experimentally feasible time interval will then depend on the fineness of subdivision of the solid, *i.e.* on its surface. It follows that at low temperatures only the outside layers of the solid will be saturated, and the apparent solubility will cease to be dependent on the mass of the solid and will depend primarily on its surface. Measurements carried out with varying surface-volume ratios will therefore no longer distinguish between adsorption and solubility.

The Variation of Sorption with Temperature

In a few cases the solubility of gases in solids decreases with increasing temperature, for example the solubility of hydrogen in palladium, titanium, and vanadium.[1] In the majority of cases, however, the solubility increases as the temperature increases. In the case of oxygen and silver the solubility passes through a minimum at 400°C. and commences to rise again at low temperatures. This is the only known case of such behaviour, but few systems have been thoroughly investigated, and there is some theoretical justification for the assumption that minima would be obtained in other systems if accurate low temperature measurements were made.[2]

Adsorption, on the other hand, usually decreases as the temperature increases. It follows that the variation in the total sorption by a catalyst as the temperature varies may be complicated, and maxima or minima may occur. Similarly, since definite heat effects accompany adsorption and solution, composite heats of sorption may be obtained.

The peculiar types of adsorption-temperature curves obtained with platinum and hydrogen,[3] palladium and hydrogen,[4] and copper and hydrogen,[5] are apparently due to composite effects of this sort.

The fact that the adsorption of oxygen on gold increases with increasing temperature[6] cannot, however, be explained in this way since it has been shown by Johnson and Toole[7] that oxygen is not appreciably soluble in gold. In this particular case some mechanism of the kind postulated by Taylor may be responsible for the observed behaviour.

---

[1] Kirschfeld and Sieverts: Z. physik. Chem., **145A**, 227 (1929); Z. Elektrochemie, **36**, 123 (1930).

[2] Steacie and Johnson: Proc. Roy. Soc., **117A**, 662 (1928).

[3] De Hemptinne: Z. physik. Chem., **27**, 429 (1898).

[4] Guthier, Gebhardt, and Ottenstein: Ber., **46**, 1453 (1913).

[5] Harris: unpublished, quoted from Taylor's paper.

[6] Benton and Elgin: J. Am. Chem. Soc., **49**, 2426 (1927).

[7] Unpublished work.

The Adsorption Isotherm

The fundamental characteristic of the usual adsorption isotherm is the large amount of gas which is taken up at low pressures. In the case of solubility, however, Henry's law usually holds. A small amount of solubility, therefore, will exert little influence on the total sorption at low pressures, but will have a much larger effect at high pressures. In consequence the fundamental form of the adsorption isotherm will not be greatly influenced by the presence of complicating effects due to solubility.

The main effect of such solubility will be to mask the presence of a definite saturation limit to adsorption, and to cause a slow steady rise in sorption as the pressure is increased. This is probably the cause of some of the apparent exceptions to Langmuir's theory of adsorption.

Hysteresis Effects

Since solubility is normally a slow process, it follows that the rapid heating and cooling of a solid in the presence of a gas may give rise to apparent hysteresis effects. In consequence the total sorption may be dependent upon the history of the system. This will be referred to again in connection with the system hydrogen-nickel. The hysteresis effects obtained with copper and hydrogen,[1] and oxygen and silver are undoubtedly of this type.

"Irreversible Adsorption"

On account of the slow rate of solution of gases in solids, the dissolved gas can be removed from the solid only by long continued evacuation at a fairly high temperature. This has led to much inaccurate work in which gases taken up by solids could not be recovered by evacuation. Such gas was said to be "irreversibly adsorbed". It is of course apparent that any investigation in which the adsorbed or dissolved gas cannot be completely recovered will lead to erroneous results. This point has been emphasized by Johnson[2] and the author and by Bircumshaw.

Such irreversible adsorption is direct evidence that solubility is a complicating factor.

Another cause of irreversible adsorption lies in the methods used in the preparation of many catalysts, or in their chemical composition. If, for example, a metallic catalyst is prepared by the reduction of an oxide with hydrogen, the resulting metal will contain hydrogen which will not be removed by evacuation at a low temperature. If adsorption measurements are now made with oxygen, there will of course be a permanent loss of oxygen by reaction with dissolved hydrogen to form water. All adsorption measurements in which irreversible phenomena occur should therefore be regarded with suspicion.[3]

---

[1] Harris: Master's Thesis, University of Virginia (1924), quoted from Taylor's paper.

[2] Proc. Roy. Soc., 112A, 542 (1926).

[3] Phil. Mag., (7), 1, 510 (1926).

Carbon is a notorious offender in this respect and no confidence should be placed in measurements in which there is a permanent loss of hydrogen or oxygen.[1]

Special Cases

Three or four of the experimental systems on which Taylor laid particular emphasis will now be considered in some detail.

(*A*) *Hydrogen and Nickel.*

Benton and White[2] observed that with hydrogen and nickel different amounts of adsorption occurred depending on whether the metal was kept exclusively at low temperatures, or was saturated at high temperatures and then cooled. This is in agreement with the idea that solubility is the cause of complications. The rate of solution is negligible at low temperatures, and nickel which is cooled rapidly will thus contain all the hydrogen which was dissolved at high temperatures.[3]

The data of Benton and White on the rate at which equilibrium is attained also support the assumption of solubility. Thus at very low temperatures (−183°) equilibrium is rapidly established. At such temperatures any dissolved hydrogen will remain in solution, while no more will dissolve on account of the immeasurably slow rate of solution. The whole process is therefore one of adsorption and the rate is consequently high.

At higher temperatures Benton and White found that equilibrium was established fairly rapidly at very low pressures, slowly at moderate pressures, and somewhat less slowly at high pressures. At such temperatures the rate of solution will be appreciable and adsorption will be complicated by the resulting solubility. On account of the different forms of the adsorption and solubility isotherms, solubility will be inappreciable at very low pressures. Adsorption will therefore be the predominating process and equilibrium will be rapidly established. At higher pressures the solubility becomes more pronounced and the rate of the whole process is much slower. The rate of solution in nickel will, by analogy with the oxygen-silver system, be proportional to the square root of the pressure. Hence at high pressures equilibrium will be established somewhat more rapidly than at intermediate pressures.

The nickel-hydrogen system, which has been cited as furnishing the best evidence for the activation energy theory, is thus excellently explained on the basis of solubility.

(*B*) *Hydrogen and Oxide Catalysts.*

Taylor cites the results of Garner and Kingman,[4] who found that hydrogen adsorbed at low pressures on $ZnO-Cr_2O_3$ catalysts was given off on heating to 100-120°, and was then readsorbed in 20 or 30 minutes.

In the first place, adsorption measurements with hydrogen on an oxide should be regarded with a certain amount of suspicion, since there is always

---

[1] See particularly Lowry and Hulett: J. Am. Chem. Soc., 42, 1408 (1920); Rhead and Wheeler: J. Chem. Soc., 101, 831 (1912); 103, 461 (1913).

[2] J. Am. Chem. Soc., 52, 2325 (1930).

[3] Hydrogen has been shown to be moderately soluble in nickel by Sieverts: Z. physik. Chem., 77, 611 (1911).

[4] Nature, 126, 352 (1930).

the possibility of a reaction between the hydrogen and the oxide, or between hydrogen and oxygen dissolved in the oxide.[1] However, even if the measurements are trustworthy, the behaviour is simply explained by the assumption of a combined adsorption and solubility. At low temperatures adsorption will predominate on account of the very slow rate of solution. As the temperature is raised the adsorption decreases in the usual way, adsorption equilibrium is rapidly attained, and some gas is desorbed. This is then followed by a slow solution of the gas in the oxide, since the solubility usually increases with increasing temperature.

The experiments of Williamson[2] on the adsorption of hydrogen by manganous oxide, in which "irreversible adsorption" was observed, are to be suspected in common with all experiments in which complete desorption is not obtained.

(C) *Hydrogen and Quartz.*

According to Taylor, the re-investigation of the hydrogen-quartz system is necessary in order to ascertain if complicating effects occur due to solubility. This would hardly seem to be necessary in view of the large number of workers who have found that hydrogen is soluble in quartz to a small but definite extent, and will diffuse[3] through it.

Conclusions

It may therefore be concluded that the experimental evidence strongly favours the assumption that the slow effects accompanying adsorption processes are due to the solubility of the gas in the solid concerned.

It should again be emphasized that the mere determination of the surface-volume ratio will not settle the question at very low temperatures. At such temperatures solubility equilibrium is never reached, only the outside layers of the solid are saturated, and the apparent (non-equilibrium) solubility is dependent on the extent of the surface.

It is regrettable that the majority of investigators who are interested in adsorption processes are inclined to overlook entirely the large amount of available experimental data on the solubility of gases in solids.

Summary

The experimental evidence cited by Taylor in support of the hypothesis of an activation energy for adsorption processes has been reexamined. It is concluded that irreversible adsorption, and slow effects accompanying adsorption processes may be simply explained on the basis of existing data regarding the solubility of gases in solids.

Physical Chemistry Laboratory,
McGill University, Montreal, Canada.

---

[1] The solubility of oxygen in lower oxides at temperatures at which the higher oxides are unstable has been proved by LeBlanc: Ann., **6**, 480 (1846), and by LeBlanc and Sachse: Z. Elektrochemie, **32**, 204 (1926).

[2] Unpublished, quoted from Taylor's paper.

[3] See for example: Steacie and Johnson: Proc. Roy. Soc., **117A**, 662 (1928); Bodenstein and Kranendieck: Nernst Festschrift, **1912**, 100; Wustner: Ann. Physik, **46** 1095 (1915); Williams and Ferguson: J. Am. Chem. Soc., **44**, 2160 (1922); **46**, 635 (1924); Villard: Compt. rend., **130**, 1752 (1900); Berthelot: **140**, 821 (1905); Richardson and Richardson: Phil. Mag., **22**, 704 (1911); Mayer: Phys. Rev., (2) **6**, 283 (1915).

THE SINGLE ELECTRON BOND*

BY J. H. SIMONS

The concept of the electron has been very useful to correlate and describe the phenomena of valence. The present conception of the normal chemical bond is that it consists of two electrons. The binding force holding the two electrons together and thereby holding the atoms is conceived to be magnetism. A single electron in an atom has been shown, in the case of the hydrogen atom by Phipps and Taylor,[1] to be a small magnet. Two electrons in the same molecular species, as for example in the hydrogen molecule, result in the neutralization of the magnetic field of each of the electrons. Atoms with an odd number of electrons have been shown in the classical experiments of Stern and Gerlach[2] on atomic silver to be magnets. The magnetic fields of all the electrons except one can be neutralized and the resulting magnetic field is due to the unpaired electron. The Magneton Theory of Parsons[3] was based on this principle of the neutralization of the magnetic fields of the electrons and the theories of valence of Lewis[4] have made use of this concept and have shown the basic stability of the pair of electrons in a chemical bond.

Prideaux[5] suggested that in certain cases a single electron could act as the connection binding the atoms together in the molecule. This was to explain the molecular structure of pentavalent and hexavalent compounds and still keep an eight electron shell. Sugden[6] has made use of this suggestion to account for certain irregularities in the function which he has called the parachor. This function is related to surface tension by the equation $P = \frac{\gamma^{1/4}M}{D-d}$ in which M is the molecular weight, D is the density of the liquid, d the density of the vapor in equilibrium with the liquid, and γ is the surface tension. All these properties are taken at the same temperature. Sugden[7] has shown this function to be approximately independent of temperature and the molecular parachors to be an additive property[8] of the atomic parachors, provided constants are added for structural features. For certain compounds he has used a constant which he has assigned to a single electron bond and has obtained a check between calculated and experimental values of the parachor by this means.

---

* Contribution from the Chemical Laboratory of Northwestern University.

[1] Science, 64, 480 (1926).

[2] Z. Physik, 9, 349 (1922).

[3] Smithsonian Inst. Pub., 65, No. 11, 80 (1915).

[4] "Valence and the Structure of Atoms and Molecules," (1923).

[5] Chem. and Ind., 42, 674 (1923).

[6] J. Chem. Soc., 129, 1173 (1927), 1929, 316.

[7] J. Chem. Soc., 125, 32 (1924).

[8] J. Chem. Soc., 125, 1177 (1924).

As ordinary compounds in which all the valences are pairs of electrons are used to calculate the atomic parachors, the parachor value for the pair of electrons is zero. The double bond, a sharing of four electrons, gives a constant of approximately +20[1] to be added to the sum of the atomic parachors to obtain the molecular parachor. For a triple bond, which can be considered a sharing of six electrons, the constant is about double this or +40. Each electron over the single pair, Sugden argues, adds to the sum of the atomic parachors 10 units, and so one electron less than the pair should subtract from the sum the same amount, 10 units. By applying this to certain compounds an agreement between calculated and observed values of the parachor are obtained.

The compounds for which it is necessary to subtract this value are all of higher valence types such as pentavalent antimony and phosphorus, tetravalent selenium and tellurium and the metals in chelate organic compounds. It should be noted, however, that in all the cases where the single electron bond has been assumed, the atomic parachor has been calculated by using compounds in which the valence of the atom is less than its valence in compounds in which the single electron bond is assumed. For antimony and phosphorus the atomic parachors are calculated for trivalent compounds and for selenium and tellurium the divalent compounds are used. The ordinary compounds of the metals which form chelate compounds are used to calculate their atomic parachors.

It is necessary to assume other structural constants besides those for double and triple bonds in order to account for molecular parachors. For ring organic compounds different constants are used depending on the number of atoms in the ring. In a refinement of Sugden's method and a recalculation of the atomic parachors, Mumford and Phillips[2] have shown that in organic compounds the kind and number of that kind of atom that is attached to the carbon atom makes a difference and that a constant must be added to account for this. In the same way the increase in the number of electrons in the valence shell could be considered a structural feature and a constant applied for this. If this value is −9.5 units for each additional electron in the valence shell or −19 units for each additional pair of electrons, all the parachors of the compounds in which single electron bonds are assumed can be explained without postulating this new type of valence, which is very difficult to appreciate theoretically.

Sugden[3] has attempted to refute this argument by two examples. The first is that the parachor for mercury in mercury diphenyl and in liquid mercury are the same. He assumes that liquid mercury is monatomic and that it has two electrons in the valence shell. In mercury diphenyl it would certainly have four electrons in the valence shell. The argument using measurements on the liquid metal is a weak one, for the condition of the atoms is unknown

---

[1] This value is 23.2 on Sugden's original calculation but 19 by the recalculation of Mumford and Phillips: J. Chem. Soc., 1929, 2112.

[2] J. Chem. Soc., 1929, 2112.

[3] J. Chem. Soc., 1929, 316.

and certainly with the free electrons or the electrons made free readily, as shown by the metallic conductivity, we have a condition very different from that in the liquids from which the atomic parachors were calculated.

In his second example which he considers a better one, he finds the atomic parachor the same for thallium in thallous compounds, in ethyl thalloacetoacetate and dimethyl thallium benzoylacetone (the last two with the assumption of the single electron bond). The use of these compounds as a test of the single electron bond has been destroyed by the recent work of Sidgwick and Sutton.[1] They have shown that some of the "so called" thallous organic compounds are highly polymerized apparently to give thallium a valence shell of six to eight electrons. They have worked with two compounds which Sugden has used in his calculations, thallous ethoxide and ethyl thalloacetoacetate. The former they have shown to have four single molecules associated together and the latter two. They point out in their discussion that this polymerization leads to difficulties in reconciling the parachor and the single electron bond with the possible structure.

If we use the concept of the enhanced valence shell decreasing the parachor by about ten units, we can account for the parachor data fairly well. For this we shall assume a parachor of about 80 for thallium with four electrons in the valence shell, i.e., unassociated thallous thallium. This is in as good agreement as Sugden's value 64 with the parachors of neighboring elements in the periodic table as the following comparison shows.[2]

$$\begin{tikzcd}
 & \text{Ga } 50 \arrow[r, "-14"] \arrow[d, "+19"] & \text{Ge } (36) \arrow[d, "+22"] \\
 & \text{In}(69) \arrow[r, "-11"] \arrow[d, "+11"] & \text{Sn } (58) \arrow[d, "+18"] \\
\text{Hg}69 \arrow[r, "+11"] & \text{Tl } (80) \arrow[r, "-4"] & \text{Pb } 76
\end{tikzcd}$$

This figure is close to the parachor for thallium in thallous nitrate (85) which Sugden excluded from his calculations. For six electrons in the shell the value would be about 60. This would correspond to unassociated thallic compounds or thallous compounds in which the association or polymerization supplied an additional pair of electrons to the thallium atom. This agrees well with the determined value 62.2 for thallium in thallous ethoxide. The structure of this compound has not been worked out but some of the formulas that can be assigned to it give a six electron shell to thallium. Thallous acetate and formate probably also come in this class with parachors of 70.0 and 64.2 for the thallium. For eight electrons in the valence shell the parachor values will be about 40 which is near the determined parachor in ethyl thalloaceo-

---

[1] J. Chem. Soc., 1930, 1461.

[2] Compare table, page 185, "The Parachor and Valency" by Samuel Sugden (1930).

acetate (37.0) and dimethyl thallium benzoylacetonate (41.4) when the assumption of the single electron bond is not made. The structures of neither of these compounds is worked out, but most of the formulas that can be assigned would give an eight electron shell to the thallium.

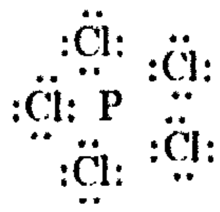
The author wishes to point out that he is not attempting to use the parachor to arrive at chemical structure in the above paragraph, but that he is only trying to show that parachors can be accounted for without using the assumption of the single electron bond.

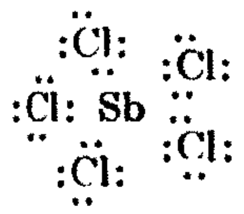
Sugden considers the parachor an atomic or molecular volume which has been corrected for difference of internal pressure, the surface tension being the measurement of internal pressure. The additive property of this function is on this consideration related to the additive property of molecular volumes. Structural features such as double bonds, strained ring formation, etc., which would normally be expected to increase the volume increase the parachor. Reasoning in the same manner the sharing of a greater number of the valence electrons with the electronegative elements would be expected to decrease the atomic volume and the parachor.

Mumford and Phillips have shown that an additional factor which they call a strain constant is necessary in order to account for the parachors of organic compounds. They show that this constant is dependent upon the kind of group which is attached to the carbon atom and the number of groups of this kind which are so attached. For example the parachor of carbon tetrachloride is less than the sum of the atomic parachors by 9 units when the parachor of carbon is calculated from hydrocarbons. As this introduces an additional factor it still further destroys the parachor as a proof of single electron bonds.

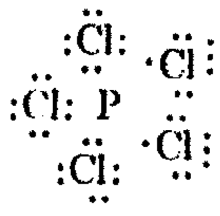
It should be pointed out that the dimensions of the parachor are not those of volume but are $m^{1/4}\ l^3\ t^{-1/2}$. Why a function of these dimensions should be independent of temperature is difficult to explain.

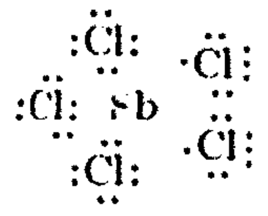
The assumption of single electron bonds leads to somewhat different structures for the molecules for which they are assumed than are obtained on the basis of the Lewis theory, and these in turn lead to different consequences in the relations of the properties of these compounds. The structure of phosphorus pentachloride and antimony pentachloride are given by Lewis as,





and by Sugden as,

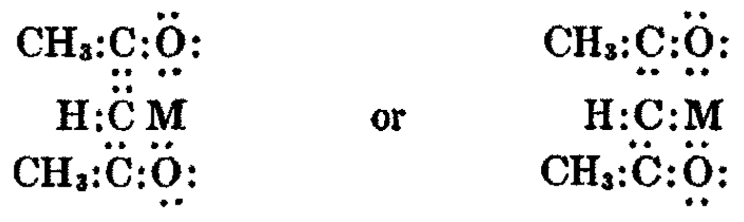




On the Lewis theory these compounds are given a symmetrical structure in which the central atom has a ten electron shell, but on the Sugden theory three of the chlorine atoms are held by pairs of electrons while two of them are held by single electron bonds. Symmetry in the structure of compounds is associated with non-polar properties as shown, for example, in carbon tetrachloride and sulfur hexafluoride. Sugden's structure for antimony and phosphorus pentachlorides are not symmetrical and so one would expect some polarity. These compounds have low melting and boiling points, are quite soluble in non-polar solvents such as carbon tetrachloride, have low dielectric constants and low conductivities in the liquid state, and measurements for their electric moment in carbon tetrachloride solution, which the author has made[1] give a zero value. They are also diamagnetic. The Lewis theory is definitely favored by the properties of these compounds.

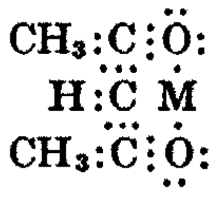
Sugden argues that as the single electron bonds occur in pairs in the molecules the magnetic fields of electrons are neutralized. This could occur only in antimony or phosphorus pentachloride, if the single electron bonds were very close together, for the two magnets must be adjacent in order to neutralize the external field, but this structure would certainly have an electric moment. With the single electron bonds on the opposite sides of the central atom and the normal valences in a plane perpendicular to them, the electric moment could be zero but it is difficult to see how the magnetic fields could be neutralized with the electrons so far apart. If both structures existed, we have the possibility of isomers.

The postulation of single electron bonds for chelate compounds is objectionable in that it violates many of the bonds in the compounds and involves the additional assumption of three electron bonds. On the Lewis theory the structure of the diketone is,



$$\begin{array}{ccc} \mathrm{CH_3{:}C{:}\ddot{O}{:}} & & \mathrm{CH_3{:}C{:}\ddot{O}{:}} \\ \mathrm{H{:}\ddot{C}\ M} & \text{or} & \mathrm{H{:}C{:}M} \\ \mathrm{CH_3{:}\ddot{C}{:}\ddot{O}{:}} & & \mathrm{CH_3{:}\ddot{C}{:}\ddot{O}{:}} \end{array}$$

but with single electron bonds this becomes,



$$\begin{array}{c} \mathrm{CH_3{:}C\vdots\ddot{O}{:}} \\ \mathrm{H{:}\dddot{C}\ \dot{M}} \\ \mathrm{CH_3{:}\dddot{C}\vdots\dot{O}{:}} \end{array}$$

according to Sugden. It does seem as if this were merely juggling electrons about in order to preserve the single electron link.

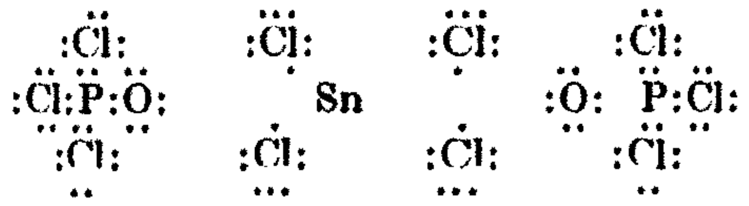
Single electron bonds have been used to assign a structure to higher valence compounds, chelate organic compounds, molecular compounds or double salts and coordination compounds. Garner and Sugden[2] give as an

---

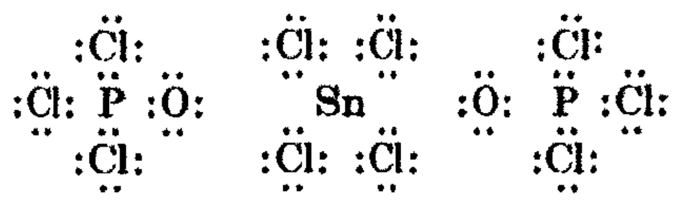
[1] Simons, J. Am. Chem. Soc. 53, 1263 (1931).

[2] J. Chem. Soc., 1929, 1298.

example of a molecular compound $SnCl_4(POCl_3)_2$ and assign the structure,



which on the Lewis theory is,



in which the tin atom has a 12 electron shell. The latter is a more probable structure and has the same parachor. The coordination compound $(Co{\cdot}4NH_3{-}{\cdot}2NO_2)Cl$ will have on Sugden's structure four single and two double electron bonds around the cobalt atom. This gives possibilities of isomerism. If six single electron bonds are assigned to the cobalt to overcome this difficulty, the value of the single electron bond in preserving the group of eight as fundamental is destroyed.

The magnetic properties of compounds agree well with the Lewis theory of valence even for such difficult cases as the complex iron salts.[1] An odd electron in the molecule has been shown experimentally to result in a paramagnetism equivalent to one Bohr magneton. We should expect each single electron bond to have this same effect. We should not expect two single electron bonds to result in zero paramagnetism for two unpaired electrons result in a paramagnetism equivalent to two Bohr magnetons as shown in some of the iron compounds. Some of the compounds for which single electron bonds have been postulated or must be postulated on the Sugden theory and which are diamagnetic as shown by experiment are $SbCl_5$, K_2PtCl_6, $(NH_4)PtCl_6$,[2] PCl_5, $Sb(CH_3)_3Cl_2$, $Sb(CH_3)_3Br_2$, $Sb(CH_3)_3I_2$, $Te(CH_3)_2Cl_2$, $Te(CH_3)_2Br_2$, $Te(CH_3)_2I_2$,[3] $K_3Co(CN)_6$, $K_4Co(CN)_6$,[4] $Co(NH_3)_6Cl_3$, $(CO(NH_3)_4NO_3)Cl$, etc.[5]

Sugden's theory would have to assume that in sulfur hexafluoride there were two normal and four single electron bonds. This compound is very stable, has a low boiling point and is apparently non-polar. The stability of the single electron bond must be very high in this compound. This is surprising in view of the fact that the only single electron bond that there can be no dispute about is in H_2^+ and this molecular species only exists for a fraction of a second under special conditions in a vacuum tube. This connection seems to be only an electrostatic attraction between a hydrogen ion

---

[1] Welo and Baudisch: Nature, **116**, 606 (1925).

[2] International Critical Tables.

[3] Lowry and Gilbert: Nature, **123**, 85 (1929).

[4] Welo and Baudisch: Nature, **116**, 606 (1925).

[5] Rosenbohm: Z. physik. Chem., **93**, 693 (1919).

and a hydrogen atom and this connection is weak. We would expect from ordinary considerations that all single electron bonds would be just as weak as this one.

The assumption of the single electron bond as a valence connection is not only unnecessary to account for chemical properties but leads to properties which are contrary to fact. The only value that it has had has been in explaining certain discrepancies in molecular parachors and these are as easily explained on the alternate basis of the enlarged valence shell. It does enable one to picture compounds without exceeding eight electrons in the valence shell, but there is no theoretical reason why more than eight electrons cannot be in this shell. In doing this it violates the most fundamental concept in the electron valence theories, the pair of electrons, which does have considerable theoretical reasons for its stability. Lewis has shown this and all chemical evidence supports the idea of the fundamentality of the pair of electrons as the valence bond.

In a recently published paper Pauling[1] has given a formal proof by means of quantum mechanics for the pair of electrons as the basis for the chemical bond. He has also established by the same means the magnetic moment of a molecule or complex ion as being due to unpaired electrons. This adds further justification for the argument set forth in this paper.

The above argument tends to show that the single electron bond for normal chemical compounds violates the basic principle of the electronic theories of valence, the pair of electrons which owe their stability to the neutralization of the individual magnetic fields; that its assumption leads to chemical properties which are contrary to fact; that its assumption involves the use of additional assumptions in order to substantiate it; that the crucial test of this type of bond which Sugden himself has proposed, the parachor of thallium in thallous compounds and in dimethyl thallium benzoylacetone, has failed to support it; that parachor discrepancies could be completely explained on other hypotheses and that the parachor, both theoretically and practically, could not be used to establish this type of valence bond.

---

[1] J. Am. Chem. Soc., 53, 1367 (1931).

13-147

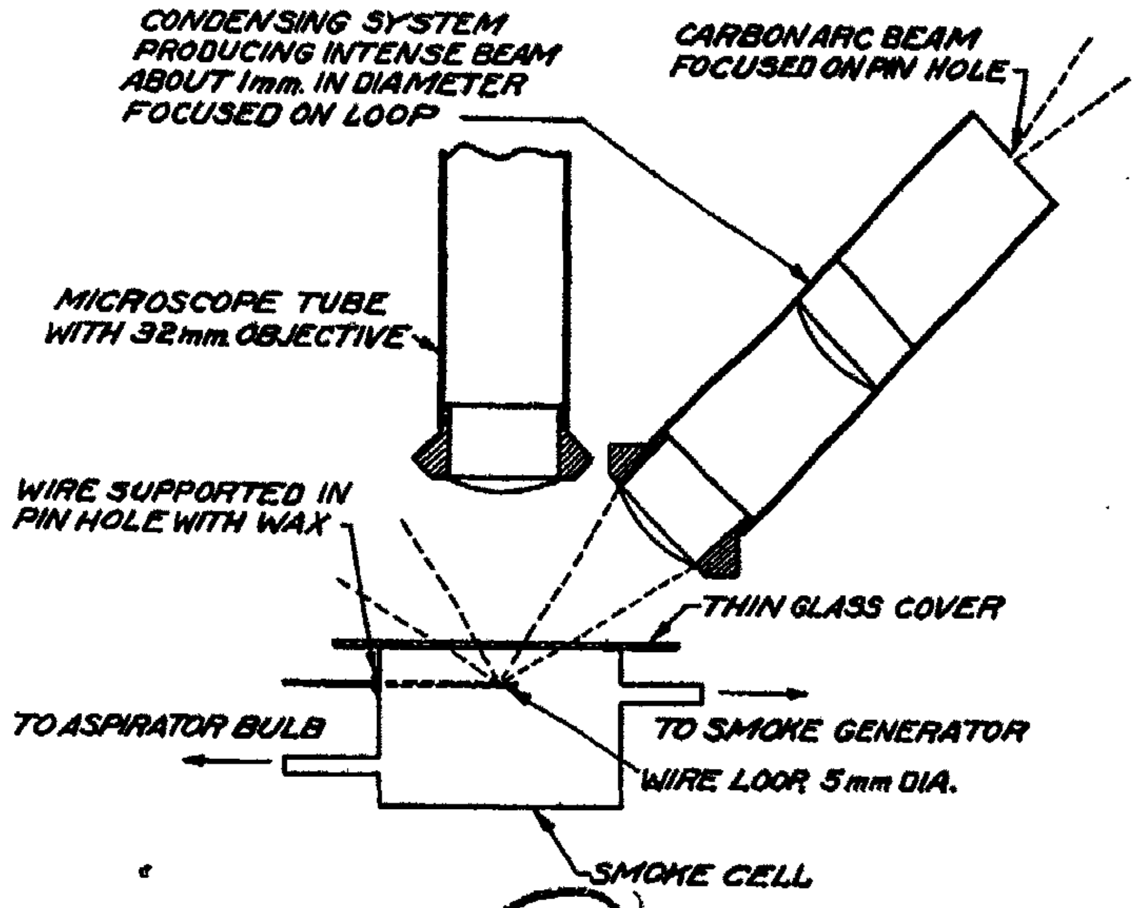
USE OF THE ULTRAMICROSCOPE FOR OBSERVING SMOKE PARTICLES FALLING ON LIQUID FILMS

BY P. D. WATSON AND A. L. KIBLER

In connection with a study of the physiological effect of smokes irritating to mucous membranes a new ultramicroscope technic has been developed which may be of interest in other fields. In the course of this study it became of importance to know something of the behavior of smoke particles when falling on films of water and of olive oil. The method developed consisted, in brief, of focusing a microscope vertically upon a horizontal liquid film which was illuminated by a beam of light focused upon it at an angle of 45°. The liquid film was held upon a small wire loop, approximately 5 millimeters in diameter, made from No. 36 Therlo wire. This loop was mounted in the center of a glass cell approximately one and one-half inches in diameter and one inch deep. The cell was painted on the outside with heavy, black paint and closed at the top by means of a thin cover glass sealed on with vaseline or deKhotinsky cement. Two side tubes provided inlet and outlet for the smoke. Illumination was furnished by an arc lamp and a series of condensing lenses which projected a fine beam of light through the cover slip and into the cell. The microscope was provided with a 32-mm. objective. Smoke was generated in a small generating vessel and sucked into the observation cell by means of a hand aspirating bulb. A sketch of the optical system used is shown in Fig. 1.

Some difficulty was experienced at first in getting the proper adjustment and focus of the microscope, but after some experience the oil and water surfaces could be easily distinguished. When the smoke was not so dense as to obscure the films the particles could easily be distinguished as they floated in the air and approached the film surface. When the film was comparatively clear of smoke particles it acted as a mirror and gave perfect mirror images of the particles floating closely above it. This phenomenon greatly aided the observations since it was easy to distinguish an individual particle with its accompanying mirror image as they approached each other and finally merged as the particle touched the film surface. In the case of smokes which were readily soluble in the water film, these observations were very striking and beautiful, and were suggestive of snow flakes falling on a wet pavement except that this analogy fails in respect to the mirror image of the smoke particles and their zigzag Brownian movements.

All smokes were not equally easy to observe. In some cases doubt existed as to whether the particles dissolved or not. In a few instances the appearance of the film indicated a decomposition of the particles, sometimes by an opalescence, sometimes by a violent movement of the particles, and sometimes by the fact that the particles remaining appeared much smaller than when they first fell on the film. Certain smoke materials produced particles which were much easier to observe than others. The water films and the oil films presented characteristic differences in appearance. The water film reminded one of a stretched membrane, and the surface appeared brighter than that of the oil. When insoluble particles fell on it they remained riding on the surface, generally in a fixed position, and were apparently not wet by it. When soluble particles fell on the film they disappeared immediately. Sometimes particles appeared slowly soluble, in which case they usually appeared partially submerged and wet. The oil film was usually in streaming motion due to convection currents set up by heat from the light beam. This effect may



1079

1/2

Quinn

Fig. 1

Apparatus for the Study of the Solubility of Smoke Particles in Liquid Films

be reduced by the use of a cupric chloride cell. When insoluble particles fell on it they were dragged beneath the surface and the streaming oil gradually became full of particles which could still be seen as they streamed to the surface. When soluble particles fell on it they disappeared and the oil did not show an increase of particles. Particles which were partially soluble or slowly soluble in oil were more difficult to judge than in the case of water films. Both oil and water films contained ultra-microscopic particles and it was necessary to eliminate as many of these as possible by filtering for oil and by distilling for water. Both films showed the mirror effect described above.

Suitable water films were more difficult to prepare and to preserve than oil films. Their initial appearance before exposure to smoke varied greatly, and seemed dependent upon their thickness. After a short time the visibility improved because evaporation reduced the curvature of the surface. A little water was generally put in the bottom of the observation cells in order to prevent excessive evaporation and consequent rupture of the water films.

It was observed that, if the oil films were exposed unnecessarily to the atmosphere before use, particles usually soluble in oil did not submerge, but appeared to rest upon the surface. In this case solution may have been retarded by the presence of a layer of condensed moisture upon the oil.

Fine smoke particles settled very slowly over olive oil films, and were observed to play for long intervals just above the surface before finally striking it. The particles appeared to enter water films more rapidly than those of oil; this difference was probably due to the condensation of moisture upon the particles which, of course, increased their weight.

It was recognized early in the work that smoke particles behave differently towards an oil film, depending on whether they were generated in moist or dry air. When generated in moist air there was apparently a film of water condensed around them which prevented solution. This effect was usually very marked and constitutes direct evidence of the moisture films on smoke particles so frequently discussed on theoretical grounds. On account of this effect, observations on oil films were made with smokes generated in saturated air and smokes generated in dry air. The smokes for the water films were generated in ordinary air, since preliminary experiments indicated that moisture was not a factor here.

Incidentally, this work furnished direct evidence in regard to the attraction between smoke particles. The coalescence of smoke particles in air occurs so infrequently and the particles can approach each other from so many different planes that it is a subject of some dispute whether an observer has ever seen the coalescence of two particles. In the case of insoluble particles on water films the motion of the particles is slowed up and the approach of two particles is limited to one plane so that actual coalescence has been observed many times. This seems to occur only when two particles are quite close together as is to be expected. When large numbers of insoluble particles fell on the films, the particles were observed to form into chains and clusters. It is believed that an increased attractive force has been observed for large aggregates of particles. For example, a smoke particle once fell near the center of a clear space on the film and remained there for several seconds. Another particle then fell near it and the two particles moved towards each other and stuck fast. These two combined particles then moved over and coalesced with a large group of aggregates at the edge of the clear space. It is recognized that these movements may have been due partly to surface tension phenomena.

An interesting case of a reaction between smoke particles and a gas was also rendered visible by means of this set-up. A smoke which was known to react with chlorine was introduced into the cell containing a water film on the wire loop. The smoke was insoluble in the water film and in a short time the film surface was thickly studded with particles. A little chlorine was then introduced into the cell and observations continued. The Brownian movement of the particles in the cloud was enormously increased. The particles rushed madly around and dived into the water film with a far greater speed than ever observed previously. In about two minutes the bright fixed aggregates on the water film were seen to be slowly growing smaller and losing their brilliance. After several minutes the excited movements of the particles in the air slowed down to a normal speed. The particles on the water film disappeared as they dissolved in the water as a consequence of their altered solubility resulting from reaction with chlorine.

Interesting observations were also made upon the effect of certain substances dissolved in water and in oil upon the solubility of smoke particles in films formed from such solutions. For example, the presence in olive oil of a small amount of an emulsifying agent (sodium oleate) greatly increased the solubility of smoke particles formed from a substance which, in bulk, is soluble in oil but which, as smoke particles, is rendered insoluble by being generated in moist air.

This method was also used for a study of the solubility of fine particles of various solid organic compounds which were dispersed in the form of a mist. Concentrated solutions of these compounds were prepared with a suitable solvent such as acetone and then atomized within a flask. This mist was aspirated through a charcoal filter which removed the solvent vapor completely but permitted the passage of a large proportion of the dry particles.

The technic described above seems promising as a means of studying phenomena relating to the presence of liquid films on smoke particles which is known to be closely related to the stability and precipitation of smokes. It may also be of value in connection with a study of the physiological effect of substances upon tissue and tissue constituents.

Technical Divisions, Chemical Warfare Service,
Edgewood Arsenal, Md.

MEASUREMENT OF PARTICLE SIZE FOR NITROCELLULOSE DISPERSION*

BY HENRY B. DEVORE** AND WHEELER P. DAVEY***

A water-spreading method of measuring the particle size of the disperse phase of a colloid has already been described by one of us.[1] This method uses, in the measurement of the sizes of colloidal particles, the technique described by Langmuir[2] for the measurement of molecular dimensions. A shallow rectangular tray filled with water is provided with an aluminum float extending the width of the tray with gaps at either side. Glass strips sliding on the tray edges and making contact with the water serve to limit the free surface of the water. A small quantity of dispersion is carefully dropped on the water surface upon which it immediately spreads. The dispersing phase disappears either by solution or by evaporation, leaving a monoparticle film of the disperse phase on the water surface. Jets of air directed along the surface of the water at the ends of the aluminum float prevent the escape of the surface film through these gaps. The surface film is compressed by moving the glass strips toward the aluminum float and the force exerted by the film is measured by a torsion balance attached to the float.

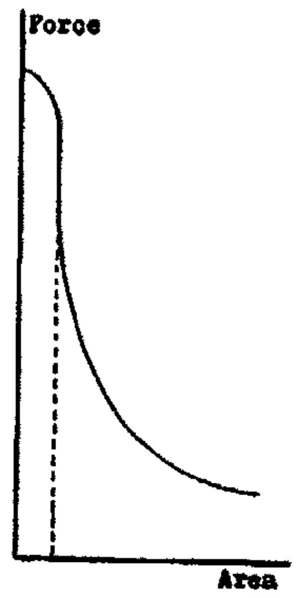


FIG. 1
Schematic Force-Area Curve

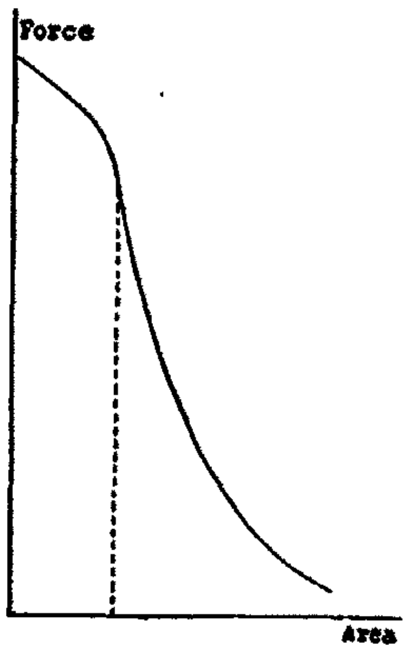


FIG. 2
Force-Area Curve for Nitrocellulose

A typical force-area curve is shown diagrammatically in Fig. 1. The vertical portion of this curve is obtained when the colloid particles are in

---

* The experimental work recorded here was done at the Pennsylvania State College during the summer of 1927. It was supported by E. I. duPont deNemours & Company, Inc.

** At present physicist; Experimental Station, E. I. duPont deNemours & Company, Inc., Wilmington, Delaware.

*** Professor of Physical Chemistry, School of Chemistry and Physics, Pennsylvania State College, State College, Pa.

[1] W. P. Davey: Science, 64, 252 (1926) and Eighth Colloid Symposium (1930).

[2] Langmuir: J. Am. Chem. Soc., 39, 1881 (1917).

contact with one another and any further decrease in area requires sufficient additional force to pile the particles up two or more deep. It is the area corresponding to this vertical portion of the curve (A) which is used in the calculation of particle size. In the case of nitrocellulose on water the vertical part of the curve degenerates to a point at which the curvature of the graph changes sign. A representative curve obtained in this way for a nitrocellulose dispersion is shown in Fig. 2.

In the experiments described here a sample of nitrocotton was dispersed in ethyl acetate. A measured amount of the dispersion was spread on clean water and the ethyl acetate allowed to disappear into the air or into the water. For sufficiently dilute dispersion, the film left on the surface of the water may be assumed to be composed of separate particles of nitrocotton corresponding to the separate particles of the disperse phase. In these experiments we used a medium viscosity nitrocotton containing 12.4% nitrogen. However, since we were interested only in the method of measuring the particle size of the nitrocotton, its technical characteristics were of very little importance. It was sufficient for our purpose to make our dispersions always from the same sample and to make up all of the dispersions at the same time. The concentrations used ranged from 1×10^{-3} gm. per cc. to 7.8×10^{-6} gm. per cc.

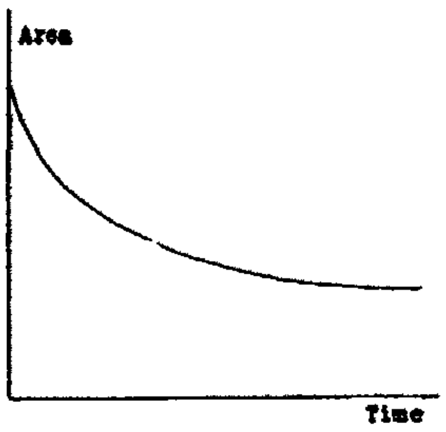


FIG. 3
Time-Area Curve at Constant Force

The films had a tendency to shrink after being spread on the water. This was probably due partly to the slow rate at which the last traces of solvent were given up by the nitrocellulose. It is quite possible that a part of the shrinkage may be due to a drying of the nitrocellulose in tiny patches or islands which orient themselves with time to give a closer and closer packing. Such a picture is consistent with the work of Zocher[3] who found by optical examination that dried films of nitrocotton show areas whose thickness varies discontinuously after the fashion of soap films. For a given compressive force on the film the area decreased with time as shown in Fig. 3. It was therefore an essential part of the technique that only the final values of curves like Fig. 3 be used in plotting the force-area curves. The points of inflection on the force-area curves from which the particle sizes were calculated were much more easily determined for the high concentrations than for low. This may be explained on the basis of larger particles since more force would be required to move them from the water surface and pile them up two deep. This would tend to make the determinations for the higher concentrations more accurate than for the lower. The most concentrated dispersion required ten drops (0.25 cc) for its determination and gave a monoparticle film 20 cm. long in a tray 23 cm. wide. The most dilute dispersion tried gave a film length of only 4.5 cm. when 120 drops (3 cc.) were used. At lower concentrations the quantity of dispersion was more than sufficient to cover the sur-

---

[3] H. Zocher and F. Stiebel: Z. physik. Chem., **147A**, 401 (1930).

face of the water, so that part of the dispersion rested not on water but on a layer of still more of the dispersion. This had the effect of increasing the concentration before a monoparticle film could be obtained. This again leads to the conclusion that the measurements made with the concentrated dispersions were somewhat more reliable.

The height of the nitrocotton particles was found to decrease with decreasing concentration from 3.69×10^{-7} cm. for the solution containing 0.001 gm. per cc. to 1.54×10^{-7} cm. for the solution containing 0.000,0078 gm. per cc. When the heights of the particles were plotted against the logarithms of the concentrations all but three of the points were found to fit a straight line within the limits of experimental error (Fig. 4). Two of these three points which were off the line were measured at the same concentration. Their average falls almost exactly on the line.

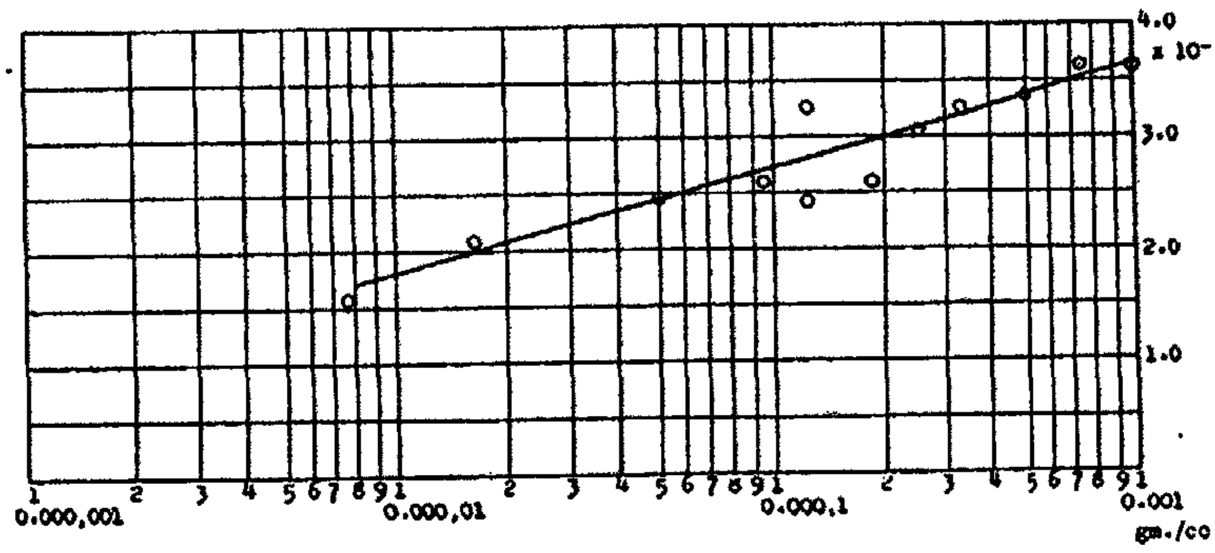


Fig. 4
Variation of Particle Height with Logarithm of Concentration

It is obvious that the line of Fig. 4 can not be extrapolated below the height of a single "molecule" of nitrocellulose. At this height it must become horizontal. Although we have no direct evidence to indicate what this limiting height is, our measurements show that it is not in excess of 1.7×10^{-7} cm. It is presumable smaller, since at this point the curve has not given any indication of becoming horizontal. It is interesting to compare this figure with the values given by Herzog [4]. From X-ray diffraction studies he finds for the unit cell of cellulose nitrate the dimensions 10.1, 8.6, and 10.8×10^{-8} cm., and for cellulose 8.60, 7.78, and 10.22×10^{-8} cm. These values are so close to our lowest dimension that it seems reasonable to assume that they are not far from what we would have found if we had been able to use solutions sufficiently dilute to bring the curve of Fig. 4 to a horizontal. It is true that the values which we have measured represent the average size of the dispersed particles. It is also true however, that the particles of the disperse phase must be multiples of an ultimate particle size which can not be smaller than the chemical molecule itself. We feel justified, then, in believing that the ultimate particles in a nitrocellulose dispersion are not greatly different in size from the unit cell of cellulose or of nitrocellulose.

---

[4] R. O. Herzog: J. Phys. Chem., 30, 457 (1926); Pulp Paper Mag., Can., 24, 697 (1926).

NEW BOOKS

Quantitative Clinical Chemistry. *By John P. Peters and Donald D. Van Slyke. Vol. I. 24 × 16 cm. pp. xvi + 1264. Baltimore: The Williams and Wilkins Company, 1931. Price: $12.00.* The chapters are entitled: total metabolism; carbohydrates; lipoids; non-protein nitrogen and nitrogen metabolism; urea; ammonia; amino acids; uric acid; creatine and creatinine; total organic acids—lactic acid, and ketones; phenols; hemoglobin and oxygen; proteins of the blood plasma, urine, and other body fluids; the volume of the circulating blood; total base, sodium and potassium; calcium; magnesium; carbonic acid and acid-base balance; chlorides; phosphorus; sulfur.

"The human organism appears to be incapable of oxidizing the common fatty acids unless a certain amount of carbohydrate or material capable of forming glucose is burned simultaneously. Shaffer and others have adduced evidence that the influence of carbohydrate in facilitating the combustion of fat follows a quantitative law. Apparently one molecule of glucose is required for the oxidation of two molecules of fatty acid. From calculations of the quantities of glucose and of fatty acid that can be formed from each food stuff Shaffer has estimated that fat can not be oxidized completely to CO_2 without ketone bodies as end products unless the molecular ratio of fatty acid derivable from the fat and protein burned to glucose, derived from protein, fat, and carbohydrate, as calculated by the following equation, is 2:1 or less," p. 33.

"It takes no more than ordinary powers of observation to recognize that among different individuals there is a distinct variation in the tendency to acquire fatty tissue. Among both those who tend to obesity and those who tend to keep spare certain persons can be found in whom the characteristic can be definitely traced to some disease or recognizable disturbance of the activity of one of the endocrine glands. In still another group less obvious endocrine disorders are suspected. This is especially true of the sudden increases of weight observed in adolescence, after pregnancy and after the menopause. It is also easy to detect the effect of heredity in determining either the fat or the lean pattern.

"In all types of obesity, whether of known or unknown origin one is forced to conclude that the immediate cause of the abnormal accumulation of fatty tissue is the ingestion of food in excess of the metabolic needs. Any other conclusion would contradict the law of the conservation of energy. This, however, does not mean that all fat people are gourmands or even extraordinarily heavy eaters. Gulick, who was of the lean type, experienced great difficulty in increasing his weight by the use of a high caloric diet. Even if all obese persons ate more than their contratypes it would still be necessary to explain why the latter had neither the desire nor the ability to eat as much. However, numerous experiments have shown that many of those with the fattening tendency do not lose weight even when they are given less than their usual allowance of food.

"There is no escape from the conclusion that obese people live more economically than thin ones. This seems paradoxical, because every motion made by a fat man entails a greater expenditure of energy than a similar motion by his lean fellow. The distinction between them does not appear to depend on any obvious difference in activity. One can find extremely nervous and active members among the heavy groups. Because no easy explanation of the difference between the two types could be found by simple methods of observation, and to aid in the more rational treatment of obesity, attention has recently been directed toward the detection of the characteristic of metabolism that determines the tendency to accumulate fat," p. 35.

"Obesity is due to the consumption of unnecessarily large amounts of food and may be overcome or prevented by reduction of diet. The term 'unnecessarily large' is not meant to connote 'unusually large' amounts. Obesity is almost the result of a personal abnormality, presumably a metabolic abnormality, as well as a tendency to excessive eating. Certain individuals resist attempts at fattening as others resist reducing measures. In just what respects the metabolism of these two types differs is still largely conjectural," p. 284.

"Of the carbohydrates of the usual foods, some are celluloses and pentosans entirely incapable of absorption, others are polysaccharides capable of hydrolysis by the digestive processes into monosaccharides that can be absorbed, while others are already monosaccharides capable of absorption without hydrolysis.

"To the *unassimilable carbohydrates belong in general the celluloses and gums of plants.* The cellulose fibres of plant stems and the cellulose envelopes of the cells of leaves are quite incapable of assimilation by man. The ruminants can hydrolyze them, but in man they pass out in the feces, without further physiological effect than that referable to their influence on the physical state of the gastrointestinal contents. In moderate amounts they appear to act as normal stimulants of peristalsis. In excessive amounts, as in 'war bread' filled with wood flour, they may produce irritation to a pathological degree. The softer tissues of the leaves and roots commonly used for food are less irritating; and such material, when the extractives have been removed by repeated boiling, has been fed in the fasting treatment of diabetes without yielding any significant amount of assimilable material to the organism.

"The assimilable polysaccharides, starch, glycogen of meat, lactose of milk, sucrose and maltose, are all rapidly hydrolyzed by the various digestive enzymes to their constituent monosaccharides, which are then absorbed into the portal circulation. Unhydrolyzed polysaccharides are not absorbed in appreciable quantities from the alimentary canals of normal animals. Glucose constitutes a large portion of the monosaccharides: all that formed from starch, glycogen and maltose, and half that from sucrose and lactose. The remainders of the latter two disaccharides consist of fructose and galactose respectively.

"It was at one time believed that all sugars were converted into glucose in the course of their passage from the intestine to the portal circulation. It is now known that monosaccharides of all kinds are absorbed as such into the blood stream and are only converted to glucose after they have reached the liver," p. 78.

"The glycogen of muscles, in contrast to that of liver, behaves as though it were tenaciously retained *in situ* for local consumption only. The muscles do store up glycogen after feeding, but not, like the liver, in amounts so hugely in excess of their own immediate requirements (see section above on Distribution). Furthermore, Mann has found that when a dog's liver is excised the glucose content of the blood, if the animal is not fed, falls in a few hours to 0.04 to 0.05 per cent, and convulsions similar to those of insulin hypo-glycemia result. The convulsions in both cases are relieved by glucose administration. It is evident that in the dehepatized dog muscle glycogen is not available to maintain the blood glucose concentration, despite the desperate need of the organism to have it maintained. Absorption of glucose by the muscles seems to approximate an irreversible process, the absorbed glucose being at once condensed into glycogen and retained until burned by the muscle, regardless of the needs of the rest of the body," p. 95.

"The lipides can be distinguished from other lipoids and from one another by solubility. As a group they are sparingly soluble in acetone, a characteristic which permits their separation. All are more easily miscible with water than the fats, tending to form stable suspensions or colloidal solutions, from which they can, however, be precipitated by salts, protein, etc. They are easily absorbed with proteins, forming adsorption compounds from which they can not readily be separated. In fact, it is believed by many that the lipides in their natural state occur chiefly in conjunction with proteins. Like the fatty acids they tend to form monomolecular films on aqueous surfaces. They also possess the property of 'growing and budding' into myelin forms in water," p. 224.

"The quantity of protein required by an individual depends on certain environmental factors and also on the composition of the non-protein portions of the diet. In order to enable a person to maintain nitrogen equilibrium on the smallest possible amount of protein it is essential that sufficient carbohydrate and fat be available to meet his caloric requirements. The effect of carbohydrate and fat in preventing nitrogen loss on low protein diets is usually spoken of as a 'protein-sparing action.' The carbohydrate and fat do not in any true sense take the place of protein in the bodily economy. They spare protein merely by preventing its consumption. The animal engine consumes its own structural substance for fuel when fat and carbohydrate supplies run low," p. 274.

"Grabfield, Alpers and Prentiss found that the administration of as little as one gram of *potassium or sodium iodide* a day to a normal adult caused a quite appreciable increase of the blood non-protein nitrogen of adults, attended usually by increased nitrogen excretion," p. 292.

"The amino nitrogen concentration in the tissues has been studied with the nitrous acid method of Van Slyke and Meyer and by Luck, and has been found to be approximately 5 to 10 times as great as that in the blood. Amino acids injected intravenously or absorbed with unusual rapidity from predigested proteins fed *per os* are concentrated at once in the tissues. Van Slyke and Meyer found that in the tissues of the dog a saturation limit appeared to be reached when the muscles had an amino nitrogen content of about 75 mg. per cent, but that the liver could take up much larger amounts. The physicochemical mechanism by which the amino acids enter the tissues in so much greater concentration than in the blood has not yet been explained. There appears to be an equilibrium, for the tissues quickly take up amino acids when the concentration of the latter is increased in the blood. Also when the supply in the blood is no longer renewed by food, in starvation, the tissues apparently pass amino acids back into the blood, for the content in the latter is maintained. But the nature of the equilibrium is such that it maintains a much greater content of amino acids in the cells than in the extra-cellular fluids," p. 390.

"The evidence that urea formation occurs exclusively in the liver has been presented in the urea chapter. Practically all of the amino acid nitrogen that is not retained in the body appears to be excreted in the form of urea or ammonia. Levene found that nitrogen administered to dogs in the form of various amino acids was completely recovered in the urine in the form of urea. In case the accompanying metabolism of other substances results in the formation of acid products, more or less of the nitrogen will be excreted as ammonia instead of urea; but apparently it is first turned into urea in the liver and then back into ammonia in the kidneys (see urea chapter). Except under unusual conditions, such as may be encountered in rapidly growing animals, where the demand for synthesis of body protein is great, by far the greater part of the nitrogen of absorbed amino acids appears to be at once turned into urea. Van Slyke, Cullen and McLean found that in fact liver does not even wait, during absorption of a protein meal, until the tissues have obtained a supply of amino acids, before it begins to transform them into urea. On the contrary, wasteful as it seems, the liver begins to turn into urea the first amino acids that reach it in the portal blood. Even in a dog that has been fasted, so that there was presumably a demand for useful nitrogen in the tissues, the blood urea began to rise within 20 minutes after a meal of meat, or about as soon as the first chyme could enter the intestine and begin to be absorbed. There is undoubtedly some regulatory process which permits the organism during rapid growth or during convalescence from wasting diseases, to retain unusual proportions of ingested nitrogen for tissue formation. It would seem, however, from the observations cited, that the mechanism for inhibiting destruction of absorbed amino acids by the liver at best only partially prevents such destruction," p. 394.

"This conception of the formation of a definite amount of uric acid per day from hypoxanthine of the muscles is analogous with the observed formation of a definite amount of creatinine per day, almost certainly from the creatine of the muscles. In confirmation of his belief that endogenous uric acid originates chiefly in the muscles Burian later observed that severe gymnastics could increase the hourly excretion of endogenous uric acid 3 to 5 fold. Furthermore, when an isolated, perfused dog muscle was stimulated it gave off uric acid to the perfusing blood," p. 428.

"Creatine, methyl-guanidine-acetic acid, is very unevenly distributed in the body, about 98 per cent of the total occurring in the muscles alone, and most of the remainder in the brain. It appears in low concentration in the blood, but is not found in the urine of normal adults. It is presumably derived from protein. Its restricted distribution and its absence from normal urine show clearly that it is not one of the waste products of metabolism, but a substance that probably serves a useful function in the muscles. This impression is further strengthened by the fact that if creatine is administered to an animal a large part is retained," p. 455.

"If shed blood is allowed to stand, the glucose in it gradually disappears, being converted to lactic acid. This process can be prevented by poisoning the blood by fluoride or other preservatives or by the simple expedient of laking the blood cells with water. The glycolysis is apparently due chiefly to leucocytic activity. Similar autoglycolysis may be observed in exudates containing leucocytes and may occur in the body. It is, apparently, this process which is responsible for the low sugar and high lactic acid content of cerebrospinal fluid in meningitis and of synovial fluids in arthritis," p. 477.

"The fact that in reduced hemoglobin the iron is in the ferrous state symbolized above as Fe^{++}, while in methemoglobin it is in the trivalent ferric state, Fe^{+++}, has been shown by recent work of Conant and his collaborators, discussed later in the section on methemoglobin. Only reduced hemoglobin, with divalent ferrous iron, can form the reversible molecular compounds with O_2 and CO.

"Methemoglobin, with the Fe oxidized to the trivalent form, has not this power, hence it is no oxygen carrier. On the other hand, it is only methemoglobin that can combine with cyanide to form cyanhemoglobin. Hence cyanide kills by its effect on the tissues, not on the blood: it can not alter the circulating hemoglobin because it encounters none in the form of methemoglobin," p. 521.

"The exact determination of the O_2 or CO combining capacity per gram of pure hemoglobin is a surprisingly hard task, because during purification hemoglobin changes readily into a tautomeric form which does not bind either gas." p. 524.

"Certain so-called 'capillary poisons', of which *histamine* can be considered representative, either by causing capillary paralysis and dilation or by direct effect on the capillary endothelium so alter the permeability of the vascular membrane that excess fluid and protein may escape from the circulation. Hemoconcentration results. Govaerts has recently shown that uranium salts have a similar effect on capillary permeability," p. 559.

"Castle has shown that products as effective as liver for the treatment of pernicious anemia are produced in the stomachs of normal individuals during the digestion of ordinary protein foods, such as round steak. Such foods, removed from the normal stomach at the height of digestion, incubated to complete digestion and then fed by gavage to patients with pernicious anemia caused remissions of the disease. These results appear to reveal pernicious anemia as a deficiency disease of a peculiar nature: the deficiency arises from the fact that faulty gastric digestion interferes with the production from protein foods of some substance without which the bone marrow is unable to carry on its function in a normal manner. This substance or substances, which can ordinarily be formed from other protein foods can, by the pernicious anemia patient, be produced only from liver and kidneys," p. 568.

"The reactions of ferricyanide, nitrite and aniline on blood *in vitro* have been studied quantitatively by Van Slyke and Vollmund. Nitrite and ferricyanide added to laked blood, both react almost instantly and quantitatively, 1 mol of each on 1 mol of hemoglobin, to form methemoglobin. When added *in vitro* to whole blood, however, these two substances show a surprising difference. Ferricyanide does not penetrate the cells and forms methemoglobin only after blood is laked. Nitrite at once penetrates the cells and forms methemoglobin within them. Aniline mixed with blood begins to form methemoglobin only after a latent period of over 4 hours at 25° and in 16 hours forms only about one-fourth mol of methemoglobin per mol of aniline. The behavior suggests that aniline may resemble some other aromatic substances studied by Heubner, which changed hemoglobin to methemoglobin only after they themselves had been oxidized to more active oxidizing agents," p. 633.

"Of two patients with equal plasma protein content and on similar regimes, edema may be more difficult to control in one than in the other. Likewise the same patient, with unaltered plasma proteins and regime, may at one time retain fluid and at another lose it, for no observable reason (e.g. see Table 47, also Linder, Lundsgaard and Van Slyke). Nevertheless, the accumulated data indicate that the constant and dominating factor in producing nephritic edema is plasma albumin deficit, the effect of which is only somewhat modified in degree by other influences," p. 682.

"According to the theory of Starling which has been adopted as the basis of the present discussion, the fluid which finds its way to the tissues from the blood stream under normal conditions is a practically protein-free filtrate of plasma. Injury, inflammation, extreme vasodilatation and other factors may, however, alter the permeability of the capillaries to *such an extent that not only proteins, but even blood cells, may escape from the blood* stream. Such tissue fluid can be maintained only if it has accumulated in some accessible part of the body as the result of disease. Examination of edema fluids from patients with cardiac and renal edema has revealed minimal amounts of protein. Salvesen and Linder found from 0.05 to 0.35 per cent of the total protein in edema fluid from one patient with nephrosis and three with cardiac decompensation. The fluids with angioneurotic edema and of edema caused by the administration of paraphenylenediamine, on the other hand, have been shown to contain larger amounts of protein. Govaerts infers from this that the production of angioneurotic edema is associated with disturbances (possibly vasomotor) that render the vessel walls more than usually permeable. Schade, Claussen and others have shown that purulent material from abscesses, even if it is freed from cells by centrifugation, may contain as much or more protein than serum. The proteins in this case are presumably in large part derived from disintegrated cellular tissue, only part of which has its origin in the blood stream," p. 696.

"That potassium is the predominant base in human muscle and blood cell, sodium in the extracellular fluids, has been noted above. Concerning the origin of this inequality we have no explanation. We merely know that it exists. Its continued existence can be possible, however, only because potassium is prevented from diffusing out of the cells by a membrane or other restraining factor. The unequal distribution of sodium and potassium may depend not on impermeable membranes, but on the inherent characteristics of the cellular and extracellular media. To describe the facts, however, and refer to the restraining factor without resorting to specific terms is so difficult that the words 'permeable,' 'impermeable,' and 'membrane' will be employed as a matter of convenience in this discussion.

"The membrane, or some restraining factor which acts like a membrane, appears also to be impermeable to sodium. Various authors have determined the base of the cells and serum of blood after submitting it to changes of CO_2 tension which altered the bicarbonate and chloride distribution to the physiological limits. Under such conditions they have found no evidence that any sodium goes into the cells or that any potassium comes out," p. 755.

"Sweating may become so extreme, when heavy muscular exercise is carried on at high temperatures, that it causes great depletion of the salt and the water content of the body. The *ingestion* of large amounts of water, under these circumstances, will produce serious symptoms commonly known as stokers' or miners' cramps. Moss has shown that these can be prevented if thirst is slaked with salt solution instead of water. Apparently miners' cramps are akin to water intoxication to which the subject is rendered more susceptible by previous depletion of body salts. Profuse sweating seems to have much the same influence on the urinary response to the administration of salts as a previous salt-poor diet, promoting retention of chloride, base and water, diminishing the effect of diuretic and exaggerating that of anti-diuretic measures," p. 773.

"Tetany or spasmophilia may be described as a symptom complex characterized by the *development of excessive irritability of the motor nervous system. In the mildest forms it* can be detected only by determination of the electrical reactions of the muscles, which present characteristic alterations, or by the presence of certain abnormal reflexes. In more outspoken cases active spasms, varying from typical contractions of the extremities (carpopedal spasm) to general convulsions, are observed. This condition occurs spontaneously in both infants and adults, especially the former. It has been produced by removal of the parathyroid glands or administration of alkaline phosphates which lower the serum Ca concentration. It is caused also by heavy, excessive breathing, persistent vomiting, the continuous removal of hydrochloric acid from the stomach or the administration of excessive bicarbonate, all of which increase the pH of the blood plasma. *Hence it appears that* factors causing either alkalosis or a diminished concentration of physiologically active serum calcium lead to a state of tetany. As mentioned before, the fraction of calcium held in solution by protein does not appear to be physiologically active, and calcium reduction caused by reduction of serum proteins does not cause tetany.

"MacCallum and Voegtlin first demonstrated a consistent reduction of the serum calcium *in the tetany which follows parathyroidectomy. This* observation has been repeatedly verified and there can be no doubt that hypocalcemia is one of the characteristic sequellae of parathyroid removal and that it can be relieved by administration of parathyroid extract. Moreover it seems to be clearly established that the administration of calcium salts in such a form that they are readily absorbed raises the serum calcium and rapidly relieves the symptoms of tetany. Tetany may be expected to supervene after parathyroidectomy when the serum calcium falls below 7 mg. per 100 cc.," p. 822.

"Calcium deficiency is not the only chemical disturbance of the blood noted after parathyroidectomy. Greenwald, in 1913, reported an elevation of the inorganic phosphate, which has been verified by subsequent observers. A little later Binger induced typical tetany in dogs by the injection of dibasic sodium phosphate. In these experiments he found that serum phosphate rose while calcium fell and that tetanic symptoms appeared only after the calcium had diminished to about 7 mg. per 100 cc. The administration of acid phosphate, *in spite of the fact that it produced similar changes in the serum calcium and* phosphorus, did not cause spasmophilia. These observations also have received ample confirmation and, indeed, it has been demonstrated by Adlersberg and Porges and others that tetanic symptoms may be relieved by the administration of the acid ammonium phosphate $(NH_4)H_2PO_4$, which causes acidosis," p. 824.

"Although alkalosis proved to be unessential for the production of parathyroid tetany, it was not long before evidence began to accumulate that reduction of the hydrogen ion concentration of the blood, whether produced by increase in plasma bicarbonate or fall in in CO_2 tension was often followed by tetany. McCann showed that gastric tetany, a well-recognized symptom complex, could be reproduced by continuous removal of gastric hydrochloric acid. This resulted in a reduction of blood chloride which was compensated by an increase of bicarbonate. A little later MacCallum, Lintz and associates confirmed McCann, showed that the symptoms could be relieved by the injection of hydrochloric acid, or even sodium chloride and that a somewhat similar syndrome developed after the injection of excessive amounts of bicarbonate. These results were rapidly and repeatedly substantiated and seemed to establish alkalosis firmly as one of the causes of spasmophilia," p. 825.

"Besides those effects which it shares in common with the other bivalent alkaline metals, calcium and strontium, magnesium has a characteristic effect of its own, the power to depress motor and sensory activity. It acts as a sedative, and even as an anesthetic when administered subcutaneously, intravenously or intraspinally, and has been used especially to overcome excessive motor activity in convulsive conditions. This action undoubtedly contributes to its value as an antispasmodic in tetany.

"The chief importance of magnesium compounds from the standpoint of clinical medicine lies in their therapeutic effects; as cathartics, diuretics and acidifying drugs, when given by mouth; as anesthetics and diuretics, when given parenterally," p. 865.

The reviewer has found this book both interesting and helpful.

Wilder D. Bancroft

Radioelements and Isotopes: Chemical Forces and Optical Properties of Substances. *By Kasimir Fajans. 23 × 16 cm; pp. x + 125. New York: McGraw-Hill Book Company, 1931. Price: $2.50.* The author held the George Fisher Baker Non-Resident Lectureship in the spring of 1930. The present volume is not identical, however, with the lectures either as to form or contents. "The systematic, although brief presentation of the subjects of Radioactivity and Isotopy, as given in the lectures, have been omitted because numerous works, including one by myself, deal with them. The corresponding chapter is restricted to an exposition of the development of the problem of the origin of actinium, a question about which interest still centers and which was discussed with my students at Cornell in one of our colloquia. The explanation of atomic structure and the bases of the Quantum Theory—necessary introductions to the lectures on Chemical Forces—have also been omitted, as they also have been well presented in numerous publications. On the other hand, more detailed attention has been devoted to some questions, *e.g.* the adsorption of ions, than they received in my lectures," p. ix.

The book contains the introductory lecture and chapters entitled: the origin of the actinium series and the stability of isotopes; outline of atomic and crystal structures; the ideal ionic linkage; general remarks on the deformability of ions; change of the refractivities of ions in the molecules and crystals; transitions between ideal ionic linkage and non-polar linkage; adsorption of ions on salt-like crystals with applications to volumetric analysis; photochemical applications of ion adsorption.

"The most probable values for the atomic weights of the members of the actinium series are: protactinium = 231; actinium = 227; actinium-lead (AcD) = 207. These atomic weights make improbable a genetic relation between the actinium and the uranium series, but do not exclude it, transportations other than those of the known alpha or beta ray types being possible. The fact that protactinium and actinium are found only in uranium minerals should be explained, then, as Piccard and many others have done, by assuming that protactinium is derived from a relatively long-lived isotope of uranium (actino-uranium), presumably having an atomic weight of 235," p. 45.

"In connection with the problem of chemical forces, one can distinguish three main limiting types of lattice: atomic lattice; ionic lattice; molecular lattice," p. 52. Under ionic lattices we have the face-centered cube of sodium chloride and the body-centered lattice of caesium chloride, p. 52. Under the atomic lattices we have the diamond lattice, characteristic of the following tetravalent non-metallic elements: diamond, silicon, germanium, and gray tin, p. 56. "This diamond lattice is, like the typical ionic lattice, a co-ordination lattice having specifically the co-ordination number 4. The difference between the two kinds of lattice is that the ionic lattice has oppositely charged ions next to each other, while in the diamond lattice the neighboring atoms are alike; it is a case of non-polar linkage between the atoms just as in the elemental molecules (*e.g.* H_2). But in the diamond lattice we have no distinctly indicated molecules, the linkage of the atoms extends to the periphery of the crystal in a similar manner, so that in a certain sense one may liken the whole crystal to a molecule," p. 58.

From the consideration of the atomic forces on the one hand and of the molecular forces on the other, it appears very probable that hydrogen (H_2) crystallizes in a molecule lattice. This cannot be proved directly by X-ray analysis, however, because the hydrogen atom, having but one electron, exerts too weak an effect on X-rays and therefore the position of the hydrogen atoms in the lattice cannot be determined. "In the case of tin tetraiodide, however, it is quite certain that it has a molecule lattice, such as is shown in Figure 12. As there shown, every Sn atom occupies the center of a tetrahedron at each of whose four corners stands an I atom all of which, on the one hand, are closer to the contained Sn atom than are the other I atoms. On the other hand these four I atoms are less distant from that Sn atom than from any other Sn atom. In this case, then, the molecule SnI_4 is definitely recognizable and the lattice is a typical molecule lattice," p. 55.

"The lead ion is colorless, as shown by its colorless aqueous solution as well as by its colorless solid chloride, nitrate and sulphate. The iodine ion, within the range of the visible spectrum, also shows no appreciable absorption. When a lead ion is combined with an iodine ion, however, the yellow lead iodide is precipitated, therefore the color of at least one of these ions must have changed under the influence of the other. Now since light absorption depends upon the state of the system of electrons that are involved, we must conclude that when the lead ion combines with the iodine ion the electron shell of one or of both of these ions has experienced a change (deformation)," p. 68.

"In the series AgF, AgCl, AgBr, AgI, the refractivity of the anions, which is a measure of their deformability, rises from 2.5 for the slightly deformable F^- to 19.2 for the readily deformed I^-. Just as in the sodium halides we here find that silver fluoride is a readily soluble, strongly dissociating salt, while the three other halides are substances whose solubility decreases in the order given above, and in the case of the yellow silver iodide amounts to only 10^{-7} mol/liter. On closer examination it can be shown that the above gradation for this series stands in direct connection with the increasing deformation of the anions by the Ag^+ ion, and the same is true of the behavior of these substances in respect of other properties like electrical conductivity, lattice distance and lattice energy, which change gradually from silver fluoride (close to the alkaline halides) up to silver iodide (approximating gray tin). Here we shall discuss the peculiarities in the lattice distances," p. 88.

"This new principle of mass analysis may be very strikingly demonstrated by the following experiment. Take a liter of an aqueous solution of the sodium salt of eosin at a concentration of about 1 gm in 300 liters of water. The salt is wholly dissociated into ions, and the greenish fluorescence as well as the yellowish-red color of the solution transmitted by light is due to the free eosin ions. If one adds to the eosin solution about 5 drops of a 1 *N* solution of silver nitrate no appreciable change in the color of the eosin takes place; at this high degree of dilution the difficultly soluble silver salt of eosin is still dissolved and also extensively dissociated. But if one now adds to this solution one drop, *i.e.* a deficiency, of a 1 *N* solution of potassium bromide, there may be noted a pronounced deepening in the color, which changes into red, and a diminished fluorescence. What has taken place? Silver bromide has been produced and, since the solution has remained perfectly transparent, it is evidently in the very finely subdivided colloidal form with a great superficial development. Since the solution contains an excess of Ag ions the colloidal silver bromide is present as a positively charged silver-body. This adsorbs the negative eosin anions, whereby the latter are deformed and change their color and power to fluoresce. A continuation of the experiment will demonstrate the truth of this conclusion. On adding 2 or 3 more drops of potassium bromide the first effect is a further deepening of the red color, for the amount of silver bromide and thereby the amount of adsorbed dye-stuff has increased. A total addition of 4 drops is followed by a lightening of the coloration and when the point of equivalency (6 drops of potassium bromide) is passed the solution regains its original yellowish-red color and the fluorescing power of the free eosin ions. This recovery is due to the bromine-body produced by the excess of potassium bromide, the eosin ions being thereby displaced from the surface and returned into solution. At this stage, by alternate additions of silver nitrate and of potassium bromide, one can repeat the play of colors at will, bringing the dye onto the surface by producing the positive silver-body or displacing it by producing the bromine-body." p. 96.

"In order that a dye may serve as a suitable adsorption indicator it is evident, then, that its adsorption curve must be very steep, when drawn as a function of the excess of Ag or of Br ions. Just as erythrosin is unsuited for titrating bromine ions, so eosin is not adapted for titrating the even more weakly adsorbed Cl ions. In this case one must employ a dye that is adsorbed correspondingly less than is eosin, and it has been found that fluorescein or dichlorfluorescein are very suitable. The considerable difference in adsorbability between iodine ions and chlorine ions makes it possible to titrate iodine ions with silver ions in the presence of chlorine ions. Thus, if the indicator is eosin or dimethyldiiodofluorescein, then on adding silver nitrate to a mixture of iodide and chloride there is a color change when the iodine ions are completely precipitated. The reason is that the adsorption by silver iodide of the dye mentioned—accompanied by the change in color—is hindered by the readily adsorbed iodine ions but not by the chlorine ions," p. 102.

"We may therefore regard the silver ion not only as a chemical acceptor but also as a spectral sensitizer in the photolysis of the silver halides. Of course the yet deeper question is also of great interest, viz., How are we to explain the proved influence of the adsorbed ions on light absorption? It is possible that here the adsorbed ions influence the optical behavior of the halogen and the silver ions of the lattice in a manner similar to that considered in Chapter V when discussing refraction and its explanation on the theory of deformation of the ions," p. 113.

The name of Grotthuss is spelled wrongly; but that may be the fault of the proof reader.

Wilder D. Bancroft

Essentials of Organic and Biological Chemistry. *By E. Wertheim. 23 × 16 cm.; pp. v + 175. Easton: The Chemical Publishing Co.; Tokyo: Maruzen Co., 1931. Price: $2.50.* This book was written to aid instruction in a combined course of organic and biological chemistry which the author has conducted for several years in the University of Arkansas. The chapters are entitled: introduction; saturated hydrocarbons; ethylene series; acetylene series; halogen derivatives of hydrocarbons; alcohols and ethers; aldehydes and ketones; acids and their derivatives; polybasic acids and urea; amines; optical activity; carbohydrates aromatic compounds; proteins; enzymes; digestion and absorption of foods; metabolism; nutrition; dietary necessities; foods and beverages.

"Esters of inorganic acids are often of importance. Thus ethyl sulfate and methyl sulfate are used in chemical synthesis. Ethyl nitrate is dispensed in 'sweet spirits of niter' for medicinal use. Amyl nitrite is of value in the treatment of asthma and for checking the onset of epilepsy," p.40.

"We call ptomaines the amine-type compounds, some of which are mentioned above, that result from the bacterial putrefaction of protein material. This putrefaction may take place at any time in protein foods, if they are improperly kept. The accumulation of poisonous amines will then cause violent illness, when such food is eaten.

"The name ptomaine poisoning is applied also to those cases in which food contains the bacillus botulinus. This bacterium secretes a soluble toxin of great potency. It may be present in canned foods, such as green beans, when sterilization has not been sufficiently thorough, and is a source of grave danger if it multiplies in the body," p. 75.

"The preparation of pure d- and l-substances is not merely a matter of theoretical interest. Often the d- and l-isomers are entirely different in their physiological effects. Thus l-nicotine is more poisonous than d-nicotine, while l-adrenaline is about twelve times as active a drug as the d-isomer. d-Glucose is an important food, but l-glucose does not serve as a food. Any study of the action of foods or drugs in the body, or of the chemistry of plants must take cognizance of optical activity," p. 82.

"Among monosaccharides the hexoses have to us the greatest importance, and they also have the best representation in nature. Sugars with five carbon atoms are not found free, but they are produced upon the hydrolysis of the pentosans, which occur in plants. By loss of water pentoses are converted to the substance furfural, $C_5H_4O_2$. This is an aldehyde having a ring structure, and distantly related to benzene compounds. Its uses include the preparation of resins of the Bakelite type, preservative, disinfectant, rubber accelerator, solvent, insectide. It is made cheaply from pentoses of corn stalks and cobs, and from oat hulls, peanuts, etc.

"Among the pentoses we find arabinose, $C_5H_{10}O_5$, which results from hydrolysis of gum arabic, xylose obtained from straw, corn cobs, and similar material by hydrolysis, and others of lesser importance. Pentoses are not digested in the human body, but are utilizable by farm animals. Pentoses are not fermentable by yeast," p. 87.

"Mercerized cotton (J. Mercer, inventor) has been treated with sodium hydroxide, which transforms it ultimately to a hydrocellulose. This has a lustre unknown to cotton fiber. It is not only made more attractive by the process, but is much stronger after treatment, and capable of taking dyes better than the untreated fiber," p. 92.

"While pectin is known to belong among the carbohydrates, but little is yet established with reference to its chemical makeup. It is made on a large scale from the apple refuse of the cider mill, as well as from lemon, orange, and grape fruit culls. Those fruits whose juices form jellies all contain pectin. It has long been the practice among housewives to add a certain proportion of these when working with such fruits as strawberry, which do not 'jell'. Pectin is now a commercial product under the name of 'Certo'. We have here another of those cases where chemical research has thrown light on the mysteries attending cookery," p. 93.

"Certain of the ductless glands of the body elaborate secretions which profoundly affect our well-being. The substances called hormones secreted by these glands act as regulators of the chemical processes taking place throughout the body, probably as catalysts. Like other catalysts with which we are familiar, hormones are extremely potent, mere traces sufficing to produce the most remarkable effects when administered to those who naturally lack a sufficient supply.

"Two hormones have been thoroughly investigated and synthesized by organic chemists. These are adrenaline, a product of secretion of the adrenal glands, small bodies which lie above the kidneys, and thyroxime, which is elaborated by the thyroid gland.

"Adrenaline has the power to constrict the capillaries and stimulate the heart, thus raising the blood pressure. The substance is secreted into the blood in times of fright or stress, when the body is required to act at its highest efficiency. It is used in surgery to check surface bleeding, for the relief of bronchial asthma, and treatment of heart failure," p. 108.

"Concentrated nitric acid gives a yellow color when applied to a protein. This becomes orange upon treatment with ammonium hydroxide. This explains the stains on the skin caused by nitric acid, which resist removal by washing. The color depends upon the nitration of phenyl groups in the protein molecule," p. 114.

"In the digestion of food the body carries on chemical reactions in a manner which has so far proved baffling to chemists and impossible of accomplishment in their laboratories. Foods are broken down into simple water-soluble units, and are quickly adapted for the production of energy, the building of tissue, or for storage against future needs. All of these reactions are carried out without recourse to high temperatures or pressure, which are such useful adjuncts to ordinary laboratory operations.

"Reactions in the body are, however, greatly expedited by catalysts, to which we give the name of enzymes (the name means 'in yeast', where the first enzyme was discovered). These enzymes are elaborated in various glands; many are found in the normal secretions of the glands and do their work outside the secreting gland. These are the exocellular enzymes, such as occur in saliva or gastric juice. Others work within the secreting cells (endocellular enzymes).

"Experiments have definitely shown that we are justified in calling these substances catalysts. By definition a catalyst is a substance which (1) speeds a chemical reaction, but (2) does not increase the amount of material finally transformed. (3) The catalyst is not a part of the final reaction product. (4) A small amount of catalyst will effect the transformation of a relatively large amount of material. Enzymes conform to these definitions. They differ somewhat from most of the inorganic catalysts in that they are specific, a given enzyme catalyzing a particular reaction and none other. Again a given enzyme may catalyze both phases of a reversible reaction (under different sets of conditions). Thus in the laboratory lipase may be used either to promote the hydrolysis of fats or their synthesis from glycerol and fatty acids," p. 123.

"Previous to being absorbed, the fats are hydrolyzed by the enzymes of the intestinal and pancreatic juice, as already noted. Probably these same enzymes assist in the resynthesis of fats from the hydrolysis products. This synthesis appears to take place in the cells of the villi, and the resynthesized fats are then passed to the lacteals of the villi, and so carried to the general circulation. A small amount of fat passes to the blood system of the villi, thence to the liver. The presence of the bile, by enhancing the solubility of fatty acids in the intestinal contents, greatly promotes fat absorption.

"Amino acids from the digestion of proteins are taken into the lacteals of the intestinal villi, but far larger amounts pass into the capillary circulation of the villi. From these simple units the body manufactures the unique and typical protein molecules necessary for its tissues. The absorption of larger protein units, such as peptones or proteoses, or of complete protein molecules, produces a state of shock. This may be noted when certain serums are directly injected into the body in the effort to combat disease. We also have the rather numerous cases in which people are unable to eat certain types of protein food. In such cases it is probable that the complete protein, instead of its final hydrolysis products, is absorbed. The synthesis of the body proteins from the amino acid building blocks takes place in the tissues of the body.

"Practically all of the digested protein, carbohydrate, and fat of the diet is absorbed in the small intestine. These digested food factors may be absorbed by the large intestine (rectal feeding may become necessary in certain cases where the stomach cannot be used), but the rate of absorption is far slower than in the small intestine.

"Cellulose which is undigested in the small intestine is not subject to hydrolysis in the large intestine, since there is no enzyme present to catalyze the reaction. Bacterial action, however, causes the breakdown of such unattacked food residues, and some of the resulting products are absorbed by the large intestine," p. 132.

"Glucose, which is absorbed into the blood stream is withdrawn by the liver and muscles, and there stored as glycogen. The liver may store as much as 300 grams of glycogen, about one-sixth of its weight, while the muscles carry about 2 per cent. As the total weight of muscle tissue is far in excess of that of the liver, the actual amount of glycogen in the former may easily exceed the amount stored by the liver.

"The concentration of sugar in the blood is maintained at a constant value of about 0.1 per cent by this rapid removal and storage process. The total amount of glucose in the blood circulation is about 5 grams. The formation of the glycogen from glucose is termed glycogenesis. The reverse of the above (glycogenolysis) occurs when glucose is needed by the body.

"One stage of the breakdown of glucose is its change to lactic acid; it may be said in passing that this change is reversible, and that both glucose and glycogen may be formed in the body from lactic acid. Lactic acid is formed from glucose during muscular contraction. In the resting phase of the muscle a portion of the acid is reconverted to glycogen, the balance being oxidized to carbon dioxide and water," p. 135.

"It is significant that normal oxidation of fats occurs only when the intake of carbohydrate is adequate and its metabolism is proceeding as it should. In starvation the carbohydrate reserves are first called upon, and when the glycogen is used up, fat metabolism becomes incomplete, as it does in diabetes, where we have faulty carbohydrate utilization," p. 139.

"It has already been mentioned that certain proteins are deficient in particular amino acids. Also that there are certain amino acids which are absolutely essential for our maintenance. These essential amino acids are those which the body cannot synthesize for itself. They include lysine, tryptophane, histidine, cystine, tyrosine, and some others. A diet lacking one or more of these building blocks would not sustain life," p. 141.

"Coffee consists of the seeds of coffee arabica, a shrub which grows in Brazil, Arabia, Africa, etc. It contains cellulose, gums, sugars, fats, tannin, and the alkaloid caffeine. Preparatory to marketing it is roasted, to bring out the color and aroma. A cup of coffee contains about 0.1 g. of caffeine, while maximum single dosage of pure caffeine is about 0.6 g. The physiological effect of caffeine is threefold. It is a heart tonic, it has a diuretic action, (produces an increased flow of urine), and it has an exciting action upon the brain. We are all familiar with the latter effect from tea and coffee drinking. The drinking of tea, coffee, and cocoa, does not in itself increase the body metabolism, though it must be borne in mind that the latter has considerably greater food value than either tea or coffee," p. 166.

Wilder D. Bancroft

A Textbook of Practical Physical Chemistry. *By K. Fajans and J. Wüst. Translated by Bryan Topley. 21 × 14 cm; pp. xv + 233. New York: E. P. Dutton Company, 1930. Price: $4.95.* This is really a laboratory manual with accompanying text. The chief sub-heads are: general introduction; molecular weight determinations in solutions; vapour pressure and distillation of liquid mixtures; surface tension of liquids; the internal friction of liquids; adsorption from solutions; coagulation of a sol by electrolytes of different valencies; determination of hydrogen ion concentration by means of indicators; calorimetry; metallography; the transformation of radio-elements; velocity of chemical reactions; refractometry; quantitiative spectrophotometry in the visible region; ultra-violet spectrography; electrical conductivity of electrolytes; transport numbers; electromotive force; electrochemical preparations; the lead accumulator.

The lowering of the partial pressure with the concentration is expressed, p. 9, in terms of the Raoult ideal formula instead of in terms of the van't Hoff formula.

"It is now known that these considerations, which formerly were considered to be of general validity, should be applied in this form only to weak electrolytes, for which the position of the equilibrium which shifts with increasing dilution towards the side of the dissociated particles is practically the only factor which determines the deviation from the behaviour of undissociated substances.

"On the other hand, for strong electrolytes such as strong acids and bases and many salts, a very large degree of dissociation is assumed at all concentrations; indeed for some time now it has been customary to speak of complete dissociation. Formerly, the deviations from the proportionality to the concentration, of the changes of specific conductance, of osmotic pressure and of catalytic activity, in the case of strong electrolytes as well were referred to different degrees of dissociation at different concentrations. But more exact measurements have shown that at the same concentration the degree of dissociation calculated from conductivity measurements is somewhat different from that calculated from measurements of lowering of the freezing point or raising of the boiling-point or from the catalytic activity of the ions. These discrepancies are now explained as being caused by the electrostatic forces which the ions exert reciprocally and upon the molecules of the solvent, and which affect the conductivity, the osmotic pressure and the catalytic activity somewhat differently. These forces are stronger, the higher the concentration and therefore the smaller the distance apart of the ions. With increasing dilution they become weaker, and at the same time the ions approach more closely the state in which they no longer influence each other, but behave as completely freely moving independent particles. This state is identical with that which had previously been assumed as the state of complete dissociation at infinite dilution. The reduction in free mobility and activity undergone by the ions as a consequence of their mutual action arising from the electrostatic forces makes it appear that the concentration of free ions is less than that corresponding to the assumption of complete dissociation. The factor by which the ionic concentration corresponding to this assumption must be multiplied in order to obtain the concentration of non-mutually influencing ions which would show the same behaviour as that actually observed, is called the 'osmotic coefficient,' the 'conductivity coefficient,' or the 'activity coefficient,' as the case may be. The two latter can also be referred to as 'the apparent degree of dissociation.' The behaviour of any electrolyte solution containing ions of different kinds may (in dilute solution) be approximately calculated additively from the coefficients of the ions in question," p. 16.

On p. 22 the Beckmann thermometer is set for the freezing-point of benzene by trial and error with benzene. It seems to the reviewer that time and trouble would be saved by adjusting it in water by comparison with an absolute-reading thermometer. On p. 29 it is stated that "alterations in the size of the flame affect the observed boiling-point by several thousandths of a degree." This is not necessary with the Davis apparatus.

On p. 61 the authors attempt to justify using the initial concentration in the solution in the case of adsorption rather than the equilibrium concentration, saying that the two do not differ appreciably. This is a rather remarkable mis-statement.

"The colorimetric indicator method depends upon the fact that the change of colour of different indicators takes place at various $H^{\cdot}$-concentrations. According to W. Ostwald, indicators are to be regarded as weak acids or bases with which the undissociated molecule shows a different colour anion or cation formed by dissociation. [According to more recent views the change in colour on formation of an undissociated molecule, say of an acid, from the ions may be looked upon as a result of the deformation of the electronic system of the anion under the influence of the $H^{\cdot}$ nucleus taken up. In many cases (Hantzsch) a shifting of the atoms or bond within the molecule takes place as a result of the adding on of the $H^{\cdot}$, and the colour change is then referred to differences of constitution between anion and acid (e.g. benzenoid and quinonoid forms)]," p. 66.

Since Richards invented the term coulometer, it is unfortunate to substitute the clumsy word coulombmeter, p. 170.

On p. 197 the authors discuss the behavior of the calomel electrode in terms of the hypothetical concentration of $Hg^{\cdot}$ as ion. In a foot-note they say: "Actually, the ions present in mercurous salts are mainly $Hg_2^{\cdot\cdot}$ ions; but since these are in equilibrium with $Hg^{\cdot}$ ions ($2Hg^{\cdot} \rightleftharpoons Hg_2^{\cdot\cdot}$), the quantitative statement of the relationships in terms of the $Hg^{\cdot}$ ions is correct, and this will be done for the sake of greater simplicity in the formulae." The reviewer thinks that it would have been better to have shown how to formulate the problem properly instead of leaving the unfortunate student up in the air. The reviewer thinks that it would also have been wiser to have pointed out somewhere in the book that determinations of hydrogen ion concentrations in chloride solutions are always subject to an error because of the displacement of the water equilibrium. It is only fair to add that the reviewer did not expect to find any such statement. The temptation to ignore errors is strong even among scientific men.

Wilder D. Bancroft

Qualitative Chemical Analysis. *By H. T. Briscoe. 22 × 14 cm; pp. iv + 279. New York: D. Van Nostrand Company, 1931. Price: $2.25.* This book was written with the intention of presenting "a comprehensive treatment of qualitative analysis which can be used and mastered by elementary students with at least one semester of preparatory work in general chemistry."

The first half of the book is devoted to the presentation of the theories and principles of electrolytic solutions, in which is included chapters on (1) A comparison of molecules of gases with molecules in solutions; (2) Avogadro's hypothesis and the van't Hoff theory as applied to solutions of electrolytes; (3) The structure of matter; (4) Reactions in solutions; (5) Chemical equilibrium; (6) Hydrolysis; (7) Oxidation and reduction; (8) Formulas and equations and (9) Colloids. The material is well presented but might be considered to be more comprehensive than is necessary for the study of qualitative analysis, especially when such a course is followed later by the study of physical chemistry.

The second half of the book is devoted to the analysis of the cations, anions and of substances which contain any or all of the different cations and anions. The order of study of the different analytical groups of the cations is the reverse of the ordinary method of presentation. The author states that this "is the order which has been found most consistent with the previous knowledge of the student and the ease with which he may be expected to master the theoretical principles upon which his understanding of the laboratory procedures will depend." The laboratory directions are well written and comprehensive notes and study questions are placed at the end of each group. With large classes, the use of the cyanide separation for copper and cadmium seems rather dangerous, especially when no mention is made of the danger involved and it would be preferable to use the terminology of ammonium thiostannate instead of ammonium sulphostannate, etc.

M. L. Nichols

Quantitative Organic Microanalysis. *By Fritz Pregl. Second English edition. Translated from the third German edition by E. Fyleman. 25 × 15 cm; pp. xiv + 237. Philadelphia: P. Blakiston's Son and Co., 1930. Price: $4.00.* The second English edition of this book is somewhat larger than the previous one and contains the new methods which have been recently developed and tested by Pregl and his co-workers. The importance of this method of analysis has increased greatly in recent years and, although many other chemists are now making contributions to this field, it is a great satisfaction that we have at least one more edition revised by Pregl, before the development of microanalysis was deprived of his inestimable services by his untimely death last December.

The book contains very explicit directions concerning the experimental details of organic microanalysis and is indispensable to the library of any one making analyses by this method or carrying out investigations in this field.

M. L. Nichols

THE EFFECT OF PRESSURE ON THE ELECTRICAL CONDUCTIVITY OF SOLUTIONS OF SODIUM CHLORIDE AND OF OTHER ELECTROLYTES

BY L. H. ADAMS AND R. E. HALL

Although a considerable amount of data on the conductivity of solutions under pressure is available, it became necessary, in connection with another investigation, to make a number of measurements on the effect of pressure on the conductivity of sodium chloride solutions. The principal object was to determine the variation of conductivity with concentration (at various pressures) in nearly saturated solutions, but some measurements were made at lower concentrations. Somewhat higher pressures were used than in previous investigations, and it is believed than an improved technique has allowed the attainment of greater precision. In this paper we present our results for dilute and concentrated sodium chloride solutions, for dilute potassium sulphate solutions, and for one potassium chloride solution; and we add a brief discussion of the various factors which determine the conductivity of electrolytes under pressure.

Apparatus and Method. The conductivity cell, of a type suitable for use in the limited space within the pressure bomb and capable of furnishing a sufficiently high resistance with concentrated solutions, is shown in Fig. 1. It was constructed of "Kavalier" glass and the electrodes were small rings of platinum made by bending the end of a piece of 0.4 mm wire into a loop and then closing the loop by soldering with gold. The platinum wires were sealed through the side of the cell, and just outside the cell were fused to gold wires in order to minimize the resistance of the leads. The electrodes were covered with a layer of platinum black by electrolyzing a solution of platinic chloride.[1] Several cells of somewhat different sizes were employed; usually they were about 5 mm inside diameter at the narrow part and about 4 cm between electrodes. The bottom was provided with a removable joint in order to facilitate cleaning and also to permit the use of the same cell for another line of work. The solutions were made up by weight from salts, which had been twice recrystallized.

Pressure was applied to the cell and its contents within a bomb illustrated in Fig. 2. Attention is directed to its simplicity of construction. The bomb was made of machine-steel and consisted essentially of a cylinder 7.5 cm outside diameter and 29 cm long with a cylindrical cavity 1.9 cm in diameter and 13.4 cm long. At the bottom the pipe through which oil was pumped was connected by a cone joint. Closure at the top also was effected by a cone joint, on the central stem or part that contains the insulated leads for conducting current through the cell. These insulated leads were made by in-

---

[1] *vide* Kohlrausch und Holborn: "Das Leitvermögen der Electrolyte," p. 9 (1898).

serting two steel wires through holes in a cylinder of soapstone, and placing the cylinder in a hole, 7 mm in diameter and 2 cm deep, which had been drilled in the inner end of the central stem, and then ramming the cylinder firmly into place by applying a force of several tons. The steel wires at their upper end had been hard-soldered to copper wires, the joint being placed just below the top of the soapstone; above the packing each copper wire, surrounded by an insulating sheath, passed through a small hole to the top of the stem. Pressure was generated by a hand pump and pressure-intensifier and was measured to within 1 bar by an electrical resistance-gauge that

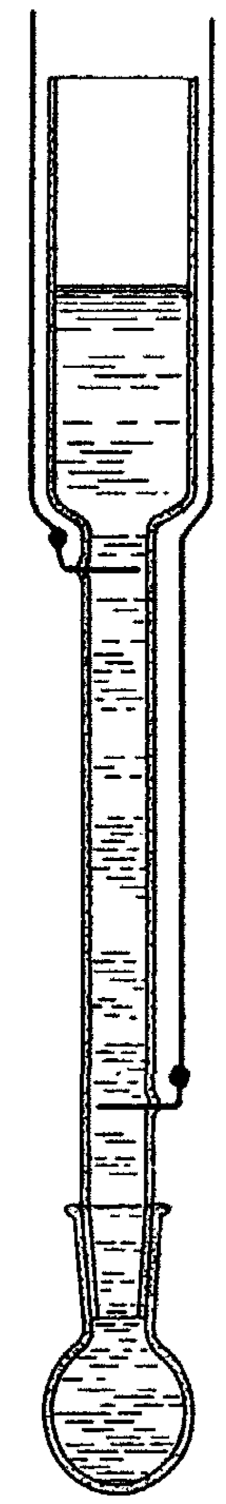


Fig. 1

Cross-section of conductivity cell used for electrolytes under pressure. The electrodes are small rings made of platinum wire (about natural size).

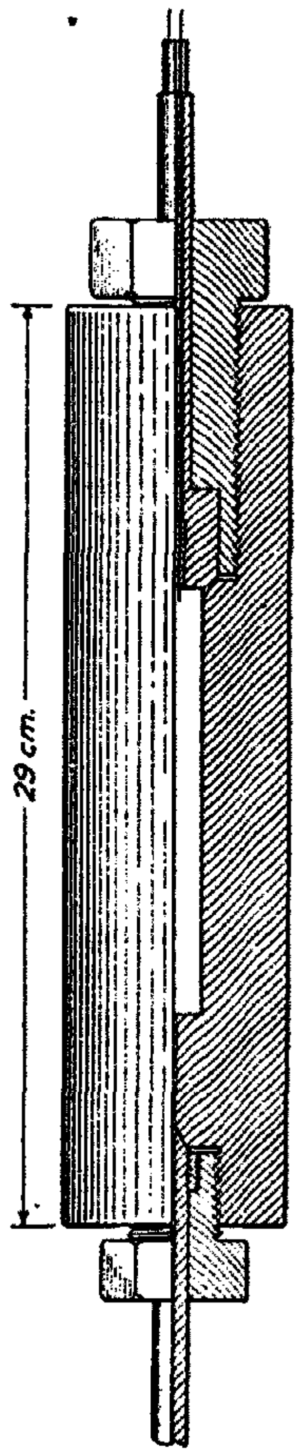


Fig. 2

The bomb in which the cell and contents are subjected to pressure. Two insulated leads pass through the central stem at the top. A pump and gauge are connected through the fitting at the bottom of the bomb.

had been calibrated against an absolute gauge of the free-piston type. Connections between pump, intensifier, gauge and bomb were made with steel tubing, 12 mm in outside diameter and of 1.5 mm bore, the necessary valves and joints being similar to those described in a previous publication[1] from this Laboratory. The medium for transmitting pressure was a light grade of petroleum oil. This was of about the same viscosity as the commercial grades of lubricating oil now designated as "S.A.E. 10." At ordinary temperatures oils heavier than this become so viscous under a pressure of 4000 bars that they transmit pressure only very slowly. Since commercial oils contain a considerable amount of various impurities, the top part of the cell before being placed in the bomb was filled with Nujol, which was found to produce no effect on the resistance of the underlying solution even after being in contact with it for a long period.

The thermostat in which the bomb was placed contained kerosene as the liquid, and the temperature of the bath was read with a ten-junction copper-constantan thermel and a potentiometer, and was maintained constant to within about 0.001°. Thorough stirring insured uniformity of temperature. Heat was supplied by an incandescent lamp immersed in the kerosene, and for convenience the bath contained also a copper coil through which either hot or cold water could be circulated.

For measuring the resistance of the cells an alternating current Wheatstone-bridge was used. The electrical connections are shown diagrammatically in Fig. 3. Alternating current at 1000 cycles was supplied to the bridge by a toothed-wheel generator (Leeds and Northrup "high frequency generator") and was measured with a vacuum thermocouple. The current through the cell was about 0.5 milliampere for a cell-resistance of 100 ohms and correspondingly less for higher cell-resistances. This represented the maximum energy that could be supplied to the cell, even though the current was allowed to flow only while the reading was being made, because otherwise there would be a noticeable heating effect and a consequent drift in the reading. With currents so small as this it was impossible to obtain satisfactory precision in determining the balance-point of the bridge by the use of the telephone alone, although a very sensitive one was available. This was a very real difficulty and was primarily due to the limited size of cell which could be used within the pressure bomb; it was obviated, however, by amplifying the unbalanced e.m.f. of the bridge by means of a two-stage electron-tube amplifier, which enabled the slide-wire setting to be made as closely as it could be read.[2]

The bridge, amplifier, and telephone were placed in a sound-proof booth at some distance from the bomb and thermostat. In series with the wires leading from the alternator were two condensers, of 3 microfarads capacity on each side, and across these wires at the booth was a condenser the capacity of which could be varied from 0.5 to 10 microfarads. These condensers, be-

---

[1] Johnston and Adams: Am. J. Sci., 31, 501-17 (1911).

[2] Hall and Adams: J. Am. Chem. Soc., 41, 1515-1525 (1919).

sides cutting down the current through the bridge below what it would have been without them, served to reduce the relative magnitude of the undesired high and low frequencies and hence to increase the purity of the tone heard in the telephone receiver. This facilitated the obtaining of a silent minimum. It was also necessary to balance out the capacitances and inductances in the various parts of the bridge, the most important of these factors being the effective capacitance of the cell. For this purpose it was sufficient to have the variable condenser C_3 (Fig. 3) so arranged that it would be connected in parallel either with the cell or with the variable resistance R. This condenser was adjusted for each cell until, by moving the slide wire, a sharp and silent minimum could be obtained. The resistance R, which consisted of non-inductive Curtis coils, was always set at a value nearly equal to the resistance of the cell, so that the setting on the slide-wire was very near the middle. This procedure simplified the calibration of the slide-wire and materially increased the accuracy of the readings.

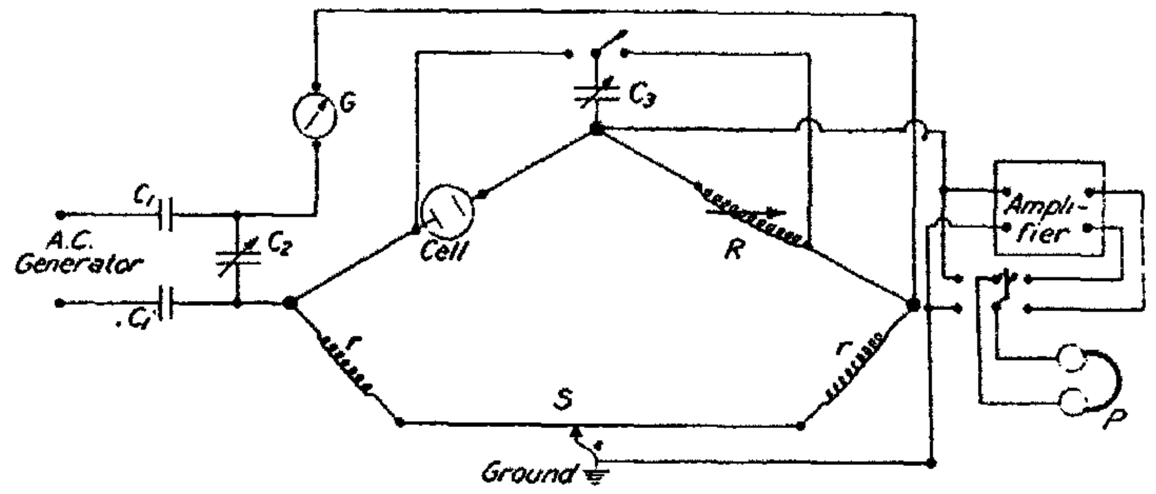


FIG. 3

Electrical circuit for the Wheatstone-bridge and appurtenances. S is a Kohlrausch slide wire, with extension coils, rr. The unbalanced e.m.f. from the bridge is amplified by an electron-tube amplifier inserted between the bridge and the telephone receiver, P.

The Kohlrausch slide-wire, S, consisted of 10 turns and the measuring-drum was provided with 200 divisions, making 2000 divisions for the total length of wire. The extension coils, rr, were each of 4.5 times the resistance of the slide-wire, so that the slide-wire resistance was one-tenth of that of the whole tract. The settings could readily be made to one-tenth of a division, or better, and hence to within one part in 200,000 of the resistance of the tract. It may be shown that this corresponds to a precision of one part in 50,000 in the resistance of the cell, and duplicate readings with slight variation in R verified this conclusion. This, of course, pertains only to the accuracy of the setting, and in order to realize the theoretical degree of accuracy it was necessary to guard against temperature effects, stray e.m.f.'s, unbalanced capacitances, and other sources of error. A useful criterion of freedom from certain errors is afforded by a comparison of the resistance as determined with alternating current and with direct current on the bridge. It was found that when a coil of about 200 ohms was put in the place ordinarily occupied by the cell, the a-c. resistance agreed, as closely as could be read, with the resistance obtained by supplying direct current to the bridge and determining the balance-point with a d-c. galvanometer. It was also observed that the resistance of the cell filled with solution as a rule did not change with time, except for a small initial effect due to equalization of temperature. After one series of measurements with a concentrated NaCl solution, in which the resistance at atmospheric pressure was 90.963 ohms, the experiment was interrupted by other work and the apparatus with cell in place stood undisturbed for more than a year. At the end of this time the resistance was measured again at the same temperature and at atmospheric pressure and was found to be 90.964. The constancy in resistance was quite gratifying; there were sometimes, however, small changes in the resistance before and after subjecting the cell to pressure.

Experimental Results. The measurements on solutions are collected in Table I, which shows the resistances of the various solutions under pressures ranging from 1 bar to about 4000 bars (ordinarily). Most of the measurements were made at 25°, although some of the earlier ones were at 30°, and one series was at 0°. Several different cells of nearly but not quite the same dimensions were used in the course of the work but all of the results are made comparable by tabulating the values of the relative resistance, R/R_0, that is, the ratio of the resistance of the cell at the given pressure to the resistance at atmospheric pressure. It is this relative resistance which represents most simply the effect of pressure on the resistivity of solutions. In the present investigation little attention was paid to absolute resistivity. Although this could have been determined by taking account of the cell-constant for each cell, it was not considered worth while, because the cells themselves were not of the most favorable form for obtaining absolute values. As is well known, there is a minimum area of electrodes for a given cell[1] below which slight errors in the resistivity may occur, but the resistance ratio, R/R_0, is affected very little by the size of the electrodes or the form of the cell.

Carefully prepared "conductivity water" was used in making up the solutions for the earlier measurements. It was noted that when the cell was allowed to remain in place within the pressure apparatus the conductivity of the water increased at a noticeable rate. On the other hand, when what would be called a poor conductivity water (conductivity, 2×10^{-6} reciprocal ohms) was used, the change with time was much slower. The question then arose: What effect would a high conductivity of the water used in making up the solutions have on the values of R/R_0 for the solutions? In order to answer this question, the effect of pressure on the conductivity of the water was measured. The results for water are shown in Table II. Since the resistance of the cell at atmospheric pressure had changed during the experiment the values of R_0 at the various times were determined by simple interpolation, and these interpolated values were used in calculating R/R_0 at the several pressures as shown in the last column. The influence of the water

---

[1] For absolute measurements it is desirable for the area of either electrode in cm² to be at least 200 divided by the resistance of the cell in ohms.

TABLE I

Results for conductivity of solutions under pressure

Pressure (bars)	R	R/R_0
NaCl, 20.26%; temp., 29.93°		
1	64.31	1.0000
243	64.26	.9992
497	64.28	.9995
754	64.38	1.0011
999	64.53	1.0034
1516	65.06	1.0117
2032	65.80	1.0232
2427	66.52	1.0344
3145	67.98	1.0571
1	64.31	1.0000
245	64.26	.9992
485	64.29	.9997
744	64.38	1.0011
1014	64.55	1.0038
1492	65.03	1.0112
2018	65.77	1.0227
2421	66.46	1.0334
3040	67.74	1.0534
3455	68.74	1.0689
3901	69.90	1.0869
2788	67.20	1.0449
1808	65.43	1.0174
863	64.42	1.0017
1	64.31	1.0000
NaCl, 23.79%; temp., 24.93°		
1	90.963	1.0000
294	91.181	1.0024
528	91.463	1.0055
791	91.868	1.0099
1046	92.344	1.0152
1282	92.853	1.0208
1540	93.475	1.0276
NaCl, 23.92%; temp., 29.93°		
1	59.85	1.0000
241	59.98	1.0022
495	60.17	1.0053
764	60.43	1.0097
988	60.69	1.0140
NaCl, 23.92%. temp., 29.23°		
1472	61.37	1.0254
1985	62.26	1.0403
2486	63.26	1.0570
3089	64.65	1.0802
3515	65.74	1.0984
3893	66.78	1.1158
2683	63.68	1.0640
1885	62.03	1.0364
1198	60.94	1.0182
715	60.36	1.0085
1	59.88	1.0005
NaCl, 23.98%; temp., 24.93°		
1	65.92	1.0000
266	66.07	1.0023
507	66.28	1.0055
772	66.58	1.0100
1026	66.93	1.0153
1266	67.31	1.0211
1538	67.80	1.0285
2116	69.04	1.0473
2567	70.17	1.0645
3166	71.87	1.0903
3543	73.05	1.1082
3923	74.27	1.1267
2674	70.44	1.0686
1735	68.16	1.0340
826	66.61	1.0105
378	66.13	1.0032
1	65.92	1.0000
NaCl, 26.48%; temp., 29.93°		
1	58.19	1.0000
230	58.42	1.0040
499	58.74	1.0095
754	59.08	1.0153
991	59.45	1.0217
1235	59.86	1.0287
1502	60.34	1.0369
2127	61.65	1.0595

TABLE I (Continued)

Results for conductivity of solutions under pressure

Pressure (bars)	R	R/R_o
NaCl: 26.48%; temp., 29.93°		
2504	62.52	1.0744
3137	64.13	1.1021
3423	64.93	1.1158
3866	66.21	1.1378
2563	62.64	1.0765
1582	60.49	1.0395
731	59.03	1.0144
1	58.20	1.0002
NaCl, 24.76%; temp., 24.93°		
1	65.28	1.0000
273	65.50	1.0034
520	65.75	1.0072
784	66.10	1.0126
1033	66.46	1.0181
1275	66.89	1.0247
1536	67.39	1.0323
2015	68.45	1.0486
2579	69.89	1.0706
3053	71.25	1.0915
3517	72.69	1.1135
3905	73.95	1.1328
2430	69.44	1.0637
1576	67.43	1.0329
698	65.93	1.0100
1	65.29	1.0002
NaCl, 26.09%; temp., 0°		
1	132.26	1.0000
285	133.05	1.0060
477	133.83	1.0119
997	136.26	1.0302
1503	139.34	1.0535
1902	142.19	1.0751
2294	145.35	1.0990
2877	150.88	1.1408
3289	154.76	1.1701
2397	146.73	1.1094
1361	138.84	1.0497
477	134.19	1.0146
1	132.97	1.0054
NaCl, 0.5836%; temp., 25.00°		
1	533.60	1.00000
511	515.35	.96578
1021	504.28	.94504
1524	498.51	.93424
1824	496.88	.93118
2082	496.42	.93032
2340	496.75	.93094
2588	497.71	.93274
3135	501.83	.94046
3646	507.81	.95166
4168	515.67	.96638
3077	501.04	.93896
2178	496.12	.92976
957	504.91	.94624
1	533.48	.99975
NaCl, 0.1168%; temp., 25.00°		
1	2466.0	1.00000
518	2381.7	.96583
1047	2330.2	.94493
1519	2306.0	.93512
1848	2299.0	.93230
2155	2298.3	.93200
2643	2307.1	.93558
3181	2328.3	.94420
3676	2357.3	.95592
4186	2395.0	.97125
2881	2313.7	.93825
2291	2298.4	.93205
1	2465.5	.99982
NaCl, 1.1387%; temp., 25.00°		
1	285.60	1.00000
245	280.45	.98197
524	275.75	.96551
1	285.66	1.00000
252	280.40	.98159
555	275.40	.96408
790	272.44	.95372
1033	270.07	.94542
1294	268.22	.93895

TABLE I (Continued)

Results for conductivity of solutions under pressure

Pressure (bars)	R	R/R_0
NaCl, 1.1387%; temp., 25.00°		
1545	267.02	.93475
1822	266.26	.93209
2087	266.02	.93125
2352	266.22	.93195
2630	266.84	.93412
3125	268.87	.94122
3680	272.35	.95341
4195	276.54	.96807
3121	268.73	.94073
2106	265.87	.93072
1117	269.23	.94248
1	285.67	1.00003
NaCl, 0.2921%; temp., 25.00°		
1	1026.55	1.00000
497	991.98	.96636
997	970.58	.94552
1522	958.86	.93410
1869	955.67	.93100
2127	955.15	.93048
2404	956.28	.93158
2680	958.92	.93416
3470	973.39	.94826
4161	993.62	.96796
3101	965.20	.94028
1967	954.71	.93006
1	1026.34	.99984
NaCl, 1.1495%; temp., 25.00°		
1	297.40	1.00000
283	291.33	.97960
581	286.41	.96305
750	284.20	.95560
1046	281.24	.94568
1300	279.56	.94001
1552	278.49	.93642
1791	278.00	.93476
2080	277.80	.93410
2409	278.23	.93556
2678	279.02	.93818
NaCl, 1.1495%; temp., 25.00°		
3165	281.29	.94584
3690	284.87	.95788
4072	288.33	.96950
3074	280.72	.94390
2153	278.06	.93498
1176	281.12	.94526
1	297.56	1.00054
NaCl, 2.8650%; temp., 25.00°		
1	122.103	1.00000
503	118.356	.96933
1089	115.773	.94814
1588	114.741	.93968
1930	114.494	.93765
2174	114.506	.93782
2624	114.897	.94100
3451	116.660	.95540
4189	119.152	.97582
3090	115.704	.94754
2102	114.446	.93733
1	122.080	.99981
K_2SO_4, 1.6861%; temp., 25.00°		
1	287.01	1.00000
583	272.41	.94913
1055	264.70	.92227
1633	258.70	.90136
1885	256.99	.89540
2145	255.68	.89084
2606	254.39	.88634
3128	254.19	.88565
3691	255.30	.88952
2941	254.05	.88516
1368	260.88	.90896
1	286.94	.99976
K_2SO_4, 0.1739%; temp., 25.00°		
1	2234.5	1.00000
562	2144.4	.95967
1088	2092.4	.93643

TABLE I (Continued)

Results for conductivity of solutions under pressure

Pressure (bars)	R	R/R_0	Pressure (bars)	R	R/R°
K_4SO_2, 0.1739%; temp., 25.00°			KCl: 0.373%; temp., 25.00°		
1565	2064.6	.92395	2115	701.93	.92638
2096	2049.5	.91719	2705	704.10	.92925
2610	2047.0	.91609	1605	704.41	.92966
3037	2052.2	.91842	554	728.95	.96204
3698	2071.5	.92706	1	757.60	.99985
2734	2047.0	.91610			
2358	2046.1	.91568	K_2SO_4, 0.4336%; temp., 25.00°		
1	2234.5	1.00002	1	969.77	1.00000
			540	928.54	.95748
KCl, 0.3730%; temp., 25.00°			1067	902.90	.93104
1	757.71	1.00000	1720	885.10	.91269
258	742.76	.98027	2430	877.59	.90494
517	730.78	.96446	2859	877.44	.90479
766	721.68	.95245	3530	882.68	.91020
1023	714.38	.94281	4162	892.50	.92032
1285	709.07	.93581	3087	878.16	.90553
1542	705.32	.93086	2599	876.94	.90428
1848	702.75	.92747	1	969.68	.99991

itself on the values of R/R_0 for solutions will obviously be less for concentrated solutions (of low resistivity) than for dilute solutions (of high resistivity), and it can easily be shown that with the most dilute solution here investigated (0.1% NaCl) the correction to be applied to the R/R_0, on account of the conductivity of the water, will be negligible, even though the conductivity of the water be as high as 2×10^{-6}. For this reason water of about this quality was used throughout most of the work.

In Fig. 4 the conductivity of NaCl solutions at atmospheric pressure and at 4000 bars is shown as a function of concentration. As usual, the con-

TABLE II

The effect of pressure on the conductivity of water (initial conductivity 2×10^{-6} reciprocal ohms, temperature 25°)

Pressure (bars)	R (ohms)	time (minutes)	R_0 (ohms)	R/R_0
1	1,750,000	0	1,750,000	1.000
966	1,433,000	50	(1,640,000)	.874
2039	1,318,000	90	(1,552,000)	.849
3132	1,250,000	120	(1,487,000)	.840
4147	1,193,000	160	(1,398,000)	.853
1		190	1,332,000	——

ductivity, κ, is expressed in reciprocal ohms. From this diagram it may be seen that pressure decreases the conductivity of dilute solutions but increases that of the concentrated solutions. It is evident, however, that pressure does not have a very great influence on the *absolute* conductivity except in strong solutions. The effect on the *relative* conductivity is more striking and will be discussed later. The diagram also shows that at sufficiently high pressures the conductivity of NaCl solutions seems to reach a maximum at a concentration close to saturation and then to decrease. It is known that a maximum conductivity exists for several electrolytes at atmospheric pressure, as for example in the case of $CaCl_2$, for which in Fig. 4 a curve has been constructed from the data of Kohlrausch and Holborn.[1] Apparently, it has not been suspected that other salts, which at low pressures do not show a maximum, may do so at high pressures. The probable reason for this phenomenon will be given below.

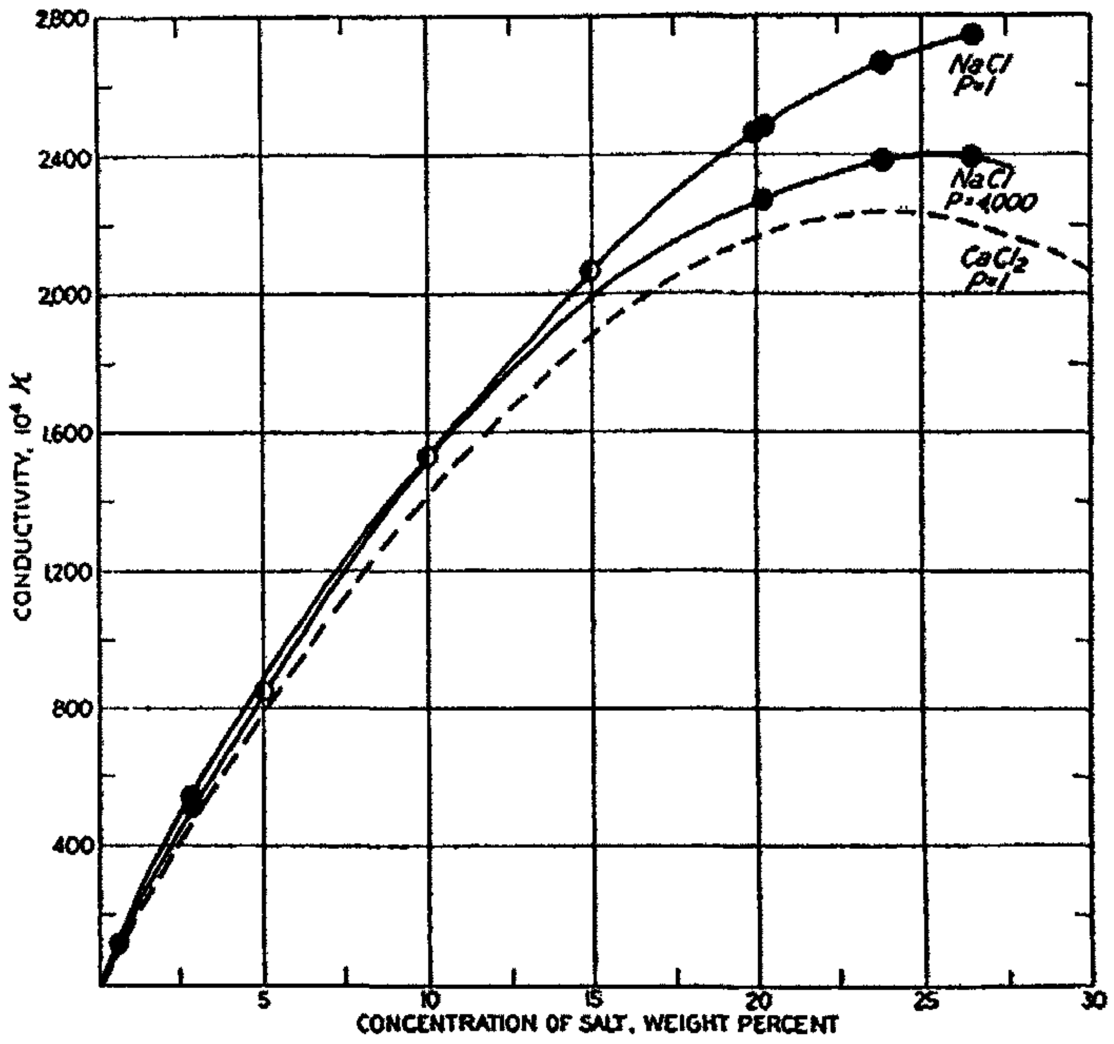


FIG. 4

The conductivity of NaCl solutions at atmospheric pressure and at 4000 bars as a function of concentration. The effect of pressure on the *absolute* value of the conductivity is not large except in concentrated solutions. At high pressures there is a maximum in the conductivity curve just as there is at atmospheric pressure for $CaCl_2$ (dashed line).

A much better way of exhibiting the changes produced by pressure is to plot the relative conductivity or the relative resistivity. In Fig. 5 are given several curves with the resistance ratio, R/R_0, as ordinate and the pressure

---

[1] *Op. cit.*

as abscissa. Here R_0 is the resistance of the cell at atmospheric pressure and R the resistance at the given pressure. The temperature is 30°, the measurements in the 2.87% solution having been reduced to 30° by applying a small temperature correction. Measurements with increasing pressure are indicated by open circles, and with decreasing pressure by half-blacked circles. In agreement with the results of previous investigations the curves of Fig. 5 show that in dilute solutions the resistance first decreases with increasing pressure and then increases, while in concentrated solutions the resistance increases throughout the whole pressure range. This diagram, however, does not show up certain relations for concentrated solutions as well as Fig. 6, in which the resistance at constant pressure is plotted against the concentration, between 20% and 26 1/2 %. The values shown are the actual resistances of a particular cell (allowable in this case because the same cell was used for the three solutions) and were interpolated at even pressures from the data of Table I. From the figure it is evident that the slope of the resistance-concentration curves in nearly saturated solutions changes to a marked extent with variation in pressure. It is also evident that in the use of the conductivity for determining the concentration of a saturated solution under pressure, the resistance-concentration gradient can be determined accurately only by measurements on a number of solutions at small intervals of concentration.

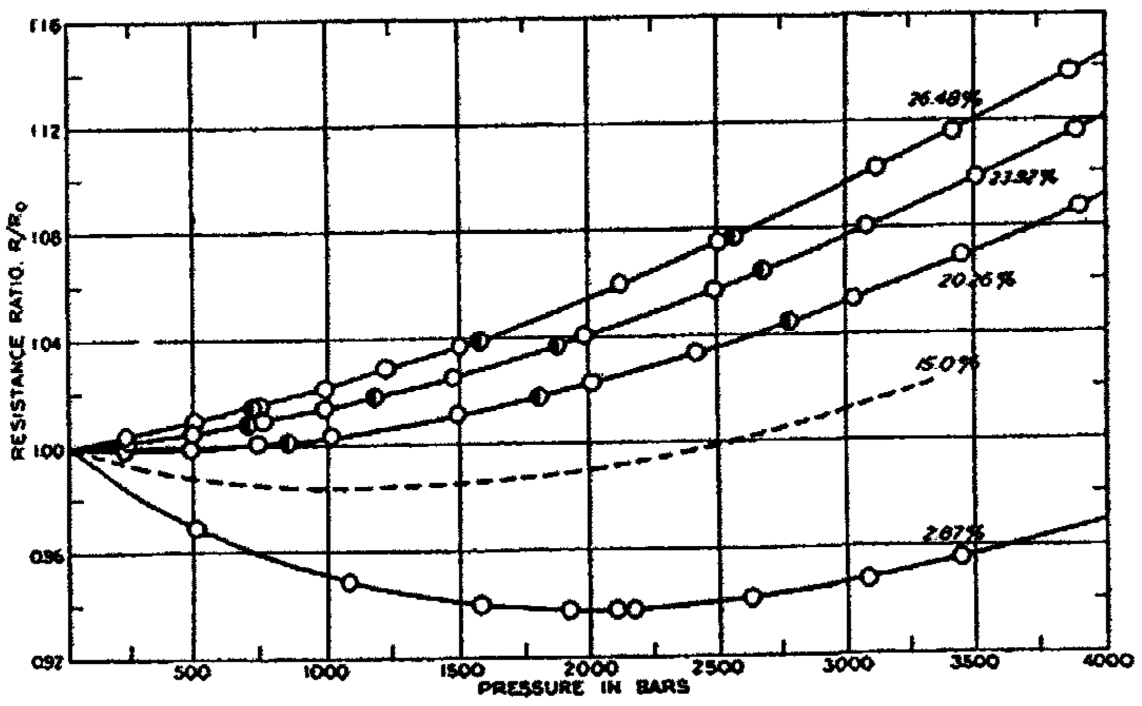


FIG. 5

The relative resistivity of several NaCl solutions as a function of pressure. Except in concentrated solutions the relative resistivity passes through a minimum.

Comparison with previous measurements. Measurements on the conductivity of electrolytes under pressure were made by Colladon and Sturm[1] as long ago as 1827, but the highest pressure used was only 30 atmospheres and their data are now of little value. Among the previous investigations

---

[1] Colladon and Sturm: Ann. Chim. Phys., 36, 231 (1827).

the most important are those of Röntgen[1] on solutions of NaCl, KCl, HCl, $ZnSO_4$, H_3PO_4, and H_2SO_4 up to 500 atmospheres; of Tammann[2] and Bogojawlenski and Tammann[3] who worked with dilute NaCl, HCl, and acetic acid solutions at pressures up to about 3500 atmospheres; of Lussana[4] on dilute solutions of NaCl and other chlorides up to 1000 atmospheres, and of Körber[5] who made numerous measurements on dilute solutions of a large number of electrolytes and on both dilute and concentrated solutions of a few salts including NaCl. The work of other investigators[6] is less pertinent to the present discussion, although it includes interesting results such as those for solutions in organic solvents.

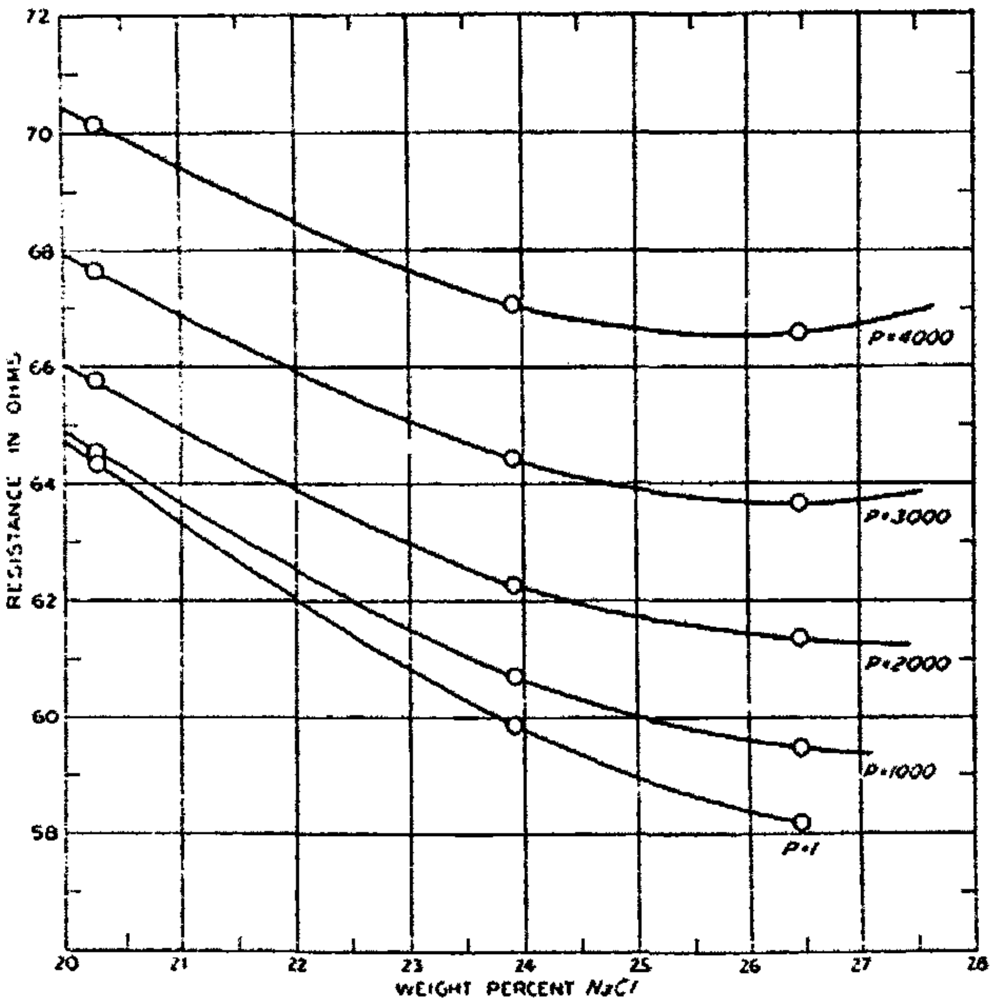


FIG. 6

These isobars for concentrated NaCl solutions show how the resistance of a particular cell changes with concentration at various pressures. In the nearly saturated solutions pressure alters the resistance-concentration gradient to a marked extent.

Owing to the great diversity of temperatures, pressures, concentrations, and substances covered by these investigations, it is difficult to show the correspondence with the present measurements, but it is possible to compare

---

[1] Röntgen: Nachr. K. Ges. Göttingen, 1893, 505.

[2] Tammann: (a) Z. physik. Chem., 17, 725 (1895); (b) Ann. Physik, 69, 767 (1899).

[3] Bogojawlenski and Tammann: Z. physik. Chem., 27, 457 (1898).

[4] Lussana: Nuovo Cimento, (4) 5, 357, 441 (1897); 18, 170 (1909); Z. physik. Chem., 76, 420 (1911); 79, 677 (1912).

[5] Körber: Z. physik. Chem., 67, 212 (1909); 77, 420 (1911); 80, 478 (1912).

[6] For example: (a) Hertwig: Ann. Physik, 160, 110 (1877); (b) Fink: 26, 481 (1885); (c) Fanjung: Z. physik. Chem., 14, 673 (1894); (d) Schmidt: 75, 305 (1911).

the results of Tammann[1] and of Körber[2] for a 24.7% solution (5.0 N), with the present results. This comparison is shown by Table III. The values of R/R_0, at round pressures, in each instance were obtained by interpolation from the original data, and the results of Tammann and of Körber have been brought to 25° by applying a temperature correction. The agreement is not very good, although Körber's results agree better with the authors' than do Tammann's. It is possible, of course, that the form of cell used may have some influence on the values of R/R_0 obtained, but it does not seem at all probable that this *relative* resistance under pressure could vary enough, with different cells, to account for the discrepancy. The authors believe that the average error of their results for R/R_0, under the conditions as described, is not greater than one or two units in the fourth decimal place, but the measurements are subject to a slight correction for the effect of pressure on the distance apart of the electrodes and on the diameter of the cell. This correction probably would decrease R/R_0 by not more than 0.0005 per 1000 bars, and would improve somewhat the agreement with Körber's results.

TABLE III

Comparison with results of Körber and of Tammann. Temp. 25.00°

Pressure (bars)	0.583% NaCl			24.7% NaCl	
	R/R_0 Tammann	R/R_0 Körber	R/R_0 A. & H.	R/R_0 Körber	R/R_0 A. & H.
1	1.000	1.000	1.0000	1.0000	1.0000
1000	.938	.947	.9455	1.0156	1.0176
2000	.920	.929	.9305	1.0448	1.0478
3000	.919	.931	.9382	1.0837	1.0886

For the effect of pressure on the conductivity of water, Körber[3] obtained results which differ considerably from those given in Table II, but no reason for the difference is apparent. His values for R/R_0 in the case of water the conductivity of which was 1.6×10^{-6} at 20° are 0.602, 0.359, and 0.179, respectively, at 1000, 2000, and 3000 bars. Bogojawlenski and Tammann[4] at 500 bars obtained substantially the same result as Körber, and observed that with different samples of water the change in R/R_0 was somewhat greater for the water of lesser conductivity.

Temperature-coefficient. From the data in Table I it is possible to calculate the temperature-coefficient of R/R_0 at different pressures for a concentrated NaCl solution at approximately 25°. The results of the calculation for a 24.7% solution are given in the last column of Table IV and show that increasing temperature causes a slight diminution in R/R_0 for each pressure, the coefficient being larger at high pressures than at low pressures. The average values of $-d(R/R_0)/dt$ between 0° and 30° for a 26.1% solution were

---

[1] Tammann: Ann. Physik, 69, 767 (1899).

[2] *Op. cit.*

[3] *Op. cit.*

[4] *Op. cit.*

TABLE IV

Temperature-coefficient of the resistance-ratio, R/R_0, for NaCl solutions

Pressure (bars)	0.058% $d(R/R_0)/dt$ (Körber)	0.583% $d(R/R_0)/dt$ (Tammann)	24.7% $d(R/R_0)/dt$ (A. & H.)
1	—	—	—
1000	0.001_3	0.001_3	-0.0001_8
2000	$.001_8$	$.001_5$	$-.0004_8$
3000	$.001_9$	$.001_8$	$-.0011_2$
4000	—	—	$-.0018_6$

also calculated and found to be 0.00032, 0.00096, and 0.00186 at 1000, 2000, and 3000 bars, respectively. In dilute solutions the temperature-coefficient is of opposite sign, as may be seen from the coefficients for 0.058% and 0.583% solutions, calculated from the data of previous investigations.

The general effect of temperature on the conductivity of *dilute* solutions under pressure is well known; a family of curves obtained by plotting R/R_0 against pressure for a single (dilute) solution at several different temperatures presents the same general appearance as Fig. 5, the curves for the highest temperature being on top. Such a family of curves (isotherms) for a nearly saturated solution would be reversed in order of temperature and more closely crowded together, and for a solution of a certain intermediate concentration a single curve would apply, within limits, to a range of temperatures. The relative position of the isotherms in concentrated solutions of NaCl in water is similar to that for dilute solutions of salts in organic solvents,[1] for example, KI in ethyl alcohol.

Effect of pressure on electrolytic dissociation. Many attempts have been made to determine the influence of pressure on the degree of dissociation of electrolytes. Waiving at this time all questions concerning the desirability of so defining dissociation that strong electrolytes in aqueous solution are always 100 per cent dissociated, and, for the purposes of the present discussion, considering the degree of dissociation, α, as arbitrarily defined by the ratio of Λ, the equivalent conductance[2] to Λ_0, the limiting value of the equivalent conductance in an infinitely dilute solution, let us note briefly what conclusions have already been reached concerning the effect of pressure on α and whether any new light is shed on the problem by the present results. The principal difficulty which enters into any attempt to deal with the effect of either pressure or temperature on electrolytic dissociation arises from the fact that the conducting power of a solution is intimately connected with the viscosity. The value of Λ_0 has been found to increase with increasing temperature, and the amount of the increase is almost exactly proportional to the increase of fluidity (reciprocal of viscosity). The frictional resistance encountered in the movement of ions presumably depends on the viscosity of

---

[1] Hertwig: Ann. Physik, 160, 110 (1877).

[2] Λ is usually defined as the ratio of the conductivity in reciprocal ohms to the concentration in gram-equivalents per cm³.

the medium, and this "ionic friction" appears to be proportional to the viscosity of the solution at the various temperatures at least in dilute solutions. From the data on the conductance of numerous salts in moderately dilute concentrations it has been concluded that the dissociation decreases steadily with increasing temperature. At each temperature α is considered to be equal to Λ/Λ_0 for that temperature. This procedure takes no account of the variation of viscosity, and involves the tacit assumption that the ionic friction changes with concentration in the same way at all temperatures.

The effect of pressure on conductivity and on dissociation is analogous to that of temperature. The change in conductivity may be considered as the sum of the three separate effects of pressure on: (1) the viscosity, η, (2) the dissociation, α, and (3) the change in concentration (per unit volume) due to the compressibility of the solution. (In solutions of concentration below 0.01N the effect of pressure on the conductivity of water also is important.) Röntgen[1] noted that in dilute solutions of strong electrolytes the dissociation is so nearly complete that the principal effects are those due to changes in viscosity and in volume. The limiting value of $\Delta R/R_0$ at infinite dilution at a given pressure should therefore be equal to the algebraic sum of $\Delta\eta/\eta_0$ and the relative volume change, $\Delta V/V_0$, for pure water. For a dilute NaCl solution at 15°, Röntgen found R/R_0 to decrease 4%, which is the sum of $\Delta\eta/\eta_0$ (-2%) and $\Delta V/V_0$ (-2%) at the same temperature and pressure. At 0° the agreement also was satisfactory. Röntgen gave good reasons for believing that all electrolytes at a given temperature and pressure have the same limiting value of R/R_0 at infinite dilution (correction being made, of course, for the effect of pressure on the conductivity of the water). Furthermore, Lussana[2] observed that the temperature-coefficient of R/R_0 at infinite dilution approaches a limit which also is nearly identical for all electrolytes. From this follows the interesting conclusion that the viscosity of water under pressure could be calculated from measurements on the conductivity and compressibility of dilute solutions. Tammann[3] concluded that in aqueous NaCl solutions the ionic friction varied in the same way as the viscosity of the solutions, but the measurements of Körber[4] indicated that in general this could not be true for electrolytes because the values of R/R_0 for a number of alkali halides in 0.01N solution showed very large differences.

For solutions of moderate concentration the situation is even more complicated, but the measurements of R. Cohen[5] on the viscosity of NaCl solutions at pressures up to 600 atmospheres show so striking a resemblance to the course of R/R_0 under pressure as to leave no room for doubt that viscosity is the predominant factor in determining the effect of pressure on the conductivity of strong electrolytes. At 0° the viscosity of water[6] first decreases with

---

[1] *Op. cit.*

[2] *Op. cit.*

[3] Tammann: Ann. Physik, 69, 767 (1899).

[4] *Op. cit.*

[5] R. Cohen: Ann. Physik, 45, 666 (1892).

[6] See Bridgman: Am. Acad. Arts Sci., 61, 85 (1926); and also Hansen: Ann. Physik, 5, 597 (1901).

increasing pressure and then increases. Variation of temperature alters the course of the viscosity-pressure curve; the amount of the decrease becomes less at higher temperatures, and above 30° the viscosity increases continuously with pressure as in the case of normal liquids. The addition of sodium chloride to the water produces the same kind of change as an increase in temperature; the minimum gradually disappears, and, at a sufficiently high concentration, pressure initially and steadily increases the viscosity of the solution. The general appearance of the curves for R/R_0 in a given concentration at various pressures, as shown in Fig. 5, is similar to that of a set of curves obtained by plotting the viscosity of the several solutions against pressure. In dilute solutions the resistivity first decreases with increasing pressure, then attains a minimum value, and finally increases, while in concentrated solutions (of strong electrolytes) the effect of pressure is always to increase the resistivity. Thus, the resistance changes run parallel with the changes in viscosity. Probably viscosity also plays an important part in producing a minimum in the resistivity (maximum in conductivity) when plotted against the concentration (see Fig. 4), as observed with NaCl at high pressures and with several other electrolytes under ordinary conditions. A given pressure will increase the viscosity of a concentrated solution more than that of a dilute solution, and therefore in the case of NaCl, the increase of viscosity with concentration may under high pressures be sufficiently great to cause a falling off of conductivity with increasing concentrations.

It is evident that the intimate relationship between viscosity and conductivity makes it impossible to estimate the influence of pressure on electrolytic dissociation in strong electrolytes without having complete information concerning the viscosity (or more exactly, the ionic friction) of the solutions at all of the temperatures, pressures, and concentrations under consideration. Even then it is questionable whether this particular problem would be solved, on account of the uncertain nature of the "ionic friction" and the lack of knowledge of its relation to measurable physical quantities. The situation is somewhat different with respect to weak electrolytes (e.g. acetic acid). Here pressure causes a large decrease in resistance, even in concentrated solutions. Since the change is much greater than the accompanying effects of pressure on volume and viscosity, it may be attributed mainly to an increase in dissociation, and an approximate estimate of the degree of dissociation under pressure can readily be obtained from conductivity measurements.

Returning now to dilute solutions of strong electrolytes, we may note the values of R/R_0 for two typical salts, as shown in Table V. These resistance-ratios for several dilute solutions of NaCl and K_2SO_4 were interpolated at round pressures from the results of Table I. In Table V there are included also, in parentheses, the values of $(R/R_0)/(V/V_0)$, which may be considered the resistance-ratios as corrected for the decrease in volume (and consequent increase in concentration) under pressure. The volume-ratios, V/V_0, were determined from the compressibility measurements on NaCl and K_2SO_4 solutions by one of the authors. If, in accordance with the definition of α at atmospheric pressure, it be defined at any pressure as the ratio of Λ to Λ_0 at

TABLE V

Values of R/R_0, for dilute NaCl and K_2SO_4 solutions, with and without correction for the compressibility of the solutions.

$\frac{R}{R_0}$ and $\frac{R}{R_0}\Big/\frac{V}{V_0}$

NaCl

Pressure (bars)	0.117% (0.02 N)	0.292% (0.05 N)	0.583% (0.10 N)	1.139% (0.20 N)	2.865% (0.50N)
1	1.0000	1.0000	1.0000	1.0000	1.0000
	(1.0000)	(1.0000)	(1.0000)	(1.0000)	(1.0000)
500	.9668	.9662	.9664	.9670	.9695
	(.9876)	(.9869)	(.9870)	(.9873)	(.9895)
1000	.9464	.9455	.9455	.9464	.9506
	(.9847)	(.9837)	(.9835)	(.9842)	(.9875)
2000	.9322	.9308	.9305	.9313	.9376
	(1.0021)	(1.0004)	(.9998)	(1.0001)	(1.0050)
3000	.9410	.9393	.9382	.9387	.9469
	(1.0391)	(1.0367)	(1.0353)	(1.0354)	(1.0417)
4000	.9658	.9635	.9619	.9623	.9708
	(1.0911)	(1.0882)	(1.0858)	(1.0853)	(1.0918)

K_2SO_4

Pressure (bars)	0.174% (0.02 N)	0.434% (0.05 N)	1.686% (0.20 N)
1	1.0000	1.0000	1.0000
	(1.0000)	(1.0000)	(1.0000)
500	.9633	.9601	.9552
	(.9841)	(.9807)	(.9752)
1000	.9395	.9336	.9248
	(.9778)	(.9715)	(.9615)
2000	.9179	.9096	.8934
	(.9867)	(.9775)	(.9589)
3000	.9180	.9069	.8858
	(1.0136)	(1.0010)	(.9760)
4000	.932	.9178	.893
	(1.053)	(1.0364)	(1.006)

that pressure, the results for the equivalent conductance at a given pressure could be extrapolated to zero concentration by one of the well-known methods, and the value of α (so defined) at that pressure could thus be calculated. It can be shown that this procedure is exactly equivalent to calculating α by the equation,

$$\left(\frac{\alpha_p}{\alpha_{p=1}}\right)_x = \left(\frac{B_{x=0}}{B_x}\right)_p$$

in which B is the "corrected" resistance ratio, $(R/R_0)/(V/V_0)$, and in which the subscript p refers to pressure and the subscript x to concentration. This equation states that the ratio of α at a given pressure to α at $p = 1$ (for a specified concentration) is equal to the ratio of the limiting value of B at infinite dilution and at a given pressure to B at the same pressure and at the given concentration.

By inspection of Table V it may be seen that for NaCl the values of B at constant pressure decrease up to a concentration of about 1% and then start to increase.[1] For K_2SO_4 solutions B falls off more rapidly and presumably begins to increase at higher concentrations. The application of the above equation for α to the results of Table V, the influence of viscosity being neglected, indicates that pressure increases the dissociation of NaCl in solutions up to at least 1% in concentration and in K_2SO_4 up to higher concentrations. This may be compared with the effect of temperature in decreasing dissociation[2] and means that the dissociation proceeds with decrease of volume and evolution of heat.

An explanation of the increase in B at moderate concentrations necessarily involves the change in viscosity with pressure.[3] The viscosity of aqueous solutions of NaCl and K_2SO_4 (and of nearly all salts) increases with concentration at atmospheric pressure and probably at any other pressure, and it is also probable that the rate of increase is greater at the higher pressures, or in other words that pressure causes a greater increase in the viscosity of the more concentrated solutions. If the "ionic friction" follows the same course as the viscosity, there would be a tendency with increasing concentration to offset the decrease in B and finally to cause an increase in its value in spite of the higher degree of dissociation.

With NaCl the values of B for the 2.86% solution are at each pressure higher than the values of B for the most dilute solution (0.117%) and therefore higher than the corresponding values of B_0. Hence, if we adhere to the definition of α as the ratio of Λ to Λ_0 at any pressure, we are forced to conclude that at concentrations above 2 or 3% the dissociation of NaCl is diminished by pressure. On the other hand it is questionable whether this definition of α is either reasonable or convenient except in very dilute solutions, that is, within so limited a range of concentration that variations in viscosity can not play an important part. A degree of dissociation defined as simply Λ/Λ_0 has been one of the most useful and interesting concepts in the physical chemistry of dilute solutions, but a considerable variation in any one of the three variables, concentration, temperature, or pressure, renders it of doubtful value unless some account of viscosity (or ionic friction) be taken in its definition. Otherwise, it would follow that pressure decreases the dissociation of moder-

---

[1] This effect was noted by Körber (*op. cit.*) for $ZnSO_4$, but his measurements on NaCl do not show it.

[2] *Cf.* A. A. Noyes: "The Electrical Conductivity of Aqueous Solutions," Carnegie Inst. of Wash., Publ. No. 63, pp. 53, 340 (1907).

[3] For a discussion of the relation between viscosity and conductivity see H. C. Jones: "Conductivity and Viscosity in Mixed Solvents," Carnegie Inst. of Wash., Publ. No. 80, (1907).

ately dilute solutions of NaCl although increasing the dissociation in very dilute solutions—which is entirely improbable.

In conclusion we may note that although much effort has been expended by numerous investigators on the properties of electrolytes under pressure, it can not yet be said that the extent of our knowledge in this field is very satisfactory. This condition arises from the interrelation of a large number of physical factors which are difficult to disentangle and from a failure to define quantities clearly and uniquely in all instances, and is not altogether surprising in view of the fact that progress is still being made in advancing our ideas concerning the nature of an electrolyte *for the most simple case*, namely in dilute solutions at ordinary temperatures and at atmospheric pressure.

Summary

Measurements on the electrical conductivity of dilute and concentrated NaCl solutions, of dilute K_2SO_4 solutions and of one KCl solution have been carried out at pressures somewhat above 4000 bars (metric atmospheres). Pressures were measured to within 1 bar with an electrical resistance gauge that had been calibrated against an absolute gauge of the free-piston type, and the arrangement for measuring the conductivity under pressure was sufficiently sensitive and reliable that the error of reading was no more than 1 part in 50,000.

The principal object was to investigate the behavior of concentrated solutions under pressure. It was found that at high pressures the conductivity of NaCl, as a function of concentration, passes through a maximum, just as the conductivities of certain other salts do at atmospheric pressure. Not much attention was paid to the absolute conductivity, the results usually being expressed in terms of the resistance ratio, R/R_0, R being the resistance of the cell at a given pressure and concentration, and R_0 the resistance at atmospheric pressure. The temperature-coefficient of R/R_0 for concentrated NaCl solutions was found to be positive, while for dilute solutions it is negative.

The significance of the changes, produced by pressure, in the conductivity of solutions is discussed, and the important influence of the viscosity of the solution is emphasized. It is shown that in dilute solutions of strong electrolytes such as NaCl, the degree of dissociation, as ordinarily defined from conductivity measurements, is increased by pressure, although to a much smaller extent than in the case of weak electrolytes. For concentrated solutions of strong electrolytes a definite conclusion concerning the change of this dissociation with pressure can not be obtained without further information concerning the influence of pressure on other physical factors.

Geophysical Laboratory,
Carnegie Institution of Washington,
March, 1931.

GELATIN WITH AMMONIA AND HYDROGEN CHLORIDE*

BY BURTON C. BELDEN

Introduction

Many scientific theories excite no opposition when they are enunciated. Either they are so obvious they should have been recognized before, or else people think they represent too little contribution to the store of scientific knowledge to merit much attention.

On the other hand, when we see a conflict of able scientific minds arising around some attempt to state a principle, then we can well presume that the point in question is one of importance. And what is more significant, we can presume that the pros and cons of this challenged principle will be ferreted out to a much greater degree as each contestant reaches down into his bag of tricks to extract evidence in support of his contention.

Science depends upon the critical state of mind to test its hypotheses—to subject its theories to the rigid scrutiny which calls forth the best efforts of their proponents to produce substantiating evidence. Science can thank its critics who protect it from a too ready acceptance of what time may prove to be a false principle.

Not the least of the controversial subjects which have enlivened the chemistry of the past thirty years and have sharpened chemists' wits has been the question of the nature of the combination of proteins with acids and bases. That proteins do "combine" with acids and bases or, as is the popular statement of it, that proteins "bind" acids and bases, is an old story. One can read as early as 1866 the statement of Platner[1] that one and the same protein can combine with both acids and bases. At the beginning of an article published in 1906 Robertson[2] lists twenty-eight references to the literature of 1874 to 1906 in which this ability of proteins to combine with acids and bases is reported.

In the light of the chemistry of 1900, one would naturally suppose that this combination is simply one of neutralization; that in the presence of an acid a protein will act as a base, the interaction yielding an ionizable protein salt, and in the presence of a base the converse will obtain, yielding a metal proteinate. The protein, then, is an amphoteric substance, conducting itself in a manner analogous to inorganic amphoteres. And thus was the nature of the combination of proteins with acids and bases early presumed to be settled.

---

* This work is done under the programme now being carried out at Cornell University and supported in part by a grant to Professor Bancroft from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University.

[1] Z. Biol., 2, 417 (1866).

[2] J. Phys. Chem., 10, 524 (1906).

Moreover, this view appears to be consistent with our belief that the protein molecules are made up of a large number of amino acids and are themselves endowed with some of the characteristics of amino acids. Thus we know that protein possesses free amino groups and we suppose it contains free carboxyl groups to about the same number. Here we have the necessary conditions for an amphoteric substance: the presence of terminal amino and carboxyl groups. Reaction with both acids and bases appears most reasonable.

Unfortunately, or fortunately, as one looks at it, the situation is in no wise so simple as it must have appeared in 1900. All manner of difficulties were encountered. It appeared, for instance, that the binding power of the various proteins for hydrochloric acid was in excess of that which could be expected from the known $-NH_2$ content. Furthermore, the amount of hydrochloric acid a given protein would bind appeared to differ when determined by different investigators and by different methods. Again, if an ionized protein salt is formed, it would be a real help to isolate that salt and analyze it; it is not at all agreed that anyone accomplished this. A simple situation had now acquired some complexities.

Adversity is said to be a boon to endeavor. A large number of workers attacked the problem from varied angles and a voluminous and frequently bewildering literature resulted. One may conclude that it is a great credit to chemists that they have worked so long trying to untangle this question, or else one might very reasonably lament the fact that chemists have focussed so much investigation on this point without entirely clearing it up.

The original view that the nature of the combination of proteins with acids and bases is one of chemical union has persisted and been upheld capably by many workers. In 1912 this contention was presented clearly by Robertson[1] and his position may be summarized as follows: the proteins form true solutions and not colloidal suspensions and they react in stoichiometric proportions with acids and bases to form definite compounds. Further support of this view one can find, among others, in Loeb[2] and Wilson.[3]

The foregoing statement of Robertson's stand leads us to the consideration of an opposing theory which has been advanced to elucidate the nature of the combination of proteins with acids and bases. Robertson holds that proteins are in true solution. If, however, it be supposed that the proteins form colloidal suspensions in water, then it is a probable consequence, though not a necessary one, that the combination with acids and bases is one of adsorption and that stoichiometrical relations do not necessarily hold. If our protein constitutes a second phase, adsorption will be a large part, if not the whole, of the story.

This, then, is the theory adhered to by Bancroft and others, differing from Robertson on these two points: proteins form colloidal suspensions and not

---

[1] "Die physikalische Chemie der Proteine" (1912).

[2] Loeb: "Proteins and the Theory of Colloidal Behavior," (1924).

[3] Wilson: "The Chemistry of Leather Manufacture," Chapter V, (1928).

true solutions in water, and they bind acids and bases largely, if not entirely, by adsorption. We are more interested in the second part of it, for it is the nature of the combination of proteins with acids and bases which we are discussing. But the first point has this important bearing on the second: if proteins form true solutions, then there exists no second phase and we can have no phenomenon of adsorption. If, however, proteins form colloidal suspensions we will unquestionably have adsorption of acid or base, and adsorption may be the sole method by which protein binds acid and base.

People do not agree which type of "solution" a protein forms. If one will accept the proposition[1] that anything which can be removed from solution by an ultra-filter is not in true solution, then one has relegated gelatin and casein to the limbo of colloidal suspensions. But for the time being, it appears that the principal point of attack is on the question itself: do or do not acids and bases combine in stoichiometric proportions with proteins?

In passing, it might be well to note that Robertson[2] in 1923 suggested that it is more or less a matter of definition if we "are reluctant to admit a purely chemical mechanism of neutralization and prefer to invoke a physical mechanism, that is, molecular attraction between the colloidal particles of protein and the molecules of acid and base which are neutralized.... It follows that 'adsorption' of dissolved substances by surfaces may itself be an expression of chemical affinities. . . ." True as this last sentence probably is, *adsorption remains a function of the surface and of the equilibrium concentration* of the adsorbed substance in the liquid phase, so that the amount of adsorption can be varied continuously within limits. This is not what we usually mean by chemical reaction in stoichiometric proportions.

Probably the most fundamental difficulty which lies in the road of those who would establish the truly chemical nature of the union of proteins with acids and bases is the complex and uncertain nature of protein molecules. Admittedly they are large, but how large? Estimates of the molecular weights of various proteins range from two thousand to a hundred thousand. Interesting, certainly, is this statement concerning casein:[3] "From the analysis of Hammarsten it appears that if casein possesses this molecular weight (17,600 *as estimated from electrochemical data) then its empirical formula* must be, approximately:

$$C_{777}H_{1241}N_{197}O_{250}S_4P_4."$$

If one insists that it is the combining weight, not the molecular weight, we are interested in, the various estimated combining weights of gelatin can be cited. *These range from 768 (Procter and Wilson) to 96,000* (C. A. Smith), *not to* mention the 332 which this research indicates for some circumstances.

That the structure of the protein molecules cannot be entirely or even largely the linking together of the carboxyl and amino groups of amino acids after the manner of Emil Fischer's synthesis of polypeptides has been recog-

---

[1] Bancroft: J. Phys. Chem., 29, 966 (1925).

[2] Robertson in Alexander: "Colloid Chemistry," 2, 255 (1928).

[3] Robertson: "The Physical Chemistry of the Proteins," 343 (1918).

nized for a good many years. A recent review of the various proposals with regard to protein structure[1] lists one hundred twenty-six references to chemical literature, which serves to indicate the intricate nature of the subject. Probably more germane to the subject is the very strong probability that we are never dealing with one protein molecule, but with a mixture of several, or many. Robertson, for instance, states:[2] "We have no proof of the chemical individuality of the majority of our protein preparations, even when, as sometimes happens, they are crystallizable." Alexander, in discussing the various estimations of the combining weight of gelatin, says:[3] "It is still to be demonstrated that these compounds [various gelatins] possess the definiteness which is at present connoted by the expression chemical compound." Doubtless when extractions of a native protein are carried out under uniform conditions, the mixtures of the protein molecules obtained will be likewise uniform, and the various analyses will agree fairly closely. Conversely, it seems probable that the differing analyses of many of the proteins which can be found in the literature reflect quite as much different methods of extracting the proteins as they do variations in the accuracy of the analyses.

As a matter of fact, the complexity of the protein molecule has led to a "stoichiometric" explanation of the ability of the protein molecule to hold varying amounts of acid and base. The big molecule possesses a multiple combining capacity; that is, contains almost any convenient number of equivalents per molecule. Robertson says, for instance:[4] ". . . as a rule, a protein can combine with not only one but several equivalents of a base or acid, so that on adding acid or alkali to a solution of a protein we obtain a continuously varying mixture of the various possible salts." This may be the sort of thing which Wood and Hardy have in mind when they say:[5] ". . . proteins react with acids and alkalies to form salts, but the reactions are not precise, an indefinite number of salts of the form $(B)_nBHA$ being formed. . . ." This has led to the concept of the "maximum binding capacity" of a protein for acids and bases, the point at which presumably all the units of combining power of the protein have been satisfied by either acid or base. This might be quite convincing, except that the maximum combining powers of the several proteins differ widely as they are determined by different investigators and by different methods.[6] While this emphasis on the multiple combining power of the proteins may serve to reconcile some of the facts with the "stoichiometric" theory, it does not help us to distinguish between chemical combination and adsorption.

The principal methods which have been employed in the attempt to demonstrate the formation of protein salts are of at least brief interest to us. They divide themselves in two groups: the direct method of precipitating

---

[1] Klarmann: Chemical Reviews, **4**, 51 (1927).

[2] "The Physical Chemistry of the Proteins," 14 (1918).

[3] "Colloid Chemistry," **2**, 301 (1928).

[4] "The Physical Chemistry of the Proteins," 85 (1918).

[5] Proc. Roy. Soc., **81**, 38 (1908).

[6] Hoffman and Gortner: Colloid Symposium Monograph, **2**, 240 (1925).

out the alleged protein salt and analyzing it, and the several indirect or static methods of learning the composition of the salt without disturbing it. The latter group of methods is now considered more reliable than the precipitation method since, in spite of the fact that this method has been widely used, one is rarely sure that the precipitating agent has not in some manner altered the salt. Ammonium sulphate and alcohol are two popular precipitating agents. Robertson believes[1] that Van Slyke and Hart successfully precipitated calcium caseinate with alcohol but that almost all other work in this line is open to question. "At the present state of our knowledge, the direct method of demonstrating the existence of protein compounds cannot be trusted to yield accurate quantitative data, and results and conclusions based upon this method are to be accepted with the greatest caution."

A method which cannot be said to leave the protein salt quite undisturbed and therefore is somewhat a direct method was the early-used procedure of titrating a protein with acid or base, using an indicator. As we now know, when we titrate a weak acid with a strong base, or a strong acid with a weak base, we must select our indicator with some consideration for whether the indicator's color change occurs at the pH which obtains when the acid and base are present in stoichiometric proportions—the vertical or nearly vertical part of the electrometric titration curve. The early literature abounds in measurements of acid- and alkali-binding capacities of proteins, all varying with the indicator used. As an example,[2] at neutrality to litmus one gram of casein binds 50×10^{-5} gram equivalents of base, and at neutrality to phenol phthalein 80×10^{-6} gram equivalents. An amphotere rates as a very weak acid and base, and its titration rarely gives a sharp end point, no matter how carefully chosen may be the indicator. In this connection there should also be considered what is nowadays called the protein error of indicators: the adsorption of indicators (and dyes) by proteins, which interferes with indicator action.

Measurements of conductivity have been invoked to show the nature of the combination of proteins with acids and bases. The reasoning is this: on adding a protein to an acid or a base the conductivity is lowered, and this lowering is presumed to be due to the fact that the protein salt which is immediately formed is less highly ionized than the original acid or base. After repeated additions of protein the conductivity approaches constancy and this should mean that all the acid or base has been bound by the protein, the remaining conductivity being due to the ions of protein salt. This may be correct; the same result will also be expected, however, if colloidal protein particles adsorb some of the high velocity hydrogen ions (or hydroxyl ions, as the case may be) of the electrolyte. These "agile"ions, now fixed to massive protein particles, will migrate with greatly diminished velocity and the conductivity of the solution will be lowered.

The procedure which stands in the highest favor to-day with those who would show the chemical nature of the binding of acids and bases by proteins

---

[1] "The Physical Chemistry of the Proteins," 69 (1918).

[2] Roberston: "The Physical Chemistry of the Proteins," 90 (1918).

is that of electrometric titration. By this method we have fairly direct measure of the amount of acid or base in combination with protein. Say we start with an acid solution whose strength we have measured with the hydrogen electrode. We add a given amount of protein. When equilibrium is attained, our hydrogen electrode will show a decreased hydrogen ion concentration, and this decrease presumably represents the hydrogen ion (that is, the acid) bound by the protein. We know quite accurately the partition of acid between protein and solution. If we do this for a number of initial concentrations of acid, then we can plot the variation of protein-bound acid with (equilibrium) concentration of acid in solution. Almost always, these graphs show that the acid bound by protein decreases with rising pH up to a certain limit. A similar situation usually holds for bases. There arises little doubt that this is a correct observation. In discussing quite another method of attack, Robertson says:[1] "It will be seen that the quantity of HCl which is bound by one gram of vitellin increases with increasing concentration of HCl in solution. We shall see that this phenomenon is a general one where proteins are concerned. It appears that the binding capacity of the vitellin reaches a maximum for the higher concentrations of the acid." The facts of the situation are clear. Rather, it is in the interpretation of these observations that the difficulties lie.

We could, for instance, adopt this explanation: protein hydrochloride, the salt of a strong acid and a very weak base, will hydrolyze appreciably according to the relation:

$$\text{Protein hydrochloride} + \text{water} \leftrightarrows \text{Protein} + \text{HCl}$$

The higher the HCl concentration, the less the hydrolysis, from Mass Law considerations. The higher the HCl concentration (the hydrogen ion concentration) the more acid will be bound by the protein. Beyond a certain HCl concentration, hydrolysis will be negligible and the protein binds a maximum constant amount of acid.

If we do not like that interpretation, we can recall our previous suggestion that the protein has multiple combining properties. The maximum combining capacity will not be shown by the protein at hydrogen ion concentrations near neutrality. But, as we increase the acid concentration, this maximum will be approached and reached; beyond that point the protein combines with no further acid in spite of the further addition of acid to the solution. We might also add that the curve shows no hint of a stepwise nature that one might reasonably expect if successive hydrochlorides are being formed. However, one can presume enough hydrochlorides so that the individual steps are indistinguishable and blend into the smooth curve.

Finally, we can quite reasonably say we have an adsorption isotherm, pure and simple. It may or it may not adhere closely enough to the Freundlich equation to satisfy everyone. But this is not a necessary criterion for adsorption; the only requirement is[2] "that the concentrations [of the acid]

---

[1] "The Physical Chemistry of the Proteins," 72 (1918).

[2] Bancroft and Barnett: J. Phys. Chem., 34, 451 (1930).

in the solution and in the adsorbent vary continuously," which means that we will get some sort of smooth curve. A survey of the literature shows that where these potentiometric curves have been plotted correctly they look, in most cases, like orthodox adsorption isotherms. Frequently the initial adsorption is very high, but this is not unusual in adsorption isotherms.

In recent years the Donnan equilibrium has been shown to give a successful basis for explaining some of the physical properties of proteins, the swelling of gelatin, for instance. Because the Donnan equilibrium is usually applied to the ions of a dissolved salt (one ion of which cannot pass through a membrane), it has been concluded that people were here dealing with a soluble, ionized, gelatin salt. This reasoning is in error, for the Donnan equilibrium applies to adsorption phenomena quite as well as it does to cases of chemical combination, as has been pointed out in some detail by Donnan himself.[1]

In the foregoing there has been presented a brief survey of the differences of opinion which have arisen concerning the nature of protein combination with acids and bases, and the principal arguments and experimental evidence which have been marshalled in support of the definite compound theory have been summarized. It should be fairly apparent that this evidence is in no wise conclusive proof of this theory; that most of it lends itself quite as well to the support of a theory of adsorption, if one cares to interpret the evidence in that direction. We still need the key experiment which will decide for us the fates of these rival contentions.

Normally, it is no great risk to demonstrate a case of adsorption. We do not do it by separating the solid phase and analyzing the adsorption complex, for during such treatment the adsorption complex would change composition. But we do have a very nice indirect method which does not disturb the solid phase. If we shake up equal amounts of activated charcoal with acetic acid solutions of varying strengths, the charcoal will adsorb acetic acid from solution. We can learn the amount of this adsorption in any case by determing the initial and equilibrium concentrations of the acetic acid, the difference representing the acetic acid adsorbed on the charcoal. From a series of such measurements we can plot the amount of acid adsorbed against equilibrium concentration of acid in solution and obtain our adsorption isotherm. The important feature of this procedure is that we can analyze pure solution, devoid of any charcoal.

Not so in the case of proteins. They are present in colloidal suspension and we cannot pipette out samples of pure solution for purposes of analysis. Our usual demonstration of adsorption is ruled out.

The next move that is suggested, then, is to eliminate the solution phase entirely and to work with a solid (powdered) protein and a volatile acid or base. In so doing, we will have eliminated the difficulties we faced in trying to make indirect analysis of the adsorption complex when the solid phase is peptized in a solution phase. Further, we will have the simplest kind of instantaneous measure of the amount of base or acid in contact with the solid:

---

[1] Chemical Reviews, 1, 87 (1924).

the pressure of the gaseous phase. The other value we need to know, the amount of acid or base held by the solid, we can learn from the decrease of pressure of the gaseous phase as the solid takes up its equilibrium concentration of the volatile acid or base—providing, of course, we know the volume of our apparatus. If now we plot these pairs of values, in the same manner that we did those of acetic acid and charcoal mentioned above, we will have a graph which shows us how the amount of acid or base bound by protein varies with the concentration of the gaseous acid or base in contact with protein. If the amount of protein-bound acid or base varies continuously, approaching a maximum value, we have adsorption and our graph shows an adsorption isotherm. If definite compounds of protein with acid (or base) are formed, Phase Rule considerations show us we will have a stepwise curve.

The reasoning involved in the preceding statement is this: if a compound—call it protein hydrochloride—is formed as HCl gas is being added to the system, there will be present at any moment during the formation three phases: HCl gas, protein, and protein hydrochloride. The number of components is two. From the Phase Rule, $F = C - p + 2$, we know that this system possesses one degree of freedom. Because we are working at constant temperature, we have fixed the temperature variable (i.e., used up our one degree of freedom) and our system is defined. This means that the equilibrium pressure in the system must be some constant value which does not change with addition of HCl to the system. Here, then, will be a flat in our curve, and it will persist until all the protein is converted into protein hydrochloride, and we have passed to a two-phase, bivariant system. If successive compounds are formed, each will have its special flat with its characteristic pressure, and our curve will be stepwise. Finally, if we are dealing with adsorption, we have two phases over the whole range and the system is everywhere bivariant, permitting us variation of pressure with concentration of acid even though the temperature variable is fixed.

In eliminating acid and alkaline solutions from our experimental work and substituting volatile acids and bases, we are presuming that the action of powdered protein solid with the gases will be very much the same as the action of peptized protein colloids with acids and bases in solution. To some this may appear an unwarranted presumption and to them we must grant the privilege of doubting. However, if a given protein clearly shows adsorption, for instance, of a given volatile base, we can certainly say that the weight of evidence is very much in favor of the view that the same protein adsorbs that same base from solution.

If the peptized protein is anhydrous, the sequence of solid phases containing only protein and acid or base must be the same in the solution as with the gas, though dissociation of a stoichiometric compound may vary very much in presence of a solution. If the protein phase contains dissolved or adsorbed water, the same phases cannot occur in the solution as with the gas, though the differences in the ratios of protein to acid are not necessarily large. Potassium iodide and iodine are the only stable solid phases at 25° in presence of chloroform, but $KI_7.xC_6H_6$ occurs[1] in presence of benzene.

In the present investigation, it is proposed to apply these methods to a particular protein, gelatin, and to use as the volatile acid and base, hydrogen chloride and ammonia, respectively. It is further proposed to make the conclusions of the investigation more convincing by applying these methods to a hydrolyzed gelatin, whose amino acid content should make the sample show to a considerable extent compound formation where the native gelatin showed adsorption.

Apparatus and Procedure

The general type of apparatus used in this study has been described in brief in the article by Bancroft and Barnett.[2] The present form of the apparatus, which has been arrived at in this laboratory after a number of revisions, is shown in the accompanying diagram, Fig. 1. It will be seen that the set-up is essentially simple; although it lends itself to refinements and adaptations for special purposes, the present simplified form proved fairly satisfactory equipment for this research. In its present form this apparatus has the very distinct advantage that it can be moved about readily. Built as it is to set at right angles to the front of the laboratory desk, it takes up desk spaces actually not in excess of twelve inches. In the case of a bank of these set-ups, two feet of desk space for each one allows ample room to operate them and to accommodate the necessary hydrogen chloride generator, ammonia cylinder, and vacuum pump.

The details of the apparatus are these:

(1.) The front support of the apparatus rests upon the desk proper; the back support on the reagent shelf. To give the apparatus added stability, the back support is clamped to the shelf.

(2.) The reaction flask is a 100 cc., round-bottom, long-neck flask with a "normal-ground" mouth, such as can be had from Greiner and Friedrichs, connected to the apparatus through a glass spiral which permits shaking the flask. The normal-ground feature has the advantage that the flask is replaceable and further that the size of the slip joint (diameter about 25 mm.) on these flasks is sufficient to give a good area of contact and reduce the possibility of leakage. The long neck eliminates the possibility of shaking the powdered solid into the immediate region of the slip joint where, if there is an excess of stopcock grease, the powder would cling. The flask is located high enough above the desk so that heating and cooling jackets may be placed around it, in case such procedure is desired in any experiment.

(3.) The principal thing to be said about the manometer is that mercury and an atmosphere's pressure of hydrogen chloride gas slowly yield a black smudge on the inside of the glass, so that after several week's operation under these conditions the mercury level on the apparatus side of the manometer becomes difficult to read. We therefore expected to replace the glass tubing

---

[1] Private communication from Professor Foote.

[2] J. Phys. Chem., 34, 462 (1930).

occasionally. A slip joint can be installed, if one wishes, between the manometer and the rest of the apparatus, so that the manometer can be removed, cleaned and replaced without involving any glass-blowing. Since we had no reason to read pressures more accurately than to one millimeter, we were satisfied to use a usual meter stick for this manometer.

(4.) The gas burette has 100 cc. capacity and has a two-way stopcock. Because of the slow reaction of HCl gas and mercury, one should be careful not to leave samples of the gas in the burette for any length of time,

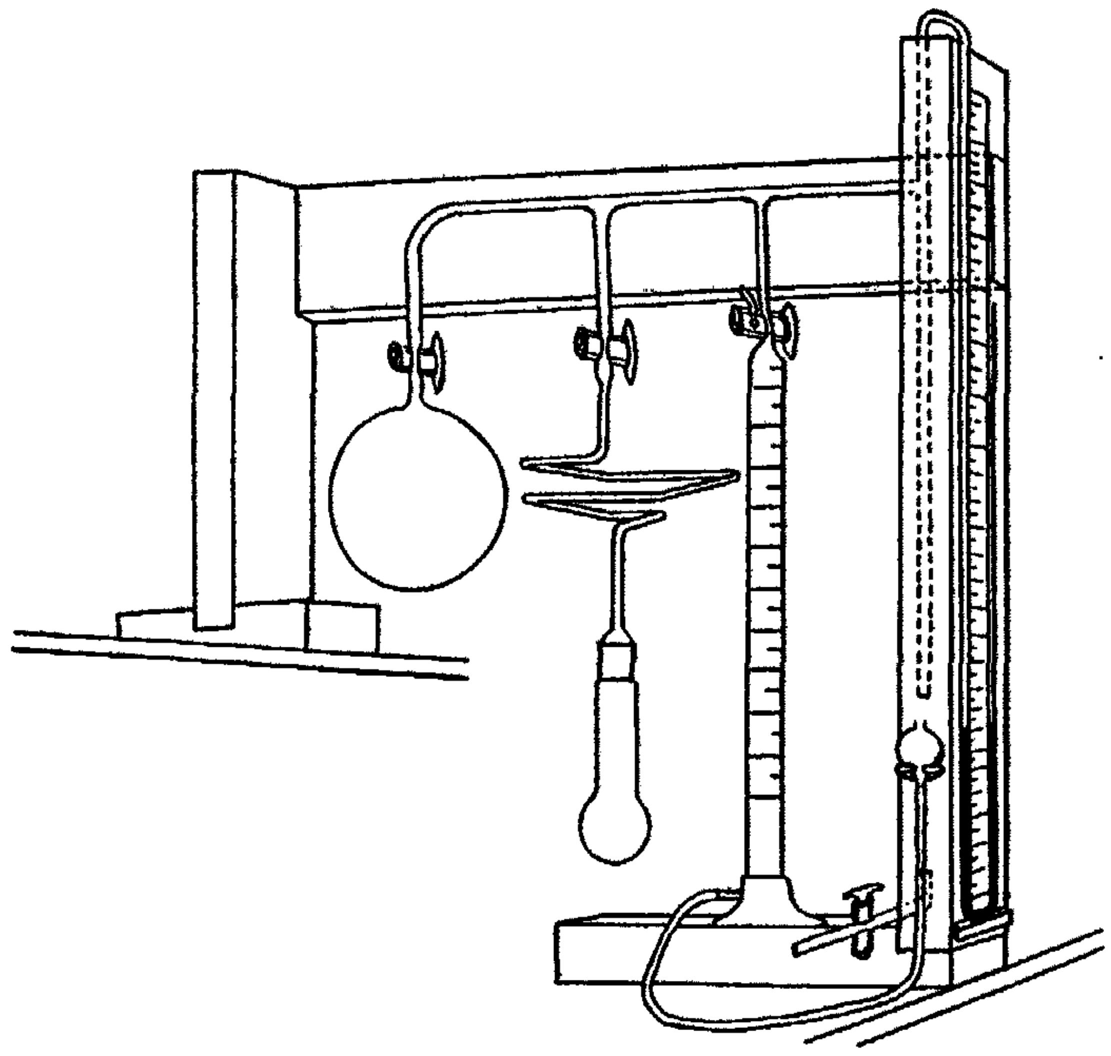


FIG. 1

(5.) The reserve flask has a capacity of about 1000 cc. and advisedly might have a greater volume. Its function may not at first be apparent. It is not difficult to evacuate a system to a sufficiently low pressure (say, less than one millimeter) if the burette into which one is drawing the gas has a volume many times as large as the system being evacuated. Thus the necessary vacuum might be obtained by drawing the gas into the burette a half dozen times. On the other hand, if the system is large in comparison to the burette, this process quickly becomes a tedious one. So it is, if we are removing gas from the system when the pressure is less than two hundred millimeters by means of the burette, whose volume is less than half that of the reaction flask, we will be able to remove but a small volume of the gas each time. The tediousness and decreased accuracy of this procedure can be avoided by using the previously evacuated reserve flask to "draw off" a volume of gas from the smaller reaction flask. Because we know the volume of the reserve flask and can read on the manometer the pressure of the gas it contains, we can quickly calculate the standard volume of the gas removed. This calculation made, we can evacuate the reserve flask and it is ready for further use.

(6.) Miscellaneous. The vacuum-pump connection is made at the base. After using a number of stopcock grease preparations, of both commercial and home-made origins, we concluded we got the most dependable results from "Airco Hy-vac Stopcock Lubricant" made by the Air Reduction Sales Co. We of course did not require the stopcock grease to hold X-ray tube vacuums; the principal requirement was that the ground-glass joints be kept gas-tight for a period of several weeks, which proved to be too much of a requirement for some of the preparations we tried. The apparatus should be calibrated in three parts; the reaction flask, the reserve flask, and the connecting tubing which, it will be noticed, must vary somewhat with the level of the mercury in the manometer.

The refinements which this general type of apparatus is capable of when it is desired to undertake more precise Phase Rule investigations can be seen by referring to some of the papers of A. W. Browne and his students.[1]

The operation of this apparatus should, in brief, be this: A powdered sample of known weight is placed in the reaction flask. The system is evacuated and the stopcock in the line connecting the reserve flask with the rest of the system closed. Known volumes of gas are added to the system and, after each addition time enough is allowed for the solid to take up its equilibrium concentration of gas. At any given equilibrium, we can calculate the amount of gas present in the gas phase (i.e., the uncombined gas) from the pressure it exerts and the calibrated volume of that part of the apparatus. We know the total gas we have added to the system, so the difference must represent the gas combined with the solid sample. When these points are obtained for pressures up to atmospheric (or higher), the curve should be checked by removing samples of gas, in the lower pressures using the reserve flask. In many cases, particularly with some amino acids, the procedure here outlined has been adhered to very closely.[2]

With many solids, however, such as almost all of the proteins, and with gelatin, in particular, this method is subject to considerable revision, for we must give some consideration to the time element involved in the attainment of equilibrium conditions. We do not mind spending a week or so with one solid; but we do object to spending months, especially when the apparatus will probably cease to be gas-tight before that interval is over. The rate at which the system will approach equilibrium conditions is at all times proportional to two things: (1) how far the system is removed from equilibrium, and (2) the pressure of the gas phase. From this it can be seen that the system will be particularly tardy in reaching equilibrium at low gas pressures, especially if we are dealing with a case of high initial adsorption where a given equilibrium pressure might be as low as fifteen millimeters, or lower. Granted

---

[1] For instance, Browne and Houlehan: J. Am. Chem. Soc., 35, 650 (1913); Friedrichs: Z. anorg. allgem. Chem., 116, 153 (1921).

[2] Bancroft and Barnett: J. Phys. Chem., 34, 449 (1930).

that the system will approach equilibrium conditions with satisfactory speed when the gas pressure is seven hundred millimeters, it is easy to see that the same system might approach equilibrium at a painfully slow rate when the pressure is but fifteen millimeters. Temporally speaking, the regions of low pressure are the ones that trouble us.

The obvious procedure to minimize this difficulty is to work as far as possible at high gas pressures—to start at the top of the curve (seven hundred millimeters, or whatever maximum seems suitable) and examine the curve downward. Then the large initial consumption of gas needed for high initial adsorption or for compound formation can proceed at a respectable speed. True, it may take two or three days for this top equilibrium point to be arrived at, as in the case of gelatin with ammonia, because the sample has this relatively large amount of gas to adsorb or combine with. But once this first point is established, succeeding points can be determined with a much greater speed. Not only that, the down curve for both cases of adsorption and of compound formation can be carried very nearly to the zero pressure axis without undue difficulty, and the curve investigated in the reverse direction, whereas it would have been almost impossible to investigate the up-curve starting originally at the low pressure. The high initial consumption of gas took place at a reasonable rate when the gas pressure was seven hundred millimeters.

Another worthwhile modification of technique, particularly in dealing with adsorption curves, is this: if, say, our system is at equilibrium at 700 mm. and we want next an equilibrium at about 600 mm., we normally would remove a sample of gas such that the pressure is immediately lowered to perhaps 560 mm. The solid now holding more than equilibrium amount of gas, HCl or NH_3 is gradually released until the equilibrium pressure is built up. For the case of gelatin and ammonia, this will require perhaps six hours. The time can be reduced materially if, in the first place, we remove a much larger sample of gas, such that the pressure is reduced to, say, 300 mm. The rate at which solid will release gas will of course be greater. At the end of an hour enough gas is restored to the system to bring the pressure back to about 600 mm.; if we have selected the proper time and the proper size of gas samples, the system will now be very nearly at equilibrium. A second hour should give us an accurate equilibrium point. In an instance such as this one, we shall be satisfied we have equilibrium conditions if the gas pressure does not vary perceptibly in thirty minutes. It will be very possible, for instance in the case of some protein hydrolysates, that the rate of adsorption or release of gas will be sufficiently slower so that thirty minutes will not be an adequate test of equilibrium.

Changes of temperature can be utilized to hasten equilibrium. A protein in process of releasing gas will do so more rapidly if the temperature is raised, for instance by putting a beaker of warm water around the reaction flask. A protein in process of adsorbing more gas may do so more rapidly if the temperature is lowered, for at the lower temperature the system is removed farther from equilibrium conditions (the process of adsorption has a negative temperature coefficient). Of course in these cases we must be sure that the whole system has returned to the temperature of our isotherm before we proceed to read an equilibrium point. One must use judgment, too, in warming a sample of gelatin, for it is easy to reach the region of agglomeration when particle size will be very much increased.

In general, the exact procedure which one uses in "running" one of these curves will need to be governed by the nature of the solid substance and the nature of the gas, the principal consideration being how fast the solid binds the gas. Action with hydrogen chloride will usually be more rapid than action with ammonia. Action with more finely powdered solids will be faster than with less finely powdered ones. Action with proteins will be slower than with organic acids and bases; action with protein hydrolysates will be slower still. Usually a little careful attention to the manner in which a given solid yields its first equilibrium point will indicate whether the rate is slow enough to justify use of the "short-cut" procedures discussed above.

Experimental Work

All gelatin samples used in this investigation were obtained from the Eastman Kodak Company. Unless otherwise noted, the gelatin is the best ash-free quality. Hydrogen chloride gas was made by passing concentrated hydrochloric acid through concentrated sulphuric acid, a method which is quite the reverse of one regularly described,[1] but which gave us the steady flow of hydrogen chloride gas which we desired. The gas was further dried by passing through two Friedrichs wash-bottles containing concentrated sulphuric acid. Ammonia was taken directly from Matheson Company lecture bottles.

There is probably a quick and efficient way of reducing the "plates" of ash-free gelatin to a finely powdered form, although at the close of this investigation we were still looking for it. Whatever means are employed, they must not heat the gelatin markedly, for the gelatin will become sticky and practically halt the grinding process. A power-driven clipper mill, used for grinding feeds, gave us a twenty-mesh gelatin without undue difficulty, but this hardly approaches what we usually mean by a "powder." A power-driven grinder was hopeless, due to the heating and gumming of the gelatin. Our best and most tedious method was to grind the gelatin in a modest coffee mill, and this was the method regularly employed. Samples of 40-60 mesh were generally used, and samples of 60-80 mesh could be had. A good method of reducing gelatin to a really fine powder would have been a genuine aid to this research.

The hydrolyzed gelatin was obtained by treatment of gelatin with sulphuric acid.[2] This procedure has the advantage over treatment with hydrochloric acid that at the conclusion of the hydrolysis the acid can be precipitated out as barium sulphate. The details of the process were these: 100 grams of

---

[1] Gmelins "Handbuch der anorganischen Chemie," **6**, 96 (1927).

[2] Plimmer: "The Chemical Constitution of the Proteins," **1**, 11, 55 (1917); Dakin: J. Biol. Chem., **44**, 499 (1920); Mitchell and Hamilton: "The Biochemistry of the Amino Acids" (1929).

ash-free gelatin was dissolved in 260 grams of water and 120 grams of sulphuric acid (Sp. G. 1.84) and was refluxed for forty-five hours on an oil bath at about 108°. After standing five days at room temperature, the acid solution was heated and treated with a hot solution of barium hydroxide until neutrality had almost been reached, as shown by Congo Red paper. The barium sulphate was filtered off by suction. The hydrolysate was evaporated down at 70° and thereafter kept in a desiccator because of its tendency to take up moisture. This method gave a light brown solid which could be readily powdered for use in the Phase Rule apparatus.

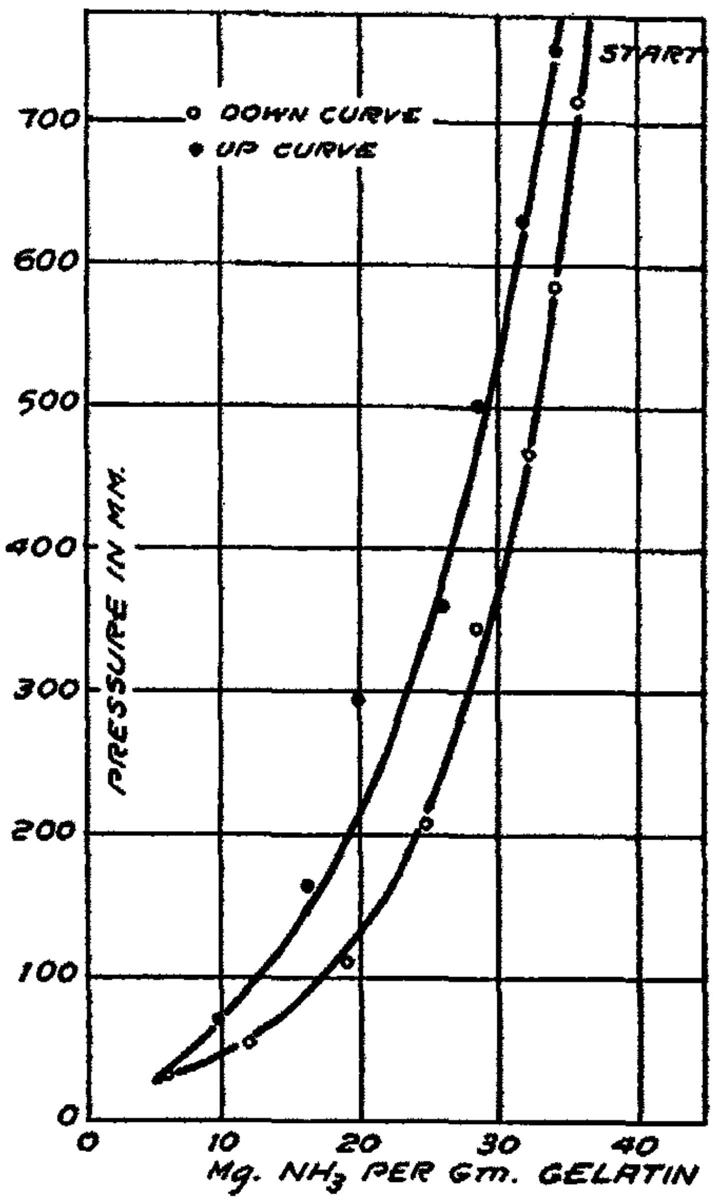


FIG. 2

Gelatin and Ammonia. Up to seven hundred millimeters pressure, gelatin and ammonia always show adsorption, with no suggestion of compound formation. The amount of this adsorption varies somewhat from one gelatin to another, but the general shape of the curves remains the same. Up-curves generally do not quite coincide with down-curves, showing the "hysteresis" which is characteristic of adsorption isotherms. A typical pair of curves is shown in Fig. 2, plotted from the data of Table I.

TABLE I

Gelatin and Ammonia

Sample 4.19 grams

Vol. NH_3 added cc.	Total vol. cc.	Equilibrium press mm.	Volume remaining cc.	Volume taken up cc.	Weight taken up mgr.	Weight taken up per gram mgr.
555.9	555.9	714	360	196	149	35.6
Removed						
74.2	481.7	584	293	189	143	34.1
72.1	409.6	467	233	177	134	32.0
82.2	327.4	344	170	157	119	28.4
87.7	239.7	208	103	137	104	24.8
79.9	159.8	111	54.5	105	79.7	19.0
67.0	92.8	54	26.4	66.4	50.3	12.0
43.7	49.1	32	15.6	33.5	25.4	6.1
Added						
38.9	88.0	70	34.3	53.7	40.8	9.7
81.0	169.0	163	80.1	88.9	67.5	16.1
87.4	256.4	294	146	110	83.5	19.9
64.9	321.3	360	179	142	109	26.0
86.2	407.5	500	250	158	120	28.6
85.2	492.7	631	318	175	133	31.7
75.7	567.9	752	380	188	143	34.1

It appears that when gelatin stands for a time in the presence of ammonia, its ability to adsorb ammonia decreases slightly. That is, if a second pair of down- and up-curves be run on a given sample of gelatin, they will tend to fall a little to the left of the corresponding curves in the first pair. Data for such a case are given in Table II and plotted in Fig. 3.

Because we are finding that the up-curves correspond with the down-curves fairly closely—within the limits of the hysteresis we might reasonably expect—we conclude that we have been reaching, or closely approaching, true equilibrium conditions and that we will be safe in depending upon a single down-curve for our information about a given gelatin. Henceforth, a single down-curve will be presented for each gelatin.

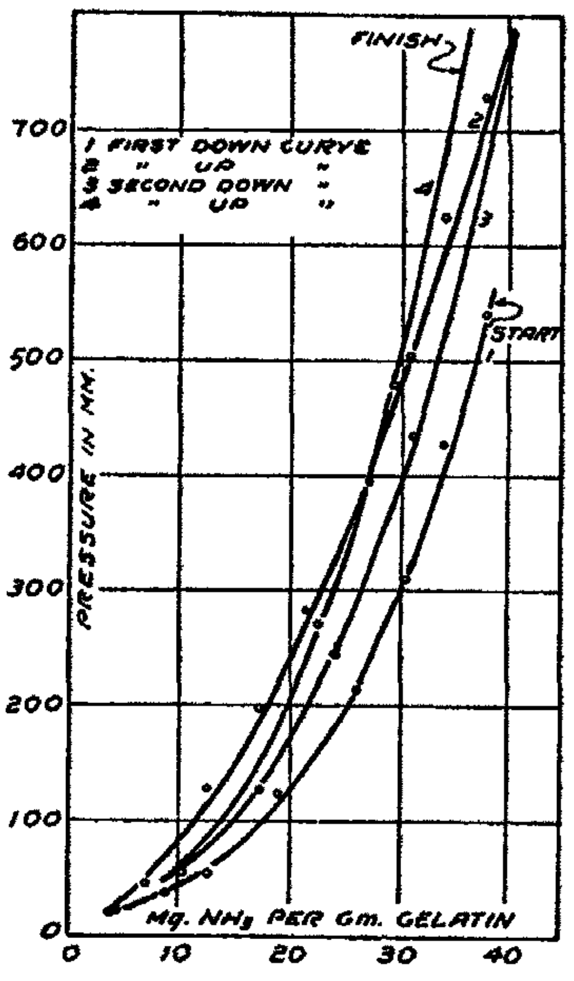


FIG. 3

TABLE II

Gelatin and Ammonia

Sample 3.77 grams.

Vol. NH_3 added cc.	Total vol. cc.	Equilibrium press. mm.	Volume remaining cc.	Volume taken up cc.	Weight taken up mgr.	Weight taken up per gram mgr.
457.2	457.2	541	269	188	143	38.0
Removed						
75.9	381.3	428	212	169	128	34.0
77.5	303.8	311	153	151	115	30.5
70.3	233.5	215	105	129	98.0	26.0
78.6	154.9	125	60.9	94.0	71.3	18.9
65.2	89.7	55	26.8	62.9	47.7	12.7
27.8	61.9	37	18.0	43.9	33.3	8.8
28.7	33.2	23	11.4	21.8	16.5	4.4
Added						
25.1	58.3	47	22.8	35.5	26.9	7.1
27.6	85.9	77	37.4	48.5	36.8	9.8
40.4	126.3	130	63.4	62.9	47.7	12.6
56.3	182.6	199	97.2	85.4	64.8	17.2
64.6	247.2	284	140	107	81.2	21.5
82.6	329.8	396	195	135	102	27.1
74.2	404.0	505	251	153	116	30.8
78.0	482.0	627	313	169	128	34.0
75.2	557.2	733	368	189	143	38.0
Removed						
186.8	270.4	437	216	154	117	31.0
131.2	239.2	245	120	119	90.4	24.0
91.5	147.7	127	61.9	85.8	65.1	17.3
68.4	79.3	57	27.7	51.6	39.2	10.4
Added						
165.8	245.1	271	133	112	85.0	22.6
140.5	385.6	480	238	148	112	29.8
151.3	536.9	725	364	173	131	34.8

The effect of the fineness of the gelatin powder upon the amount of its adsorption of ammonia was found to be about nil; rather, the increasing fineness of the gelatin increased only the rate at which equilibrium conditions were reached. Data to show this are given in Table III and plotted in Fig. 4.

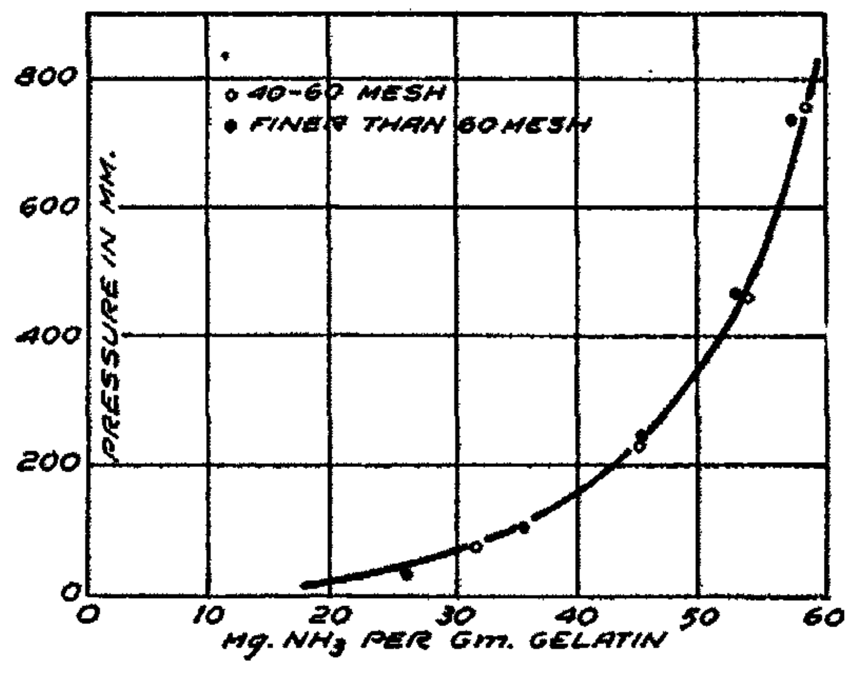


Fig. 4

TABLE III

Gelatin and Ammonia
Sample 40-60 mesh
Weight 1.85 grams

Vol. NH$_3$ added cc.	Total vol. cc.	Equilibrium press. mm.	Volume remaining cc.	Volume taken up cc.	Weight taken up mgr.	Weight taken up per gram mgr.
448.4	448.4	752	305	143	108	58.4
Removed						
133.3	315.1	460	184	131	99.4	53.8
113.9	201.2	230	91.0	110	83.5	45.1
94.5	106.7	75	29.5	77.2	58.5	31.6

Time required to reach first equilibrium point: 65 hours.

Same gelatin, ground to finer than 60 mesh
Weight 1.52 grams

Added						
436.8	436.8	733	322	115	87.3	57.4
Removed						
128.7	308.1	467	202	106	80.5	52.9
111.1	197.0	248	106	91.0	69.1	45.3
82.9	114.1	102	43.1	71.0	53.9	35.4
48.6	65.5	32	13.5	52.0	39.5	25.9

Time required to reach first equilibrium point: 24 hours.

An observation of some interest was made on a sample of gelatin which was ground in a clipper mill previously used to grind various seeds. Although the mill had been carefully cleaned, it was apparent the gelatin sample was contaminated with a very small amount of vegetable oil. The amount of adsorption was considerably less than in the case of the same gelatin ground in the usual coffee mill; further the amount of adsorption increased slowly with time, so that at the end of twenty-one days the adsorption of ammonia at six hundred millimeters pressure had increased about 29%. Certain impurities, then, can be said to reduce at least temporarily the adsorption of ammonia by gelatin. The comparison is shown in the data of Table IV and in Fig. 5.

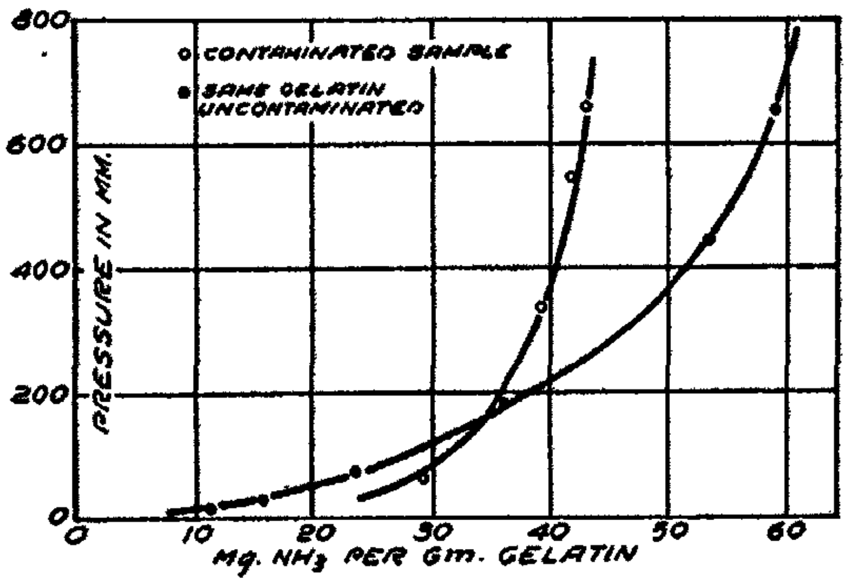


FIG. 5

TABLE IV

Gelatin and Ammonia

Sample slightly contaminated with vegetable oil

Weight 2.62 grams

Vol. NH_3 added cc.	Total vol. cc.	Equilibrium press. mm.	Volume remaining cc.	Volume taken up cc.	Weight taken up mgr.	Weight taken up per gram mgr.
437.3	437.3	660	289	148	112	42.9
Removed						
55.2	382.1	545	238	144	109	41.7
101.5	280.6	338	146	135	102	39.1
153.7	126.9	62	26.2	101	77	29.2

Same gelatin, uncontaminated

Weight 1.42 grams

Added						
402.7	402.7	654	293	110	83.5	58.8
Removed						
106.2	296.5	447	197	100	75.9	53.5
148.9	147.6	185	80.4	67.2	51.0	35.9
70.5	77.1	75	33.2	43.9	33.3	23.4
35.9	41.2	31	12.7	28.5	21.6	15.2
13.0	28.2	16	7.5	20.7	15.7	11.1

The idea presented itself that the amount of adsorption of ammonia by gelatin samples might serve as a useful indication of the uniformity or lack of uniformity of the several gelatins. For the purpose of testing this possibility, the Eastman Kodak Company sent us six gelatin samples which varied quite widely in appearance, two of them looking about like ash-free gelatin samples, the other four appearing darker and "dirtier." These six samples showed adsorption of ammonia which varied from 50.0 to 59.3 milligrams ammonia per gram of gelatin at seven hundred millimeters pressure. Five of them varied only from 54.7 to 59.3 milligrams. Furthermore, the curves for the two purest gelatins lay in the midst of the other four. From this we concluded that however good the idea may have appeared at first, it had not materialized and did not provide us a good method of differentiating various gelatins. The data for these curves are given in Table V and the top portions of the curves are plotted in Fig. 6. All samples were ground uniformly to 40-60 mesh fineness.

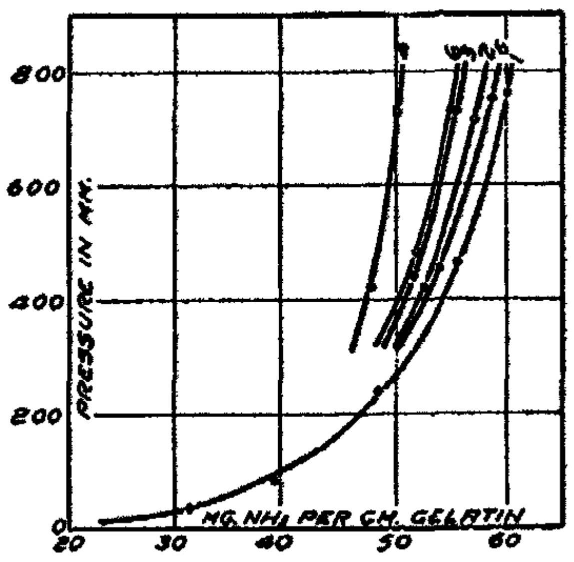


Fig. 6

Table V

Gelatin No. 1 and Ammonia
Weight 1.69 grams

Vol. NH_3 added cc.	Total vol. cc.	Equilibrium press. mm.	Volume remaining cc.	Volume taken up cc.	Weight taken up mgr.	Weight taken up per gram mgr.
468.6	468.6	763	336	133	101	59.8
Removed						
141.3	327.3	468	203	124	94.1	55.6
115.2	212.1	242	104	108	82.0	48.5
87.5	124.6	87	36.5	88.1	66.9	39.5
37.1	87.5	39	17.1	70.4	53.3	31.6

Gelatin No. 2 and Ammonia
Weight 1.54 grams

Added						
406.1	406.1	717	290	116	88.0	57.1
Removed						
128.8	277.3	426	171	106	80.4	52.2
110.0	167.3	200	79.1	88.2	67.0	43.5
63.6	103.7	86	33.5	70.2	53.3	34.6

TABLE V (Continued)

Gelatin No. 3 and Ammonia
Weight 1.56 grams

Vol. NH_3 added cc.	Total vol. cc.	Equilibrium press. mm.	Volume remaining cc.	Volume taken up cc.	Weight taken up mgr.	Weight taken up per gram mgr.
Added						
417.9	417.9	731	304	114	86.5	55.4
Removed						
129.5	288.4	444	183	105	79.7	51.7
99.7	188.7	232	94.5	94.2	71.5	45.8
102.4	86.3	58	23.4	62.9	47.7	30.6
Gelatin No. 4 and Ammonia Weight 1.86 grams						
Added						
427.1	427.1	730	304	123	93.4	50.2
Removed						
133.9	293.2	426	176	117	88.9	47.7
98.0	195.2	225	92.2	103	78.2	42.0
83.6	111.6	77	31.1	80.5	61.1	32.8
Gelatin No. 5 and Ammonia Weight 1.85 grams						
Added						
448.4	448.4	752	305	143	108	58.4
Removed						
133.3	315.1	460	184	131	99.4	53.8
113.9	201.2	230	91.0	110	83.5	45.1
94.5	106.7	75	29.5	77.2	58.5	31.6
Gelatin No. 6 and Ammonia Weight 1.67 grams						
Added						
459.3	459.3	757	339	120	91.0	54.5
Removed						
132.6	326.7	484	213	114	86.5	51.8
114.0	212.7	259	113	100	75.9	45.5
142.2	70.5	37	16.2	54.3	41.2	24.7

Gelatine Hydrolysate and Ammonia. The story of hydrolyzed gelatin with ammonia is quite different, as it should be. When equilibrium conditions have been reached, the sample binds in excess of eighty milligrams of ammonia per gram of sample at seven hundred millimeters pressure. On examining the curve downward it appears that forty-one milligrams of this are held in chemical combination, the rest of it being adsorbed. How many individual compounds this flat portion of the curve represents we do not know; each, in theory, has its own flat, but actually in this range of low pressures and with a gelatin hydrolysate which reaches equilibrium conditions very slowly (much more slowly than the original gelatin) these flats cannot be investigated at all readily. The important thing is the total amount of ammonia bound in chemical combination. Data and curve are presented in Table VI and Fig. 7.

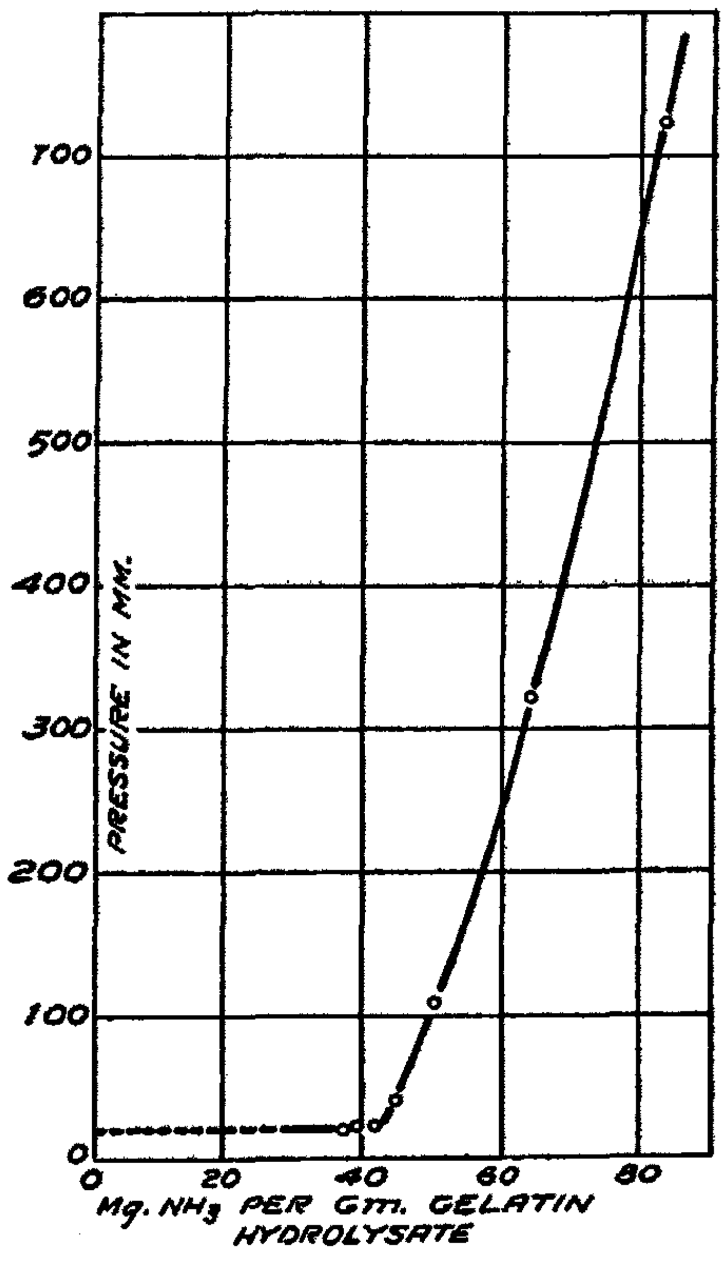


Fig. 7

Table VI

Gelatin Hydrolysate and Ammonia
Weight 3.98 grams

Vol. NH$_3$ added cc.	Total vol. cc.	Equilibrium press. mm.	Volume remaining cc.	Volume taken up cc.	Weight taken up mgr.	Weight taken up per gram mgr.
805.2	805.2	724	370	435	330	83.0
Removed						
306.5	498.7	322	163	336	255	64.1
180.5	318.2	110	55.1	263	199	50.2
63.7	254.5	42	21.4	233	177	44.6
23.6	230.9	24	11.8	219	166	41.7
12.9	218.0	22	10.5	207	157	39.5
11.0	207.0	20	9.7	197	149	37.4

Time required to reach first equilibrium point: 10 days.

The question naturally arises: to what amino acid products of the hydrolysis of gelatin can we attribute this compound formation. According to the analysis of Dakin,[1] one gram of gelatin upon hydrolysis will yield:

Class 1	Glycine	255 milligrams
	Alanine	87
	Leucine	71
	Phenylalanine	14
	Serine	4
Class 2	Proline	95
	Hydroxyproline	141
	Histidine	9
Class 3	Aspartic Acid	34
	Glutamic Acid	58
Class 4	Arginine	91
	Lysine	59
	Ammonia	4
	Unaccounted	78
		1000 milligrams

Class 1	Monoamino monocarboxylic acids
Class 2	Heterocyclic compounds
Class 3	Monoamino dicarboxylic acids
Class 4	Diamino monocarboxylic acids

---

[1] J. Biol. Chem., **44**, 524 (1920); Kossel and Gross: Z. physiol. Chem., **135**, 167 (1924).

In Class 1 we know that glycine does not react with ammonia[1] and we found the same to be true of alanine when we treated it with ammonia. Presumably the other members of Class 1 act in the same manner. We would not expect ammonia to react with members of Class 4, which already have two amino groups to one carboxyl group. Assuming that each of the acids in Class 2 and Class 3 react with one mol of ammonia, the amount of ammonia held in chemical combination would be:

Proline	(95 mgr.)	14.0 mgr. NH_3
Hydroxyproline	(114 mgr.)	18.3
Histidine	(9 mgr.)	0.9
Aspartic Acid	(34 mgr.)	4.4
Glutamic Acid	(58 mgr.)	6.7
	Total	44.3 mgr. NH_3

Table VII

Gelatin and Hydrogen Chloride. 1.
Weight 3.06 grams

Vol. NH_3 added cc.	Total vol. cc.	Equilibrium press. mm.	Volume remaining cc.	Volume taken up cc.	Weight taken up mgr.	Weight taken up per gram mgr.
557.1	557.1	680	276	281	458	149
Removed						
215.0	342.1	206	81.8	260	424	138
87.3	254.8	60	24.2	231	377	123
23.0	231.8	25	10.0	222	362	118
12.2	219.6	15	6.1	214	349	114
Gelatin and Hydrogen Chloride. 2. Weight 4.90 grams						
Added						
487.4	487.4	269	138	349	570	116
Removed						
150.0	337.4	23	11.4	326	532	108
15.5	321.9	15	7.9	314	512	104
Gelatin and Hydrogen Chloride. 3. Weight 1.50 grams						
Added						
356.7	356.7	520	210	147	239	159
Removed						
230.9	125.8	46	18.1	108	176	117
16.9	108.9	22	8.5	100	163	109
10.1	98.8	16	6.2	93	152	102

---

[1] Bancroft and Barnett: J. Phys. Chem., 34, 475 (1930).

Actually we found 41 mgr. ammonia had reacted with one gram of gelatin hydrolysate, and if the theoretical amount is calculated correctly above, then we had about 93% complete compound formation. To justify this deviation, one can always point to the possibility of some variation in the products of hydrolysis. It is also quite possible that histidine does not bind one mol of ammonia, for it contains one amino group, one imino group, and one carboxyl group; in this case, compound formation was about 95% complete.

Gelatin and Hydrogen Chloride. In contrast to the case with ammonia, where adsorption curves alone were obtained, gelatin and hydrogen chloride form a compound (or compounds) with each other, to the extent of about 110 milligrams hydrogen chloride per gram of gelatin. Beyond this point, the solid phase also shows adsorption of hydrogen chloride. Apparently, then, gelatin possesses an equivalent weight of about 332. Data and graphs for three typical runs are given in Table VII and Fig. 8.

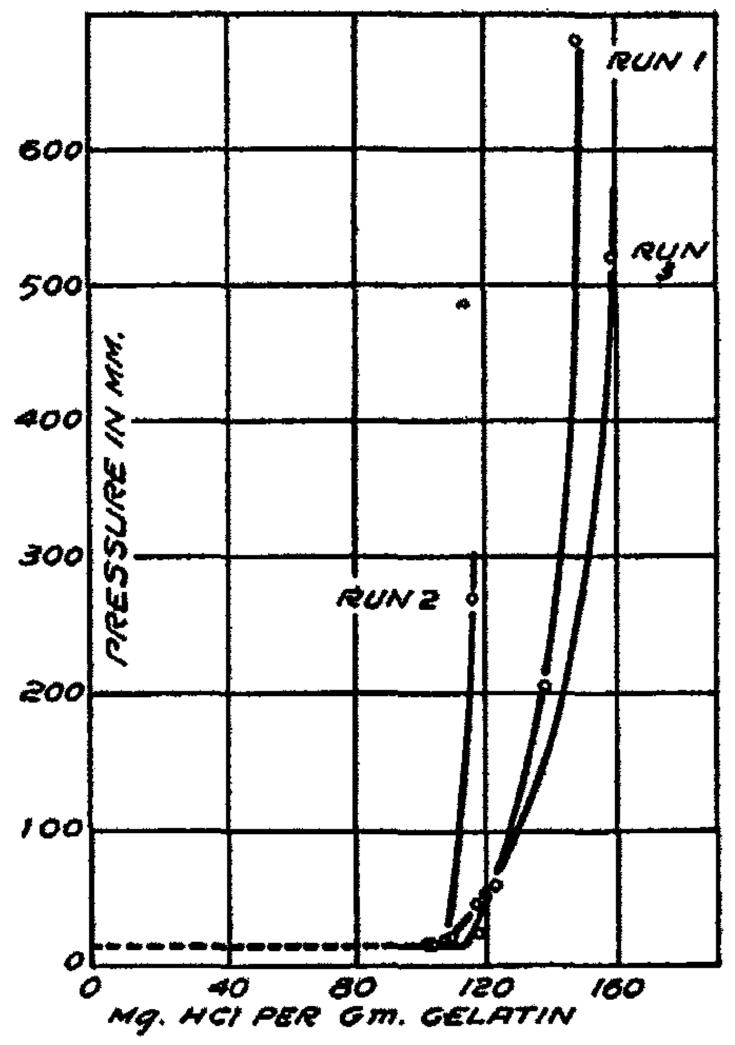


FIG. 8

In general, hydrogen chloride reacts with proteins more rapidly than ammonia; this is true with gelatin. However, hydrogen chloride has the disadvantage that it disintegrates gelatin slowly, the disintegration being accompanied by discoloration. This can be seen in the fact that the right-hand end of the flat portion of the curve (which represents compound formation) creeps slowly to the right over the period of many days while the sample darkens. The problem, then, is to know when hydrogen chloride ceases to be taken up by chemical combination and is further taken up only through the process of disintegration of the gelatin. However, under proper conditions (particularly when a sufficiently finely powdered gelatin sample is used), the rates of combination of the hydrogen chloride through these two processes are markedly different, and guesswork is largely eliminated in determining the point at which chemical combination ceased. Run No. 1 in Table VII covered fifteen days (which was longer than necessary), at the end of which time the sample was a little darkened and some disintegration had doubtless occurred. In Run No. 2 the pressure of hydrogen chloride was purposely kept under three hundred millimeters to minimize disintegration. Run No. 3 used a gelatin sample of considerably greater fineness and the first equilibrium point was reached in six hours. Disintegration was believed to be slight in this run, and the compound formation very nearly complete. From these considerations we estimated the extent of compound formation to be from 105 to 110 milligrams hydrogen chloride per gram of gelatin; the 110 value is used in the calculation of equivalent weight given above.

If no appreciable disintegration of the gelatin occurred during treatment with hydrogen chloride, then there should be little or no increase of free amino content of the gelatin as determined in the Van Slyke apparatus. This test was made on the gelatin of Run No. 3, following closely the procedure described by Van Slyke and Birchard.[1] One modification was made. Enough hydrochloric acid was added to the sample of gelatin to make it equivalent to the hydrogen chloride content of the HCl-treated gelatin (from Run No. 3). Due to this, the free amino content of the gelatin appeared higher than (in fact, more than double) the accepted value: 3.1% of the total nitrogen as amino nitrogen. Finally, the amino nitrogen content of a hydrolyzed gelatin was determined. The results of these determinations are given in Table VIII.

TABLE VIII

Van Slyke Determinations

Original gelatin	6.8% total N as amino N
HCl-treated gelatin	8.4
Hydrolyzed gelatin	49

If we assume that the increase from 6.8% to 49% represents complete hydrolysis, then we can say that the HCl-treated gelatin had undergone the equivalent of about 4% hydrolysis. This evidence supports our belief that this hydrogen chloride treatment of gelatin did not include appreciable disintegration.

Whether the flat portion of the curve represents one compound or several compounds (in which latter case the curve is stepwise) we do not know; it probably represents several compounds. Attempts to establish steps in the pressure range below twenty millimeters, with the present form of apparatus at least, and when working with proteins and their hydrolysates, are tedious and frequently unsatisfactory.

---

[1] J. Biol. Chem., **16**, 539 (1913).

Gelatin Hydrolysate and Hydrogen Chloride. Chemical combination of hydrogen chloride with the hydrolysis products of gelatin is nearly three times as great as its combination with the original gelatin. By observing several curves, a typical one of which is presented in Table IX and Fig. 9, we concluded that the amount of this chemical combination lay between 285 and 290 milligrams hydrogen chloride per gram of gelatin. It should be pointed out that the curve in Fig. 9 includes something which had not been attempted in the two previous cases where we were dealing with compound formation: the determination of points along the flat portion of the curve. The procedure consists of admitting into the apparatus an atmosphere's pressure of hydrogen chloride, leaving it until compound formation was partly completed, removing it until the pressure of the remaining gas was less than two millimeters, and then letting the solid release enough hydrogen chloride to build up equilibrium pressure. The process is costly in time, but inasmuch as we are not concerned here with any disintegration of the solid by hydrogen chloride, the method should not thereby be less accurate. If the points thus obtained are true equilibrium points, as we have every reason to believe they are, they show the compound portion of the curve to consist of several (at least three) separate flats, which is as it should be. Because of the unfavorable time element in the attainment of equilibrium conditions, it would have been about impossible to obtain enough points in this region of the curve to fix the lengths of the individual flats.

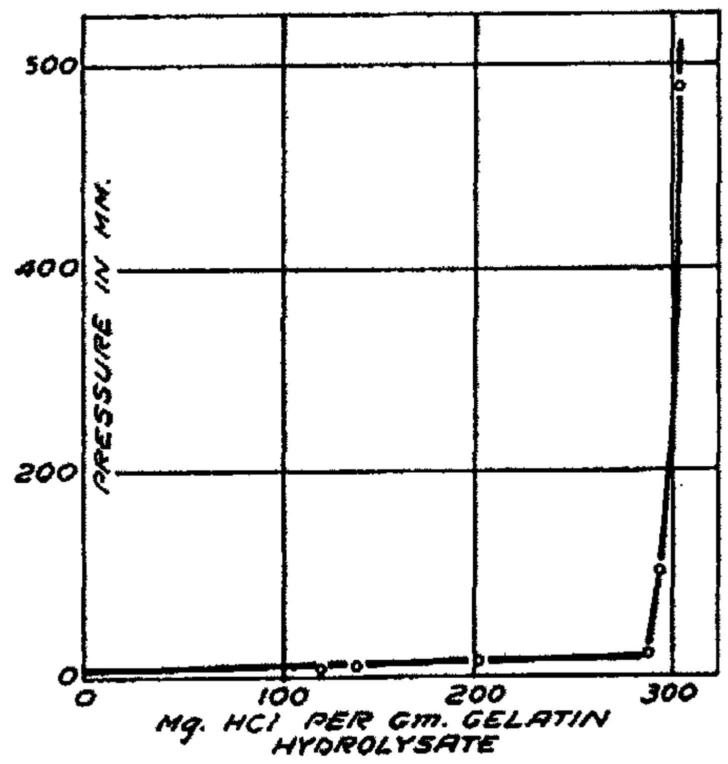


FIG. 9

When gelatin hydrolysate is treated with hydrogen chloride, the reaction proceeds for a few minutes with considerable speed. Regardless of how vigorously the reaction flask is being shaken, however, the powdered sample soon cakes and the rate immediately diminishes. An attempt was made to eliminate this caking by mixing the powdered sample with purified sand, in the

TABLE IX

Gelatin Hydrolysate and Hydrogen Chloride
Weight: 1.89 grams

Vol. NH_3 added cc.	Total vol. cc.	Equilibrium press. mm.	Volume remaining cc.	Volume taken up cc.	Weight taken up mgr.	Weight taken up per gram mgr.
302.0						
Removed						
159.4	142.6	6	2.8	140	228	121
Added						
343.6						
Removed						
316.3	169.9	9	4.4	166	270	143
Added						
383.0						
Removed						
311.6	241.3	15	7.5	234	382	202
Added						
407.5	648.8	577	296	353	575	304
Removed						
259.7	389.1	101	51	338	551	292
44.8	344.3	20	10	334	545	288

hope that the sand would prevent the agglomeration of the hydrolysate particles; the caking continued to occur even in the presence of the sand. There is probably some feasible means of keeping such a sample as this ground up without opening the apparatus. Such an addition to the apparatus would be amply justified for this work.

To what amino acid products of the hydrolysis of gelatin can we attribute this ability to hold 290 milligrams of hydrogen chloride in chemical combination? Referring to the list of these amino acids on page 2185, one would say that the Class 1 acids should follow the lead of glycine[1] and take up one mol of hydrogen chloride. In all probability the acids of both Class 2 and Class 4 will combine with one mol of hydrogen chloride. The behavior of aspartic acid and glutamic acid (Class 3) we particularly examined. Both acids combine with one mol of hydrogen chloride but they do so extremely slowly. A sample of purified Eastman Company glutamic acid weighing 3.31 grams had at the end of twenty-one days taken up 83% of one equivalent of HCl; at the end of fifty days had come to practically a standstill at 98% HCl. During some of this time the temperature had been raised to 80°C. to expedite compound formation. Similarly, a sample of Kahlbaum "Asparaginic Acid for

---

[1] Bancroft and Barnett: J. Phys. Chem., 34, 479 (1930).

scientific purposes," weighing 1.53 grams, had at the end of seven days taken up 75% of one mol HCl, and at forty days had apparently reached equilibrium conditions at about 102% HCl. Again, elevated temperature had been used some of the time to hasten the reaction. From this it can be seen that in the run reported in Table IX, which covered a period of thirteen days and was carried on at room temperature, combination of hydrogen chloride with the glutamic and aspartic acid portions of the hydrolysate was only partly completed; that if the run had been continued to a total of fifty days, the flat portion of the curve would have extended itself slowly to the right (to a value probably not exceeding 313 mgr. HCl per gram sample) as the aspartic and glutamic acids completed their casual compound formation. The amount of hydrogen chloride which should be held in chemical combination by the several amino acids is:

Glycine	(255 mgr.)	123.9 mgr. HCl
Alanine	(87 mgr.)	35.7
Leucine	(71 mgr.)	19.8
Phenylalanine	(14 mgr.)	3.1
Serine	(4 mgr.)	1.3
Proline	(95 mgr.)	30.2
Hydroxyproline	(141 mgr.)	39.3
Histidine	(9 mgr.)	2.1
Arginine	(91 mgr.)	19.4
Lysine	(59 mgr.)	14.7
Glutamic Acid (58 mgr.; combination with HCl estimated to be about 40% complete		5.8 (100% = 14.4 mgr.)
Aspartic Acid (34 mgr.; combination with HCl estimated to be about 50% complete		4.7 (100% = 9.3 mgr.)
	Total	300.0 mgr. HCl

It would be fine for our purposes if glutamic and aspartic acids did not react with hydrogen chloride, for the total of the first ten acids in the above list is 289.5 mgr. HCl, which falls within the 285-290 mgr. estimate made from the investigations in the Phase Rule apparatus. If the theoretical amount of the combination with hydrogen chloride is calculated correctly above, then we obtained about 96% complete compound formation.

Summary

Thus do we see that adsorption plays a large role in the binding of volatile acid and base by gelatin. With ammonia, the process of adsorption is the whole story. With hydrogen chloride it is a part of the story; chemical combination constitutes the other part. It is probably true that hydrogen chloride reaches the realm of chemical combination through the intermediate stage of adsorption. Whatever else this investigation may or may not accomplish, it throws a weight of evidence against the view that the proteins always react in stoichiometric proportions with acids and bases to form definite compounds. It shows that under some circumstances adsorption is unquestionably the mode of combination, and it suggests that under all circumstances adsorption probably is a factor which needs must be reckoned with. The fact that we show chemical union for a given case does not eliminate adsorption.

The principal points which appear in this paper are these:

1. A statement is given of two conflicting views concerning the nature of the binding of acid and base by protein.

2. A brief review is presented of the evidence which is said to support the theory that acids and bases react with proteins in stoichiometric proportions to form definite compounds.

3. The method of using dry protein powder and volatile acid and base to distinguish between chemical union and adsorption is discussed.

4. An apparatus is described which has proved reasonably satisfactory for Phase Rule investigation of the action of volatile acid and base on a solid.

5. Gelatin and ammonia show adsorption and no compound formation. The amount of adsorption varies somewhat with the gelatin and with the conditions. Gelatin is sufficiently porous, apparently, so that the fineness of the gelatin powder does not alter the amount of the adsorption. The presence of some impurities, for instance a trace of vegetable oil, lowers the adsorption, at least temporarily. It does not appear that the amount of adsorption of ammonia can be used satisfactorily as a test of the uniformity or lack of uniformity of gelatin samples.

6. The hydrolysis products of gelatin show chemical combination with ammonia to the extent of about 41 milligrams ammonia per gram of hydrolysate, and this can be accounted for on the very reasonable assumption that ammonia combines with the glutamic acid, aspartic acid, proline, hydroxyproline, and histidine portions of the hydrolysate. The hydrolysate, after its union with 41 milligrams of ammonia, adsorbs further ammonia.

7. Gelatin and hydrogen chloride show chemical combination to the extent of 110 milligrams hydrogen chloride per gram of gelatin. In addition, they show adsorption or, more accurately speaking, the product of the chemical combination of gelatin and hydrogen chloride adsorbs further hydrogen chloride. From this we conclude gelatin shows a combining weight of 332 toward hydrogen chloride. If left for a period of time in the presence of hydrogen chloride, gelatin darkens and decomposes.

8. The hydrolysis products of gelatin show a greatly increased ability to combine chemically with hydrogen chloride, one gram of hydrolysate combining with about 290 milligrams of hydrogen chloride. Assuming under these conditions that the hydrogen chloride reacts partially with the glutamic and aspartic acid portions of the hydrolysate, and completely with the remaining ten amino acids, we find this combination with hydrogen chloride to be within 4% of the calculated value.

9. Stress is laid on the necessity of considering adsorption when we are dealing with the action of proteins with acids and bases.

Acknowledgment

When it is one's rare good fortune to work under the able direction and constant inspiration of Professor Wilder D. Bancroft, one has, indeed, reason to be very grateful.

Cornell University.

CATALYTIC EQUILIBRIUM BETWEEN ACETALDEHYDE AND ALCOHOL*

BY WILDER D. BANCROFT AND AVERY B. GEORGE

Introduction

The catalytic decomposition of ethyl alcohol has been studied by several investigators, and the products obtained have been found to be dependent on the nature of the catalytic agent employed. It was first observed by Berthelot and Jungfleisch[1] that when ethyl alcohol is passed through a heated tube, it begins to decompose at about 500°C, the decomposition consisting of two distinct superposed reactions, the dehydration to ethylene and water, and the dehydrogenation to acetaldehyde. In contact with various catalytic agents it is now known that dehydration may take a third course, or rather, stop at an intermediate stage giving ether.

Ipatiev showed that the proportion in which alcohol undergoes these changes is very much modified by the presence of catalysts. With different catalysts, the decomposition products of ethyl alcohol vary by widely different factors, and Sabatier has drawn up a table in which the relative dehydrating and dehydrogenating influences of various oxides are compared. This work was done in the later stages of Sabatier's investigations on the catalysis of organic compounds at solid surfaces. This aspect of the subject was especially studied by Sabatier and Mailhe,[2] who found that, for example, ethyl alcohol was converted into ethylene and water or, alternatively, into hydrogen and acetaldehyde, by the oxides quoted in Table I.

The direction and importance of the activity of the various oxides can be shown clearly by a comparison of the volume and composition of the gas evolved by them, when equal volumes of them are used at 340°-350°C with the same amount of ethyl alcohol. All of the oxides have been prepared below 350°C. From Table I it is clear that thoria, alumina, and the oxides of tungsten and chromium are pre-eminently dehydrating catalysts, whilst a large number of others promote both types of decomposition. Finally, a few oxides, notably those of zinc, tin, cadmium, manganese and magnesium are almost exclusively catalysts of dehydrogenation.

It is necessary, especially from a technical standpoint, to consider not only the relative proportions of the two types of reaction, but also to bear in mind the intensity of the change set up by any given oxide. As a matter of fact, the dehydrogenating oxides are almost wholly of feeble activity, and consequently have not been utilized in technical practice, in the production of an

---

*This work is done under the programme now being carried out at Cornell University and supported in part by a grant from the Heckscher Foundation for the Advancement of Research established by August Heckscher at Cornell University.

[1] Berthelot and Jungfleisch: "Traité élémentaire de Chimie organique," 1, 256 (1886).

[2] Ann. Chim. Phys., (8) 20, 289 (1910).

TABLE I

Oxide	Vol of gas in cc./min.	Composition of gas % C_2H_4	% H_2
ThO_2	31.0	100	trace
Al_2O_3	21.0	98.5	1.5
W_2O_5	57.0	98.5	1.5
Cr_2O_3	4.2	91.0	9.0
SiO_2	0.9	84.0	16.0
TiO_2	7.0	63.0	37.0
BeO	1.0	45.0	55.0
ZrO_2	1.0	45.0	55.0
UO_2	14.0	24.0	76.0
Mo_2O_5	5.0	23.0	77.0
Fe_2O_3	32.0	14.0	86.0
V_2O_3	14.0	9.0	91.0
ZnO	6.0	5.0	95.0
SnO (Initial)	45.0	0.0	100.0
CdO (Initial)	11.2	0.0	100.0
MnO	3.5	0.0	100.0
MgO	traces	0.0	100.0
Cu	110	0.0	100.0

aldehyde or ketone from an alcohol. For dehydrogenation processes the finely divided metals such as nickel, copper, platinum and cobalt have been found to be the most active catalysts, the first two named being used to a considerable extent in technical processes. The action of a metallic catalyst is connected to some extent, although not exclusively, with its capacity for adsorbing hydrogen, so that catalysis by metals can usually be placed in the categories of hydrogenation or dehydrogenation. The metallic oxides display little tendency to act simply as hydrogenating or dehydrogenation catalysts; they are more usually concerned either in the removal of the elements of water from organic compounds or in processes of more or less oxidation.

The dehydrogenation of alcohols was first studied by Ipatiev,[1] but it is to Sabatier and Senderens[2] that we owe a complete understanding of the dehydrogenation of alcohols. They showed that when primary saturated alcohols are passed over finely-divided copper, they are regularly decomposed into aldehydes and hydrogen. The action begins at about 200°C, becomes rapid at 250°C, and is almost the exclusive reaction up to 300°C. This is a very advantageous method for the preparation of aliphatic aldehydes, particularly for those which, on account of low volatility, are difficult to prepare by oxidation of the alcohols. The transformation can never be complete, even when a long train of copper is used, since the hydrogen which is formed can be added to the aldehyde by copper above 200°C. Hence the reaction is

---

[1] Ber., 34, 3579 (1901); 35, 1047 (1902).

[2] Compt. rend., 136, 921 (1903); Ann. Chim. Phys., (8) 4, 463 (1905).

limited, but the conditions are favorable to the decomposition because the operation is carried on in the presence of a small concentration of hydrogen.

$$C_2H_5OH \rightleftarrows CH_3CHO + H_2$$

The equilibrium is favorable to hydrogenation at a low temperature, dehydrogenation becoming more pronounced as the temperature is raised. An increase of pressure, as would be expected from Le Chatelier's rule, is favorable for the hydrogenation process. By operating under reduced pressure, there is the double advantage of a more readily volatilization of the alcohols and a diminishing of the reverse action of hydrogenation, so consequently increasing the practical yield.

At higher temperatures the aldehydes begin to decompose into carbon monoxide and a hydrocarbon. In the case of ethyl alcohol at 420°C, 16% of the acetaldehyde is destroyed, and the gas collected contains carbon monoxide and methane as well as hydrogen.

$$CH_3CHO \longrightarrow CO + CH_4$$

Reduced nickel acts similarly, but more energetically and at a lower temperature than does copper. Decomposition takes place from 150°C up, while the reaction is rapid above 230°C. At 180° almost a third of the aldehyde formed is decomposed, and at 330°C its destruction is complete. Platinum sponge acts on alcohols as does nickel, but its action does not begin till above 250°C, at which point the acetaldehyde formed is mostly decomposed into carbon monoxide and methane.

The reverse reaction, the hydrogenation of acetaldehyde, takes place readily at 140°C with active nickel, while at 180° the formation of methane and carbon monoxide begins. Copper on account of its weak activity, relative to that of nickel, requires a higher temperature before it exerts any action, in which case dehydrogenation of the alcohol becomes the predominating change, at the temperature necessary for hydrogenation. For example, alcohols in contact with copper are not attacked below 230°C, at which temperature, under ordinary pressures of hydrogen, dehydrogenation takes place. Finely divided platinum is unsuitable for the regular transformation of aldehydes into the alcohols by hydrogenation, since at the temperatures necessary for action, which are above 200°C, the metal acts powerfully to break up the aldehyde molecule into carbon monoxide and hydrocarbon.

There has been much work done on the behavior of ethyl alcohol at a copper surface, while with nickel there has been very little done since the mechanism was first put forward by Sabatier. Palmer[1] and his associates have made a rather extensive study of the activity of a copper catalyst. Thinking that a pure metal was necessary for high activity, he prepared pure metallic copper by the electrolysis of a copper salt, but found this to be catalytically inactive. However copper obtained by reduction of the oxide is active in the dehydrogenation of alcohol, and he considers that the activity

---

[1] Proc. Roy. Soc., 98A, 13 (1920); 99A, 412 (1921); 101A, 175 (1921); 106A, 250 (1924); 107A, 255, 270 (1925).

is due to a kind of copper produced from cuprous compounds. There would, of course, only be "cupric" copper in the deposit on an electrode and hence, according to Palmer, this would be inactive as a catalyst.

At temperatures below 300°C Palmer[1] found that pulverulent copper decomposes ethyl alcohol into acetaldehyde and hydrogen, with no formation of secondary products; but if a mixture of acetaldehyde and hydrogen is passed over the copper catalyst between 250° and 300°C, much of the aldehyde is decomposed. The author accounts for this apparent discrepancy by assuming that alcohol is adsorbed selectively by copper from a mixture of alcohol and aldehyde vapors, so that the surface of the copper during dehydrogenation is covered by a layer of alcohol molecules, these latter preventing the adsorption and consequent destruction of the aldehyde. Palmer[1] believes that the dehydrogenation of alcohol involves three stages.

(1) Adsorption of alcohol molecules over the surface of the catalyst.

(2) Activation of certain alcohol molecules by adsorption of energy.

(3) Evaporation of acetaldehyde and hydrogen away from the adsorption surface into the alcohol stream flowing past the catalyst.

Bancroft[2] has suggested that such cases might be called "protective poisoning."

The velocity of decomposition of alcohol at the surface of a solid catalyst has been shown by Rideal[3] to be very much higher than the reverse reaction of hydrogenation.

He states that "although the dissociation of the alcohol to aldehyde and hydrogen takes place relatively rapidly at the commencement, yet the reverse reaction proceeds but slowly, and a long period of contact is necessary even to approximate to equilibrium conditions. According to the general concept of catalytic mechanism, an alcohol molecule striking the surface of the catalyst may either undergo decomposition or it may evaporate from the surface unchanged. For the combination of aldehyde and hydrogen, a molecule of each species has to strike adjacent molecules of the catalytic surface, a much less frequent phenomenon." Rideal makes a calculation to show that, unless the number of alcohol molecules striking the surface and evaporating again unchanged is extraordinarily large, the reverse reaction will proceed much more slowly.

Since partial poisoning may be secured, it is evidently possible that use may be made of it to achieve certain reactions whilst obviating others. A very obvious application is in the case where a catalytic process proceeds too far with an active catalyst. By minimizing the activity of such a catalyst or poisoning the more highly reactive patches with the requisite poison, the reaction may be stopped at the desired stage. An example of this has been found by Armstrong and Hilditch,[4] who have shown that in the catalytic dehydrogenation of ethyl alcohol in the presence of copper, the presence of water in the alcohol improves the yield of acetaldehyde relative to that of hydrogen.

---

[1] Proc. Roy. Soc., **98A**, 13 (1920).

[2] J. Ind. Eng. Chem., **14**, 545 (1922).

[3] Proc. Roy. Soc., **99A**, 153 (1921).

[4] Proc. Roy. Soc., **97A**, 259 (1920).

Thus at 300°C, whereas anhydrous alcohol only gave an aldehyde-hydrogen ratio of 67 percent, alcohol containing eight percent water gave a 95 percent ratio. With the anhydrous alcohol, there is a marked increase in the yield of gaseous products, so it is evident that secondary decomposition of aldehyde is much more pronounced than with alcohol containing water. Evidently the water acts as a beneficial poison in that it poisons the catalyst for such secondary decompositions. Armstrong and Hilditch showed, by passing aldehyde vapor together with water over a copper catalyst, that the water had a considerable protective influence on the aldehyde.

In the hydrogenation whilst water protects the aldehyde from decomposition, the effect of even a small proportion of water is to retard hydrogenation considerably, in fact to render it almost negligible. The authors state in regard to this that, "the protection afforded by water in the dehydrogenation process may be ascribed to the influence it exercises on the removal of the molecules of aldehyde from the sphere of action. The reason for no influence on the reverse process may be that the conditions cannot well be made the same in the two cases; in other words the behavior of a surface at which the aldehyde is being produced towards hydrogen and water may well be different from that of a surface saturated with water towards a mixture of aldehyde and hydrogen."

During the years 1917-1919 this principle of protective poisoning was used for the production of ethylene from alcohol in presence of kaolin. Instead of a low temperature process, the reaction was conducted at red heat and the products were protected from decomposition by using alcohol-water mixtures, even though the process was dehydration. Hoover and Rideal[1] find that the presence of water affects the ratio in which the competing dehydration and dehydrogenation reactions occur at the surface of thoria.

Armstrong and Hilditch obtained some data on the dehydrogenation of a 92 percent ethyl alcohol-water solution over nickel at 250°C, the aldehyde-hydrogen ratio being only 35.7 percent, and the evolved gas contained 60 percent hydrogen, 20 percent carbon monoxide, and 15-17 percent methane. Evidently, in this case, the 8 percent of water in the alcohol used was not sufficient to protect the aldehyde produced. Russell and Marschner[2] studied the effect of water on the decomposition of ethyl alcohol at a nickel surface. They worked at 200°C, and found that over a wide range of concentrations the effect of water was, (a) to increase the amount of alcohol undergoing reaction, and (b) to decrease the percentage of the aldehyde decomposed.

It was the object in this work to determine the point of equilibrium between ethyl alcohol and acetaldehyde, employing finely-divided nickel as the catalyst. The effect of a platinized asbestos catalyst on this reaction was also studied under the same conditions. Then there was a general study of the reaction, bringing out certain points. The temperature employed was 140°-145°C, in which range nickel does not cause any appreciable decomposition of the acetaldehyde.

---

[1] J. Am. Chem. Soc., 49, 114 (1927).

[2] J. Phys. Chem., 34, 2554 (1930).

Experimental Procedure

Materials. Electrolytic hydrogen was used in this work, and it was further purified by passage through a tube containing platinized asbestos at a dull red heat, then over solid potassium hydroxide. Finally, to dry the hydrogen it was passed through a tube containing soda-lime and then phosphorus pentoxide.

Anhydrous ethyl alcohol was used, which gave no test for water by the anhydrous copper sulphate test. The acetaldehyde employed was obtained by distilling paraldehyde after having added a few drops of concentrated sulphuric acid. The acid depolymerizes the paraldehyde to acetaldehyde, which is distilled over and condensed. The alcohol-water and the acetaldehyde-water mixtures used were prepared by diluting these liquids with distilled water.

The finely-divided nickel and also the platinized asbestos catalysts employed in this work, were very kindly furnished by Dr. Stine of E. I. du Pont de Nemours & Company, to whom our thanks are given.

Apparatus and Procedure. The apparatus consisted of a purifying system for the hydrogen, with a flow meter interposed in the path of the hydrogen, then a flask for vaporizing the liquid, this being connected to a reaction tube heated by an electric furnace, with a system for condensing the product at the other end. A thin layer of the catalyst was spread along the reaction tube for a length of 39 cm. Before making a run the furnace was heated to 300°C with a slow stream of hydrogen flowing through the apparatus, and this condition was maintained for thirty minutes. Then the temperature of the tube was lowered to 140°-145°C, at which temperature all of the runs were made. In the case of the hydrogenation, a measured amount of the acetaldehyde was put into the flask through a funnel at the top. At the end of a run the amount of liquid left was measured, then the amount of acetaldehyde actually used could be determined. The flask containing the acetaldehyde was immersed in an ice bath, at which temperature the vapor pressure of the aldehyde was 331 mm. The flow of hydrogen was adjusted to the desired rate, and with the delivery tube extended nearly to the bottom of the flask the run was started. The hydrogen admixed with the vapor of acetaldehyde was passed through the catalyst tube, the product being condensed and collected on emergence from the heated tube. The experiments were carried out for a period of two and one half hours, and the rate of hydrogen was varied over a fairly wide range. After the vapors passing through were condensed, the liquid was collected in a small flask which was surrounded by an ice bath. The products obtained consisting of a mixture of alcohol and acetaldehyde were analyzed, after the weight of the product had been determined.

Some work was done on devising a method for analyzing the product by specific gravity and index of refraction determinations. However the relations obtained were only qualitative in most cases, so these methods were not used. An attempt to separate the acetaldehyde-alcohol mixtures by fractional distillation did not yield quantitative results. So the acetaldehyde was determined in an aliquot portion of the sample by the method of Ripper.[1] On later comparison it was found that the results obtained from one set of specific gravity data agreed very well with the amount of acetaldehyde as found in the product by using the procedure of Ripper. So a method of analysis along this line could no doubt be worked out for this case.

The method of analysis actually used consisted essentially in adding a measured excess of sodium bisulphite solution to the sample, and after at least fifteen minutes the amount of excess is determined with iodine solution. This solution was standardized against sodium thiosulphate solution. Under the conditions of these experiments, the alcohol present in the product was obtained by difference.

In the case of the dehydrogenation of the ethyl alcohol, practically the same procedure was followed as given above. Hydrogen was passed through the apparatus until the measured quantity of alcohol was put into the flask, then the flow of hydrogen was shut off. The flask containing the alcohol was immersed in an oil bath, and the rate at which the alcohol vapors were allowed to pass over the catalyst, was controlled by varying the temperature of the oil bath. The product was collected as before in a small flask surrounded by ice, and then a delivery tube led from this into a solution of sodium bisulphite, which served to absorb any acetaldehyde that may have passed over in the vapor. An aliquot portion of the product was analyzed for acetaldehyde as before, and the necessary data obtained.

Hydrogenation of Acetaldehyde

A series of runs were made on the hydrogenation of acetaldehyde employing finely-divided nickel as the catalyst, and the rate of hydrogen flow was varied between 56 cc./min. to 148 cc./min. The principle involved was to plot the percentage yield of alcohol obtained against the rate of hydrogen flow, and on extrapolating the curve, the percentage of alcohol at zero rate or the equilibrium value could be determined. A few runs were made using the same catalyst each time, the assumption being that the activity of the nickel catalyst was the same in each case. The procedure followed was to heat the catalyst to 300°, and to maintain this temperature for thirty minutes, then to lower the temperature to 140°-145°C before starting a run, the catalyst also being cooled in an atmosphere of hydrogen after the completion of a run. The results obtained were not consistent, and they seemed to indicate that the activity of the catalyst must have undergone some change. In order to get away from this difficulty, a series of runs were made using a fresh portion of catalyst each time, in which case the various runs were comparable. The results obtained are given in the following table.

Rate of Hydrogen cc./min.	% Alcohol
56	94.0
74	91.2
95	90.0
148	85.9

---

[1] Monatsheft, 21, 1079 (1900).

These data were plotted and a straight line relation obtained. The mechanism of this decrease in activity of the catalyst, and to what extent the poisoning took place, was an interesting point for consideration. From some of the data obtained, the indications were that there was a rapid initial poisoning action, after which the activity of the nickel surface either remained constant or changed but slightly. This was further realized experimentally by a series of runs using the same catalyst for each run, the only treatment being the heating and cooling of the nickel surface in an atmosphere of hydrogen, before and after each experiment. The following set of data was obtained.

Rate of Hydrogen cc./min.	% Alcohol
56	88.8
	88.3
95	87.3
	85.6
148	79.8
	79.3

These runs were made employing a nickel catalyst which had been previously used, so it had lost its initial activity. Since the reaction takes place in or at the surface, it follows that any substance, which cuts down the rate at which the reacting substances reach the catalytic surface[1] or which prevents them from reaching it, will decrease the reaction velocity and may destroy the catalytic action entirely. In this case it seems that the nickel surface possesses spheres of different activity. The more active points would be those showing the greatest adsorption and activation of the reactants. During its initial run certain points of the nickel surface must become altered and thus poisoned to any further reaction at these points. On preparing the catalyst for another run by the treatment outlined above, certain spheres of the surface, which are no doubt the most active portions, remain unaltered during this procedure, thus giving the catalyst a lower activity for this experiment. Thus after the initial run the reaction must take place at the unaltered points of the nickel surface, these points having a lower adsorption so the activity of this surface would be less than that of the original surface. So from this it must mean that the activity is gradually decreased during the initial run with the nickel catalyst. This point has been realized experimentally, for by taking samples at intervals during an initial run, it was found that the amount of alcohol formed decreased with increase of time. In the second case, after this initial poisoning had taken place, the amount of alcohol formed remained practically the same throughout a run. Considerable work has been done by Palmer and Constable[2] on the activity of a copper catalyst, using this reaction for study. The work dealt primarily with the activity of the catalysts with temperature.

---

[1] Taylor: Trans. Am. Electrochem. Soc., 36, 149 (1919).

[2] Proc. Roy. Soc., 99A, 412 (1921); 101A, 175 (1922).

Of course in our case it may be possible to restore the nickel catalyst to its original activity, but by the treatment given in this work, a certain portion of the surface was not reactivated.

A series of runs was next made using as the catalyst some of the nickel which had become poisoned, in other words whose initial activity had been lost. The following set of results was obtained.

Rate of Hydrogen cc./min.	% Alcohol
56	88.5
74	86.5
95	86.5
148	79.5

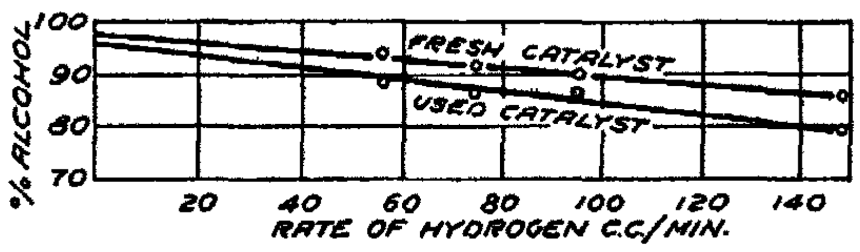


Fig. 1
Hydrogenation of Acetaldehyde with Nickel

The data obtained by using some fresh catalyst each time were plotted, the percentage of alcohol against the rate of hydrogen flow, and a straight line relation was obtained. On extrapolating the line to zero rate, a value of 96-97% alcohol was obtained which will correspond to the equilibrium value as reached from one end of the reaction. The data given above which were obtained by using some of the poisoned catalyst, were plotted as in the other case, and the straight line resulting, on extrapolating to zero rate, intersected at practically the same point as did the line obtained from using fresh catalyst each time. This means that the same equilibrium value will be obtained in each case, but that it would be reached more slowly using a poisoned catalyst, than when a fresh catalyst was employed. These results are what would be expected for, in the case of the poisoned catalyst, the reaction takes place on areas which have a lower adsorptive power than those of the fresh catalyst, and consequently the reaction velocity is less in the case of the poisoned catalyst.

Effect of Water. The hydrogenation of a water solution of acetaldehyde was carried out and some interesting results obtained. A 10% and a 25% solution of water in acetaldehyde were made up, and these two solutions were hydrogenated, the same temperature being used as in the above cases, and the rate of hydrogen passing through being 95 cc./min. The yields of alcohol obtained were approximately 94% and 96% respectfully, which shows that the presence of water increased the amount of alcohol formed, for by making a run under similar conditions using anhydrous acetaldehyde a 90% yield of alcohol was obtained. The presence of water was also found to increase the yield of alcohol when using a poisoned catalyst. So the water tends to reactivate the nickel surface, and also the activity of the catalyst does not diminish as rapidly when water is present. It may be that the action of the water is a specific action, and thus involving its preferential adsorption, on the nickel surface, to that of poisons thereby allowing more acetaldehyde to react. According to this then, the reactivation by water would mean that the water displaces the adsorbed poisons on certain points.

Dehydrogenation of Ethyl Alcohol

The reaction was now approached from the other side, that is, by dehydrogenating the ethyl alcohol. Some runs were made on this reaction by varying the rate of alcohol passage over the nickel catalyst from 7 cc./hr. to 26 cc./hr., over which range the yield of acetaldehyde obtained remained practically constant. This is in agreement with what Armstrong[1] found, for he states that the reaction velocity of the dehydrogenation of ethyl alcohol was found to be independent of the rate of flow of alcohol vapor over the catalyst between 7 cc. and 35 cc. of liquid vaporized per hour. In view of this fact all future runs were made at the higher rate, that is 26 cc./hr. due to the experimental advantages involved.

One of the important results of the work of Palmer[2] and his associates was that, on a given copper catalyst, the rates of dehydrogenation of the primary alcohols, ethyl, propyl, butyl, isobutyl and isoamyl, are all equal within the limits of experimental error, and the temperature coefficient is the same for all. Constable,[3] in the last of the series of these researches, showed that the reaction velocity at 250°C with ethyl and butyl alcohols was independent of the pressure in the range 10-140 cm. of mercury. It is evident therefore that, in this pressure range, the surface is practically covered with alcohol molecules and the mean life of the molecule in the activated unimolecular layer changes only slowly with the pressure over the range investigated.

Some runs were made on the dehydrogenation of alcohol using a fresh portion of catalyst each time, the temperature being the same as in the hydrogenation of the acetaldehyde, that is, 140°-145°C. The following table gives the results obtained.

Rate of Alcohol cc./hr.	% Acetaldehyde
26	2.96
26	3.08

Average—3.0% Acetaldehyde

On making some runs employing a nickel catalyst which had been previously used, a little lower yield of acetaldehyde was obtained than is given in the above table, the average value being about 2.68% acetaldehyde. So in the dehydrogenation of ethyl alcohol there is also a decrease in the activity of the nickel catalyst, the mechanism of which is probably the same as in the hydrogenation of the acetaldehyde. The heat treatment of the nickel sur-

---

[1] Proc. Roy. Soc., **97A**, 259 (1920).

[2] Proc. Roy. Soc., **107A**, 255 (1925).

[3] Proc. Roy. Soc., **107A**, 279 (1925).

face before and after a run was the same in the hydrogenation and the dehydrogenation processes.

Effect of Water. The effect of the presence of water on this reaction was determined by dehydrogenating a solution containing 10% water and 90% ethyl alcohol, the following results being obtained.

Rate of Solution Passed cc./hr.	% Acetaldehyde
26	2.97
26	3.11

Average—3.04% Acetaldehyde

So from these data it can be seen that the equilibrium in this case is not displaced by the presence of ten percent water. Armstrong[1] has shown that water has a considerable protective influence on the acetaldehyde, but under the conditions of these experiments the amount of acetaldehyde that is decomposed would be very small, thus the presence of a small amount of water should have but little effect in protecting the acetaldehyde against decomposition. However the presence of water does tend to reactivate the nickel surface, as can be shown in the following manner. A nickel catalyst which had been used once, thus having lost its initial activity, was employed in the dehydrogenation of a 10% water and 90% alcohol solution. The results instead of showing about a 2.68% yield of acetaldehyde as obtained in the case of a poisoned catalyst, the percentage yield of acetaldehyde approached very closely to the value obtained when using a fresh portion of catalyst. So under these conditions the presence of a small amount of water will bring an apparently poisoned nickel catalyst approximately back to its initial activity. This was also stated by Russell and Marschner[2] in their work on the effect of water on the decomposition of ethyl alcohol in the presence of a nickel catalyst. They state that, "increasing the water concentration causes a considerable reactivation of the catalyst, but not as complete as with the hydrogen treatment at 350° C." In this case the poisoning seems to be most complete with the anhydrous alcohol, so in the presence of water more of the active areas may be restored to their original activity due to the preferential adsorption of the water.

The behavior of ethyl alcohol at a nickel surface is similar to its behavior with other catalysts. Constable[3] has found that the activity of a copper catalyst decays with time when exposed to the vapors of pure ethyl alcohol at temperatures above 280°C. The curves given in the work of Russell and Marschner by plotting the yield of aldehyde against time are entirely similar to those obtained by Constable in the temperature range of 300°-330°C. The same initial rapid decrease in aldehyde yield, followed by a much slower rate of decrease, was found. Palmer[4] also observed that the catalytic activity of a supported copper catalyst decreased with use although everything was pure,

---

[1] Proc. Roy. Soc., 97A, 259 (1920).
[2] J. Phys. Chem., 34, 2554 (1930).
[3] J. Chem. Soc., 1927 II, 2995.
[4] Proc. Roy. Soc., 98A, 13 (1920).

however, after oxidation and subsequent reduction the initial activity again returned for about an hour of use. The curves obtained by Adkins and Millington[1] show a similar behavior for ethyl alcohol with oxide catalysts. They noted that "reheating a catalyst for thirty minutes in dry air after it has been in use for an hour or two restored the percentage of ethylene to approximately its former level."

In view of the fact that, in the dehydrogenation of ethyl alcohol, the reaction velocity is independent of the rate of flow of alcohol vapor, over a fairly large range, which is not true in the hydrogenation of acetaldehyde, the dehydrogenation reaction must proceed at a faster rate than does the hydrogenation of acetaldehyde. So in this case the equilibrium value is obtained at a much faster rate in the dehydrogenation process. The 3 percent acetaldehyde obtained by approaching the reaction from this end, corresponds very well to the equilibrium value obtained by extrapolating the hydrogenation curve, which gave 96-97 per cent ethyl alcohol. A high temperature favors the dehydrogenation reaction, so at the relatively low temperature employed in this work 140°-145°, the equilibrium would be expected to be far on the ethyl alcohol side.

The Effect of Platinized Asbestos as Catalyst. The hydrogenation of acetaldehyde employing platinized asbestos as the catalyst, was tried under the same conditions as the above work was carried out, the temperature being 140°-145° C. The rate of hydrogen flow was varied over a fairly wide range, but no ethyl alcohol was obtained in any case. It was thought that perhaps water would have some effect on this reaction; but, on attempting the hydrogenation of a water solution of acetaldehyde, no alcohol was formed. So under these conditions the presence of water has no effect on the hydrogenation process. However, with a platinized asbestos catalyst at much higher temperatures, when there is a partial hydrogenation of the acetaldehyde, it might be that the presence of water would exert some appreciable effect.

As no hydrogenation took place with platinum under the above conditions, it was desirable to run an experiment in order to determine whether hydrogen was taken up by an acetaldehyde solution in the presence of platinum. This was carried out in the following manner. A 50 percent solution of acetaldehyde and water was made up, and about 250 cc. of this solution put into a 500 cc. round-bottom flask. Then after platinizing a platinum cylindrical electrode, this was put into the flask so as to have about two-thirds of it immersed in the solution. The air was displaced from the flask by passing in hydrogen, then a mercury manometer was attached to the flask, into which hydrogen was now forced, and the pressure read on the manometer. The apparatus was allowed to stand, and if any hydrogen was taken up, it could be recorded by the drop in pressure as shown by the manometer. The results were, that hydrogen was apparently taken up, as shown by the drop in pressure of the manometer, but very slowly, the pressure drop being about one cm. of mercury

---

[1] J. Am. Chem. Soc., 51, 2455 (1929).

in three to four hours. However, this did not tell exactly how the hydrogen was taken up, so another experiment was made in the same way as the above one except that no platinum electrode was used. The object of this experiment was to show whether hydrogen was absorbed by the acetaldehyde-water solution. It was found that hydrogen was taken up, but more slowly than in the first case, the pressure drop being about one cm. of mercury in seven hours. It is also known that platinized platinum adsorbs hydrogen, but even though hydrogen was taken up in these two cases, the process was slow. So apparently the hydrogen did not reduce any of the acetaldehyde to ethyl alcohol, for no test could be obtained for alcohol from the solution, after being in an atmosphere of hydrogen for a long time.

The reduction of acetaldehyde electrolytically was next taken up. Formaldehyde and acetaldehyde, the simplest of the aliphatic aldehydes, under certain circumstances are almost quantitatively reduced in alkaline solution at a copper or silver cathode. On the other hand in an acid solution they are not so easily reduced. Platinum and silver cathodes are without action, but copper or mercury cathodes lead to the formation of small quantities of methane when formaldehyde is the starting material, or to ethane when the acetaldehyde is used. This formation of a hydrocarbon is enhanced by the use of a cadmium cathode, and so pure propane may be prepared in good quantities from the propionaldehyde, but not in such large quantities as are obtained by the reduction of acetone.[1] In the reduction of aliphatic aldehydes, mercury and lead electrodes as a rule give excellent results, but the yields are always lower than those obtained with a cadmium electrode. In the use of lead and mercury cathodes with aldehydes no metal alkyl compounds are formed, as in the reduction of acetone at these electrodes.[2]

The industrial production of acetaldehyde and paraldehyde from acetylene has led to the development of several interesting methods for their reduction to a variety of products, that are of immense value, especially alcohol and ethyl acetate. These methods are covered by patents, and the electrolyte is 5-10 percent sulphuric acid, sodium sulphate, or orthophosphoric acid. The presence of a mercury salt, which acts as a catalyst, in the solution permits the passage of the acetylene directly into the electrolyte without being converted into acetaldehyde by a previous and separate process.[3] The formation of alcohol requires the use of a diaphragm to prevent anodic oxidation, but ethyl acetate is so stable that no diaphragm is needed when it is the end product. The cathode material should be of lead or mercury. The temperature, the acidity, the concentration of the unreduced aldehyde, the current density and the duration of the reaction must be held as low as possible, as otherwise there will be too large a formation of undesired by-products.

In this work an attempt was made to reduce acetaldehyde electrolytically at a platinized-platinum cathode. Two experiments were made, one using a 50 percent and the other a 10 percent solution of acetaldehyde in water, with

---

[1] F. Muller: Dissertation, Dresden (1921).

[2] Brockman: "Electro-Organic Chemistry," page 287.

[3] British Patents, 140115 (1918); 140527 (1919); Pascal: Swiss Patent, 88188 (1921).

a little 10 percent sulphuric acid as the electrolyte. The acetaldehyde solution was put into a porous cup, with a cylindrical platinized-platinum electrode immersed in the liquid. A 10 percent sulphuric acid solution was used as the anode liquid, with a platinum flag as electrode. On passing a current through the solution, gas was evolved immediately at the two electrodes, this occurring in both concentrations employed. Of course this means that if there is any reduction it must be very inefficient, but these runs were allowed to go for a sufficient length of time to get some reduction, if such a process took place. A current density of about 0.01 amperes/sq. cm. of cathode surface was used. The cathode liquid was tested for ethyl alcohol by using the Schotten-Baumann reaction, the odor of ethyl benzoate being detected in the presence of ethyl alcohol. However, no positive test could be obtained, so it seems that the acetadehyde is not reduced electrolytically, to ethyl alcohol, with a platinized-platinum cathode.

The dehydrogenation of ethyl alcohol over a platinized-asbestos catalyst at 140°-145° C was carried out. However, the alcohol passed over the catalyst apparently unchanged, as no acetaldehyde could be detected in the resulting product. So a platinized asbestos catalyst will cause neither the hydrogenation of acetaldehyde, nor the dehydrogenation of ethyl alcohol at the temperature employed in this investigation.

The Effect of adding Oxygen in the Dehydrogenation of Ethyl Alcohol using a Nickel Catalyst. The dehydrogenation of ethyl alcohol takes place according to the following reaction.

$$C_2H_5OH \rightleftarrows CH_3CHO + H_2$$

It was thought that by adding oxygen to the reaction, the oxygen and the hydrogen would unite to form water, so by removing one of the products of the reaction it would be displaced towards the right with the formation of more acetaldehyde than the equilibrium value.

A few experiments were carried out, in the same way and under the same conditions as the dehydrogenation runs above, except that a slow rate of oxygen was passed into the reaction tube during the runs. The following data shows how the yield of acetaldehyde obtained varied with the rate of oxygen passage, all other conditions remaining the same.

Rate of Oxygen	% Acetaldehyde
8 cc./min.	4.10
22 cc./min.	5.30
55 cc./min.	3.80
22 cc./min.	5.35

The equilibrium value as found above was 3 percent acetaldehyde, so while the amount of acetaldehyde formed was increased by the addition of oxygen, the extent of this increase was not particularly alarming. The first two rates showed an increase in the yield of acetaldehyde, but with a very fast rate, 55 cc./min., the yield of aldehyde dropped off. This may be due to two causes, first the oxygen may carry the alcohol over the catalyst at such a rapid rate as to prevent contact with the catalyst for reaction, and secondly this rate of oxygen is much in excess of the amount of hydrogen given off from the alcohol, so the catalyst is probably acting as a nickel oxide surface rather than that of metallic nickel. This experiment was also made in order to determine whether alcohol was oxidized to acetaldehyde over the catalyst in the presence of an excess of oxygen, but as the yield of acetaldehyde decreased this was not the case. A second run was made at the slower rate in order to determine whether or not check runs could be obtained, and the data show that the run was substantiated. So in this work, it has been shown that a slow rate of oxygen passing into the reaction tube over the catalyst will increase the practical yield of acetaldehyde, but this increase is not very great.

The Effect of Excess Hydrogen in the Dehydrogenation of Ethyl Alcohol using a Nickel Catalyst. The dehydrogenation of ethyl alcohol was carried out at 180°C, at which temperature a certain amount of the acetaldehyde formed was decomposed into carbon monoxide and methane. The liquid product was collected, as was also the evolved gas, the latter being collected in a large bottle acting as a gas holder. After making an analysis of the products it was found that a little less than one third of the acetaldehyde was decomposed into gaseous products. This is in agreement with the results of Sabatier,[1] for at 178°C he obtained some acetaldehyde, but about a third was decomposed into carbon monoxide and methane.

Now another run was made, and this time a slow stream of hydrogen was passed over the catalyst, in order to find out whether or not the decomposition of the acetaldehyde was diminished by the presence of the excess of hydrogen. However, the results show that the decomposition of the acetaldehyde is practically the same in each case, so the hydrogen apparently has no protective influence in this case. The percentage yield of acetaldehyde was less in the latter case which would be expected, as an excess of hydrogen would tend to suppress the dehydrogenation reaction, and favor the reverse process. The actual amount of decomposition gases is less in the latter case, but the percentage decomposition is about the same, for there is less acetaldehyde formed in the presence of an excess of hydrogen.

Summary

1. The equilibrium value of the ethyl alcohol-acetaldehyde reaction was found to correspond to 96-97% ethyl alcohol, when acetaldehyde was hydrogenated at different rates, this value being obtained on extrapolating the percent ethyl alcohol-rate of hydrogen flow curve to zero rate of flow. On approaching the reaction from the other side, that is the dehydrogenation of the ethyl alcohol, an equilibrium value of 3 percent acetaldehyde was obtained, which checked very well with the value from approaching it by the hydrogenation of acetaldehyde.

2. The nickel catalyst employed showed a rather rapid initial poisoning action, after which the activity of the nickel surface remained practically

---

[1] Compt. rend., **136**, 738 (1903).

constant. So it seems that the nickel surface must possess spheres of different activity, the more active points would be those showing the greatest adsorption and activation of the reactants. The more active points would be those most easily poisoned, so after the initial run the reaction must take place at the unaltered points of the nickel surface, these points having a lower adsorptive power, so the activity of this surface would be less than that of the original surface.

3. On extrapolating the plotted data obtained in the hydrogenation of acetaldehyde, using some catalyst which had lost its initial activity, the line intersected the zero rate line at practically the same equilibrium value as when using fresh catalyst. This means that the same equilibrium value will be obtained in each case, but that it would be reached more slowly when using a poisoned catalyst.

4. The presence of water has an activating effect on the nickel surface, from whichever side the reaction is approached. In the hydrogenation of acetaldehyde the presence of water increased the amount of alcohol formed. It may be that the action of the water is a specific one, and thus involving its preferential adsorption, on the nickel surface, to that of poisons thereby allowing more acetaldehyde to react. In the case of the dehydrogenation, while the presence of 10 percent water did not appreciably displace the equilibrium, it did have an activating effect on a used nickel catalyst.

5. A platinized asbestos catalyst will cause neither the hydrogenation of acetaldehyde nor the dehydrogenation of ethyl alcohol at the temperature employed. It has also been shown that acetaldehyde is not reduced to ethyl alcohol electrolytically with a platinized-platinum cathode.

6. In the dehydrogenation of ethyl alcohol, the yield of acetaldehyde can be increased by passing a slow rate of oxygen into the reaction tube over the catalyst, but the amount of this increase is not very great.

7. Passing an excess of hydrogen over the nickel catalyst in the dehydrogenation of ethyl alcohol, does not appreciably affect the percentage of acetaldehyde that is decomposed into the gases carbon monoxide and methane.

Cornell University

A STUDY OF ORGANIC ACID IRON SOLUTIONS

II. Colloidal Properties

BY NORMAN J. HARRAR AND FRANK E. E. GERMANN

Introduction

In a previous paper,[1] the purpose and the plan of this work were explained in detail. Quantities of freshly precipitated ferric hydroxide were dissolved in various organic acids, to give concentrations of about one gram of iron in 250 c.c. of one normal acid solution. Standard methods of analysis were used to find the exact amounts of iron and of acid present in each case. The colors of the solutions, the colors on dilution and the relative color intensities were determined for each combination.

The theory was advanced that, "the most important factor in determining the color (and, therefore, the structure) of these complexes, is the strength of the acid involved." It was found that an arrangement of the acids tested, in the order of their dissociation constant values, would show definite division into two groups—strong acids with green colored solutions, and weak acids with red colored solutions. It was then planned to examine these combinations by a number of different methods.

Dialysis

The subjection of these organic iron solutions to dialysis experiments was due to an idea that some of them, at least, appeared to possess colloidal properties. It was necessary to conduct a series of preliminary experiments, mostly with formic, acetic, propionic, oxalic, malonic, succinic and glutaric acids, before a uniform method of treatment was worked out. Thus, the color descriptions, recorded in Table IV, were checked a number of times and found applicable even with some variations in quantities, concentrations, times, and temperatures. The quantitative values depend directly upon the conditions of the experiments.

In order to be certain that the comparison of results could be based upon similar conditions, the following procedure was finally adopted and applied to all solutions: A parchment cup of about 50 c.c. capacity was placed in a dish containing 150 c.c. of distilled water and a 30 c.c. portion of the solution was poured into the cup. The liquid outside was removed and replaced by pure water, three times at intervals of four hours, and then allowed to stand over night. All portions thus removed were saved for an iron analysis and checks were run on the part remaining in the cup. All determinations were made in duplicate and then, as in the color experiments, the entire process was repeated with two samples of another preparation.

---

[1] Harrar and Germann: J. Phys. Chem., 35, 1666 (1931).

TABLE IV

Acid K	Original Colors	Colors Inside	Colors Outside	g. of Fe through
Formic 2.14	Intense red	Dark red	Colorless Pale green Pale Yellow Orange	.049
Acetic .18	Intense red	Dark red	Yellow Orange red	.035
Propionic .14	Blood red	Dark red	Yellow Orange red	.036
Butyric .15	Orange red	Orange red	Orange	.029
Oxalic 380.	Vivid green	Very pale green	Green	.113
Malonic 16.1	Green	Colorless	Pale green	.101
Succinic .66	Orange red	Orange red	Pale orange	.007
Glutaric .47	Red orange	Red orange	Very pale orange	.004
Adipic .37	Red orange	Orange	Almost colorless	.002
Tricarballylic 2.2	Red orange	Red orange	Colorless (trace of green?)	.006
Maleic 120.	Orange red	Orange red	Green Pale yellow green	.066
Fumaric 10.	Colorless	Colorless	Colorless	Some
Mesaconic 7.9	Colorless	Colorless	Colorless	Some

TABLE IV (Continued)

Acid K	Original Colors	Colors Inside	Colors Outside	g. of Fe through
Chloracetic 15.5	Red	Orange red	Pale green	.067
Dichloracetic 500.	Green yellow	Orange	Very pale green	.090
Trichloracetic 2000.	Very pale green	Pale orange	Colorless	.093
Benzoic .66	Colorless	Colorless	Colorless	Some
Phenylacetic .50	Colorless	Colorless	Colorless	Some
Phthalic 12.6	Pale green	Colorless	Colorless	Some
Hydrochloric	Green	Orange	Very pale green	.087
Sulfuric	Pale green	Pale orange	Very pale green	.103

In Table IV is recorded the information obtained from the dialysis experiments. The first column lists the acids used and their dissociation constant values, as given before in Table I. The second column gives the colors of the original solutions, as recorded previously in Table II. The third column states the color of the solution left inside the cup at the end of the dialysis, as there were, in some cases, significant changes produced. The fourth column describes the colors appearing outside the cup and the last column gives the quantity of iron which passed through the parchment. Since some of the solutions contained but very small amounts of iron at the start, quantitative determinations were of little value. In these cases, tests with NH_4CNS served to show whether or not any iron was passing through the dialysis cup.

An examination of Table IV shows that, when a weak acid combination is involved, the solution outside the cup develops a yellow or pale orange color. On the other hand, the strong acids, even when the normal solutions are red, first give a green color outside the cup. Some of the solutions contain so little iron that a definite color outside the cup cannot be observed.

These facts are in accord with the results obtained in the dilution experiments and Table V has been compiled to illustrate the division suggested. Omitting those which do not give colors, the acids are listed in the table in the order of their dissociation constant values and the colors appearing outside the cups are tabulated.

TABLE V

Acid	$K.10^4$	First Color outside
Dichloracetic	500.	Very pale green
Oxalic	380.	Green
Maleic	120.	Green
Malonic	16.1	Pale green
Chloracetic	15.5	Pale green
Tricarballylic	2.2	Colorless (trace of green?)
Formic	2.14	Pale green
Succinic	.66	Pale green
Glutaric	.47	Very pale orange
Adipic	.37	Almost colorless
Acetic	.18	Yellow
Butyric	.15	Orange
Propionic	.14	Yellow

It should be noted that in Table III, based on dilution colors, tricarballylic and formic were classed with the weak acids, while in Table V they are listed in the strong group. The formate solution was one of the first to be examined and since its dialysis action was so different from the results obtained with the acetate and propionate, it was checked and rechecked a number of times. When the tests were extended to include the maleic and chloracetic combinations, which undergo a shift from red to green merely on dilution, the reasons for the formate change were made less obscure.

All the evidence obtained seems to lead to the conclusion that those solutions which, under various conditions, show red or green colors, actually contain both red and green complexes all the time, in a sort of equilibrium. The appearance of a different color outside the cup may, therefore, be due to:

1. Increase in Acid Strength by Dilution.

It was previously shown that in the maleic and chloracetic acid solutions, a shift from red to green was produced by mere dilution. The change on dialysis might, therefore, be ascribed to a dilution, which certainly does occur as the acid and the iron complex pass into the water outside the cup. It should be noted, however, that a change in the formate could not have been brought about by dilution alone.

2. Increase in Amount of Acid relative to Iron.

It seems reasonable to suppose that the simple acid radicals present, pass through the parchment more rapidly than either of the iron complexes. The concentration of acid outside the cup would be increased, therefore, relative to the iron, and this would tend to favor the existence of the green form. Further work along this line, with the formate, will be described later.

3. Different Diffusion Speeds of Red and Green Forms.

The facts regarding the composition of the red and green forms, which will later be discussed in detail, seem to show that the red is a much more complex form than the corresponding green one. The appearance of a green color outside the cups may be partly due, therefore, to the more rapid diffusion of that form.

No less significant than the colors which appear outside, are the changes which take place inside the cups. Omitting those combinations which exhibit no colors whatever, Table VI has been drawn up to classify the types of changes observed.

TABLE VI

Original Colors	Green		Orange Red	
Colors Outside	Green	Green	Green	Orange
Colors Inside	Green	Orange	Orange	Orange
Acids in each class	Oxalic Malonic	Hydrochloric Sulfuric Trichloracetic Dichlor-acetic	Maleic Chloracetic Tricarballylic Formic	Succinic Glutaric Adipic Acetic Butyric Propionic

The evidence contained in this table is entirely in accord with the idea that the excess of acid is rapidly removed on dialysis and that, inside the cup, the equilibrium is shifted towards the orange form. In the cases of some of the weaker acids, the resulting hydrolysis finally brings about a precipitation. It should be noted that, in this respect also, the oxalate and malonate solutions furnish striking exceptions to the general rule, showing no tendency to undergo any noticeable color change.

The qualitative and quantitative examinations of the solutions outside the cups showed that in every case, at least some iron passed through the parchment walls. These quantities, as recorded in Table IV, represent a wide variation in actual amounts and in percentages of iron present. A study of the percentage relations will again yield a classification of these acids upon the basis of their relative strengths. In order to illustrate this point, Table VII has been compiled, listing those acids with which it was possible to obtain quantitative results.

The grouping in this table parallels the divisions suggested by the color evidence and further supports the theory that acid strengths are the most

TABLE VII

	Acids	$K.10^4$	g. Fe (30 c.c.)	g. Fe through	Per cent through
Strong Acids	Hydrochloric	—	.109	.087	79.81
	Sulfuric	—	.122	.103	84.43
	Trichloracetic	1000.	.112	.093	83.04
	Dichloracetic	500.	.114	.090	78.95
Intermediate Strengths	Oxalic	380.	.121	.113	93.39
	Malonic	16.1	.113	.101	89.38
	Maleic	120.	.111	.066	59.46
	Chloracetic	15.5	.118	.067	56.78
	Tricarballylic	2.2	.020	.006	33.33
	Formic	2.14	.125	.049	39.37
Weak Acids	Succinic	.66	.060	.007	11.67
	Glutaric	.47	.024	.004	16.67
	Adipic	.37	.010	.002	20.00
	Acetic	.18	.115	.035	30.44
	Butyric	.15	.049	.029	59.18
	Propionic	.14	.084	.036	42.86

important consideration. The percentage figures bring out the contrasts in properties very clearly.

There are two factors, however, which produce apparent contradictions, especially with the weak acids, and these should be explained. Solutions containing but small amounts of iron give higher percentages of iron outside the cups, though the actual quantities are less. It seems reasonable to suppose that the greater excess of acid over iron in such cases, is responsible for this action. The effect of this factor is very evident in both the dibasic and monobasic series of acids.

Again, solutions containing monobasic acids give larger amounts, as well as higher percentages of iron outside the cups, than do the dibasic acid preparations. This effect may be ascribed to the more ready passage of the simpler substances. The low results obtained with the tribasic tricarballylic acid solution appear to further support this explanation.

As a result of this study of the dialysis of these preparations, it is not possible to say whether the iron is in true solution or present in colloidal particles. There is no individual case, even, in which the evidence is entirely conclusive. On the contrary, it appears most probable that a satisfactory explanation of the facts, in many cases, must assume the existence and presence of both forms.

Tyndall Effect

As a test of colloidal properties, the Tyndall Effect has been shown to be of somewhat doubtful value. With a large number of possible comparisons, however, any information regarding the light-reflecting properties of these preparations, may be useful in checking the results obtained by other methods.

Therefore, each solution was examined with a strong beam of light and the results are indicated in Table VIII. Since conclusions must not be based upon any individual case, no attempt was made to estimate degrees of intensity of the effects. The table merely classifies the solutions into groups representing: a very definite positive effect, a very weak or negative result and a rather indefinite intermediate condition.

Table VIII

Pronounced Tyndall Effect	Intermediate Effect	Practically no Effect
Formic		Oxalic
Acetic		Malonic
Propionic	Maleic	
Butyric		Trichloracetic
	Chloracetic	
Succinic	Dichloracetic	Benzoic
Glutaric		Phenylacetic
Adipic		Phthalic
	(Fumaric)	
Tricarballylic	(Mesaconic)	Hydrochloric
		Sulfuric

Taken as a whole, it may be stated that definite Tyndall cones are produced in the orange or red solutions, while in the green or colorless solutions, almost no effects are observed. It is not intended to put a great amount of emphasis upon the results of this test, but it should be noted that they were in accord with the general conclusions reached, by means of the other methods employed.

Diffusion

It was found to be possible to check the relationship of acid strengths to colors by conducting some simple diffusion experiments. A 100 c.c. graduate cylinder was cut at the 50 c.c. mark and the two parts connected by a short piece of large rubber tubing. The solution of the formate preparation was poured into the lower half of the cylinder and the tubing clamped. Then an equal quantity of distilled water was poured into the upper half and the clamp very gradually removed. The tube was stoppered and kept at a fairly constant temperature of 27°C. Similar tubes were prepared with the acetate, propionate, oxalate, malonate, succinate and glutarate solutions, and all were set aside for a period of thirty days.

The results were entirely in accord with those obtained in the other tests applied and may be classified into three types as follows:

1. Diffusion was most rapid in the oxalate and malonate solutions. The characteristic green color gradually spread into the upper half of the tube until, at the end of the period, there was but little difference throughout. A portion removed from near the surface gave, of course, a very strong iron test.

2. Diffusion was slow in the acetate, propionate, succinate and glutarate solutions. From the lower red layer there was a gradual fading into orange and yellow, but, even at the end of thirty days the color did not extend very far up the tube. A portion taken from near the surface gave only a weak test for iron. This might be expected for, as it may be recalled, the red combinations retain a noticeable color to a high degree of dilution, and in these tests the solutions near the surface were colorless.

3. Diffusion in the formate solution produced a change of color. From the lower red layer there was a gradual shift into orange, yellow and then, green. Furthermore, the solution near the surface was colorless, but yielded a good iron test. These facts, together with the results of the color and dialysis experiments, seem to indicate that in the formate solution there exists a simple, more rapidly moving, green complex, as well as the intensely red complex. The latter must, ordinarily, completely mask the presence of the less intensely colored green form.

The idea just advanced was submitted to still other methods of examination and the results of these experiments will be described later. It is obvious that the acids of intermediate strengths supply the most stringent tests of the generalization that the nature of the complex is determined by the strength of the acid involved. As the evidence accumulates, it appears more and more certain that the formate furnishes an excellent example of a border line condition.

Colloidal Properties

It should be obvious, from the very nature of the foregoing experiments that, although the term itself has not been made prominent, the possibility of colloidal properties was being considered. In order to be able to make a real comparison, a colloidal ferric hydroxide was prepared, and some of the tests developed were applied to it.

The colloid was made by pouring 20 c.c. of a saturated ferric chloride solution into about 300 c.c. of boiling water, and subjecting this mixture to a long dialysis. As with the organic acid preparations, this was made to have an iron concentration equivalent to one gram in 250 c.c. of solution.

The color of the colloid was an intense orange red and upon dilution, this very gradually faded out through orange and yellow. The dilution was carried to the 16th bottle (as compared with 13 for acetic and propionic) until a solution was obtained, which appeared to be colorless. A beam of light produced a good Tyndall cone. A diffusion test showed very little iron in the upper part of the tube, at the end of thirty days. A pale yellow color in the upper layer was further evidence of the color intensity, for tests showed a very low iron concentration.

There are certainly many marked similarities between the properties of the weak acid preparations and the colloidal ferric hydroxide. The latter could be and undoubtedly is formed, to some extent, in solutions of this type. However, the experiments made have all indicated that some iron remains in solution. On the other hand, even this iron may be present in highly complex ions which, in some cases and in varied amounts, may approach colloidal dimensions.

The results of still other types of tests designed to determine the form in which the iron exists in these organic preparations will be described in a later article.

Summary

A further study has been made of the properties of a number of organic iron combinations, prepared as described in a previous article. These preparations were then compared upon the basis of dialysis phenomena, tests for Tyndall effects and some simple diffusion experiments.

The results obtained provide further support for the generalization that the most important factor in determining the color and structure of any combination is the strength of the acid involved. There are some cases, notably that of the formate, in which the acid is of an "intermediate" strength, and in which intermediate properties are exhibited.

Many similarities were observed between the properties of a colloidal ferric hydroxide and those of the weak acid preparations, but the latter all appeared to contain some iron in true solution. It seems probable that a satisfactory explanation of the facts must assume that some sort of an equilibrium exists between several different complex forms. Further work along this line will be presented in a later article.

University of Colorado.
Boulder Colorado.

HYDROGENATION OF BENZENE WITH NICKEL AND PLATINUM*

BY WILDER D. BANCROFT AND AVERY B. GEORGE

Introduction

The statement is usually made that a nickel or copper catalyst will do things that a platinum catalyst will not. If we consider only the hydrogen, this is impossible, because the catalyst can apparently only increase the rate by increasing the amount of monatomic hydrogen. This action may be merely a question of rate, or there may be a specific effect of the nickel on the substance to be reduced. The object of this work was to find out the reason for the different action of catalytic nickel and platinum. It was desired to pick a case in which nickel is said to be a better catalyst than platinum. So the reaction, benzene to hexahydrobenzene, was chosen for carrying out this investigation.

The use of metallic catalysts has provided a method capable of fairly general application to the hydrogenation of the benzene nucleus. According to Sabatier it is undoubtedly the most important of the operations that reduced nickel has rendered possible in synthetic organic chemistry. At temperatures in the neighborhood of 180°C the aromatic nucleus may readily be hydrogenated in presence of nickel without isomerisation of the products or production of secondary reactions.

Early experiments of Lunge and Akunoff[1] had demonstrated a partial hydrogenation of benzene to cyclohexane, in presence of platinum black, at the ordinary temperature, or better at 100°C. Palladium sponge, on the other hand, yielded cyclohexane, C_6H_{10}. The composition of the products was deduced from the contraction in volume of the gases and is therefore uncertain. The catalytic activity of the metal also rapidly diminished. The work of Sabatier and Senderens demonstrated the efficiency of the reduced nickel catalyst.

The direct hydrogenation of benzene to cyclohexane, C_6H_{12}, takes place with nickel above 70°C. Its speed increases with the temperature up to

$$C_6H_6 + 3H_2 \rightarrow C_6H_{12}$$

170°–190°C, where it is rapid without any side reaction. Above that, and particularly above 300°C, a part of the benzene is reduced to methane, and carbon is deposited on the nickel.[2] Recently prepared platinum black can transform benzene into cyclohexane at 180°C for a time, but its activity diminishes rapidly and soon disappears. Platinum sponge has not this power.[3]

---

* This work is done under the programme now being carried out at Cornell University and supported in part by a grant from the Heckscher Foundation for the Advancement of Research established by August Heckscher at Cornell University.

Zelinsky[4] affirms that both platinum and palladium are as efficient as nickel in this and other hydrogenations of the aromatic nucleus. Cobalt[3] also catalyzes the hydrogenation of benzene at 180°C, but soon loses its activity.

Dougherty and Taylor[5] made a study of the mechanism of the catalytic reduction of benzene to hexahydrobenzene. The results indicated that the reaction does not occur at all according to the stoichiometric equation, as calculated from gas concentrations, but at rates governed by the distribution of the reacting materials between the catalyst and the gas phase. Pease and Purdum[6] have made copper catalysts reactive in this synthesis, contrary to the statements of Sabatier that copper would not reduce benzene to hexahydrobenzene. An excess of benzene was found to inhibit the reaction, and this was explained as due to the hydrogen adsorption being blocked by preferential adsorption of benzene.

The reverse of hydrogenation, or the process of dehydrogenation takes place as the temperature becomes more elevated. Cyclohexane, which cannot be formed by the direct hydrogenation of benzene by the aid of nickel above 300°C, suffers a partial dehydrogenation to benzene above this temperature, but a part of the benzene is transformed to methane by the liberated hydrogen.[7]

$$3C_6H_{12} \rightarrow 2C_6H_6 + 6CH_4$$

The presence of a current of hydrogen stabilizes the molecule to a certain extent so that it is only slightly broken up at 350°C. At 400°C about 30% of the cyclohexane passing over the nickel with the hydrogen is decomposed into benzene.[8]

Experimental Procedure

Hydrogenation

In order to ascertain whether or not the apparently greater action of a nickel catalyst was a question of rate, some experiments were made on the hydrogenation of benzene vapor in the presence of a nickel catalyst and a platinum catalyst. From the work of Sabatier and Senderens,[2] it was known that benzene can be readily hydrogenated at 180°C in the presence of a nickel catalyst. Freshly prepared platinum black can be used for hydrogenating benzene; but its activity diminishes rapidly. This action may be due to the sintering of the platinum black, so we used platinum on an asbestos support, which prevents sintering. The finely-divided nickel and the platinized asbestos catalysts were very kindly furnished by Dr. C. M. A. Stine of the Du Pont Company, to whom we extend our thanks.

The procedure of the hydrogenation consisted essentially in passing the hydrogen, admixed with benzene vapor, through a combustion tube containing the catalyst at the proper temperature, the product being condensed and collected on emergence from the heated tube.

Electrolytic hydrogen was used, and this was further purified by passing the gas through a tube containing platinized asbestos at a dull red heat, then over some solid potassium hydroxide. To dry the hydrogen it was passed through a tube containing soda-lime, and finally through phosphorus pentoxide. In order to regulate the flow of gas a flow-meter was interposed in the path of the hydrogen. A thin layer of the catalyst was spread along the reaction tube, the same amount being used in each experiment. Before making a run the furnace was heated to 300°C with a slow stream of hydrogen flowing through the apparatus, and this condition was maintained for thirty minutes. Then the temperature of the tube was lowered to 180°–185°C, at which temperature all of the runs were made. A measured amount of the benzene was put into the flask through a funnel at the top. At the end of a run the amount of liquid left was measured, then the amount of benzene actually used could be determined. The dry hydrogen was then bubbled through the benzene contained in a flask, which was immersed in a water bath kept at 35°C, at which temperature the vapor pressure of the benzene is about 145 mm. With the flow of hydrogen at the desired rate, and the delivery tube extending nearly to the bottom of the flask the run was started. The hydrogen admixed with the vapor of benzene was passed through the catalyst tube, the product being condensed and collected on emergence from the heated tube. The experiments were carried out for periods of three hours, and four and one half hours.

The product contained, in addition to the cyclohexane formed, some unchanged benzene that passed over. The cyclohexane is not attacked by fuming sulphuric acid, while the benzene is, so this offers a method of separation of the two. The product was treated with some fuming sulphuric acid, the benzene forming benzene sulphonic acid and this was separated from the cyclohexane by use of a separatory funnel, the top layer being the cyclohexane portion. The cyclohexane was then dried over a little calcium chloride, and the percentage yield of the resulting product was calculated.

A series of experiments were carried out using nickel and platinized asbestos as catalysts. A few runs were made employing the same rate of hydrogen in each case. Then some experiments were made with the platinum catalyst, in which the rate of hydrogen flow was diminished to two thirds of the initial rate, and the run was allowed to go one and a half times as long. The time for the initial runs was three hours, while the latter ones were carried out for a period of four and a half hours. The average values of the results obtained are given in the table below, this also includes some physical constants taken on the products.

Catalyst	C_6H_{12} % Yield	Boiling Point	Specific Gravity
Nickel	36.8	78.0°–79.0°C	0.778_{20}°
Platinum	27.8	75.5°–76.5°C	0.795_{20}°
Platinum	51.7	77.5°–78.5°C	0.787_{20}°
Platinum	52.4	77.5°–79.0°C	0.784_{20}°

The results given in the above table were obtained under similar conditions, except for varying the rate of hydrogen flow. In the first two sets of data the hydrogen flow was the same, and while the last two sets were at the same rate, the flow of hydrogen in these cases was two thirds of that in the first sets of data. This means that the rate of hydrogen flow is the important factor, in comparing the relative amount of hydrogenation of benzene in the presence of a nickel and of a platinized-asbestos catalyst. For by using a nickel and a platinized-asbestos catalyst in the presence of the same rate of hydrogen, a larger percentage yield of the cyclohexane is obtained with the nickel catalyst. However by diminishing the rate of hydrogen flow in the case of the platinized-asbestos catalyst the percentage yield of product was greatly increased. So at a given rate of hydrogen, there is a larger amount of monoatomic hydrogen present at the surface of the nickel than at the surface of the platinized asbestos. In other words hydrogen is activated more strongly by nickel than by platinum. The efficient utilization of a platinized-asbestos catalyst, therefore, hinges on the fact that a slow current of hydrogen must be employed in the hydrogenation.

Dehydrogenation

The reaction was now approached from the opposite side by employing a much higher temperature, which favors the dehydrogenation process. The dehydrogenation can take place in the presence of an excess of hydrogen, and in some cases the excess of hydrogen, far from hindering the reaction, regulates it by favoring the maintenance of the cyclic structure and diminishing the tendency to the breaking up of the molecule into many fragments. At 300°C the cyclohexane first formed is then reduced to methane using a nickel catalyst.

$$3C_6H_{12} \rightarrow 2C_6H_6 + 6CH_4$$
$$C_6H_6 + 9H_2 \rightarrow 6CH_4$$

The experimental procedure in this dehydrogenation was practically the same as in the hydrogenation of benzene. The furnace was maintained at a temperature of 300°C, and a slow current of hydrogen was bubbled through the benzene in the flask. In this case the gas issuing from the apparatus was analyzed, a sample being collected after the run had proceeded for about an hour. The analysis of the gas was carried out in the following manner. First any benzene vapor or unsaturated hydrocarbons were removed by absorbing them in fuming sulphuric acid, then the hydrogen was removed by passing the gas over hot copper oxide, at 270°C. Finally, the remaining portion of the original sample was burned in a combustion pipette, the total contraction volume and the amount of carbon dioxide formed being determined. This latter portion would consist of saturated hydrocarbons.

A series of runs was made using a nickel catalyst at 300°C, and the evolved gas analyzed according to the procedure outlined above. After removing the unsaturated hydrocarbons and hydrogen, the remaining gas was combusted and the average value for n, in the series $C_n H_{2n+2}$, was found to be 1.04 which shows that the gas was methane. The percentage composition was calculated after having subtracted the volume of hydrogen from the original volume. The average composition then of the remaining gas was about 90% methane, with a little ethane present, and 10% of benzene vapor and unsaturated hydrocarbons.

From these results it was thought that with nickel at 250°C the amount of methane formed would be less than that obtained at 300°C, so a few experiments were carried out under these conditions. After analyzing the gas evolved, by the same method as employed above, about 15% of the original volume was found to be of the saturated group, as compared to about 60% obtained at 300°C. By running a combustion on this remaining gas, the average value of n was found to be 2.1, which showed that there were other gases present rather than just methane. These data did not tell the proportions of the various gases present, so some method of analysis of the mixture had to be devised.

The following method was devised and used in this case. The mixture was thought to contain methane, ethane, and probably some propane, for from the first gas analysis the mixture might contain methane and propane, ethane and a little propane, or a combination of all three of these. The solubility of these gases in absolute alcohol is as follows.

Methane	52.2 cc./100cc. alcohol
Ethane	46.0 cc./100cc. alcohol
Propane	790.0 cc./100cc. alcohol

So the method employed was to run a combustion on one sample of gas after removing the unsaturated hydrocarbons and hydrogen, thus leaving only the saturated hydrocarbons. Then another sample of gas was taken, and before combusting it, the saturated hydrocarbon gas was shaken up with 4.5 cc. of absolute alcohol. After removing the alcohol, the last traces with water, a combustion was run on the remaining gas. This amount of alcohol would remove all the propane which might be present, so by finding the value of n, from the combustion data, of the remaining gas the amounts of methane and ethane in this gas can be determined. The solubility of the gases in 4.5 cc. of absolute alcohol is as follows.

Methane	2.2 cc.
Ethane	1.6 cc.
Propane	36.0 cc.

The volume of gas removed by the alcohol was recorded, and on analyzing the remaining gas an average value of 1.3 was obtained for n, which shows the ratio of methane to ethane in this gas.

By assuming that the alcohol used became saturated in respect to methane and ethane, the volume of propane present in the original gas could be found by difference, which was actually done. The volumes of methane and ethane in the gas remaining after the absorption with absolute alcohol, was calculated from the combustion data. Then the total volumes of these constituents in the gas were found by adding the volume absorbed by the alcohol to the volumes as calculated above. With these data the percentage composition of the three gases methane, ethane, and propane in the total volume of saturated hydrocarbons was calculated. The amount of oxygen necessary to burn this mixture was calculated, and the values agreed very well with the amount of oxygen actually used in the combustion. The average percentage composition of the gases present in the saturated hydrocarbon gas was as follows.

Methane	60%
Ethane	25%
Propane	15%

Now to put these values on the same basis as in the above case, that is, the composition of the evolved gas after removing the hydrogen, the following results were obtained.

Unsaturated hydrocarbons	25%
Methane	45%
Ethane	20%
Propane	10%

More hydrogen was obtained in the gas evolved using nickel at 250°C, than at 300°C, and as there is a much larger percentage of methane obtained at the latter temperature, this means that more hydrogen is used for reducing the benzene to methane. At 250°C the nickel causes a certain decomposition of the benzene, but somewhat partial as compared to that at 300°C. There are more of the unsaturated hydrocarbons, and there being some of the higher members of the saturated series, this means that the reduction has not been carried so far as occurs at 300°C, when almost all of the evolved gas was methane. This action must be due to the increase in temperature, and the more important factor the increased activity of the nickel catalyst at the elevated temperature.

With these data on the effect of a nickel catalyst, the dehydrogenation was next carried out using a platinized asbestos catalyst. The first series of runs were made at 300°C, in the same manner as in the case of nickel, samples of the issuing gas being collected and analyzed as before. After removing the unsaturated hydrocarbons and hydrogen, there remained only about 3% of the saturated series as compared to about 60% with nickel under the same conditions. These percentages are based on the original volume of gas as evolved from the apparatus. After removing the hydrogen from this volume, the average percent of unsaturated hydrocarbons was 75%, and of the saturated hydrocarbons 25%. From this marked change in percentage composition, it can be seen that there must have been a large amount of hydrogen present in the evolved gas. These figures can be compared with the data obtained by using a nickel catalyst in the following manner.

Catalyst	Temp.	% Unsaturated	% Saturated
Nickel	300°C	10	90
Platinum	300°C	75	25

This means that nickel is a more active catalyst than platinized asbestos under these conditions, and so causes a much greater decomposition of the benzene to saturated hydrocarbons. A run was made with the platinized asbestos catalyst at 400°C, and another at 500°C; even at these elevated temperatures only a very small amount of decomposition to saturated hydrocarbons takes place.

The dehydrogenation of benzene over platinized asbestos at 250°C gave a little less of the unsaturated hydrocarbons, than obtained at 300°C, the amount of the saturated series remaining about the same. The increasing of the temperature of the benzene bath from 35°–47°C, thus increasing the concentration of the benzene in the vapor passing over the catalyst, merely increased the amount of the unsaturated hydrocarbons in the gas formed.

The next step was to substitute cyclohexane in place of the benzene. Hydrogen was passed through some cyclohexane, the water bath being at 40°C, and the vapor passed over platinized asbestos at 300°C, as in the above cases. The results obtained were similar to those given by benzene under the same conditions. Cyclohexane is probably formed first on dehydrogenating benzene in the presence of hydrogen, and then this is dehydrogenated, in which case the same results would be expected whether starting with benzene or with cyclohexane.

Conclusions

1. In the hydrogenation of benzene with a nickel and a platinized asbestos catalyst, the rate of hydrogen flow is the important factor. A slow rate of hydrogen is necessary in the case of the platinum.

2. With nickel at 300°C, the decomposition of the benzene is more marked than at 250°C. About 90% methane is formed in the former case, and 75% of mixed members of the saturated series at the latter temperature.

3. Platinized asbestos at 300°C gave much less of the saturated hydrocarbons than did nickel at the same temperature, the activity of the latter catalyst being much greater.

4. At temperatures up to 500°C only a small amount of decomposition to saturated hydrocarbons was obtained with platinized asbestos.

5. At 250°C platinized asbestos gave a little less of the unsaturated compounds than obtained at 300°C. Increasing the concentration of the benzene in the vapor passing over the catalyst at 300°C, merely increased the amount of unsaturated hydrocarbons in the gas.

6. Substituting cyclohexane for benzene with platinized asbestos at 300°C gave results similar to those obtained with the benzene.

Cornell University

References

[1] Lunge and Akernoff: Z. anorg. Chem., **24**, 191 (1900).
[2] Sabatier and Senderens: Compt. rend., **132**, 210 (1901).
[3] Sabatier and Senderens: Ann. Chim. Phys., (8) **4**, 368 (1905).
[4] Zelinsky: J. Russ. Phys. Chem. Soc., **44**, 274 (1912).
[5] Dougherty and Taylor: J. Phys. Chem., **27**, 533 (1923).
[6] Pease and Purdum: J. Am. Chem. Soc., **47**, 1435 (1925).
[7] Sabatier and Mailhe: Compt. rend., **137**, 240 (1903).
[8] Sabatier and Daudier: Compt. rend., **168**, 670 (1919).

THE POLYBASICITY OF SEVERAL COMMON SUGARS

BY ALLEN E. STEARN*

I.

The instability of sugars in alkaline solution has been attributed to the formation of salts of the sugars acting as weak acids.[1 2 3] The present work was undertaken primarily to determine not only the extent to which salt formation takes place at high alkalinity, but also something of the nature of the sugar ions.

The acid-binding power of certain sugars has been investigated by measuring the effect of the sugars on the catalytic action of sodium hydroxide on saponification, by titration with the hydrogen electrode, and by the application of conductivity methods. The present paper presents results obtained by the use of the last method named. The work was completed before knowledge of the fact that Hirsch and Schlags had employed a similar method[4] in investigating the same problem. Reference to their paper showed, however, that, in the first place, they did not study the effects at the high alkalinities covered in the present paper (about .25 normal NaOH being the highest alkalinity reported, whereas the present study goes to double normal NaOH), and in the second place, though they worked with solutions as concentrated as 1.2 molal in disaccharide, they mention no consideration of viscosity corrections, which under such conditions might be nearly 100% as was found in work preliminary to the present study. Their review of the literature is comprehensive, however, so it is not repeated here.

Qualitatively their data seem to indicate very definitely that the sugars with which they worked are all at least dibasic.

II. General Method

The outstanding experimental advantage of a conductivity method over a potentiometric method in a study of the present kind lies in the fact that in the former method one is dealing with additive in place of ratio effects, an important point when one is working in strongly acid or alkaline solutions; and also the question of boundary potentials is eliminated.

The addition of sugar lowers the conductivity of a sodium hydroxide solution by replacing the fast moving OH-ion with the much slower sugar ion and by increasing viscosity. For a polybasic sugar molecule more than one OH ion may be replaced by a double or triple charged sugar ion from one molecule of sugar.

For a cell of known constant the change in conductivity due to replacement of one OH-ion per sugar molecule can be calculated.

---

* Division of Physical Chemistry, University of Missouri.

Let Λ_{OH} = equivalent conductance of the OH-ion
and Λ_S = equivalent conductance of the sugar ion

$$\text{Then } \Lambda_{OH} - \Lambda_S = \frac{1000\ k}{C} \Delta K_0 \qquad (1)$$

where k is the cell constant, C is the concentration of the sugar salt, and ΔK_0 is the change in measured conductivity due to replacing c equivalents of OH-ion per liter with the same number of equivalents of sugar ion, after viscosity change has been corrected for. From equation (1) we have

$$\Delta K_0 = \frac{(\Lambda_{OH} - \Lambda_S)C}{1000\ k} \qquad (2)$$

Thus if Λ_{OH} and Λ_S are known, ΔK_0 can be obtained for a cell of known constant for any value of concentration, C. Λ_{OH} is known,[9] but it is necessary to determine values of Λ_S for the various sugars. These latter values will be small compared to Λ_{OH} so that the accuracy of the method is not dependent on extreme precision in the values of Λ_S.

As soon as ΔK_0 is obtained for some arbitrary value of C, say C = 0.025, then experimental values of a quantity ΔK can be measured for sugar concentrations of 0.025 molal at varying NaOH concentrations. This will be the decrease in conductivity of the NaOH solution caused by adding 0.025 mol sugar per liter. The values of $\Delta K/\Delta K_0$ will then give directly the number of neutralized hydrogen equivalents per molecule of sugar.

If there were no viscosity differences between any of these various solutions the value of ΔK could be taken as merely the difference in the directly measured conductivities of the pure alkali and that containing sugar. By working with small sugar concentrations one can have a condition of negligible viscosity change between any solution pair due to sugar addition, but since the values of ΔK are to be compared with those of ΔK_0, which have been calculated for a relative viscosity of unity, and since, in the concentrated NaOH solutions necessary for bringing into play more than one ionizing hydrogen in sugars the relative viscosities are quite high, the conductivities of these solutions must be corrected as well as possible to corresponding values at unit relative viscosity.

The elimination of the worst experimental uncertainty is brought about by working with sugar solutions so dilute that the viscosity of the sugar solution may be taken as that of the pure NaOH solution. This is especially important in the normal and the double normal alkali since ΔK is small here compared to the total conductivity. Except for determining the values of Λ_S for equation (2), the highest sugar concentration used was 0.025 molal.

The viscosity correction, after much consideration, was made from the equation

$$K = K_\eta(\eta)^{.66} \qquad (3)$$

where K is the required conductivity at unit relative viscosity, K_η the measured conductivity, and η the relative viscosity. The value 0.66 for the exponent was obtained by measuring resistances of 0.1% KCl and NaCl solutions varying the relative viscosity between 1 and 3 by adding sugar (for NaCl the value 0.67 was obtained), and is in agreement with other work of the same kind[5] for such salts. Furthermore the temperature coefficient of viscosity of water at 23°, the temperature of these experiments, is 0.0238.[9] Using this value and analogous temperature coefficients for ion mobilities the value of the exponent in equation (3) for Na-ion is about 1.03 and for OH-ion about 0.68. Since the latter ion has a predominating effect in NaOH this indicates an exponent of not far from 0.7 for NaOH. Therefore the value 0.66 was taken as the probable lower limit of the value of this exponent and one which will be nearly in accord with the actual state of affairs. Larger values would tend to amplify the effects reported in this work and it was thought advisable, if a certain degree of uncertainty is a necessity, to be on the conservative side. Thus all conductivity values were corrected by multiplying by $(\eta)^{.66}$.

In all the experiments a cell with a constant 13.86 was employed. Except for the determinations of the values of Λ_S the maximum resistance range measured was 50 to 5000 ohms. The cell constant was measured using 0.1 N KCl (resistance about 100 ohms) and this value used throughout. The temperature was maintained at 23. ± .02°C. An ordinary Wheatstone bridge set up was employed using a dial resistance box of Curtis coils reading to 0.1 ohm as standard resistance, and telephone receivers as detecting instruments. The sugars studied were the monosaccharides galactose, glucose and fructose, and the disaccharides lactose, maltose and sucrose. All were Eastman products except the sucrose which was the ordinary commercial variety, and the glucose which was Baker's monohydrate.

III. Determination of Values of Λ_S for the Various Sugars

For these determinations increasing amounts of sugar were added to 0.025 normal NaOH until the base was completely neutralized as shown by no further net decrease in conductivity. The final conductivity, then, represented that of 0.025 molal sugar salt very nearly. Very small corrections were made for residual NaOH (as determined by the hydrogen electrode), and, where large concentrations of sugar were used, for the slight conductivity of the sugar blank, probably caused by impurities. These corrections do not appreciably alter the results.

The ion conductance of the sugar ion is obtained by subtracting that of the Na-ion from the limiting value of the equivalent conductance of the sugar salt. This latter is obtained from the measured conductivity of the 0.025 molal salt and the cell constant after correcting for interionic attraction. In this particular case the Onsager equation[6] can be used with a certain degree of assurance since here, with the large excess of sugar, one is dealing with a univalent salt type at a sufficiently low concentration (0.025). The equation used for 23°C. was[7]

$$\Lambda = \Lambda_0 - (.226\Lambda_0 + 57)\sqrt{.025} \tag{4}$$

from which

$$\Lambda_0 = \frac{\Lambda + 9}{.9643} \tag{5}$$

where Λ is the equivalent conductance measured for the 0.025 molal sugar salt, obtained from the relation**

$$\Lambda = \frac{1000 \times 13.86 \times K \times \eta^{.66}}{.025}$$

Thus $$\Lambda_S = \Lambda_0 - \Lambda_{Na} = \Lambda_0 - 48.4$$

where Λ_S is the equivalent conductance of the sugar ion at 23°C.

One other correction was necessary when large amounts of sugar were added, namely a volume correction. There is a decrease in conductivity due to volume increase, i.e. to dilution, without any reaction between sugar and base. These volume changes were in all cases measured and corrected for. Table I gives results for glucose. The sugar concentrations in column 1 are weight formal, i.e. the number of mols added to an ORIGINAL volume of one liter.

TABLE I

Sugar concn. (1)	Vol. cc. (2)	Res. ohms (3)	$\eta^{.66}$ (4)	k × 10^6 corrected (5)	$C_{OH} \times 10^4$ (6)
0.00	100.0	2450	1.007	411.0	
0.05	100.7	4370	1.019	216.9	
0.30	104.1	8620	1.097	132.5	
0.80	110.5	11800	1.292	121.0	2.5
1.00	112.9	13080	1.365	118.0	1.7*

* These values are really activities, but even should the actual H-ion concentration be as high as double the activity, certainly an extreme assumption, these values indicate that well over 98% of the NaOH has been neutralized.

Values in column 5 are obtained by taking the product of the values in columns 2 and 4 and multiplying that by the reciprocal of the corresponding value in column 3. The last two values for this corrected conductance, k of column 5, are practically constant, and when further corrected for the sugar blank and the free NaOH (see column 6) become, respectively, 114 and 112 × 10^{-6} reciprocal ohms.

Thus $$\Lambda = \frac{1000 \times 13.86 \times 112 \times 10^{-6}}{.025} = 62.1$$

and $$\Lambda_0 = \frac{\Lambda + 9}{.9643} = 73.7$$

and $\Lambda_S = 73.7 - 48.4 = 25.3$ for glucose.

** It is recognized that the Onsager equation itself includes the viscosity, but it also includes the dielectric constant, and until some idea of the magnitude of the change in the latter with sugar concentration is obtained, the present method of treatment is considered better, i.e. to make the empirical viscosity correction in which dielectric constant change is doubtless implicit, and then apply the Onsager correction as to a solution with the viscosity and the dielectric constant of water. That the presence of sugar has a very appreciable effect on the dielectric constant of aqueous solutions is shown by the results of Possner who finds the values 45, 50 and 60 respectively for 67, 61.5 and 50% sugar solutions.(8)

A resume of analogous results for the six sugars studied is given in Table II.

TABLE II

Sugar (1)	$K \times 10^6$ for .025 molal salt. (corrected) (2)	Λ (3)	Λ_0 (4)	Λ_S (5)
Galactose	111.	61.6	73.2	24.8
Glucose	112.	62.1	73.7	25.3
Fructose	110.	61.0	72.6	24.2
Lactose	113.	62.6	74.2	25.8
Maltose	112.	62.2	73.8	25.4
Sucrose	106.	58.8	70.3	21.9

From values of Λ_S in Table II corresponding values of ΔK_0 can be calculated from equation 2 above. These values are listed in Table III referring arbitrarily to a sugar concentration of 0.025 molal as a convenient reference concentration. Λ_{OH} at 23°C is taken as 189.5.[9]

TABLE III

Sugar	$\Delta K_0 \times 10^6$ for $c = 0.025$	Sugar	$\Delta K_0 \times 10^6$ for $c = 0.025$
Galactose	297	Lactose	295
Glucose	296	Maltose	296
Fructose	298	Sucrose	302

IV. Determination of the Basicity of the Sugars

The first determinations were made by preparing solutions 0.05 molal in sugar and varying the NaOH concentration, and comparing the conductivities of these solutions with the NaOH blanks. Such a sugar concentration in the cases of the disaccharides especially increases the viscosity of the NaOH solutions appreciably if only slightly. The values of prime interest in this work were in solutions of high alkalinity where the decrease in conductivity due to the sugar may be only about 3% of the total conductivity. In such cases, since the viscosity correction must be applied to the total conductivity a small error in viscosity determination may result in a large error in ΔK. For small NaOH concentrations good results can be obtained in this way, but the inherent magnitude of the error is such that none of these results are included in the present paper.

Increments of sugar concentration of 0.006 were found by experiment to give no detectable change in viscosity to the NaOH solutions, and even up to 0.025 molal the change was found to be inappreciable; whereas changes in conductivity even in double normal NaOH could be duplicated with accuracy. At this concentration no volume correction is necessary. Samples of dilute sugar solutions were therefore prepared using various NaOH solutions as solvents and varying the sugar concentration by about 0.006 molal increments and never exceeding a concentration of 0.025 molal. For these solutions the viscosity values were taken to be the same as those of the corresponding pure NaOH solutions used as solvent. In all cases the conductivities were measured within one to two hours after the solutions were prepared, although experiment showed that in the case of sucrose there was no change in conductivity of a 0.05 molal solution in half normal base even after a period of 62 hours at 23°C.

The NaOH concentrations finally used were 0.02 N, 0.10 N, 1.0 N, and 2.0 N. In the last two cases the pH of the solutions containing sugar were essentially the same, measured by hydrogen electrode, as of the corresponding pure base. With the 0.1 normal base, while the pH of the sugar solutions differed distinctly from that of the pure base, the pH values for like concentrations of the different sugars did not differ appreciably among themselves.

TABLE IV

sucrose concn. (1)	$K \times 10^6$ rec. ohms cor. for viscosity (2)	$\Delta K \times 10^6$ (3)	$\Delta K \times 10^6$ for 0.025 molal sugar (4)	$\frac{\Delta K}{\Delta K_0}$ [see Table III] (5)	C_H of 0.025 molal sugar solns. (6)
	A. 2 normal NaOH. $\eta^{.66} = 1.326$				
0.0000	28,363	—	—		
0.00625	28,107	256	1024		
0.0125	27,846	517	1034		
0.0250	27,329	1034	1034		9.1×10^{-15}
		Ave.	1030	3.41	
	B. 1 normal NaOH. $\eta^{.66} = 1.146$				
0.0000	14,466	—	—		
0.00625	14,281	185	740		
0.0125	14,096	370	740		
0.0250	13,729	737	737		1.8×10^{-14}
		Ave.	739	2.45	
	C. 0.1 normal NaOH. $\eta^{.66} = 1.014$				
0.0000	1,585				
0.00625	1,525	60	240	0.794	
0.0125	1,471	114	228	0.755	
0.0250	1,368	217	217	0.718	1.4×10^{-13}
	D. 0.02 normal NaOH. η nearly unity				
0.0000	329.8				
0.00625	309.8	19.9	79.6	0.263	
0.0125	293.7	36.1	72.2	0.239	
0.0250	265.6	64.2	64.2	0.213	7.7×10^{-13}

Thus in making calculations later, constant pH values are taken for these three sets of sugar solutions. With the 0.02 normal base each sugar gave a characteristic pH. It may be pointed out that these very small pH differences which, in the present method, we can safely neglect, furnish the entire basis for calculations in a potentiometric method.

Table IV gives typical data for sucrose.

In this part of the work it was decided not to attempt to correct for interionic attraction. This could be done for the most dilute solutions all right, but certainly such an attempt would have no quantitative significance in the more concentrated solutions. Even the empirical equation of Lattey[10] which is said to hold for all cases examined up to a concentration of 0.1 normal and for KCl up to normal and fairly well even at double normal, gave impossible values for normal and double normal NaOH. It should be noted, however, that such a correction would amplify the values of ΔK and thus of $\Delta K/\Delta K_0$ since the interionic effect is always such as to give a measured conductivity always lower than that in the absence of such an effect. Thus, from this point of view, the values presented here are lower limiting effects.

It will be noted from Table IV that at the lower concentrations of alkali the values of $\Delta K/\Delta K_0$ decrease with increasing sugar concentration whereas for the higher concentrations of alkali the values seem to be independent of the sugar concentration up to 0.025 molal. This is to be expected since in the latter case the base is present in great excess for all concentrations of sugar while in the other case there are some solutions in which the sugar itself is in excess.

Table V gives a digest of values of ΔK and $\Delta K/\Delta K_0$ for the final concentration, i.e. 0.25 molal, of all the sugars studied. Inspection of the values of $\Delta K/\Delta K_0$ in Table V indicates greater binding power for disaccharides than for monosaccharides though the difference shows up distinctly only at comparatively high alkali concentrations. At least four ionizing hydrogens are indicated as operative in double normal alkali for the disaccharides and at least three for the monosaccharides.

The general solution of the relation between the values of the various ionization constants, the H-ion concentration and the observed value of $\Delta K/\Delta K_0$ can be obtained as follows.

TABLE V

Sugar	2 N. base		1 N. base		0.1 N base		0.02 N. base		
	final C_H in all cases is 9.1×10^{-15}		final C_H in all cases is 1.8×10^{-14}		final C_H in all cases is 1.4×10^{-13}				
	$\Delta K \times 10^6$	$\frac{\Delta K}{\Delta K_0}$	$\Delta K \times 10^6$	$\frac{\Delta K}{\Delta K_0}$	$\Delta K \times 10^6$	$\frac{\Delta K}{\Delta K_0}$	$\Delta K \times 10^6$	$\frac{\Delta K}{\Delta K_0}$	$C_H \times 10^{12}$ of 0.025 molal sugar
Galactose	680	2.29	448	1.51	242	0.815	97.9	0.33	0.9
Glucose	695	2.35	482	1.63	269	0.909	113.8	0.384	1.0
Fructose	659	2.21	521	1.75	279	0.936	129.5	0.435	1.15
Lactose	1006	3.41	763	2.59	312	1.058	126.5	0.429	1.1
Maltose	1105	3.73	775	2.62	339	1.145	129.5	0.438	1.2
Sucrose	1030	3.41	739	2.45	217	0.718	64.2	0.213	0.77

Let there be a polybasic acid of n ionizing hydrogen equivalents per mol. and formula H_nA, and take a solution of molality c. Then

$$\left.\begin{array}{ll} & \dfrac{(H^+)\,(H_{n-1}A^-)}{(H_nA)} = K_1 \quad \text{and} \quad (H_{n-1}A^-) = \dfrac{K_1\,(H_nA)}{(H^+)} \\ \text{Also} & \dfrac{(H^+)\,(H_{n-2}A^=)}{(H_{n-1}A^-)} = K_2 \quad \text{and} \quad (H_{n-2}A^=) = \dfrac{K_1K_2(H_nA)}{(H^+)^2} \\ & \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ & \dfrac{(H^+)\,(A^{n-})}{(HA^{(n-1)-})} = K_n \quad \text{and} \quad (A^{n-}) = \dfrac{K_1K_2K_3\cdots K_n(H_nA)}{(H^+)^n} \end{array}\right\} \qquad (6)$$

$$\begin{aligned} \text{But} \quad C &= (H_nA) + (H_{n-1}A^-) + \cdots\cdots + (A^{n-}) \\ &= (H_nA)\left[1 + \frac{K_1}{(H^+)} + \frac{K_1K_2}{(H^+)^2} + \cdots\cdots + \frac{K_1K_2\cdots K_n}{(H^+)^n}\right] \qquad (7) \end{aligned}$$

$$\begin{aligned} \text{Also} \quad \frac{\Delta K}{\Delta K_0}C &= (H_{n-1}A^-) + 2\,(H_{n-2}A^=) + 3\,(H_{n-3}A^{\equiv}) + \cdots + n(A^{n-}) \\ &= (H_nA)\left[\frac{K_1}{(H^+)} + \frac{2K_1K_2}{(H^+)^2} + \cdots\cdots + \frac{nK_1K_2\cdots K_n}{(H^+)^n}\right] \qquad (8) \end{aligned}$$

Dividing (8) by (7)

$$\frac{\Delta K}{\Delta K_0} = \frac{K_1(H^+)^{n-1} + 2\,K_1K_2\,(H^+)^{n-2} + \cdots\cdots + nK_1K_2\cdots K_n}{(H^+)^n + K_1(H^+)^{n-1} + K_1K_2\,(H^+)^{n-2} + \cdots + K_1K_2\cdots K_n} \qquad (9)$$

Thus if we have n simultaneous values for (H^+) and $\Delta K/\Delta K_0$, values of the n ionization constants can be obtained. In practice however it is very difficult and quite unsatisfactory to apply this equation in the present case, since the value of (H^+) varies from over 10^{-12} to less than 10^{-14}, and it is easily seen from Table V that at least the fourth power of this magnitude will be involved.

Actually it has been found more satisfactory to adjust values of K by trial. The order of magnitude of K_1 is easily obtained from the alkali-binding power of the sugar in the 0.02 normal base assuming it alone to be effective. K_1 is in all cases predominantly large, though the remainder of the constants are in many cases of nearly equal magnitude.

Table VI gives the results of the calculations of four constants for each sugar and adjusted to the observed values of $\Delta K/\Delta K_0$ beginning with the most dilute alkali. In making these calculations the data in Table V were employed. There the individual values of the H-ion concentration for the sugar solutions in 0.02 normal base are given in the last column. With the other solutions the H-ion concentration used in the calculations is given just under the various alkali concentrations in the table headings. As explained above this did not vary measurably from sugar to sugar for 0.025 molal sugar concentration.

Table VI

Sugar	$K_1 \times 10^{13}$	$K_2 \times 10^{14}$	$K_3 \times 10^{14}$	$K_4 \times 10^{14}$	$K_5 \times 10^{14}$	$\Delta K/\Delta K_0$							
						0.02 N. base		0.1 N. base		1 N. base		2 N. base	
						obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.
Galactose	4.3	0.9	0.5	0.5		.33	.33	.815	.816	1.51	1.50	2.29	2.04
Glucose	6.0	1.4	0.45	0.45		.384	.384	.910	.905	1.63	1.63	2.35	2.13
Fructose	8.6	1.15	1.15	0.10		.435	.435	.936	.946	1.75	1.72	2.21	2.23
Lactose	7.6	3.0	1.7	1.6		.429	.427	1.058	1.064	2.59	2.59	3.41	3.26
Maltose	8.5	4.0	1.9	1.2		.438	.436	1.145	1.135	2.62	2.62	3.73	3.21
Sucrose	2.0	1.9	1.7	1.7		.213	.215	.718	.718	2.45	2.45	3.41	3.23
Sucrose*	2.0	1.9	1.7	1.4	0.35	.213	.215	.718	.716	2.45	2.45	3.41	3.42

* See text.

With the exception of fructose it will be noted that four constants are not enough to account for the alkali binding *unless the value of K_4 be taken as larger than that of K_3*, and thus at least five constants seem definitely indicated for most of these sugars coming definitely into play in alkali as concentrated as double normal. The precision of $\Delta K/\Delta K_0$ values for double normal NaOH is not considered sufficient to warrant tabulating values for K_5, though qualitatively it is thought to be definitely indicated. By way of interest five constants have been calculated for sucrose and are appended to Table VI. The use of the fifth constant affects the value of K_4 somewhat though its influence does not reach any farther back.

The only assumption implicit in this treatment not so far mentioned, namely that doubling the charge on a sugar ion doubles its molecular conductance, seems justified since the loss of a proton affects neither the mass nor the effective cross section of such a large molecule appreciably.

The constants obtained from the present data, so far as they can be compared, are in fair agreement with those in the literature as shown in Table VII, where a few representative values are listed. The somewhat lower results noted for the first constant in this work are to be expected since in most of the previous work only one constant is noted and it had to be given a value to take care of the alkali binding of any other constant operative at the alkalinity studied. So far as the author is aware Hirsch and Schlags are the only workers whose published data suggest polybasicity of common sugars and their data was not for alkali concentrations sufficiently great to indicate a basicity of more than two. Urban and Shaffer,[13] using the hydrogen electrode and working at high alkalinities have also obtained data indicating the same thing. These workers have indications that at high alkalinities some sugars have a basicity distinctly greater than two.

TABLE VII

sugar	Madsen[11] (1901) (catalysis) $K \times 10^{13}$	Michaelis & Rona[12] (1913)(potentiometric) $K \times 10^{13}$	Hirsch & Schlags[4] (1929)(conductometric) $K_1 \times 10^{13}$		Stearn $K_1 \times 10^{13}$	$K_2 \times 10^{14}$
			$K_1 \times 10^{13}$	$K_2 \times 10^{14}$	$K_1 \times 10^{13}$	$K_2 \times 10^{14}$
	25°C.	17 to 18°C.	25°C.		23°C.	
Galactose	—	5.3	—	—	4.3	0.9
Glucose	5.9	6.6	7.8	1.54	6.0	1.4
Fructose	10.2	8.8	20.3	1.56	8.6	1.15
Lactose	—	6.	10.5	3.6	7.6	3.0
Maltose	—	18.	11.6	7.7	8.5	4.0
Sucrose	2.2	2.4	3.1	3.0	2.0	1.9

VI. Summary

1. The conductivity method has been applied to a study of the alkali binding of sugars especially at high alkali concentration.

2. In double normal alkali the sugars studied act as polybasic acids, with at least five ionizing hydrogens in most cases.

3. Values for the various ionization constants of the sugars are calculated.

4. The limiting equivalent conductances of the monovalent sugar ions have been determined.

5. The validity of the treatment of the data is discussed.

References

[1] P. A. Shaffer and T. E. Friedemann: J. Biol. Chem., **86**, 345 (1930).
[2] A. P. Mathews: J. Biol. Chem., **6**, 3(1909).
[3] J. N. Nef: Ann., **376**, 1 (1910); **403**, 235 (1914).
[4] P. Hirsch and R. Schlags: Z. physik. Chem., Abt. A, **141**, 387 (1929).
[5] C. A. Kraus: "The Properties of Electrically Conducting Systems," p. 121.
[6] L. Onsager: Physik. Z., **28**, 277 (1927).
[7] C. W. Davies: "The Conductivity of Solutions," p. 196 (1930).
[8] H. Possner: Ann. Physik, (5) **6**, 875 (1930).
[9] International Critical Tables, **6**, 230.
[10] R. T. Lattey: Phil. Mag. (7), **4**, 831 (1927).
[11] T. Madsen: Z. physik. Chem., **36**, 290 (1901).
[12] L. Michaelis and P. Rona: Biochem. Z., **49**, 232 (1913).
[13] Private communication from Dr. P. A. Shaffer, covering data obtained by Dr. Frank Urban in collaboration with himself, which is in process of preparation for publication.

NEPHELOMETRIC TITRATIONS. III. THE EFFECT OF EXTRA COMPOUNDS*

BY CLYDE R. JOHNSON**

In the first paper of this series it was pointed out that atomic weight values derived from nephelometric titrations in which the equal-opalescence end-point is used are not necessarily independent of the "extra" compounds inevitably present in the analytical solutions. Further, it was suggested that these values may also depend to some extent upon certain arbitrary features of the analytical procedures now used for determining the end-point in such titrations.

The experiments described in the following report are designed to furnish information bearing upon both of the above points. They show in a general way the extent to which and the conditions under which the end-point and the stoichiometrical point coincide, in a number of typical titrations, involving a variety of extra compounds. More important, perhaps, the experiments outline and test a general method for placing the analytical procedures used in determining the end-point upon an experimental basis. That is, they provide a means of removing the arbitrary feature of these procedures when they are applied to the determination of any particular stoichiometrical ratio. The application of the method is quite simple. It consists in predetermining the conditions under which the end-point of the titration will correspond with the stoichiometrical point with the necessary precision. The actual analyses are carried out under these predetermined standard conditions, with analytical systems of definite composition and volume. The details of the method used in handling the systems and conducting the nephelometric tests then lose their arbitrary character. The various time and temperature factors important in these tests are thus brought under control; any disturbing effects characteristic of the liquid phase in the systems under investigation are eliminated. It is evident that the method is applicable whether the tests are made by the equal-opalescence method of Mulder or by the standard-solution method outlined in the second paper of this series.

The present research has been confined to experiments with systems containing silver chloride, since this compound has been employed very extensively in nephelometric atomic weight determinations. The systems used in such work consist of flocculent silver chloride in contact with one to five liters of its "saturated" solution in nitric acid. The solution generally contains an extra compound derived from the chloride undergoing analysis. Very frequently, although not necessarily, there are present various auxiliary compounds, of which ammonium nitrate is a common example. The methods by which these systems are synthesized in atomic weight determinations are described in detail in corresponding reports and will not be discussed here.

---

* Contribution from the Frick Chemical Laboratory, Princeton University.

** National Research Fellow in Chemistry.

Experimental

In the present work systems of the above type were prepared by a reverse method of synthesis from pure flocculent silver chloride, nitric acid, and various pure compounds. These syntheses were carried out in parallel with a series of nephelometric tests, as described below. The technique characteristic of precise atomic weight determinations was observed throughout. All work with the silver chloride was done in the light of Series O and OA Wratten Safelights.

Reagents. The water, nitric acid, hydrochloric acid, and the standard solutions used in this research were prepared according to the specifications outlined by Scott and Johnson.[1] The silver nitrate was obtained from silver chloride residues from previous atomic weight investigations. This silver chloride was reduced to silver with purified sugar and sodium hydroxide. The silver was thoroughly washed, dried, and fused on a bed of pure lime in an atmosphere of methane. It was then etched and dissolved in nitric acid, and crystallized as the nitrate. This material was further purified by two precipitations from saturated solution with nitric acid, after each of which it was dried by centrifuging. Before each crystallization or precipitation the solution was filtered through a platinum Munroe crucible.

The other compounds used in the work were freed from chlorides (and silver) by repeated crystallization and centrifuging. The initial crystalline material was usually 500 grams of the "reagent grade" compound; in a few cases C.P. material was used as a starting point. The compounds were subjected to four, five, or six recrystallizations, as necessary. After each of these the moist crystals were centrifuged in covered porcelain Büchner funnels, at 1500–2000 r.p.m. for about fifteen minutes. Each solution was filtered at least three times at different stages in the purification, initially through a paper filter, and at least twice through a Munroe crucible. The crystals finally obtained were placed in porcelain dishes, and dried by vacuum desiccation over fused sodium hydroxide. By this treatment it was found possible to obtain 75 to 150 grams of each compound, which met the requirements for purity described below. One exception must be noted. The initial thorium nitrate sample weighed less than 200 grams and could be recrystallized only four times. The system 0.10 M in $Th(NO_3)_4$ prepared from the final material was found to contain excess chloride equivalent to 0.00030 grams of silver per liter. It may be noted that the hygroscopic crystals of the cerium and thorium nitrates were distinctly more difficult to separate from their mother-liquor in the centrifuge, than the crystals of any of the other compounds.

Nephelometric Tests. The nephelometric tests made upon the systems finally obtained, and during their synthesis, were based upon the equal-opalescence method of Mulder,[2] with innovations and precautions suggested by Richards and Wells,[3] and Wells.[4]

---

[1] Scott and Johnson: J. Phys. Chem., 33, 1978 (1929).

[2] Mulder: "Die Silberprobir-Methode" (1859).

[3] Richards and Wells: Am. Chem. J., 31, 235 (1904).

[4] Wells: Am. Chem. J., 35, 99 (1906).

To prepare the systems for testing they were shaken vigorously 1000 times, following each change in the composition of the solutions. After this treatment they were allowed to stand for several days, with the minimum of agitation required to keep the solutions uniformly mixed. For another period of days, and later, during the course of the tests, the systems were seldom disturbed. These specifications are of some importance, as preliminary and incidental data obtained in the present investigation show. Tests accompanied by casual "occasional shaking" of the silver chloride-nitric acid-extra compound systems almost invariably indicated that the liquid phase contained excess chloride equivalent to several tenths of a milligram of silver per liter.

For each test two 20.0 cc. portions of clear supernatant liquid were withdrawn with a pipette and placed in a pair of clean, dry test tubes, which had been matched with respect to volume, clearness, and color. The suspensions to be compared were then formed in the usual manner by the addition of 1.00 cc. portions of standard solutions of silver nitrate and sodium chloride containing the equivalent of 1.000 gm. of silver per liter. These solutions were added drop by drop, with slow stirring, and each mixture was finally stirred with fifty strokes of a glass stirrer. The tubes were then covered; between thirty and ninety minutes later the suspensions were compared in a nephelometer. The comparison consisted in exposing 65 mm. of one cup and recording the mean of twenty settings of the jacket of the other. The tubes were reversed after ten readings to eliminate instrumental errors. The tests were made at room temperature, which varied from 25° to 29°C.

Comparative tests with Pyrex and soft glass nephelometer tubes showed the former to be much more satisfactory. Furthermore, one may well suspect that the opaque white patches which soon form on the soft glass tubes are due to silver chloride, although they cannot be removed by the usual reagents. The above statement may thus be extended to include the large flasks and bottles used in work of the present nature.

Preparation of Analytical Systems. Thirteen 16 gram quantities of silver nitrate were dissolved in one liter portions of water or nitric acid and mixed with one liter portions of hydrochloric acid containing either a 3% excess or deficiency of HCl, at the rate of 5 cc. per minute, drop by drop, with frequent shaking. In some cases both solutions were 0.3 M in nitric acid; in others the solutions contained no additional acid. Each silver chloride precipitate, contained in a 4-liter glass-stoppered Pyrex bottle, was washed sixteen times with 250 cc. portions of pure water, over a period of one month, with frequent shaking. The final 250 cc. washings, after standing over the precipitates for another month, were removed, acidified, and tested in the nephelometer.

After two or three additional washings the water was drained from the silver chloride samples and one liter of pure 0.30 M nitric acid was added to each bottle. The bottles were shaken; after standing for a time the supernatant liquids were again tested. The precipitates were washed twice more and then shaken vigorously with 1000 cc. of water. Concentrated nitric acid was added to make the solutions 0.25 M in HNO_3. Nephelometric tests were then made upon each system, with the precautions noted above, until three out of four consecutive tests, made over a period of a week, gave three results with an average deviation less than 3%. These last tests invariably indicated that the supernatant liquids contained equivalent amounts of silver and chloride.

Blanks. All subsequent additions to the systems were covered by two series of "equal-opalescence" blanks. The first series of tests were used during the crystallization of the "extra" compounds to insure the removal of impurities which might form opalescent suspensions with the standard solutions. The tests differed from those of the second series, described below, mainly in that the factor of sensitivity was emphasized, at the expense of uniformity, by the use of larger volumes of the precipitating reagents and greater concentrations of the compounds in the blanks. In general, the compounds were crystallized until any disturbing impurities originally present were reduced to a concentration in which they produced no effect under conditions in which sodium chloride or silver nitrate impurities equivalent to 0.02-0.04 mg. of silver per 0.1 mol of compound produced a noticeable difference of brightness in the nephelometer tubes. The second series of blanks, rather more uniform but less sensitive than the above tests, accompanied the addition of the compounds to the analytical systems. These blanks were intended to determine whether or not the compounds themselves produced any noticeable effect upon the precipitating reagents, under the same conditions used in the final tests, but with silver chloride absent.

Addition of Extra Compounds. In each case an amount of the crystalline compound sufficient to make the solution 0.050 M in the compound, plus the amount needed for the blank, was weighed out on a watch-glass. This material was made up to 20, 40, or 60 cc. with 0.25 M nitric acid, and a 1.00 cc. to 5.0 cc. aliquot portion was withdrawn and diluted with 0.25 M nitric acid until 0.050 M in the compound, for the blank. By virtue of a simple algebraic calculation, the blank test was always made upon two 20.0 cc. samples, withdrawn from a solution somewhat larger than 40 cc. in volume. These samples were tested by the usual equal-opalescence procedure. If the examination in the nephelometer showed no opalescence in either tube after two hours, the remainder of the concentrated solution was added to the main system. It was necessary to add the sodium pyrophosphate, ammonium metavanadate, and boric acid as dry powders. The blanks for these compounds were prepared from representative samples of the powders.

After the above additions, the supernatant liquids were again *regularly saturated* with silver chloride, and tested until four consecutive tests, separated by intervals of three days, gave three results with an average deviation less than 3%. In an analogous manner, the solutions were made 0.10 M in the compounds and tested again. In this case the blanks were 0.10 M in the compounds and 0.25 M in nitric acid. A few exceptions should be noted. The average deviations of the tests made upon the thorium nitrate solutions were 8% and 12%, respectively, at the 0.050 M and 0.10 M concentrations. System

No. 19 contained the equivalent of 0.025 mols of NH_4VO_3 per liter and 20 grams of silver chloride. The solution was 0.58 M in nitric acid.

Experiments similar to those described above, in which the total amounts of silver and chloride in the systems were extremely small, were also tried. The initial systems were made by diluting 1.00 cc. to 4.00 cc. volumes of the standard sodium chloride solution with 1000 cc. of 0.25 nitric acid, and adding equal (small) volumes of the standard silver nitrate solution. These experiments offered a means of separating effects due to the presence of the silver chloride precipitates, and also served to check the accuracy of the standard solutions and the burette calibrations.

Discussion of Results

Preliminary Tests. The results of the tests made during the washing of the silver chloride samples are condensed below:

Formation and Washing of Silver Chloride

System No.	Initial HNO_3 Conc.	Solution Added By Drops	Final 3% Excess	Nephelometric Ratio after:			
				Washing No. 16	Washing No. 17	Adding 0.3M HNO_3	Adding 0.25M HNO_3
1	0.3	$AgNO_3$	$AgNO_3$	1.21	1.04	0.84	1.03
2	0.0	$AgNO_3$	$AgNO_3$	1.30	0.99	0.90	0.99
4	0.0	$AgNO_3$	$AgNO_3$	1.14		1.16	1.00
6	0.3	$AgNO_3$	HCl	1.18	1.01	0.91	1.00
7	0.0	$AgNO_3$	$AgNO_3$	1.29	0.94	0.83	1.00
8	0.3	$AgNO_3$	$AgNO_3$	0.96		0.86	1.00
9	0.3	$AgNO_3$	HCl	1.01		1.02	0.98
10	0.3	$AgNO_3$	$AgNO_3$	1.49	1.19	0.90	1.02
11	0.3	HCl	HCl	0.94		0.94	1.02
12	0.0	$AgNO_3$	HCl	0.92		0.91	1.03
13	0.0	$AgNO_3$	HCl	1.50	1.06	1.10	1.00
16	0.0	HCl	HCl	1.15		0.78	0.99
18	0.0	$AgNO_3$	HCl	1.69	1.08	0.67	1.01
19	0.3	$AgNO_3$	$AgNO_3$	1.04		1.00	1.01

Notes. Each addition of acid was immediately preceded by two washings with 250 cc. portions of water.

Washing No. 16 stood for a month over the precipitates; No. 17 only a few days.

With the exception of the values in the last column each value in the table represents a single nephelometric analysis. The result of each analysis is expressed as the average ratio of the exposed length of the cup containing excess sodium chloride to that with excess silver nitrate, at the condition of equal opalescence, as shown by the nephelometer. That is, a ratio greater than unity indicates that the original samples contained excess chloride; a ratio less than unity indicates that they contained excess silver. This same convention is observed in Table I. It is a drawback of the equal-opalescence method that the results are not in terms of absolute quantities of material.

There are available no trustworthy data for effecting this conversion. As a rough approximation, holding only in certain limited cases, it may be taken that 0.01 ratio unit corresponds to about 0.01 mg. of silver or its chloride equivalent, per liter of solution.

The data tabulated above furnish a little general information concerning the precipitation and washing of silver chloride which may be passed over without comment. They also reveal a characteristic of the analytical systems which is worthy of more detailed examination. Most of the supernatant liquids, standing after fifteen washings with non-acidified water, contained an excess of chloride over silver. On the other hand, the precipitates generally held excess silver, which was removed,—at least partially removed,—only by a large increase in the concentration of electrolyte in the liquid phase. It is difficult to believe that the excess of chloride in the sixteenth washing was due to the "soaking out of occluded hydrogen chloride." This hypothesis does not explain the reasonable assumption that fifteen 250 cc. washings with water, covering an entire month, are more than enough to remove any "occluded" material which the sixteenth washing might remove, even in another month. Nor does it explain the excess of silver left in (or on) the precipitates. It is easier to accept an explanation based on the view that colloidal silver chloride, on coagulation, tends to carry down more silver than chlorine atoms.

However, without reference to any particular mechanism, it may be concluded that in working with these analytical systems one may consistently obtain tests for excess chloride in the solutions, even though the precipitates hold an excess of silver. This source of constant error, operating in any nephelometric atomic weight titration, would tend to make the calculated atomic weight too low. The departure from accuracy would also be enhanced by the constant errors in the antecedent atomic weights used in the calculation, e.g., the atomic weights of silver and chlorine. The accepted values of these constants depend to a considerable extent upon determinations involving silver chloride precipitated from dilute solution.

The Blanks. The extent to which the absence of disturbing impurities was guaranteed by the first series of blanks has already been noted. In the second series of blanks, with the exception of those covering the thorium nitrate, all of the paired tubes appeared equally "black" when viewed in the nephelometer It follows that the corresponding compounds, listed in Table 1, had no effect upon the equal-opalescence end-point due to any reactions with the standard solutions, at the concentrations used in this work. The tests also show the effectiveness of crystallization with centrifuging in removing chloride (and silver) impurities from these compounds.

Color and Stability of the Suspensions. At the risk of making a few inaccurate statements in attempting to generalize, some observations concerning the color and stability of the equal-opalescence suspensions may be recorded. All of these apply to systems practically at the end-point. When the tests were made with the necessary precautions, the two suspensions were usually quite alike, sometimes even identical, in color and appearance. No marked and regular differences in color between the two suspensions due to the action of any of the extra compounds were observed, although there were indications of small differences of this nature. The colors of the suspensions derived from the separate systems varied from blue-gray and yellow-gray to yellow-white with increasing solubility of the silver chloride in the presence of different extra compounds. In other words the color varied with the amount of material in suspension, also, of course, with its state of division. It would appear that effects due to the latter factor were largely eliminated by the uniform conditions of precipitation. In general, the above statements apply to tests made upon solutions regularly saturated with silver chloride at room temperature.

On the other hand there was a persistent tendency for the suspensions in the paired tubes to differ markedly in color and appearance. This tendency was aggravated by shaking or cooling the analytical systems or by deliberately reducing the silver chloride concentration in the nephelometer tubes by dilution. Changes usually appeared in both tubes simultaneously, and accompanied changes in the relative brightness of the suspensions in a characteristic manner, almost invariably taking the same course. The suspensions formed by addition of excess silver nitrate inclined toward bright blue and blue-gray colors, differing nevertheless from the normal colors. Those formed by the addition of excess sodium chloride became dull gray, with yellow, red, or brown tints. In comparing the suspensions with respect to their opalescence or brightness color differences were found to increase the uncertainty of the nephelometric observations, and were avoided in the final tests, as indicated.

As a rule the suspensions were quite stable. Although they often changed rapidly in relative opalescence immediately after precipitation, they did not subsequently alter for long periods. After standing for several hours they settled noticeably. The suspensions, once fully formed, were in no case observed to be very greatly affected by the presence of the extra compound.

Effect of Extra Compounds. The results of the tests designed to examine the possible effect of extra compounds on the equal-opalescence end-point are summarized in Table I. Each nephelometric ratio in the table is the average of the values obtained from at least three separate analyses. The method of obtaining these results has been described in detail; it seems to warrant the conclusion that the ratios show the correct experimental end-points of the titrations represented in the table, with an accuracy corresponding to a few hundredths of a milligram of silver or its chloride equivalent, per liter of analytical solution. Reservations concerning the solid phase in the analytical systems have been noted.

The deviations from the theoretical (equal-opalescence) value of 1.00 are in most cases quite small. Those observed for System No. 18 are mainly due to a chloride impurity in the thorium nitrate, as the blanks testify. Some of the others may be ascribed, not unreasonably, to the action of the extra compounds. Even for precise titrations these deviations are equivalent only to minor errors, which may be eliminated in any case by the use of the correct experimental end-point. In brief, when the tests are made with the necessary precautions, the accuracy claimed for the nephelometric method of analysis by investigators who have used it in atomic weight work may be attained, in so far as any effects due to the presence of extra compounds come into consideration.

The writer takes this occasion to thank Professor George A. Hulett for his interest and co-operation in this work.

TABLE I

The Effect of Extra Compounds

System No.	Wt. of solid AgCl Grams	Extra Compound Added	Observed Nephelometric Ratios in AgCl Solutions 0.25 M in HNO_3:		
			Compound Absent	Compound 0.050 M	Compound 0.10 M
1	13	None	1.03	—	—
2	13	NH_4NO_3	0.99	1.16	0.97
3	0.001	NH_4NO_3	0.99	1.00	1.01
4	13	$NaNO_3$	1.00	0.86	1.02
5	0.004	$NaNO_3$	0.98	0.89	1.00
6	13	$(NH_4)_2SO_4$	1.00	1.00	0.98
7	13	Na_2SO_4	1.00	0.98	0.97
8	13	$Ca(NO_3)_2$	1.00	1.02	1.02
9	13	$Cd(NO_3)_2 \cdot 4H_2O$	0.98	1.00	1.05
10	13	$(NH_4)_2HPO_4$	1.02	0.98	0.98
11	13	H_3BO_3	1.02	0.96	0.93
12	13	$Al(NO_3)_3 \cdot 9H_2O$	1.03	1.05	1.01
13	13	$Ce(NO_3)_3 \cdot 6H_2O$	1.00	1.07	1.06
14	None	$Ce(NO_3)_3 \cdot 6H_2O$	1.00	1.07	1.08
15	None	$Ce(NO_3)_3 \cdot 6H_2O$	1.00	1.18	—
16	13	$Na_4P_2O_7 \cdot 10H_2O$	0.99	0.85	1.14
17	0.001	$Na_4P_2O_7 \cdot 10H_2O$	1.00	0.86	1.04
18	13	$Th(NO_3)_4 \cdot 4H_2O$	1.01	1.14	1.24
19	20	NH_4VO_3	1.01	(1.03)	—

Note. Silver chloride solution 14 was saturated at room temperature; solution 15 contained 1.33 mg. of AgCl per liter.

Summary

A method for testing arbitrary features of the procedures used in precise nephelometric titrations has been outlined. The effect on the equal-opalescence end-point of thirteen compounds of various types has been studied.

Princeton, New Jersey

THE INFLUENCE OF HIGHER TERMS OF THE DEBYE-HÜCKEL THEORY IN THE CASE OF UNSYMMETRIC VALENCE TYPE ELECTROLYTES[*]

BY VICTOR K. LA MER, T. H. GRONWALL AND LOTTI J. GREIFF[**]

Introduction

I. General

The interionic attraction theory of Debye and Hückel[1] affords a theoretical solution, in the limiting region of high dilutions, of the long-standing problem of the anomalous behaviour of strong electrolytes. However, serious discrepancies between its predictions and the facts, even in these dilutions, for example, the deviations of experimental data from the theoretically predicted curves—in the case of the solubility of difficultly soluble salts in solvent salt solutions,[2 3 4 5] heats of dilution[6] and *activity coefficients from electromotive force measurements*[7]—threaten to necessitate far-reaching revision, if not rejection, of the theory. It was suggested by LaMer[8] that such discrepancies might be due, in large measure, not to the physical assumptions of the theory, but to the incomplete mathematical analysis by Debye and Hückel of their basic differential equation. In this equation the investigators expressed the relationships inherent in their physical assumptions by introducing the Poisson equation into the Boltzmann law of distribution. They expanded the right-hand member of the resulting equation into a series and, for purposes of simplification of the mathematical treatment, retained only the linear term of this series for solution. It is the theoretical predictions resulting from the solution of this simplified equation which are incompatible with the experimental data mentioned above. It is obvious that the mathematical treatment must be completed before criticism of the theory on the basis of experimental data is justified.

Gronwall, LaMer and Sandved[9] realizing that this approximation may involve serious limitations, have given a complete solution of the unabridged equation in the form of a converging infinite series, the first term of which is identical with the solution given by Debye and Hückel. They have completed the numerical evaluation of sufficient terms of this series to make it applicable to electrolytes in which the anion and cation are of the same valence, such as KCl, $MgSO_4$ (symmetric valence types) and they have shown that for such electrolytes it is in far better agreement with experimental results than was the first (or Debye) approximation. As no new physical assumptions of any

---

[*] Contribution No. 659 of the Department of Chemistry and Department of Physics, Columbia University, New York, N. Y. Received January 16, 1931. Presented at the Indianapolis Meeting of the American Chemical Society, April 1931.

[**] This paper is constructed from a dissertation submitted by Lotti June Greiff in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science in Columbia University, December 1930. Grateful acknowledgment is made to the Society of Sigma Xi for a grant which made possible the completion of this work.

kind, such as Bjerrum's ion-association[10] nor additional adjustable parameters, such as the dissociation constant involved in the further assumption of incomplete dissociation have been introduced in this development, the theory assumes added significance.

II. Statement of the Problem of this Investigation.

The greatest deviations from the predictions of the first (Debye) approximation are found where salts of unsymmetric valence type (Na_2SO_4, $BaCl_2$) are involved.[2–7] Since the numerical computations of Gronwall, LaMer and Sandved have been carried out only for the relatively simple case of symmetric valence type salts, the theory may be subjected to the most rigorous test only if the numerical treatment is extended to make it applicable to unsymmetric types also. Other attempts to solve the problem of unsymmetric valence types have already been made by Hans Müller,[11] LaMer[2] and his co-workers and Lange and Meixner.[12] None of these is as general a solution as that applied in this paper. All investigators other than those just mentioned have used only the mathematical first approximation of Debye as sufficient for testing the theory with experiment, that is, they have ignored the effect of the higher terms. As a theoretical development a comparison with the extended theory is obviously of great interest. That it is considered of immediate importance by investigators in the experimental fields involved is apparent from a survey of the very recent literature where several specific references to the non-existence of this development are to be found. Lange and Meixner[12] in their investigation: "Zur Individualität der integralen Verdünnungswärme starker Electrolyte" in the absence of this development, give a graphical solution for heats of dilution only, which is specific for each valence type. Scatchard and Tefft[7] in a report on "Electromotive Force Measurements in Cells containing Zinc Chloride" were obliged to attribute the curvature which they find on plotting $(E_D - E_0)$[a] against $\sqrt{c}$ i.e. the deviation from the Debye approximation, entirely to incomplete dissociation since "the computations which these latter authors (Gronwall, LaMer and Sandved) have promised for unsymmetrical salts are not yet published." Lucasse[13] in an investigation on the electromotive force of cadmium chloride cells and Hansen and Williams[14] in one on the activity coefficients of ions in dilute solutions of ethyl alcohol-water also mention that this development has not yet appeared.

Extension of the numerical evaluation to make the theory applicable to unsymmetric valence types, involves computation of every term in Gronwall's complete analytical solution to as many terms as will make a contribution significant with respect to the accuracy of the experimental data used for comparison. The problem which has been undertaken in this investigation is to determine the influence of the second and third order terms in Gronwall's solution of the Debye equation, and to compare the resulting theoretical de-

---

(a) $E_D = E''_0 - 0.155\sqrt{c}$ where $E'' = E + 0.088725\,[\log m - \log(1 + 0.054m) + 0.01781]$ This is similar to the E'_0 of Lewis and Randall from which it differs only by the third term, i.e. $E_D - E_0 = -0.088725 \log f - 0.155\sqrt{c}$.

velopment with appropriate experimental data involving electrolytes of unsymmetric valence types.(b)

III. Solution of the Poisson-Boltzmann Equation.

The assumptions of the Debye-Hückel theory may be stated as follows:

1. Strong electrolytes are completely dissociated.

2. The closest distance of approach of two ions "a" is the same for all kinds of ions in the solution.

3. For the purpose of calculating the electrostatic potential of an individual ion, the charges on all the other ions may be replaced by a continuous charge distribution which fills the space outside the distance of closest approach, is spherically symmetrical, and of a density determined by Boltzmann's statistical law.

4. This potential satisfies Poisson's equation, in which the dielectric constant of the solution is assumed to be the same as that of the pure solvent.

5. At the distance of closest approach to an individual ion, the potential and field strength are the same as for a point charge equal to the charge of the ion in question and placed at its center.

On the basis of these assumptions Debye and Hückel set up their fundamental differential equation now generally known as the Poisson-Boltzmann equation:(c)

$$\frac{1}{r^2}\,\frac{d}{dr}\left(r^2\frac{d\psi_i}{dr}\right) = -\frac{4\pi\epsilon}{D}\sum_{j=1}^{s}\frac{Nn_jz_j}{V}e^{-\frac{z_j\epsilon\psi_i}{kT}} \qquad (I.-1)^{*(d)}$$

with the boundary conditions,

$$\psi_i \rightarrow 0 \text{ for } r \rightarrow \infty$$

$$\frac{d\,\psi_i}{dr} = -\frac{\epsilon z_i}{D}\cdot\frac{1}{a^2_i} \text{ for } r = a_i \qquad (I.-2)$$

It is this equation for which Gronwall[9] has given a general solution. Expressing it in the form $\frac{d}{dr}\left(r^2\frac{d\psi_i}{dr}\right) - \varkappa^2r^2\psi_i = \varkappa^2r^2\Phi\,(\psi_i)$

$$= \varkappa^2r^2\sum_{\nu=2}^{\infty}\frac{(-1)^{\nu-1}}{\nu!}\left(\frac{\epsilon}{kT}\right)^{\nu-1}q_\nu\psi_i^\nu, \text{ where} \qquad (I.-4)$$

$$\varkappa^2 = \frac{4\pi N\epsilon^2}{kTD}\sum_{j=1}^{s}\frac{n_j\,z_j^2}{V} \quad (I.-5) \quad \text{and } q_\nu = \frac{\sum\limits_{j=1}^{s} n_jz_j^{\nu+1}}{\sum\limits_{j=1}^{s} n_jz_j^2} \qquad (I.-6)$$

(b) Terms of higher order may be of significance. On account of the formidable mathematical difficulties included in their evaluation this investigation has been limited to terms through the third order.

(c) ψ_i = electrostatic potential due to an ion of the i-th kind at a distance r from that ion
ϵ = unit electric charge D = dielectric constant N = Avogadro's number
k = Boltzmann's constant V = vol. of solution which contains n_0 mols of solvent and
T = absolute temperature. n_i mols of ions of the i-th kind.

(d) The notation of the present paper follows that given by Gronwall, LaMer and Sandved[9]

*(I.-1) Refers to Gronwall, LaMer and Sandved[9] equation No. 1.

he transforms it into an integral equation through the introduction of Green's function.[15] Letting $\rho = \kappa r$ and $x_i = \kappa a_i$ Green's function $\zeta(u, \rho)$ for the linear part of equation (I.-4) and boundary conditions (I.-2) is given [in (I.-19)], and the solution of I.-4 obtained by him in the form of a series in descending powers of D, is

$$\psi_i(\rho) = \sum_{m=1}^{\infty} \frac{\epsilon^{2m-1} z_i^m}{(Da_i)^m(-kT)^{m-1}} \psi_m(\rho, x_i) \qquad \text{(I.-23)}$$

Here the function $\psi_m(\rho, x_i)$ are determined by the recurrent formulas

$$\psi_1(\rho, x_i) = \frac{x_i}{1 + x_i} \cdot \frac{e^{x_i - \rho}}{\rho} \qquad \text{(I.-27)}$$

and

$$\psi_m(\rho, x_i) = \int_{x_i}^{\infty} \zeta(u, \rho)\, \Phi_m(u, x_i)\, u^2\, du, \text{ for } m > 1$$

where

$$\Phi_m(\rho, x_i) = \sum \frac{q_\nu}{\nu!} \psi_{m_1}(\rho, x_i)\, \psi_{m_2}(\rho, x_i) \ldots \psi_{m_\nu}(\rho, x_i) \qquad \text{(I.-26)}$$

$$m_1 + m_2 + \ldots + m_\nu = m,$$
$$\nu \geqq 2$$

The first term in the series for $\psi_i(\rho)$ is

$$\frac{\epsilon z_i}{Da_i} \frac{x_i}{1 + x_i} \frac{e^{x_i - \rho}}{\rho}$$

Replacing x_i by κa_i and ρ by κr, this becomes

$$\frac{\epsilon z_i}{D(1 + a\kappa)} \frac{e^{\kappa(a_i - r)}}{r}, \qquad \text{(I.-7)}$$

which is the solution originally given by Debye and Hückel, and designated as the first or Debye approximation.

Introducing successive values of m equal to 2,3,4 . . . into (I.-26) and writing Φ_m for $\Phi_m(\rho, x_i)$ and ψ_m in place of $\psi_m(\rho, x_i)$, Gronwall derives the expressions:

$$\Phi_2 = \tfrac{1}{2} q_2 \psi_1^2$$

$$\Phi_3 = q_2 \psi_1 \psi_2 + \tfrac{1}{6} q_3 \psi_1^3 \qquad \text{(I.-28)}$$

$$\Phi_4 = \tfrac{1}{2} q_2 (\psi_2^2 + 2 \psi_1 \psi_3) + \tfrac{1}{2} q_3 \psi_1^2 \psi_2 + \tfrac{1}{24} q_4 \psi_1^4$$

$$\Phi_5 = q_2 (\psi_1\psi_4 + \psi_2 \psi_3) + \tfrac{1}{2} q_3 (\psi_1^2 \psi_3 + \psi_1 \psi_2^2) + \tfrac{1}{6} q_4 \psi_1^3\psi_2 + \tfrac{1}{120} q_5 \psi_1^5$$

Now, in the symmetrical case, that is where the valences of the ions are equal in pairs, but of opposite sign

$$\nu_1 = \nu_2 \text{ and } z_1 = -z_2;\ \nu_3 = \nu_4 \text{ and } z_3 = -z_4 \ldots$$

$$q_\nu = 0$$

for those terms in which the ν's have the values 2,4,6 . . . [See (I.-6)]. It follows [from (I.-27) and (I.-26)] that $\psi_m(\rho, x_i) = 0$ when m is even, so that only the terms of the series solution (I.-23) with m odd remain in the case of symmetric valence type salts. Gronwall, LaMer and Sandved[9] have carried out the computations necessary for the evaluation of the function for salts of symmetric valence type, through the fifth order terms.

IV. Experimental Functions appropriate for Comparison with the Theory.

An expression for the free energy in terms of the potential of the ions may be obtained by introducing a thermodynamic cycle, the "charging process" of Debye.[16] This yields the general expression for F_e, the total excess free energy arising from electric charges; namely

$$F_e = \sum_{j=1}^{s} Nn_j z_j \sum_{m=1}^{\infty} \frac{\epsilon^{2m} z_j^{m}}{(Da_j)^m(-kT)^{m-1}} \cdot \frac{1}{x_j^{2m}} \int_0^{x_j} x^{2m-1}\psi_m(x,x)dx - \sum_{j=1}^{s} \frac{Nn_j z_j^2 \epsilon^2}{2D_0 a_j} \quad \text{(I.-29)}$$

The activity coefficients of solvent and solute result directly from this expression according to the definitions:

for solvent:[g] $\ln f_{H_2O} = \dfrac{1}{NkT} \dfrac{\partial F_e}{\partial n_0}$

for solute: $(\nu_1 + \nu_2) \ln f_s = \dfrac{1}{NkT} \dfrac{\partial F_e}{\partial n}$

Since, as a function of the activity coefficient of the solvent, f_{H_2O} we have its simple relationship with the osmotic deviation (θ), [h] given by the expression:

$$\theta = \frac{\ln f_{H_2O}}{10^{-3} \dfrac{\partial v}{\partial n_0} c \sum_{j=1}^{s} \nu_j}$$

and as functions of the activity coefficient of the solute, [i], f_s, we have:

1—The electromotive force (E) in accordance with the relationship:

$$E = E_0 - \frac{RT}{NF} \ln c f_s$$

2—solubility of difficultly soluble salts in solvent salt solutions:[j]

$$\ln f_s = \ln \frac{S}{S_0} - \ln f_0$$

an evaluation of the functions $\ln f_{H_2O}$ and $\ln f_s$ makes it possible to compare the theory directly with experimental data. Gronwall, LaMer and Sandved have made the computations necessary to express the theoretical functions (for single salts of symmetrical valence type, through the fifth approximation) as

---

[g] Assuming the solvent to be water. [h] osmotic deviation (Θ) defined as $1 - \dfrac{\Delta t\ obs}{\Delta t\ ideal}$ or the j function of Lewis and Randall. Δt = freezing point lowering.

[i] f_s = activity coefficient of salt.

[j] S_0 = soly. in pure solvent. f_0 = activity at 0 conc. of added salt. S = measured soly. in given solution.

sets of curves in which "a," the closest distance of approach of two ions, is the adjustable parameter. They have compared the curves so drawn with data on (1) freezing point lowerings and (2) electromotive force measurements. They have found that their theoretical curves are in far better agreement with the experimental data than is the first approximation in that they always give positive values of "a" in accord with the physical interpretation i.e. the closest distance of approach of two ions, whereas the Debye approximation often yields impossibly small or even negative values for "a" which vary markedly with the concentration.

Since the integral heat of dilution is a function of the derivative of the free energy with respect to temperature:[12], (k)

$$\frac{nH_{\text{dil.}}}{NkT^2} = \frac{\delta}{\delta T}\left(\frac{F_e}{NkT}\right)$$

experimental measurements of this nature may also be used as a test of the theory. Lange and Meixner[12] have applied the theory to this case, using the potential functions computed by Gronwall, LaMer and Sandved, and have found that the agreement in this case, also, is much better than with the first approximation, in that more plausible "a" values are postulated and the agreement extends over a greater range of concentrations. In addition they find that the order of "ion size" thus obtained for the alkali ions in solution Li < K < Cs and that for the alkaline earth ions Ca < Mg, likewise is the same as that found by Darmois[17] in experiments on the optical rotary power of tartrates through the addition of alkali and alkali earth halides.

B. The Evaluation of Functions for the Potential in the Unsymmetric Case

To determine the contribution of the second and third order terms for comparing the theory with experimental data, the functions Φ_2 and Φ_3 have been evaluated in this investigation. The second order terms had been almost completed in 1926 by Gronwall and LaMer[18] in accordance with the development given in Gronwall's contribution:[19] "Calculation of the second and third order terms in the unsymmetrical case." In this development

$$\psi_2(x,x) = q_2 X_2(x) \text{ where} \qquad (5')\ ^{(l)}$$

$$-X_2(x) = \frac{1}{2}\,\frac{x^2}{(1+x)^3}\,e^{3x}E\,(3x), \text{ and} \qquad (6')$$

since

$$Y_m(x) = \frac{1}{x^{2m}}\int_0^x x^{2m-1}X_m(x)dx \qquad (I.\text{-}74)$$

$$Y_2(x) = \frac{1}{x^4}\int_0^x x^3X_2(x)\,dx, \text{ giving} \qquad (7')$$

$$-Y_2(x) = \frac{f_1(x) + f_2(x)\,e^{3x}\,E(3x)}{2(1+x)^3}, \qquad (8')$$ $f_1(x)$ and $f_2(x)$ being power series

---

(k) $H_{\textit{dil.}}$ = *integral* heat of dilution.

(l) References to equations in[19] will be indicated by primed figures. The starred quantities exist only in the unsymmetrical case for the third approximation.

$$\text{of the form } f_1(x) = \sum_{n=2}^{\infty} a_n x^n \text{ and } f_2(x) = \sum_{n=2}^{\infty} b_n x^n \tag{11'}$$

For the third order term, Gronwall has given

$$\psi_3(x,x) = q_2 \int_x^{\infty} \xi(u,x)\, \psi_1(u,x)\, \psi_2(u,x)\, u^2\, du \tag{14'}$$

This he writes in the form $\psi_3(x,x) = q_2^2 X_3^*(x) + q_3 X_3(x)$, where

$$X_3^*(x) = \frac{1}{q_2} \int_x^{\infty} \xi(u,x)\, \psi_1(u,x)\, \psi_2(u,x) u^2 du; \text{ and} \tag{15'}$$

$$X_3(x) = \frac{1}{6} \int_x^{\infty} \xi(u,x)\, (\psi_2(u,x))^3\, u^2 du \tag{16'}$$

$X_3(x)$ and $Y_3(x)$ have been evaluated in the previous paper.[9]

The solution of (15′) gives:

$$X_3^*(x) = \frac{1}{4} \frac{x^3}{(1+x)^4} \left\{ \frac{x-1}{x+1} \left(e^{3x} E(3x) \right)^2 + 2e^{4x} \int_x^{\infty} \frac{e^{-u} E(3u)}{u}\, du \right\} \tag{17'}$$

The corresponding Y function is:

$$Y_3^*(x) = \frac{1}{6} \int_0^x x^5 X_3^*(x)\, dx \tag{18'}$$

Its solution yields:

$$Y_3^*(x) = \frac{1}{4(1+x)^5} \left\{ f_1(x) + f_2(x) e^{3x} E(3x) + f_3(x) [e^{3x} E(3x)]^2 + f_4(x) \int_x^{\infty} \frac{e^{-u} E(3u)}{u}\, du \right\} \tag{19'}$$

From (17′) (18′) (19′), introducing (I-81) an equation is obtained containing terms with $e^{4x} \int_x^{\infty} \frac{e^{-u} E(3u)}{u}\, du$; $[e^{3x} E(3x)]^2$ and $[e^{3x}\, E(3x)]$ as factors. When terms containing the same of these factors on each side, are equated, four differential equations are obtained, viz:

$$\begin{gathered}
(1+x) \frac{d}{dx} x^6 f_4(x) + (4x-1)\, x^6 f_4(x) = 2x^8 (1+x)^2 \\
(1+x) \frac{d}{dx} x^6 f_3(x) + (6x+1)\, x^6 f_3(x) = x^8 (x^2-1) \\
(1+x) \frac{d}{dx} x^6 f_2(x) + (3x-2)\, x^6 f_2(x) - 2(1+x)\, x^5 f_3(x) - (1+x)\, x^5 f_4(x) = 0 \\
(1+x) \frac{d}{dx} x^6 f_1(x) - 5x^6 f_1(x) - (1+x)\, x^5 f_2(x) = 0
\end{gathered} \tag{21'}$$

These equations are solved by power series of the form

$$f_1(x) = \sum_{n=3}^{\infty} a_n x^n;\ f_2(x) = \sum_{n=3}^{\infty} b_n x^n;\ f_3(x) = \sum_{n=3}^{\infty} c_n x^n;\ f_4(x) = \sum_{n=3}^{\infty} d_n x^n \tag{22'}$$

Equating the coefficients of x^{n+s} when the equations of (22′) are substituted in those of (21′), four equations are obtained:—

$$(n+6)d_n+(n+4)d_{n-1}+4d_{n-2} = \begin{cases} 2, n = 3 \\ 4, n = 4 \\ 2, n = 5 \\ 0, n > 5 \end{cases} \qquad (23')$$

$$(n+6)\ (c_n+c_{n-1}) + 6c_{n-2} = \begin{cases} -1, n = 3 \\ 0, n = 4 \\ 1, n = 5 \\ 0, n > 5 \end{cases} \qquad (24')$$

$$(n+6)b_n+(n+3)b_{n-1}+3b_{n-2}-2(c_n+c_{n-1})-(d_n-d_{n-1})=0 \qquad (25')$$

$$(n+6)a_n+na_{n-1}-(b_n+b_{n-1})=0 \qquad (26')$$

From these equations the d's were evaluated through d_{12}, the c's through c_{14}; the b's through b_{12} and the a's through a_{10}. These were substituted in the respective power series and the series evaluated from values of $x = 0.00$ to $x = 0.40$ in steps of 0.01 and including the value $x = 0.005$.

Values of $X_2(x)$; $Y_2(x)$; $X_3(x)$; $Y_3(x)$; X_3^* (x) and $Y_3^*(x)$(m) now being available, application may be made to the experimental functions; electromotive force measurements, freezing point depressions and solubilities of salts of any valence type in solvent salt solutions

C. Comparison with Experimental Data

I. *Electromotive Force Measurements.*

Since the electromotive force developed between a metal and the solution of one of its salts, is as direct a measure of the electrical potential of the solute as we have, and, in general, electrical measurements are the most precise and trustworthy, experimental data on the electromotive force of reversible cells should offer the most convincing test of this theory.(n)

As has already been pointed out, the relationship between electromotive force and the potential functions of this theory resides in the logarithm of the activity coefficient of the salt.

1. Log f_{salt} by the Theory as extended in this Paper.

$$\text{The definition}^{20}\ (\nu_1 + \nu_2) \ln f_s = \frac{1}{NkT} \frac{\delta F_e}{\delta n}$$

(m) Table I. (n) Researches on E.M.F. recently completed in this laboratory (1) by Dr. Irving Cowperthwaite (In press J. A. C. S., 1931) who studied the activity coefficient of $ZnSO_4$ by means of the cell

$$Zn/Hg(s), ZnSO_4\ (m), PbSO_4,\ Pb$$

and (2) by Dr. Wilbur G. Parks who made a similar study of the cell

$$Cd/Hg(s),\ CdSO_4(m),\ PbSO_4,\ Pb$$

in order to determine activity coefficients of $CdSO_4$, (J. A. C. S. *53*, June 1931) give excellent confirmation of this theory for the symmetric valence type (2,-2).

TABLE I

	$-10^2.X_2(x)$	$-10^2.Y_2(x)$	$10^3.X_3^*(x)$	$10^3.Y_3^*(x)$
0.005	0.004 547	0.000 792	0.000 029	0.000 003
.01	0.014 798	0.002 602	0.000 218	0.000 019
.02	0.045 933	0.008 182	0.001 542	0.000 174
.03	0.086 458	0.015 563	0.004 668	0.000 535
.04	0.133 074	0.024 174	0.010 014	0.001 157
0.05	0.183 723	0.033 653	0.017 804	0.002 076
.06	0.236 991	0.043 747	0.028 134	0.003 305
.07	0.291 854	0.054 267	0.041 005	0.004 847
.08	0.347 550	0.065 072	0.056 352	0.006 705
.09	0.403 498	0.076 050	0.074 064	0.008 873
0.10	0.459 255	0.087 113	0.093 998	0.011 332
.11	0.514 473	0.098 190	0.115 991	0.014 068
.12	0.568 885	0.109 225	0.139 870	0.017 068
.13	0.622 284	0.120 174	0.165 451	0.020 309
.14	0.674 510	0.130 998	0.192 553	0.023 769
0.15	0.725 440	0.141 668	0.220 996	0.027 434
.16	0.774 985	0.152 160	0.250 604	0.031 282
.17	0.823 077	0.162 455	0.281 207	0.035 292
.18	0.869 670	0.172 538	0.312 644	0.039 446
.19	0.914 735	0.182 398	0.344 762	0.043 726
0.20	0.958 256	0.192 025	0.377 417	0.048 114
.21	1.000 228	0.201 412	0.410 474	0.052 594
.22	1.040 655	0.210 555	0.443 808	0.057 148
.23	1.079 547	0.219 451	0.477 304	0.061 763
.24	1.116 922	0.228 097	0.510 853	0.066 424
0.25	1.152 803	0.236 495	0.544 358	0.071 118
.26	1.187 213	0.244 644	0.577 730	0.075 833
.27	1.220 184	0.252 545	0.610 886	0.080 555
.28	1.251 745	0.260 200	0.643 753	0.085 276
.29	1.281 931	0.267 613	0.676 264	0.089 987
0.30	1.310 775	0.274 786	0.708 359	0.094 678
.31	1.338 312	0.281 723	0.739 985	0.099 338
.32	1.364 579	0.288 428	0.771 095	0.103 963
.33	1.389 613	0.294 904	0.801 646	0.108 544
.34	1.413 449	0.301 156	0.831 602	0.113 075
0.35	1.436 124	0.307 189	0.860 931	0.117 551
.36	1.457 674	0.313 007	0.889 606	0.121 966
.37	1.478 136	0.318 615	0.917 604	0.126 316
.38	1.497 543	0.324 018	0.944 904	0.130 598
.39	1.515 932	0.329 221	0.971 492	0.134 806
0.40	1.533 337	0.334 228	0.997 354	0.138 939

in accordance with equation (I-34), and the assumptions, valid for dilute solutions, that $D = D_0$ and that $10^{-3}c \dfrac{\partial V}{\partial n}$ is negligible, takes the form:

$$(\nu_1+\nu_2)\ln f_s = -\sum_{j=1}^{2}\nu_j z_j \sum_{m=1}^{\infty}\left(\frac{\epsilon^2 z_j}{-kTDa_j}\right)^{m}\cdot\left[\tfrac{1}{2}\psi_m(x_j,x_j) - \frac{m-1}{x_j^{\,2m}}\int_0^{x_j} x^{2m-1}\psi_m(x,x)\,dx\right]$$

$$-\sum_{j=1}^{2}\frac{\nu_j\epsilon^2 z_j^2}{2kTDa_j};\qquad (1)$$

Assuming that $a_1 = a_2 = a$ whence $x_1 = x_2 = x$ and noting that $\nu_1 = -z_2$; $\nu_2 = z_1$ for a single salt composed of two kinds of ions, it follows that:

$$-\ln f_s = -z_1z_2\left\{\frac{1}{10^8a}\,B_1(x) + \frac{1}{(10^8a)^2}\,(z_1+z_2)^2B_2(x) - \frac{1}{(10^8a)^3}\,\left(z_1^2+z_1z_2+z_2^2\right)\right.$$

$$\left.\left(z_1+z_2\right)^2B_3^*(x) - \frac{1}{(10^8a)^3}\left(z_1^2+z_1z_2+z_2^2\right)^2B_3(x)\right\}\qquad (2)$$

where $B_1(x) = \dfrac{10^8\epsilon^2}{kTD}\,\dfrac{1}{2}\,\dfrac{x}{1+x}$

$$B_2(x) = \left(\frac{10^8\epsilon^2}{kTD}\right)^2\left[\tfrac{1}{2}X_2(x) - Y_2(x)\right]$$

$$B_3^*(x) = \left(\frac{10^8\epsilon^2}{kTD}\right)^3\left[\tfrac{1}{2}X_3^*(x) - 2Y_3^*(x)\right]$$

$$B_3(x) = \left(\frac{10^8\epsilon^2}{kTD}\right)^3\left[\tfrac{1}{2}X_3(x) - 2Y_3(x)\right]$$

This function may be evaluated for arbitrarily chosen values of x ($=\kappa a$) making use of the constants given by Gronwall, LaMer and Sandved[9] (q)(r) for a given temperature (25°C. in this paper) together with the functions $[\tfrac{1}{2}X_3(x) - 2Y_3(x)]$ tabulated in the former paper and $[\tfrac{1}{2}X_2(x) - Y_2(x)]$ and $[\tfrac{1}{2}X_3^*(x) - 2Y_3^*(x)]$ given in Table II.

(q) This has been done for the sake of uniformity in the absence of an accepted value for the dielectric constant of water. Wyman's[33] more reliable values have appeared since most of the calculations in this paper were completed. These newer values compared to those of Drude are:

	Drude	*Wyman*
0°C.	88.23	88.00
25°C.	78.77	78.54

i.e. the Wyman values are less than those of Drude by c0.25%. Since this difference is so slight, recalculation was considered unnecessary.

(r) The Drude equation for D: should read $D = 88.23 - 0.4044t + 0.0010035t^2$ instead of $+0.00135t^2$ as given in I. page 388.

TABLE II

	$10^2[\frac{1}{2}X_2 - Y_2]$	$10^3[\frac{1}{3}X_3^* - 2Y_3^*]$	$10^2[\frac{1}{2}X_2 - 2Y_2]$	$10^3[\frac{1}{3}X_3 - 3Y_3]$	$10^3[\frac{1}{3}X_3^* - 3Y_3^*]$
0.000	0.000 000	0.000 000	0.000 00	0.000 00	0.000 00
.005	−0.001 482	0.000 009	−0.000 69	−0.000 45	0.000 01
.01	0.004 797	0.000 071	0.002 20	0.001 70	0.000 05
.02	0.014 784	0.000 423	0.006 60	0.005 88	0.000 25
.03	0.027 666	0.001 264	0.012 10	0.011 63	0.000 73
.04	0.042 363	0.002 693	0.018 19	0.018 32	0.001 54
0.05	0.058 209	0.004 750	0.024 56	0.025 57	0.002 67
.06	0.074 748	0.007 457	0.031 00	0.033 03	0.004 15
.07	0.091 660	0.010 809	0.037 39	0.040 53	0.005 96
.08	0.108 703	0.014 766	0.043 63	0.047 87	0.008 06
.09	0.125 699	0.019 291	0.049 65	0.054 92	0.010 42
0.10	0.142 514	0.024 335	0.055 40	0.061 64	0.013 00
.11	0.159 05	0.029 86	0.060 86	0.067 92	0.015 79
.12	0.175 22	0.035 80	0.065 99	0.073 69	0.018 73
.13	0.190 97	0.042 11	0.070 79	0.079 00	0.021 80
.14	0.206 26	0.048 74	0.075 26	0.083 78	0.024 97
0.15	0.221 05	0.055 63	0.079 38	0.088 05	0.028 20
.16	0.235 33	0.062 74	0.083 17	0.091 82	0.031 46
.17	0.249 08	0.070 02	0.086 63	0.095 09	0.034 73
.18	0.262 30	0.077 43	0.089 76	0.097 86	0.037 98
.19	0.274 97	0.084 93	0.092 57	0.100 14	0.041 20
0.20	0.287 10	0.092 48	0.095 08	0.101 97	0.044 37
.21	0.298 70	0.100 05	0.097 29	0.103 37	0.047 46
.22	0.309 77	0.107 61	0.099 22	0.104 33	0.050 46
.23	0.320 32	0.115 13	0.100 87	0.104 90	0.053 36
.24	0.330 36	0.122 58	0.102 27	0.105 12	0.056 16
0.25	0.339 91	0.129 94	0.103 41	0.104 98	0.058 83
.26	0.348 96	0.137 20	0.104 32	0.104 51	0.061 37
.27	0.357 55	0.144 33	0.105 00	0.103 74	0.063 78
.28	0.365 67	0.151 32	0.105 47	0.102 68	0.066 05
.29	0.373 35	0.158 16	0.105 74	0.101 36	0.068 17
0.30	0.380 60	0.164 82	0.105 82	0.099 80	0.070 15
.31	0.387 43	0.171 32	0.105 71	0.098 00	0.071 98
.32	0.393 86	0.177 62	0.105 43	0.096 00	0.073 66
.33	0.399 90	0.183 74	0.105 00	0.093 82	0.075 19
.34	0.405 57	0.189 65	0.104 41	0.091 46	0.076 58
0.35	0.410 87	0.195 36	0.103 68	0.088 93	0.077 81
.36	0.415 83	0.200 87	0.102 82	0.086 26	0.078 91
.37	0.420 45	0.206 17	0.101 84	0.083 47	0.079 85
.38	0.424 75	0.211 26	0.100 74	0.080 55	0.080 66
.39	0.428 75	0.216 13	0.099 52	0.077 53	0.081 33
0.40	0.432 44	0.220 80	0.098 21	0.074 45	0.081 86

Introducing numerical values for the constants and converting to Briggsian logarithms, there is obtained

$$\begin{aligned}\frac{-\log f_s}{(-z_1z_2)} = {} & 1.53636\cdot\frac{1}{10^8a}\cdot\frac{x}{1+x} + 0.21740\cdot\frac{1}{(10^8a)^2}\cdot(z_1+z_2)^2\left[\tfrac{1}{2}X_2(x)-Y_2(x)\right] \\ & -0.15382\,\frac{1}{(10^8a)^3}\cdot(z_1^2+z_1z_2+z_2^2)\,(z_1+z_2)^2\left[\tfrac{1}{2}X_3^*(x)-2Y_3^*(x)\right] \qquad (3) \\ & -0.15382\,\frac{1}{(10^8a)^3}\cdot(z_1^2+z_1z_2+z_2^2)^2\cdot\left[\tfrac{1}{2}X_3(x)-2Y_3(x)\right]\end{aligned}$$

the form suitable for direct evaluation.

As can be readily seen from the equation, for a given valence type, for each value of "a" there will be a set of points obtained by introducing different values of x into the expression. Taking $x = 0.00$ to $x = 0.40$ in steps of 0.01 and including $x = 0.005$ for "a" = 2, 3 and 4Å, series of points were obtained which could be plotted as families of curves. This was done for valence types 1:2, 1:3, 1:4 and 2:3.

The curves plotted were $\dfrac{-\log f}{(-z_1z_2)10^{-8}\kappa}$ against $10^{-8}\kappa$ as the independent variable. Since κ is independent of "a" and is directly proportional to the square root of the concentration, it was used as the independent variable. Reference to the functions X_2, Y_2, X_3, Y_3, X_3^*, Y_3^* shows that if each is divided by x, there still remains a function with x as a factor in the numerator, and not in the denominator. Now, if equation (3) is divided by $10^{-8}\kappa$ there results:

$$\frac{-\log f_s}{10^{-8}\kappa(-z_1z_2)} = 1.53636\frac{1}{a\kappa}\cdot\frac{x}{1+x}+0.21740\frac{1}{10^8a.a\kappa}(z_1+z_2)^2\left[\tfrac{1}{2}X_2(x)-Y_2(x)\right]-\cdot\cdot \qquad (4)$$

Since $a\cdot\kappa = x$, this becomes:

$$\begin{aligned}\frac{-\log f_s}{10^{-8}\kappa(-z_1z_2)} = {} & 1.53636\,\frac{1}{1+x}+0.21740\,\frac{1}{10^8a}(z_1+z_2)^2\,\frac{\left[\frac{1}{2}X_2(x)-Y_2(x)\right]}{x} \\ & -0.15382\,\frac{1}{(10^8a)^2}(z_1^2+z_1z_2+z_2^2)(z_1+z_2)^2\,\frac{\left[\frac{1}{2}X_3^*(x)-2Y_3^*(x)\right]}{x} \qquad (5) \\ & -0.15382\,\frac{1}{(10^8a)^2}(z_1^2+z_1z_2+z_2^2)^2\cdot\frac{\left[\frac{1}{2}X_3(x)-2Y_3(x)\right]}{x}\end{aligned}$$

so that

$$\lim_{\kappa=0}\frac{-\log f_s}{(-z_1z_2)10^{-8}\kappa} = 1.53636\,\frac{1}{1+x} = 1.53636 \qquad (6)$$

This, then, is the limiting value of $\dfrac{-\log f_s}{(-z_1z_2)10^{-8}\kappa}$ at zero concentration for the extended series as well as for the first approximation, and is also the constant value for the limiting law.(1) As this function, so plotted, gives a series of curves all having the same origin, and, therefore, most convenient for comparison with each other and with data, it has been selected for this purpose.

---

(1) according to the limiting law $\Psi_i = \dfrac{-\epsilon z_i}{D}\kappa$ and $-\log f_i = \dfrac{z_i\epsilon^2}{2DkT}\cdot\kappa$

i.e. $\dfrac{-\log_{10}f_s}{(-z_1z_2)10^{-8}\kappa} = \dfrac{1}{2}\,\dfrac{\epsilon^2}{DkT} = 1.53636$

That the inflections noticed in the region of very small concentrations might be definitely determined for values of "a" larger than 3Å, in particular, the original potential functions (6′) (8′-each factor) (17′) (19′-each factor)

and also
$$\left\{X_3(x) = \tfrac{1}{6}\frac{x^2}{(1+x)^4}\left[1-4xe^{4x}\,E(4x)\right]\right\} \text{ and}$$

$$\left\{Y_3(x) = \frac{f_1(x)-e^{4x}\,E(4x)f_2(x)}{6\cdot(1+x)^4}, \text{ each factor}\right\}$$

were divided by x, for the values of $x = 0.005$ and $x = 0.01$. In this way the accuracy of the function for these points was increased (200 times in the first instance, and 100 times in the second). The function $\dfrac{-\log f}{(-z_1z_2)10^{-8}\kappa}$ was then computed from the values obtained, using equation (5) of this paper.

The graph of this function (Fig. 1 (a) (b) (c) (d)) shows the Debye limiting law represented by a horizontal line which has the same value for $\kappa = 0$ as each of the other curves. All other points on the curves for the Debye first approximation lie below this line, whereas the curves including the third approximation show maxima above the limiting law line at low concentrations and cross this line at higher concentrations. Inspection of Fig. (1 (a) – (d)) makes it obvious that the smaller the value of "a" and the greater the dissymmetry of the valence type, the higher is the maximum. For the 1, −2 valence type the 4Å curve for the extended approximation is very close to that for the first approximation. For "a" greater than 4Å in the case of 1, −2 salts and "a" greater than 6Å for 1, −3 salts, the first and the extended approximation are so nearly alike that the first approximation is sufficient for making comparison with data.

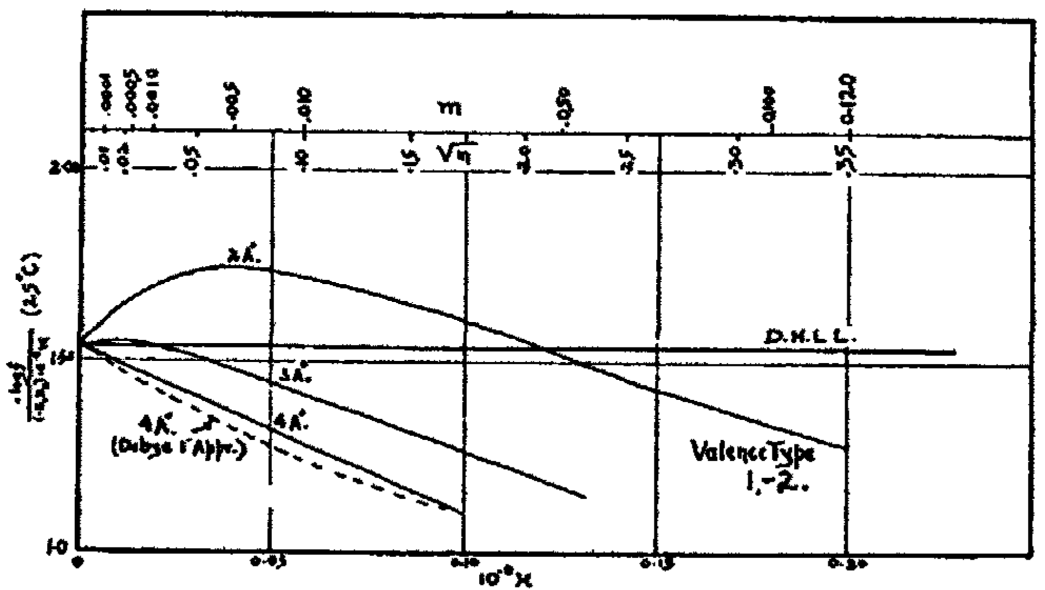


FIG. 1(a)

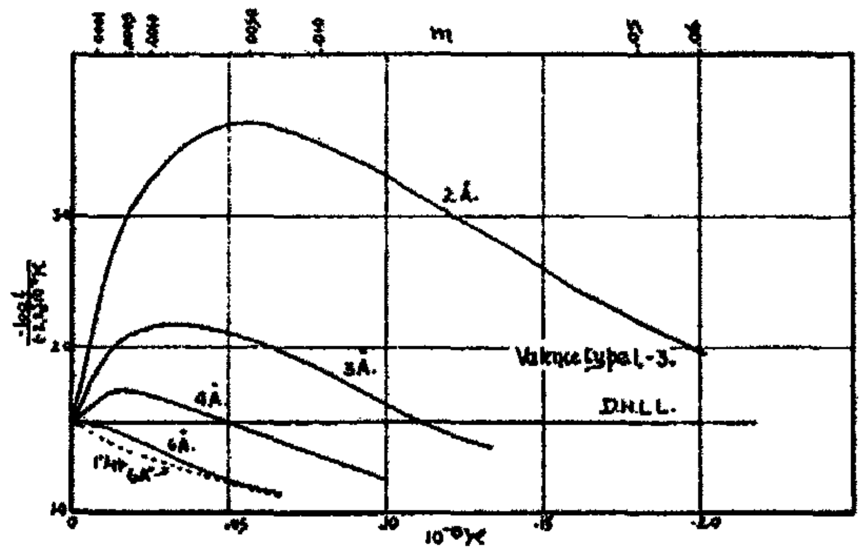


Fig. 1(b)

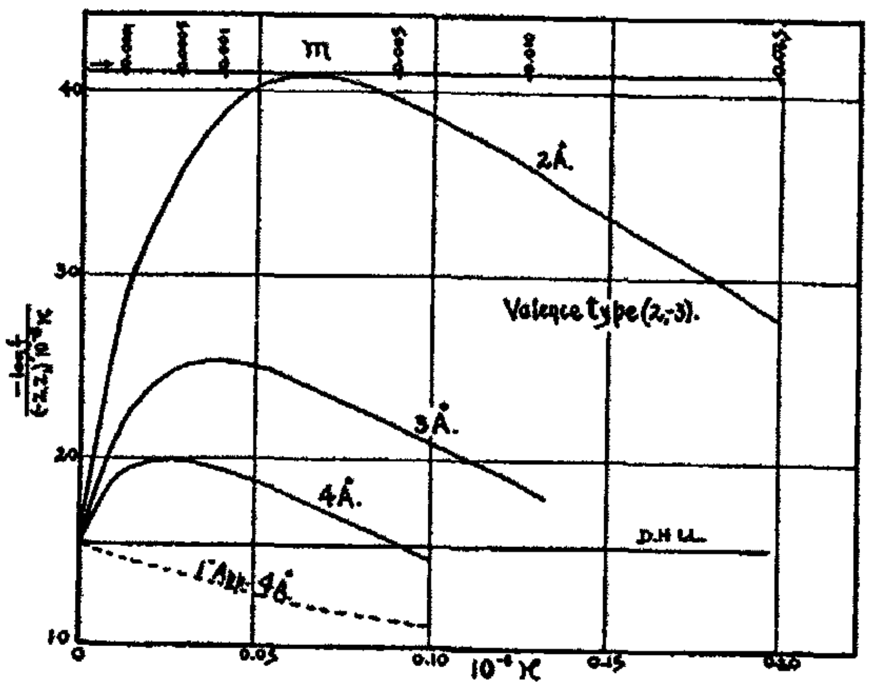


Fig. 1(c)

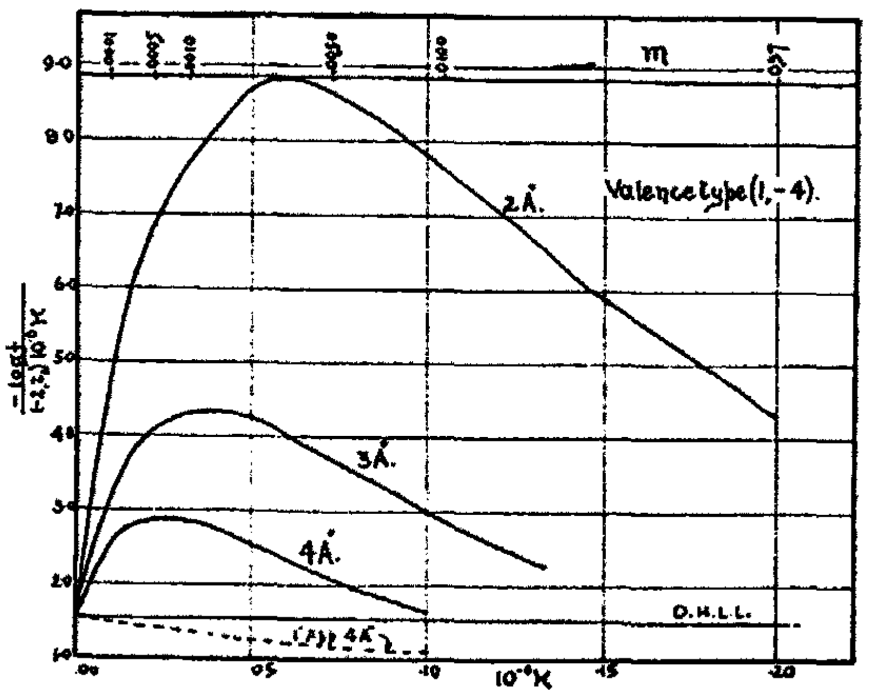


Fig. 1(d)
Theoretical Curves for Unsymmetric Salts 1°-3° Approximations

For comparison of the theory with experiment additional computations were made for intermediate values of "a" varying by 0.2Å from 2Å through 4Å including 2.5Å, 1.8, 1.5 and 1.0Å for valence type 1, −2 and 2.5, 4.5, 5 and 6Å for valence type 1, −3. A typical set of these curves is represented in Fig. (2) reduced to about 1/20 the size actually used.

2. Logf_{salt} by Experiment.

The experimentally determined quantity is the E.M.F. developed in a reversible cell, one member of which contains a known concentration of the solute salt in contact with its metallic element. These E.M.F.'s are expressible in terms of the activity of the ions of the solute salt (a standard reference state having been assumed) in accordance with the relationship:

$$E = E_0 - \frac{RT}{NF} \ln a_1^{\nu_1} a_2^{\nu_2} \text{ which becomes}$$

$$E = E_0 - \frac{RT}{NF} \ln(\nu_1 m)^{\nu_1} f_1^{\nu_1} (\nu_2 m)^{\nu_2} f_2^{\nu_2} \tag{7}$$

where m = the concentration of salt,(w) f_i = activity coefficient of the ion of activity a_i and $a_i = m\nu_i f_i$. Since, by definition $\ln(f_1^{\nu_1} f_2^{\nu_2})^{\frac{1}{\nu_1+\nu_2}} = \ln f_s$, converting to decadic logarithms and using R = 1.9885 cals./degree, T = 298.1(25°C) F = 23074 cals./volt equiv. = 96494 coulombs/gm. equiv. = 1 Faraday,[20] this becomes (for a(2,-1) salt like $PbCl_2$ or $ZnCl_2$).

$$E(\text{mv.}) + 88.725(0.2007 + \log m) = E_0(\text{mv.}) - 88.725 \log f_s = E'_0(\text{mv.}) \tag{8}$$

By plotting values of E'_0 for each value of (m), as ordinates vs. $\sqrt{m}$ as abscissae and extrapolating to zero concentration, a value for E_0 is obtained. The extrapolation of this curve to zero concentration is usually attended with considerable uncertainty since the lower values on the curve do not lie on a straight line. This difficulty has been variously treated by different investigators, as will be discussed in connection with each set of data. If this E_0 value is now introduced into equation (8) for each value of (m) a value of $\log f_s$ can be computed.

From 1-5 and the constants given by Gronwall, LaMer and Sandved(y) at 25°C.:

For 1:2 salt, $10^{-8}\kappa = 0.5686\sqrt{m}$

For 1:3 salt, $10^{-8}\kappa = 0.8041\sqrt{m}$

An experimentally determined $\dfrac{-\log f}{(-z_1z_2)10^{-8}\kappa}$

may therefore be found for each experimental concentration. By interpolation on the working curves a value of a[3](z) has been found. Values of a[1](aa)

(w) m here is molality; molarity is involved in the theory. The correction in conversion from the former to the latter for the highly dilute solutions considered here, is so slight as to be of no significance.

(y) See footnotes (q) and (r).

(z) a[3] = distance of closest approach of two ions as postulated by the theory extended through the third order terms, evaluated in this paper.

(aa) Debye or first approximation.

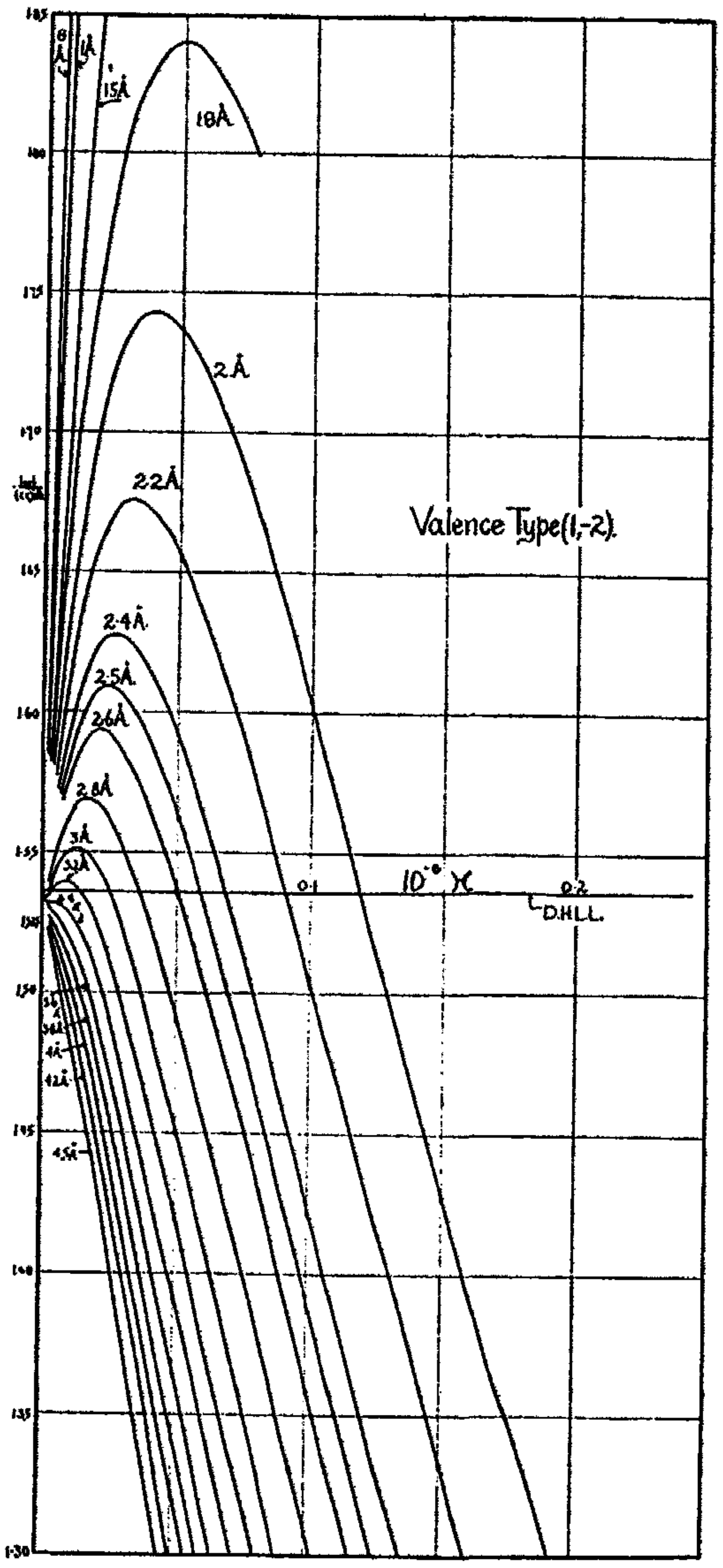


FIG. 2

$\frac{-\log f}{(-z_1 z_2)\, 10^{-8}\kappa}$ vs. $10^{-8}\kappa$

for these same points have been computed in accordance with the relationship:

$$-\log f = \frac{1.53636\ (-z_1z_2)\kappa}{1 + a_1\kappa}$$

$$a[1] = \frac{1.53636\ (-z_1z_2)\kappa + \log f}{\kappa \log f}$$

Then, on the assumption of a constant value for a[3], there has been read from the theoretical curves the corresponding value of the activity coefficient function for each concentration. By reversal of the calculation outlined a theoretical E_0 for each concentration has been determined. Various trials with different values for a[3] revealed one value which gives a most constant E_0. This is considered the most probable a[3] and the corresponding value of E_0 so obtained is designated throughout as $E_{0[3]}$.

3. Comparison of Experimental Log f_s with Theoretical Log f_s.

The cell Zn/Hg (2 phase), $ZnCl_2$(m), AgCl, Ag has been studied by Scatchard and Tefft.[7] Hydrolysis was eliminated by saturating the zinc chloride solution with zinc oxide, and correction, which never exceeded 0.1 mv., even for the most concentrated solutions, was made for this added component. The investigators arrive at their value of E_0 by means of a graphical extrapolation and the introduction of an added parameter, incomplete dissociation, to indicate the course of the curve [$(E_D$-$E_0)$ vs. $\sqrt{c}$] in the region of high dilution.(ad)

Values for E_0 obtained by various methods are considered in the present investigation:

$E_{0[i]}$ – The value given by the investigator

$E_{0[1]}$ – Calculation from Debye first approximation
(only concentration to 0.01M employed)(ae)

$E_{0[3]}$ – Calculation from extended theory as explained above
(experimental data as for $E_{0[1]}$)

Extrapolation of E'_0 given in Table III, col. 4, admits of interpretation through limits wider than the extreme differences between the values $E_{0[1]}$ $E_{0[3]}$ and $E_{0[i]}$.

This investigation was chosen first for comparison as the "a" value is large, therefore not much difference would be expected between the agreement with the first approximation and with the development in this paper.

(ad) The factor which Scatchard and Tefft include, [$-\log(1 + 0.054m)$] to relate the measurements to Raoult's law has not been included here, since the fundamental theoretical development is on the basis of molarity, and conversion to other concentration units in the dilutions involved, is so slight as to be without significance.

(ae) a: It has been shown by Gronwall, LaMer and Sandved[9]: that agreement between the *theory and experiment, in the symmetrical cases,* does not extend much beyond m = 0.01.

b: Fowler:[21] states with respect to the importance of the "fluctuation" in Poisson's equation in this theory "the condition of smallness may be taken to be satisfied for solution 1/100 normal or less."

TABLE III

$ZnCl_2$ Scatchard and Tefft[7]

(a)

	$\frac{\text{mols}}{1000 \text{ gms. } H_2O}$	E obs. mv.	$10^{-8}\kappa$. $0.568\ 59\sqrt{m}$	E_0'
1.	0.002 941	1 198.3	0.030 83	991.5
2.	0.007 814	1 165.02	0.050 26	995.88
3.	0.012 36	1 149.51	0.063 21	998.03
4.	0.021 44	1 131.01	0.083 25	1 000.76

(b)

	$E_{0[1]} = 983.93$		$E_{0[i]} = 983.4$		$E_{0[3]} = 983.71$	
	a[1]	a[3]	a[1]	a[3]	a[1]	a[3]
1.	3.46Å	4.4Å	1.24Å	3.32Å	2.55Å	3.89Å
2.	2.91	3.81	1.97	3.38	2.52	3.62
3.	3.52	4.01	2.83	3.63	3.19	3.87

(c)

	a[3] = 3.4Å mv.	a[3] = 3.8Å mv.	a[3] = 4.2Å mv.
1.	983.28+0.12	983.71−0.11	984.12−0.32
2.	983.28+0.17	983.71+0.19	984.12+0.20
3.	983.28−0.28	983.71−0.07	984.12+0.12
		983.71−0.65	

	a[1] = 2.9Å mv.	a[1] = 3.3Å mv.	a[1] = 3.7Å mv.
1.	983.73+0.07	983.93−0.03	984.13−0.13
2.	983.73+0.19	983.93+0.19	984.13+0.20
3.	983.73−0.26	983.93−0.16	984.13−0.06
		983.93−0.98	

(e)

	$\frac{-\log f}{(-z_1z_2)10^{-8}\kappa}$ Theoretical (a[3] = 3.8Å)	Experimental (E_0 = 983.7)
1.	1.433 0	1.433 9
2.	1.343 0	1.363 9
3.	1.283 0	1.276 7

That the $E_{0[3]}$ value is in somewhat better agreement than is the $E_{0[1]}$ in that the deviations of the first three values from the mean are more nearly alike, and the deviation of the value computed for the fourth point is considerably less in the case of $E_{0[3]}$, is apparent. Scatchard and Tefft[7] show wide divergence of these first four points from the value calculated by the Debye-Hückel equation for varying dielectric constant. The first three of these points deviate less than 0.2 mv. from the value computed by use of the extended theory. Although the fourth concentration is too great for this theory (assuming $D = D_0$; $a_1 = a_2 = a$ etc.) to be applicable, the divergence from the computed $E_{0[3]}$ is reasonably small. Examination of Table III, (b), reveals that the a[3] values based on $E_{0[3]}$ show greater uniformity than the "a" values computed in any way.

That they show greater uniformity than the a[1]s computed on the basis of the $E_{0[1]}$ indicates that these points are in better agreement with the theory extended through the third approximation than with the less exact first approximation.

In his study of the cell Zn(s), $ZnCl_2$(m), AgCl(s), Ag(s) in concentration below 0.001 M Horsch[22] claims a precision of 2 mv. The data are therefore hardly of sufficient accuracy for distinguishing definitely between the different theories. However, if we apply the value of a[3] equals 3.8Å(af) as derived from Scatchard and Tefft's data and introduce the small correction of 0.6 mv.(ag) due to the dilution of the zinc by the mercury, to their data, we get $E_{0[3]} = 984.3$ mv. This value differs from that obtained by Horsch—by graphical methods employing a most probable extrapolation—984.5 mv. by but 0.2 mv. (Table IV)

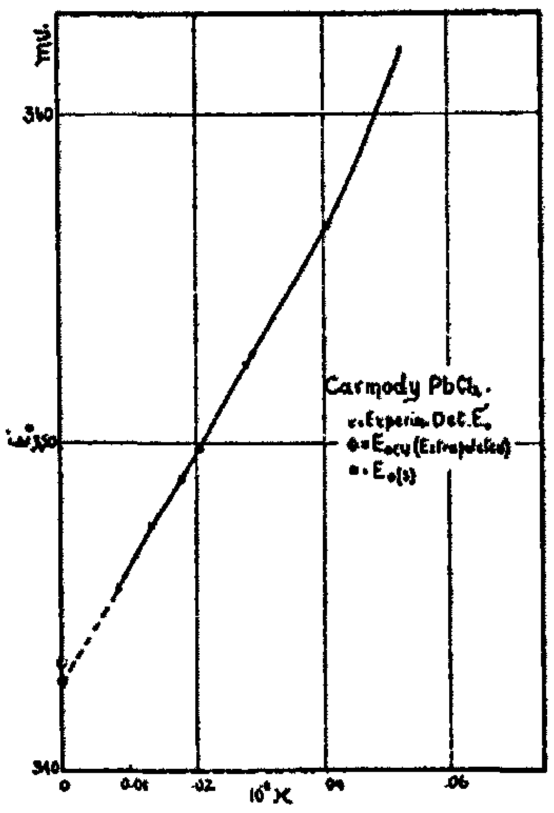


Fig. 3

Carmody[24] has made a careful study of the Pb/Hg, $PbCl_2$(m), AgCl, Ag cell. His results are particularly valuable for testing the theory since they consist of a series of eight values extending over a fifty-fold range of concentrations. The effects of the hydrolysis of the lead chloride and the solubility of silver chloride are negligible except in the most dilute solution, where they are small and of opposite sign.[24] A duplication of experimental data to 0.1 mv. is claimed. By a graphical extrapolation an E_0 of 342.6 mv. is obtained. However, as Table V shows an a[3] of 1.75Å gives an $E_{0[3]}$ of (343.2 ± 0.09) with a maximum deviation of 0.25 mv. This value differs from the graphically extrapolated value 342.6 mv. by 0.6 mv. This difference seems to be very slightly more than could be accounted for by individual interpretations in extrapolation. (Fig. 3) Since the a[1] values are all negative, an $E_{0[1]}$ is without significance. The rather small a[3] (1.75Å) may be due to the fact that lead chloride is only slightly soluble and might be expected to have a small distance of approach between two ions, the attraction between the water molecule and the ions of the salt being slight. In addition,

---

(af) Table III (c) (ag) Correction given by Cohen[23] for the potential of a Zn/Hg (1:9) amalgam vs. Zn. and employed by Scatchard.[7]

TABLE IV

ZnCl$_2$ Horsch[22]

a[3] = 3.8Å making $E_{0[3]}$ = 984.3 mv.(ah)

m	$E_{obs.}$ (mv.)	$E_{calc.}$ (mv.)	$E_{obs.}$-$E_{calc.}$ mv.
0.000 347 8	1 270.1	1 276.3	−6.2
0.000 399 5	1 269.9	1 271.1	−1.2
0.000 649	1 249.7	1 253.2	−3.5
0.000 772	1 247.5	1 246.8	+0.7
0.001 253	1 228.9	1 229.3	−0.4
0.001 453	1 221.9	1 223.9	−2.0
0.003 112	1 195.3	1 197.0	−1.7
0.006 022	1 174.2	1 174.2	±0.0
0.010 21	1 155.8	1 156.5	−0.7
			9)16.4
			1.8 mv. = a.d.

(ah) Values derived from Scatchard and Tefft's data.

the effect of further approximation on small a[3] values (less than 2Å) is probably significant, and, we think, by analogy with the symmetrical case where the influence of higher approximations is known, would yield larger "a" values, in low concentration, for the same experimental points.

Although the limit of accuracy of the further data of Horsch,[22] given in Table VI on the cell Cd/Hg, CdCl$_2$(m), AgCl, Ag, is large, 1 mv., for the least accurate portion of the data in the lowest concentration—so that the computation of a reliable a[3] value is somewhat uncertain—examination of these data in the light of this theory has been undertaken.

By graphical extrapolation of the E'_0 vs. $\sqrt{m}$. values for this cell we get E_0 = 579.0 mv. whereas Horsch arrives at a value $E_{0\,[i]}$ = 625.5 mv. through his interpretation of the graph which he has drawn E_0 vs. log c on the basis of incomplete dissociation. This value which he uses happens to be the algebraic average of his separate values, the average deviation from this mean being 1.55 mv. The difference between the $E_{0\,[3]}$ (623.0 mv.), calculated on the basis of the interionic attraction theory, with no further assumptions, and the $E_{0\,[i]}$ (625.5 mv.) is not great in the light of the accuracy of the measurements. Our value is slightly more consistent (a.d. = 1.48) than that obtained by Horsch on the basis of incomplete dissociation. The assumption that cadmium chloride is completely dissociated, at least in the concentrations under investigation, seems justified from the results of the calculations made here as well as from the figures used by Horsch to represent the degree of dissociation of cadmium chloride (0.888 for a 0.001 M solution) compared with that of zinc chloride (0.930 for a 0.001 M solution). The difference between these figures could hardly represent the difference between a "strong electrolyte" and a "weak electrolyte."

TABLE V

$PbCl_2$ Carmody[24]

(a)

	$\frac{\text{mols}}{1000 \text{ gms. } H_2O}$	E mv.	10^{-8} κ	E_0' mv.	$E_{0[1]}$ = 342.6 a[1] Å	$E_{0[1]}$ = 342.6 a[3] Å	$E_{0[3]}$ = 343.2 a[1] Å	$E_{0[3]}$ = 343.2 a[3] Å
1.	0.000 211 6	653.7	0.008 27	345.5	−26.41	ᶜ0.50	−1.46	2.85
2.	0.000 619 7	614.3	0.014 15	347.5	−14.87	1.20	−7.02	1.82
3.	0.001 034	596.0	0.018 29	348.9	−11.52	1.35	−6.96	1.73
4.	0.001 337	587.0	0.020 79	349.8	−10.30	1.40	−6.84	1.63
5.	0.002 348	567.7	0.027 55	352.2	− 7.94	1.48	−6.04	1.60
6.	0.002 620	563.9	0.029 11	352.6	− 7.17	1.50	−5.46	1.68
7.	0.005 160	541.9	0.040 84	356.7	− 5.23	1.51	−4.37	1.74
8.	0.010 39	520.5	0.057 96	362.3	− 3.43	1.68	−2.99	1.76

(b)

	a[3] = 2Å mv.		$E_{0[3]}$ a[3] = 1.75Å mv.		a[3] = 1.5A mv.	
1.	343.7	−0.6	343.25	−0.25	342.7	+0.3
2.	343.7	−0.4	343.25	−0.05	342.7	+0.3
3.	343.7	−0.3	343.25	−0.05	342.7	+0.2
4.	343.7	−0.2	343.25	+0.05	342.7	+0.2
5.	343.7	−0.1	343.25	+0.15	342.7	+0.1
6.	343.7	±0.0	343.25	+0.05	342.7	−0.1
7.	343.7	+0.4	343.25	+0.05	342.7	−0.6
8.	343.7	+0.9	343.25	+0.05	342.7	−1.6
		av.	343.25	±0.09		

(c)

$$\frac{-\log f}{(-z_1z_2)10^{-8}\kappa}$$

	Theoretical (a[3] = 1.75Å)	Experimental (E_0 = 343.2)
1.	1.663 5	1.555 0
2.	1.722 0	1.706 7
3.	1.752 0	1.760 5
4.	1.766 5	1.791 7
5.	1.805 8	1.843 9
6.	1.809 0	1.827 6
7.	1.854 3	1.870 7
8.	1.851 3	1.859 0

TABLE VI

$CdCl_2$ Horsch[22]

(a)

	$\frac{\text{mols.}}{1000 \text{ gms. } H_2O}$	(al) $E = E_{obs} + 53.4$mv mv.	$10^{-8}\kappa$	E_0' mv.
1.	0.000 102 9	959.4	0.005 77	605.6
2.	0.000 108 7	955.7	0.005 93	604.0
3.	0.000 113 7	954.5	0.006 06	604.5
4.	0.000 126 9	951.2	0.006 41	605.5
5.	0.000 152 7	946.0	0.007 03	607.4
6.	0.000 214 4	933.7	0.008 33	608.2
7.	0.000 336 3	917.8	0.010 43	609.6
8.	0.000 365 9	914.8	0.010 88	609.9
9.	0.000 479	905.	0.012 44	610.5
10.	0.000 924	883.0	0.017 28	613.8
11.	0.002 581	849.1	0.028 89	619.5
12.	0.003 519	839.8	0.033 73	622.1
13.	0.007 400	816.45	0.048 91	627.4

(b)

$E_{0[3]}$

	a[3] = 1.5Å mv.		a[3] = 1.0Å mv.		a[3] = 0.8Å mv.	
1.	624.4	−2.7	623.0	−1.4	622.1	−0.6
2.	624.4	−4.3	623.0	−3.0	622.1	−2.2
3.	624.4	−3.8	623.0	−2.5	622.1	−1.7
4.	624.4	−3.0	623.0	−1.7	622.1	−0.9
5.	624.4	−1.3	623.0	±0.0	622.1	+0.8
6.	624.4	−0.9	623.0	+0.3	622.1	+1.0
7.	624.4	−0.2	623.0	+0.9	622.1	+1.5
8.	624.4	−0.1	623.0	+1.0	622.1	+1.6
9.	624.4	±0.0	623.0	+0.9	622.1	+1.4
10.	624.4	+1.6	623.0	+2.1	622.1	+2.3
11.	624.4	+2.9	623.0	+2.1	622.1	+1.1
12.	624.4	+3.7	623.0	+2.1	622.1	+0.7
13.	624.4	+8.6	623.0	−1.3	622.1	−5.2
			a.d.	±1.48 mv.	a.d.	±1.62 mv.

(al) 53.4 mv. E.M.F. Cd, Cd/Hg.

The only E. M. F. data on more unsymmetric valence types are the recent data of Hakomori[25] on the cell In,$InCl_3$(f) HCl(0.02 f), AgCl,Ag.

The constant HCl concentration was maintained to prevent hydrolysis of the indium chloride. The limit of reproducibility that the investigator gives for his cell is for the Ag/AgCl half cell 0.2 to 0.3 mv. and for the indium electrode 0.4 mv. so that duplicate measurements on the whole cell might differ by 0.6 to 0.7 mv. In recalculating Hakomori's data we have used the figures as if the hydrochloric acid were part of the solvent, but have included its chloride ion concentration, assuming complete dissociation, in figuring the activity coefficient of the indium chloride. Our $E_{0\,[3]}$ is really $E_{0\,(.02HCl[3])}$ which is comparable with the $E_{0\,(.02HCl[1])}$ obtained by Hakomori when he extrapolated his curve of E_0' vs. $\sqrt{c}$ to an indium concentration of zero.

Ordinarily Equation 7 could be applied directly to a 3:1 salt. However the increased chloride ion concentration obviously requires modification resulting in the expression:

$$E + 19.72[\log c_{InCl_3} + 3\log(3c_{InCl_3} + 0.02)] = E_0 - 78.88 \log f_s = E_0'$$

$E_{0[3]}$ has been compared with $E_{0[1]} = 574.0$ here, rather than with the value 578.0 mv. obtained by plotting against $\sqrt{\mu}$ and extrapolating to an ionic strength equivalent to 0.02 molal, or with 575.0 mv. taken as the most probable value by Hakomori, because our method of computing $E_{0[3]}$ assumes the hydrochloric acid to be part of the constant environment, just as does the graphical method giving the value $E_0 = 574.0$ mv. The more rigorous treatment of this problem would be to consider the mixture of a 1:1 electrolyte with a 3:1 salt, in accordance with the development given in Part 3 of this

TABLE VII

$InCl_3$ in.02 M HCl Hakomori[25]

(a)

	Moles. / Liter	E mv.	$10^{-8}\kappa$	E'_0 mv.	$E_{0[1]} = 574.0$		$E_{0[3]} = 570.46$	
					a[1]	a[3]	a[1]	a[3]
1.	0.001 515	737.03	0.031 30	586.18	−2.10	4.24	−8.82	3.02
2.	0.005 332	726.44	0.058 72	596.20	−0.65	3.73	−2.90	3.21
3.	0.011 04	719.11	0.084 49	605.10	−0.14	3.35	−1.34	3.06

(b)

$E_{0[3]}$

	a[3] = 2.8Å mv.		a[3] = 3.1Å mv.		a[3] = 3.4Å mv.	
1.	567.17	+2.20	570.46	+0.39	572.70	−1.28
2.	567.17	−1.10	570.46	−1.08	572.70	−0.52
3.	567.17	−1.10	570.46	+0.69	572.70	+1.81
			a.d.	0.72		

(c)

$$\frac{-\log f}{(-z_1z_2)10^{-8}\kappa}$$

	Theoretical (a[3] = 3.1)	Experimental (E_0 = 570.46)
1.	2.070	2.122
2.	1.930	1.852
3.	1.698	1.732

chapter. This procedure, if followed, would itself be very approximate because of the uncertainty in determining an "a" value where the hydrogen ion is involved. No $E_{0[1]}$ has been determined, since all of the a[1] values are negative. The maximum deviation of the $E_{0[3]}$ values from the mean is somewhat greater than the greatest variation which would be expected in duplicate cells, but the average deviation is no greater. The a[3] value figured on the basis of this $E_{0[3]}$ show far greater constancy than do those figured on the basis of the $E_{0[i]}$, and also than the a[1] values figured on either basis.

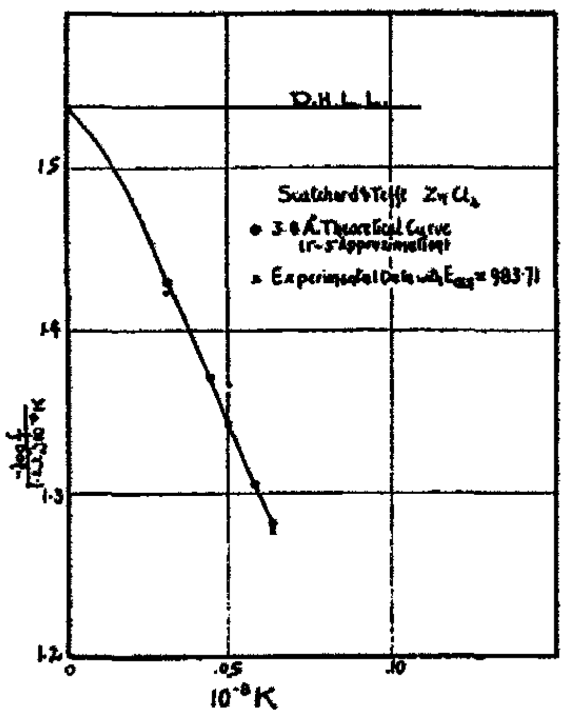


Fig. 4

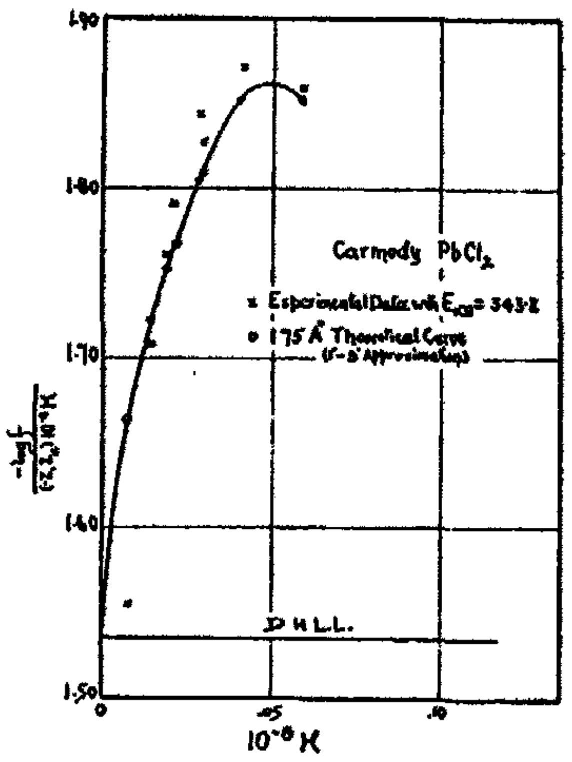


Fig. 5

In Figs. 4, 5, 6, the data shown in Tables III(e), V(c), VII(c) have been plotted. These show the position of the experimental points relative to the theoretical curves for the a[3] values postulated. The agreement in the case of the lead chloride data is seen to be most marked.

Figs. 7(a) and (b) show the variation of $E_{0[3]}$ with concentration, for the various a[3]'s postulated. (Tables V(b), VII(b), (IIIc)). As has been indicated by Gronwall, LaMer and Sandved,[9] for the symmetrical case, the extrapolation to zero concentration of each set of these values for a given a[3], leads to the same $E_{0[3]}$ as for every other set (i.e. the effect of the "ion size" is eliminated at zero concentration). As can be seen from the

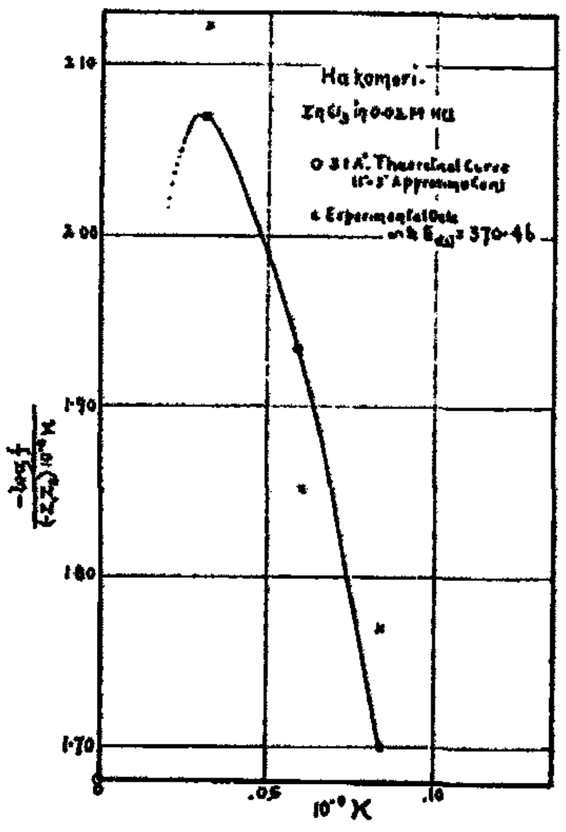


Fig. 6

graphs, this value is attained, if extrapolation is made along the most probable straight line through the points. Here, as in the preceding graphs, that for the lead chloride cell of Carmody is most convincing, since there are sufficient points to definitely fix the course of the line. It appears that the deviation of the $E_{0[3]}$ value due to difference in postulated "a" is a linear function of the concentration.

This survey of the comparison of the theory with experimental electromotive force data shows that our extension is in better agreement with experiment than is the first approximation in that

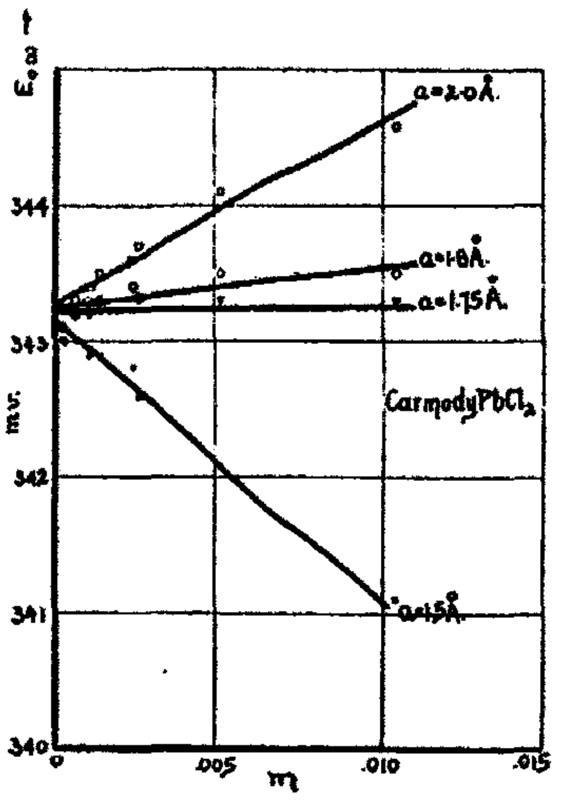


Fig. 7(a)

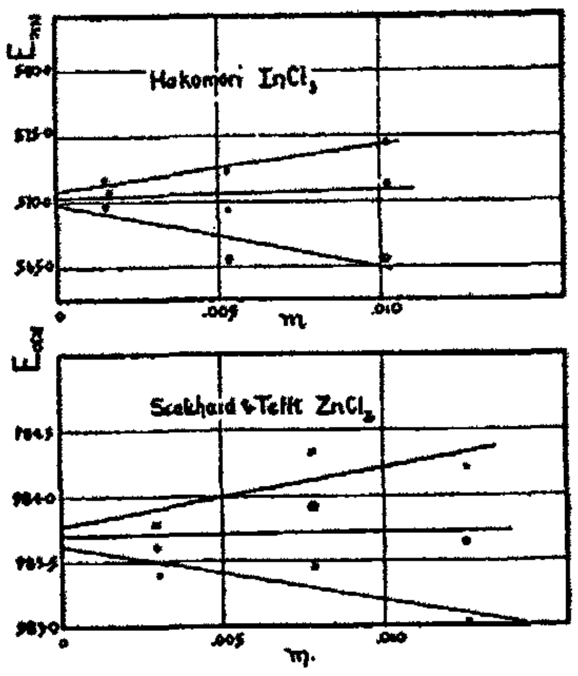


Fig. 7(b)

1. it gives more plausible values for "a"
2. a constant E_0 value may be computed from every experimental point up to 0.01 M
3. the E_0 value so computed compares favorably with that obtained by graphical methods, in that
    a. it exhibits constancy of the same order of magnitude as the experimental error
    b. it is not widely divergent from this extrapolated value
    c. it is not subject to personal interpretation as is the graphical extrapolation.

II. Freezing Point Depressions.

Since the osmotic deviation is a function of the activity coefficient of the solvent, which is in turn a function of the excess free electrical energy of the solution, measurements of freezing point depressions also serve as a test of the theory. However, such measurements do not afford as precise a test as do electromotive forces of reversible cells due to experimental difficulties attendant upon

1. establishing a true state of equilibrium between the solid phase and the solution of given concentration in contact with that solid phase,
2. measurement, to a sufficient degree of accuracy, of the extremely small temperature differences involved,
3. determination of the true concentration of the solution under consideration

The theoretical development itself requires that

1. electrical potential be converted into a function of temperature difference and
2. electrical potential due to interionic attraction between particles of solute be converted into a function of the activity coefficient of the solvent.(aq)

1. Osmotic Deviation by the Extended Theory

The osmotic deviation, Θ, equals,

$$\frac{\ln f_{H_2O}}{10^{-3}\dfrac{\partial V}{\partial n_0}c\sum\limits_{i=1}^{s}\nu_i}$$

by definition.

If the value

$$\ln f_{H_2O} = 10^{-3}\frac{\partial V}{\partial n_0}\sum_{j=1}^{s}c_j z_j\sum_{m=1}^{\infty}\left(\frac{\epsilon^2 z_j}{-kTDa_j}\right)^m$$

$$\left[\frac{1}{2}\left(1-\sum_{i=1}^{s}\frac{c_i}{D}\frac{\partial D}{\partial c_i}\right)\psi_m(x_j, x_j) - \frac{m}{x_j^{2m}}\int_0^{x_j}x^{2m-1}\psi_m(x,x)dx\right]$$

under the assumption that $\frac{\partial D}{\partial c_i} = 0$ (valid for dilute solutions) and $a_1 = a_2 = a$ making $x_1 = x_2 = x$ in the solution of a single salt consisting of two kinds of ions so that $s = 2$ and $\nu_1 = -z_2$ and $\nu_2 = z_1$, is introduced, there is obtained:

$$\Theta = (-z_1z_2)\left\{\frac{1}{10^8a}A_1(x) + \frac{(z_1+z_2)^2}{(10^8a)^2}A_2(x) - \frac{(z_1+z_2)^2(z_1^2+z_1z_2+z_2^2)}{(10^8a)^3}A_3^*(x) - \frac{(z_1^2+z_1z_2+z_2^2)^2}{(10^8a)^3}A_3(x)\right\} \quad (9)$$

where

$$A_1(x) = \frac{10^8\epsilon^2}{kTD}\left[-\frac{1}{2}\frac{1}{1+x}+\frac{1}{x}-\frac{1}{x^2}\log(1+x)\right] = \frac{10^8\epsilon^2}{kTD}\cdot\left[\frac{\sigma(x)}{6}\right]$$

$$A_2(x) = \left(\frac{10^8\epsilon^2}{kTD}\right)^2\left[\tfrac{1}{2}X_2(x) - 2\,Y_2(x)\right]$$

(aq) The theory does not consider the effect of the binding forces between the ions of the solute and the molecules of the solvent, when the solvent is strongly polar. Fowler[21] p. 315 discusses these forces and gives a rough evaluation. He makes the statements: "It appears on closer examination that this force is not quite large enough to have a serious effect on the ionic distribution laws" and "the pressure term (due to the attraction of the water dipole by the inhomogeneous field of the ion) is probably negligible."

$$A_3^*(x) = \left(\frac{10^8\epsilon^2}{kTD}\right)^3 [\tfrac{1}{2}X_3^*(x) - 3\,Y_3^*(x)]$$

$$A_3(x) = \left(\frac{10^8\epsilon^2}{kTD}\right)^3 [\tfrac{1}{2}X_3(x) - 3\,Y_3(x)]$$

This function may be evaluated in a manner analogous to that used for the function log f_s. Values of the functions $[\tfrac{1}{2}X_2(x) - 2Y_2(x)]$,

$$[\tfrac{1}{2}X_3^*(x) - 3Y_3^*(x)] \text{ and } [\tfrac{1}{2}X_3(x) - 3Y_3(x)]$$

are tabulated in Table II. The first term of the series is the first approximation, the $\sigma(x)$ function being identical with the function so designated by Debye and Hückel. Introducing the constants for 0°C one obtains:

$$\begin{aligned} \frac{\Theta}{(-z_1z_2)} &= 6.89402\,\frac{1}{10^8a}\left[\frac{\sigma(x)}{6}\right] \\ &+ 0.47532\,\frac{(z_1+z_2)^2}{(10^8a)^2}[\tfrac{1}{2}X_2(x) - 2Y_2(x)] \\ &- 0.32769\,\frac{(z_1+z_2)^2\,(z_1^2+z_1z_2+z_2^2)}{(10^8a)^3}[\tfrac{1}{2}X_3^*(x) - 3Y_3^*(x)] \\ &- 0.32769\,\frac{(z_1^2+z_1z_2+z_2^2)^2}{(10^8a)^3}[\tfrac{1}{2}X_3(x) - 3Y_3(x)] \end{aligned} \tag{10}$$

In this form it is ready for numerical evaluation.

Equation (10) is analogous to, but of course, not identical with, Equation (3) for log f_s. In the case of Θ, also, there will be for each valence type and for each value of "a" a different set of points. These points are obtained by introducing different values of x (κa) into the expression for each valence type. These may then be plotted as families of curves, one family corresponding to each valence type. This has been done for the four unsymmetric valence types previously considered through the same range of values for "a."

Curves have been plotted showing (1) Θ vs. x (Fig. 8) (2) $\dfrac{\Theta}{(-z_1z_2)}$ vs. x (Fig. 9) (3) $\dfrac{\Theta}{(-z_1z_2)}$ vs. κ (Fig. 10) (4) $\dfrac{\Theta}{(-z_1z_2)\kappa}$ vs. κ (Fig. 11)

For purposes of comparison with data, curves of Fig. 11 are best, being similar in form to the series plotted for the function of the activity coefficient of the solute.[af] Here, as in the previous case, it is preferable to employ κ as the independent variable. Theoretical considerations leading to the use of the function $\dfrac{\Theta}{10^{-8}(-z_1z_2)\,\kappa}$ are as follows:

[af] Fig. 1 (a-d).

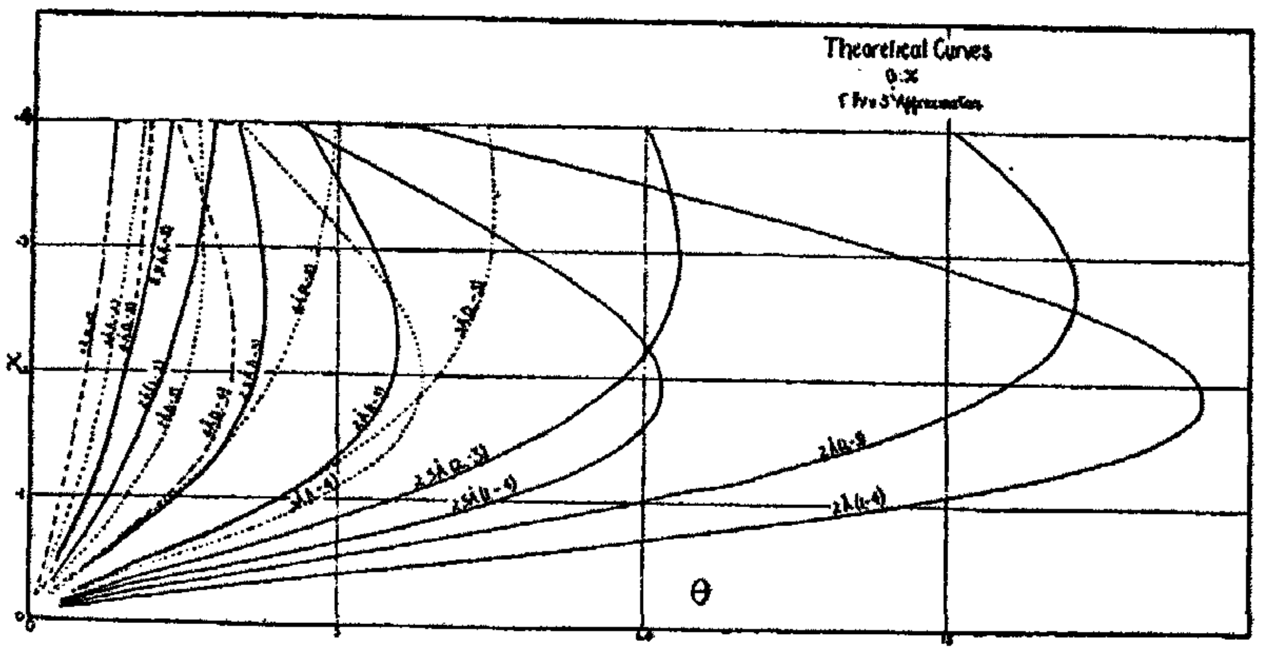


FIG. 8

The Debye limiting formula:

$$\lim_{\kappa=0} \frac{\log f_{H_2O}}{\left(\sum_{j=1}^{s} c_j z_j^2\right)^{\frac{3}{2}}} = \tfrac{1}{6}\, 10^{-3} \frac{\partial V}{\partial n_0} (4\pi N)^{\frac{1}{2}} \left(\frac{\epsilon^2}{kTD_0}\right)^{\frac{3}{2}}$$

has been shown by Gronwall[av] to remain unchanged by the addition of the higher terms. Introducing this into the value for Θ it may be seen that

$$\lim_{\kappa=0} \frac{\Theta}{(-z_1z_2)\kappa} = \tfrac{1}{6} \cdot \frac{\epsilon^2}{kTD} = \frac{1.1490}{10^8}; \text{ i.e.} \tag{11}$$

$$\lim_{\kappa=0} \frac{\Theta}{(-z_1z_2)\,10^{-8}\kappa} = 1.1490$$

The Debye limiting law gives the value

$$\frac{\Theta}{(-z_1z_2)\kappa} = \tfrac{1}{6}\frac{\epsilon^2}{kTD} = \frac{1.1490}{10^8}; \frac{\Theta}{(-z_1z_2)\,10^{-8}\kappa} = 1.1490$$

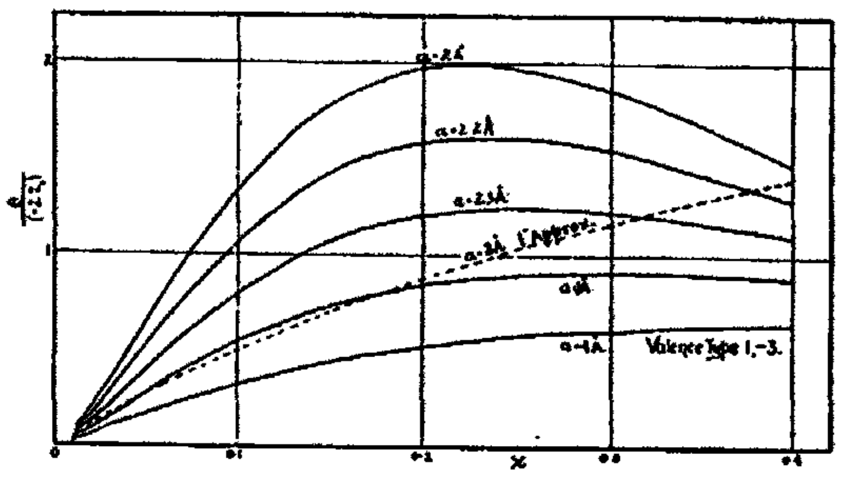


FIG. 9

[av] I p. 476.

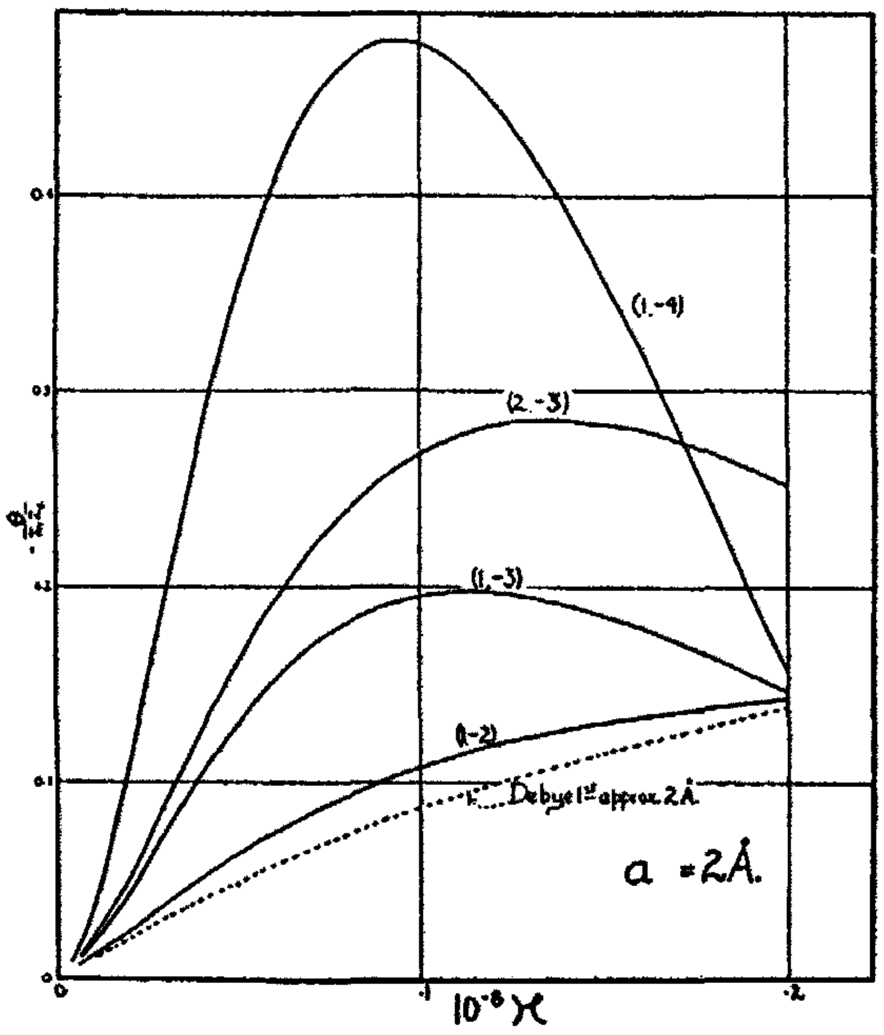


FIG. 10

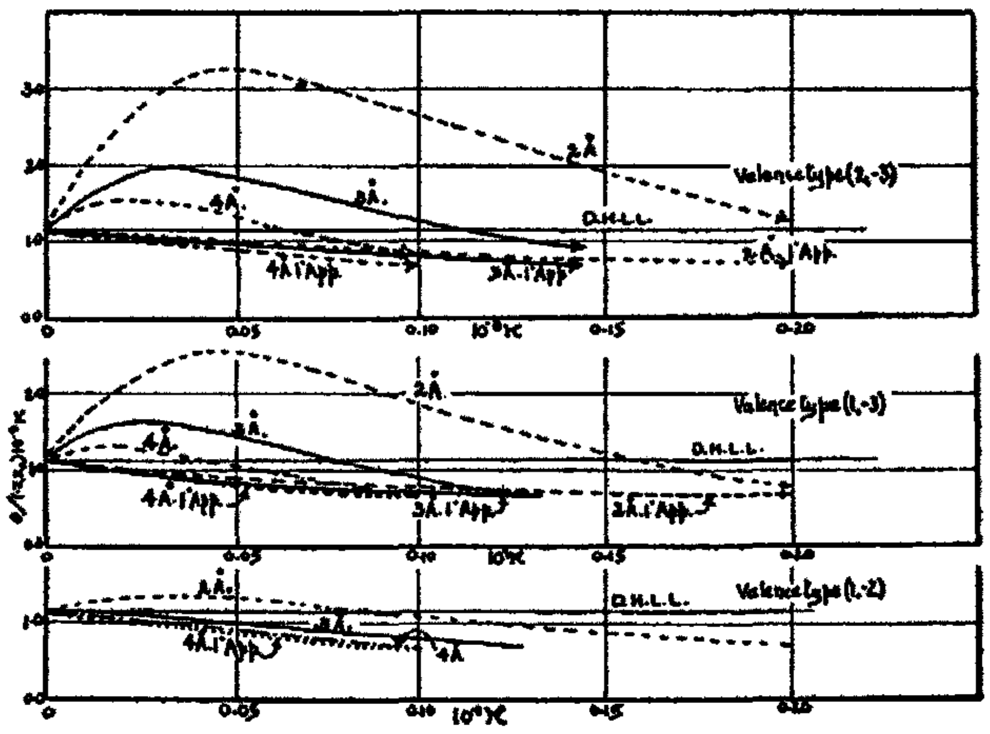


FIG. 11
Osmotic Deviations—Unsymmetric Case, thru 3′ Approximation

so that, in the graph produced in accordance with (4) above, the Debye limiting law is represented by a horizontal line which has the same value for $\kappa = 0$ as each of the other curves drawn. These curves differ from those for the log f function considered in that their maxima are not quite as high and are attained at somewhat smaller concentrations. In general form, however, the two sets of curves are very similar.

In this case also to compare the theoretical curves with experimental data it was necessary to calculate curves for intermediate values of "a." A separate graph was made for each valence type.[(ay)]

As there was doubt here also as to the presence of the inflection noticed in the regions of very small concentrations in particular for "a" $\doteq$ 3Å to 4Å the values of the original function divided by $x = 0.005$ and $x = 0.01$ were introduced into equation (10) of this paper, modified by multiplication by "10^8a" in order to convert $\frac{\theta}{(-z_1z_2)x}$ into $\frac{\theta}{(-z_1z_2)10^{-8}\kappa}$.

The value of the function for these two assumed x's was obtained throughout by means of this modified equation.

2. Effect of a Small Experimental Error on the Course of the Theoretical Curves

In order to show how the course of the curves would be changed, for the limiting values of a[3], for each valence type, if the freezing point depression were varied by a given small temperature from that theoretically postulated for the specified concentration, Table VIII has been prepared. As would be expected, this shows that the least effect of a small experimental error, for a given concentration, is found in the case of salts of the higher valence types e.g. (1:4 or 2:3). Unfortunately few data exist for such salts. The difference between the effect of such small errors in the case of 1:2 as compared with 1:3 salts is shown in Figs. 12(a) and (b) and 13 (a) (b) and (c).

3. Osmotic Deviation by Experiment

Since according to definition, osmotic deviation, θ, equals $1 - \frac{\Delta t obs}{\Delta t ideal}$ in order to obtain $\frac{\theta}{(-z_1z_2)10^{-8}\kappa}$ for the experimental point,[(bc)] κ must also be known.

At 0°C for the different valence types:

$10^{-8}\kappa$	Valence Type
$0.5611\sqrt{m}$	1,-2
$0.7935\sqrt{m}$	1,-3
$1.0245\sqrt{m}$	1,-4
$1.2547\sqrt{m}$	2,-3

[(ay)] these sets of curve are similar to the set representing $\frac{-\log f}{-z_1z_2 10^{-8}\kappa}$ shown in Fig. (2).

[(bc)] Here also the distinction between molarity and molality is insignificant in the concentrations considered.

TABLE VIII

Effect of Error of 0.000 01°C in observed Freezing Point Depressions on $\frac{\Theta}{(-z_1z_2)\ 10^{-8}\ \kappa}$ and on a[3] for Different Values of a[3] and Different Concentrations

Valence Type	a[3] Å	$10^{-8}\kappa$	$\frac{\Theta}{(-z_1z_2)10^{-8}\kappa}$	Δt calc. + Error	$\frac{\Theta}{(-z_1z_2)10^{-8}\kappa}$	a[3] Å	Δt calc. − Error	$\frac{\Theta}{(-z_1z_2)10^{-8}\kappa}$	a[3] Å
1,-2	2	.005 611	1.207 5	0.000 559	−0.36	>10.00	0.000 539	2.878	<1.00
		.007 935	1.235	0.001 102	+0.68	>10.00	0.001 082	1.808	<1.00
		.03	1.319	0.014 69	+1.307	2.05	0.014 67	1.328	1.95
	4	.005	1.137 5	0.000 445	−1.136	>10.00	0.000 425	3.41	<1.00
		.005 611	1.127 5	0.000 560	−0.45	>10.00	0.000 540	2.718	<1.00
		.007 935	1.120	0.001 104	+0.57	>10.00	0.001 084	1.695	<1.00
		.02	1.062 5	0.006 79	+1.025	4.7	0.006 77	1.095	3.55
1,-3	2	.007 735	1.802 5	0.000 72	1.163	>10.00	0.000 70	2.327	<1.00
		.010 939	1.996	0.001 40	1.829	2.20	0.001 38	2.255	1.70
		.041 25	2.676	0.014 15	2.672	2.01	0.014 13	2.680	1.99
	4	.007 735	1.221	0.000 73	0.603	>10.00	0.000 71	1.766	2.01
		.010 939	1.227	0.001 44	1.036	>10.00	0.001 42	1.432	3.35
		.015 0	1.320	0.002 63	1.273	c5.10	0.002 61	1.422	3.53
2,-3	2	.012 55	2.390	0.000 77	2.285	2.10	0.000 75	2.577	1.90
		.017 74	2.690	0.001 34	2.630	2.01	0.001 32	2.724	1.99
		.047 5	3.266	0.000 93	3.264	2.005	0.000 91	3.269	1.995
	4	.012 55	1.512	0.000 83	1.435	c4.5	0.000 81	1.714	3.20
		.017 74	1.544	0.001 56	1.512	c4.10	0.001 54	1.616	3.75
		.018 5	1.545	0.001 51	1.495	c4.2	0.001 49	1.595	3.82
1,-4	3	.010 25	2.800	0.000 83	2.601	3.2	0.000 81	3.126	2.7
		.014 49	3.115	0.001 53	3.046	3.05	0.001 51	3.232	2.95
		.027 5	3.495	0.005 06	3.486	3.005	0.005 04	3.529	2.995
	4	.010 25	2.110	0.000 86	1.830	4.60	0.000 84	2.367	3.55
		.014 49	2.240	0.001 63	2.140	4.15	0.001 61	2.312	3.90
		.017 5	2.275	0.002 29	2.214	4.05	0.002 27	2.314	3.95

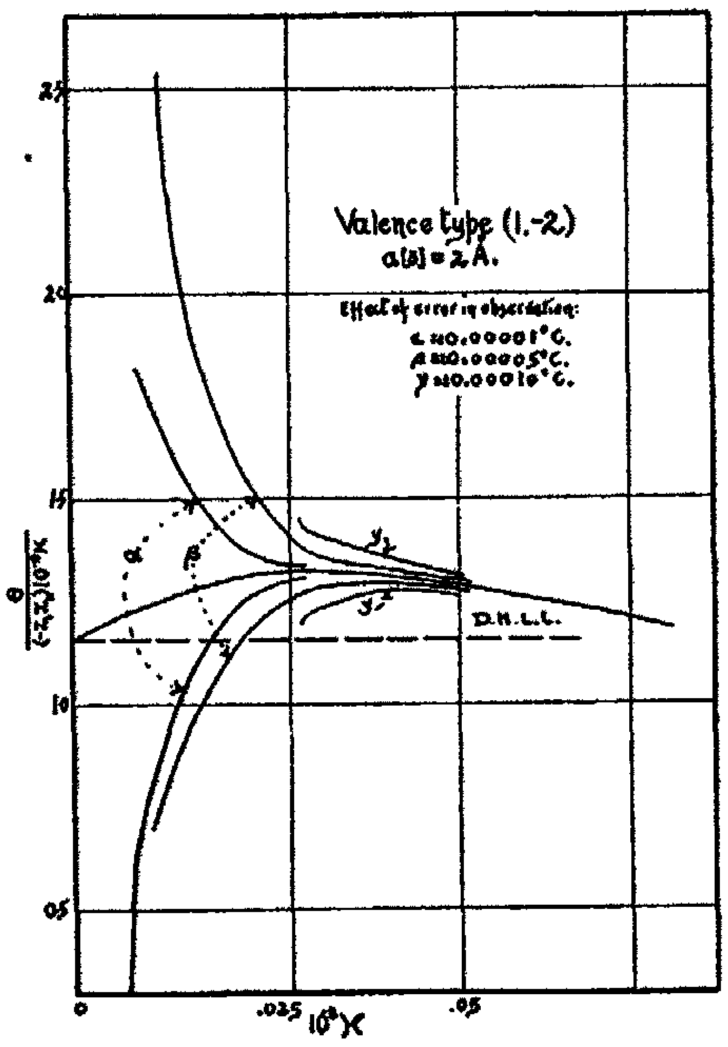


Fig. 12(a)

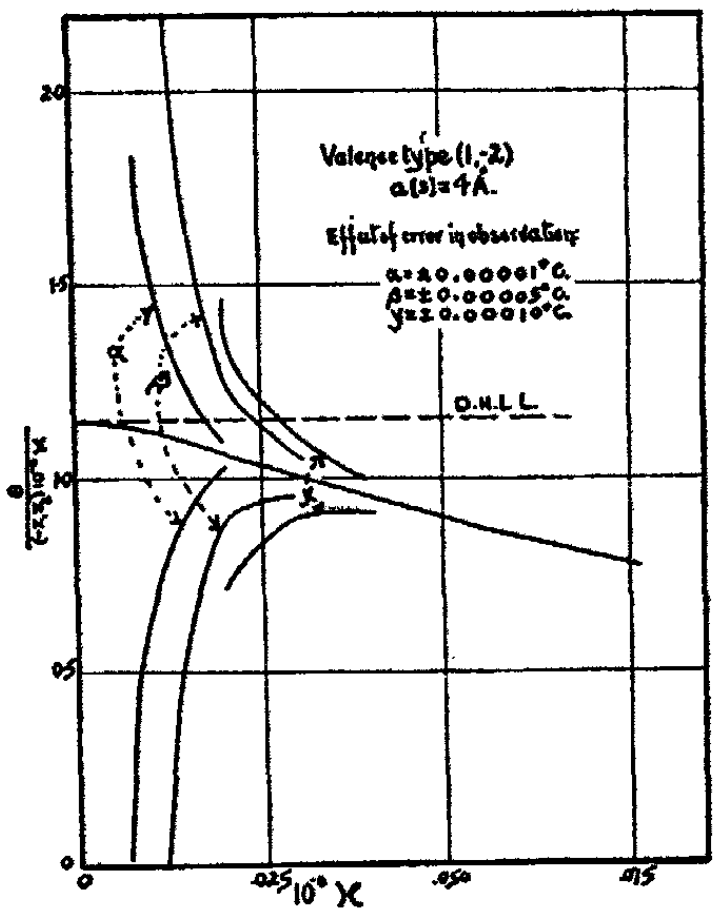


Fig. 12(b)

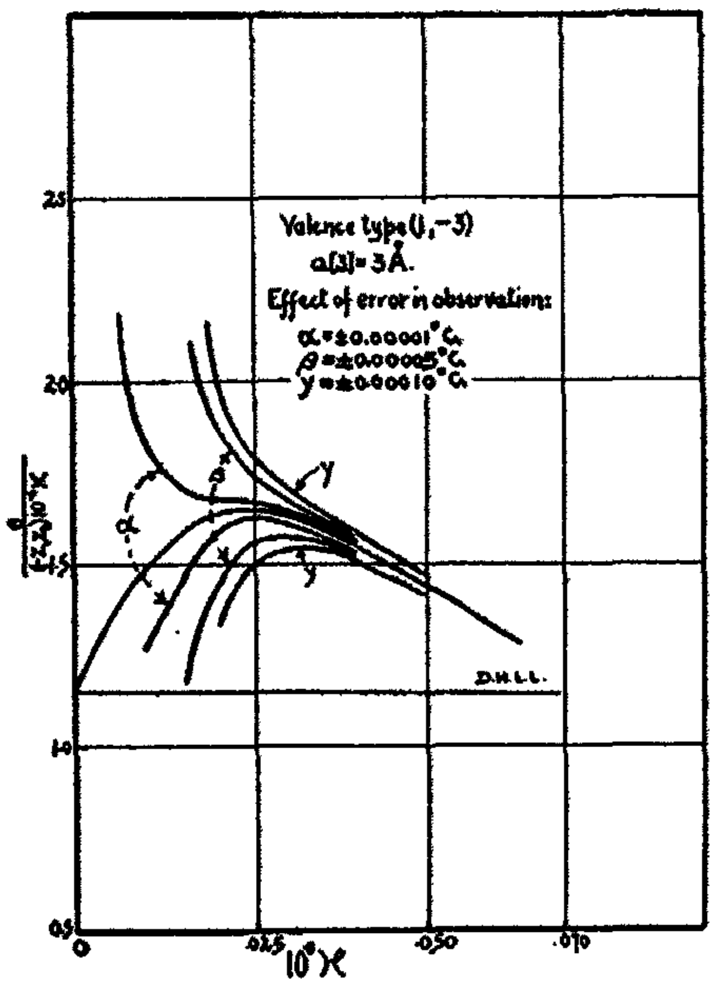


Fig. 13(a)

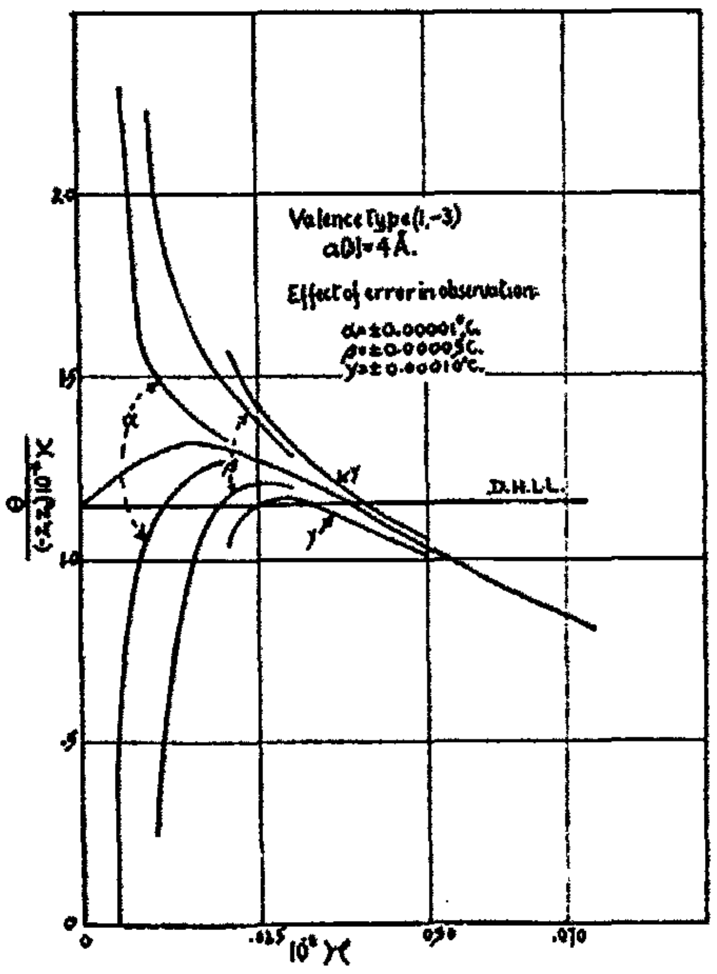


Fig. 13(b)

Now, $\frac{\theta}{(-z_1z_2)10^{-8}\kappa}$ having been found for each experimental point, an "a" value was determined for each by interpolation on the theoretical "working curves." From these "a"s, for each series of measurements, a most probable "a" was postulated.(6a) The theoretical curve for this "a" was then interpolated on the plot, and from it for each experimental concentration a theoretical value of $\frac{\theta}{(-z_1z_2)10^{-8}\kappa}$ was read. By reversal of the calculations indicated above (p. 2274) a value was obtained for the magnitude of the freezing point depression were the theory correct and the value of "a" properly chosen (theoretical freezing point depression). Exactly the same procedure was followed, the first approximation being used to give the theoretical values. In this way it was made possible to compare: (1) the most probable "a" and (2) the fit of the curves using this most probable "a" on the basis of the extended theory as compared to the first approximation.

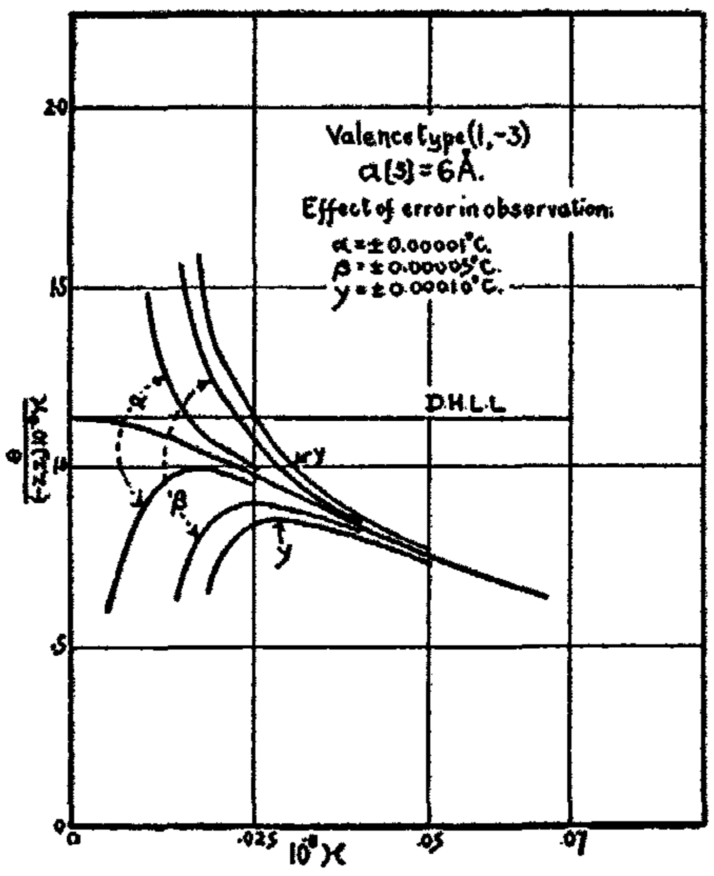


FIG. 13(c)

4. Comparison of Experimental $\frac{\theta}{(-z_1z_2)10^{-8}\kappa}$ with Theoretical $\frac{\theta}{(-z_1z_2)10^{-8}\kappa}$.

Data for comparison have been taken from the literature appearing since 1916 and from International Critical Tables. For each valence type there is a value of a[3] beyond which it varies so little from a[1] that the first approximation is sufficient for making experimental comparisons. These values are:

(6a) Actually various a[3] values were tried, that resulting in the best agreement between theory and experiment chosen as most probable.

TABLE IX

m	Δt *obs*	$10^{-8}\kappa$	$\frac{\Theta\ obs}{(-z_1z_2)10^{-8}\kappa}$	a[1] Å	$\frac{\Theta}{(-z_1z_2)10^{-8}\kappa}$	Δt_t	Δt_t-Δt_o	a[3] Å	$\frac{\Theta}{(-z_1z_2)10^{-8}\kappa}$	Δt_t	Δt_t-Δt_o
BARIUM NITRATE											
Series A[26]					Most Probable a[1] = 2Å				Most Probable a[3] = 3.10Å		
0.001 668 8	0.008 79°C	0.022 95	1.194 8	− 1.09	1.074 1	0.008 84	+0.000 05	2.55	1.123 5	0.008 82	+0.000 03
0.005 220 5	0.026 67	0.040 57	1.029 2	+ 1.87	1.021 7	0.026 69	+0.000 02	3.23	1.048 5	0.026 62	−0.000 05
0.007 381 4	0.037 15	0.048 20	1.006 0	+ 1.91	1.000 0	0.037 17	+0.000 02	3.13	1.012 5	0.037 12	−0.000 03
0.008 667 0	0.043 36	0.052 24	0.998 5	+ 1.87	0.989 3	0.043 41	+0.000 05	3.05	0.992 0	0.043 39	+0.000 03
0.011 667	0.057 43	0.060 60	0.964 3	+ 2.03	0.966 9	0.057 41	−0.000 02	3.02	0.953 0	0.057 52	+0.000 09
Series B[26]											
0.000 833 5	0.004 348	0.016 22	1.977 2	−18.99	1.095 2	0.004 481	+0.001 33	<0.30	1.144 0	0.004 474	+0.000 12
0.001 592 2	0.008 372	0.223 9	1.265 7	− 2.80	1.075 9	0.008 447	+0.000 75	2.19	1.125 0	0.008 428	+0.000 06
0.003 467 6	0.017 897	0.330 5	1.120 1	+ 0.52	1.043 8	0.017 994	+0.000 97	2.83	1.083 5	0.017 944	+0.000 05
0.005 807 0	0.029 416	0.427 6	1.066 4	+ 1.19	1.015 5	0.029 557	+0.001 41	2.92	1.037 5	0.029 496	+0.000 08
0.010 820	0.053 392	0.583 5	0.983 0	+ 1.87	0.972 8	0.053 464	+0.000 72	2.98	0.961 5	0.053 544	+0.000 15
[27]											
0.001	0.005 39	0.017 74	0.910 9	+ 9.37	1.090 9	0.005 39	−0.000 04	9.98	1.139 0	0.005 34	−0.000 05
0.005	0.025 70	0.039 68	0.981 1	+ 2.78	1.024 2	0.025 60	−0.000 10	3.71	1.052 5	0.025 54	−0.000 16
0.010	0.049 84	0.056 11	0.901 6	+ 3.10	0.978 6	0.049 62	−0.000 22	3.51	0.972 5	0.049 66	−0.000 18
						av.	0.000 45			av.	0.000 09
POTASSIUM SULPHATE											
[29] (bk)					Most Probable a[1] = 2.8Å				Most Probable a[3] = 3.6Å		
0.002 74	0.014 2	0.029 37	1.192 9	− 0.844	1.020 0	0.015 36	+0.000 16	2.50	1.070 0	0.014 31	+0.000 11
0.006 18	0.031 7	0.044 11	0.904 9	+ 3.88	0.963 8	0.031 52	−0.000 18	4.30	0.964 5	0.031 52	−0.000 18
0.010 39	0.052 0	0.057 17	0.892 2	+ 3.18	0.918 3	0.051 83	−0.000 17	3.66	0.901 0	0.051 94	−0.000 06
[27]											
0.001	0.005 26	0.017 74	1.568 8	−10.7	1.068 3	0.005 36	+0.000 10	<1.3	1.100 0	0.005 35	+0.000 09
0.005	0.025 65	0.039 78	1.001 3	+ 2.39	0.979 7	0.025 70	+0.000 05	3.49	0.991 0	0.025 68	+0.000 03
0.010	0.050 05	0.056 11	0.909 6	+ 2.96	0.921 8	0.049 97	−0.000 08	3.57	0.905 0	0.050 08	+0.000 03
						av.	0.000 12			av.	0.000 08
BARIUM CHLORIDE											
[27]					Most Probable a[1] = 2.6Å				Most Probable a[3] = 3.4Å		
0.002 73	0.014 30	0.029 32	1.031 0	+ 0.26	1.028 6	0.014 30	±0.000 00	3.96	1.062 5	0.014 27	−0.000 03
0.005 34	0.027 55	0.041 00	0.909 3	+ 4.08	0.986 6	0.027 60	−0.000 19	4.45	1.005 5	0.027 32	−0.000 23
[30]											
0.001	0.005 31	0.017 74	1.315 7	− 4.96	1.074 1	0.005 36	+0.000 05	1.9	1.115 0	0.005 35	+0.000 04
0.002	0.010 42	0.025 08	1.305 2	− 3.23	1.045 5	0.010 47	+0.000 14	2.02	1.085 0	0.010 54	+0.000 12
0.004	0.020 48	0.035 49	1.149 8	− 0.28	1.005 9	0.020 53	+0.000 23	2.62	1.033 5	0.020 66	+0.000 18
0.006	0.030 42	0.043 46	1.038 9	+ 1.59	0.977 6	0.030 47	+0.000 18	3.08	0.993 5	0.030 55	+0.000 13
0.008	0.040 24	0.050 18	0.972 0	+ 2.34	0.954 9	0.040 29	+0.000 08	3.31	0.961 0	0.040 29	+0.000 05
0.010	0.050 00	0.056 11	0.917 7	+ 2.86	0.935 2	0.050 05	−0.000 11	3.50	0.931 0	0.049 92	−0.00 08
						av.	0.000 123			av.	0.000 108

(bk) The authors increase the depression which they obtain experimentally by 0.0001°C in the concentration range which we are using. As we are consistently using experimental data as obtained, we have decreased their published values by 0.0001°C in each case.

TABLE X

m	Δt obs	$10^{-8}\kappa$	$\frac{\Theta}{(-z_1z_2)10^{-8}\kappa}$	a[1] Å	$\frac{\Theta}{(-z_1z_2)10^{-8}\kappa}$	Δt_t	Δt_t-Δt_o	a[3] Å	$\frac{\Theta}{(-z_1z_2)10^{-8}\kappa}$	Δt_t	Δt_t-Δt_o
XANTHO-COBALTIC CHLORIDE[31]											
					Most Probable a[1] = 1.5Å				Most Probable a[3] = 3.2Å		
0.001 54	0.008 03°C	0.022 02	1.455 5	− 6.68	1.099 13	0.008 16	+0.000 13	c1.6	1.117 0	0.008 16	+0.000 13
0.003 54	0.018 41	0.033 35	1.003 0	+ 2.85	1.067 78	0.018 32	−0.000 09	3.8	1.067 5	0.018 33	−0.000 08
0.003 86	0.020 00	0.034 86	1.013 2	+ 2.51	1.064 83	0.020 92	−0.000 92	3.66	1.061 0	0.019 93	−0.000 07
0.005 71	0.029 10	0.042 40	1.011 6	+ 2.10	1.043	0.029 01	−0.000 09	3.25	1.024 5	0.029 06	−0.000 04
0.007 45	0.037 40	0.048 43	1.026 8	+ 1.49	1.033	0.037 37	−0.000 03	3.00	0.994 5	0.037 53	+0.000 13
0.008 71	0.043 30	0.052 37	1.032 5	+ 1.40	1.025	0.043 34	+0.000 04	2.86	0.975 0	0.043 59	+0.000 29
0.010 92	0.053 63	0.058 63	1.014 3	+ 1.48	1.021	0.053 55	−0.000 08	2.80	0.946 0	0.054 12	+0.000 49
						av.	0.000 20			av.	0.000 17
POTASSIUM COBALTICYANIDE[28]											
Series A					Most Probable a[1] = 4.3Å				Most Probable a[3] = 5.0Å		
0.000 297 3	0.002 126	0.013 68	0.926 2	+11.21	1.054 1	0.002 12	−0.000 01	>10.	1.180 0	0.002 10	−0.000 03
0.000 492 0	0.003 419	0.017 60	1.231 3	− 2.56	1.029 0	0.003 458	+0.000 04	4.5	1.155 0	0.003 43	+0.000 01
0.002 914	0.019 17	0.042 85	0.893 3	+ 4.23	0.890 1	0.019 18	+0.000 01	5.2	0.909	0.019 13	−0.000 04
0.004 923	0.031 61	0.055 67	0.814 7	+ 4.56	0.830 4	0.031 51	−0.000 10	4.9	0.800	0.031 70	+0.000 09
Series B											
0.000 287 0	0.002 052	0.013 44	0.941 7	+10.47	1.055 5	0.002 042	−0.000 01	c10.	1.180 0	0.002 032	−0.000 02
0.000 495 5	0.003 486	0.017 66	1.009 6	+ 5.06	1.029 0	0.003 482	±0.000 00	>6.	1.155 0	0.003 458	−0.000 03
0.000 693 7	0.004 819	0.020 90	1.039 4	+ 3.30	1.009 3	0.004 830	+0.000 01	5.8	1.126	0.004 792	−0.000 03
0.002 948	0.019 40	0.043 09	0.886 2	+ 4.35	0.889 0	0.019 39	−0.000 01	5.2	0.910	0.019 33	−0.000 07
Series C											
0.000 500 0	0.003 506	0.017 74	1.061 8	+ 3.04	1.029 0	0.003 513	+0.000 01	5.95	1.155 0	0.003 488	−0.000 02
0.000 993 8	0.006 794	0.025 01	1.068 2	+ 1.97	0.985 9	0.006 840	+0.000 05	5.15	1.085	0.006 785	−0.000 01
0.000 985 0	0.006 687	0.024 90	1.159 3	− 0.20	0.985 9	0.006 782	+0.000 10	4.70	1.085	0.006 728	+0.000 04
							11).000 35				11)0.000 39
						ad. =	0.000 032			ad. =	0.000 035

Valence Type	Maximum "a" for which differences between a[3] and a[1] are significant. (> ±1Å)
1, −2	4Å
1, −3	6
1, −4	10
2, −3	10

Table (IX), based on data taken from Randall and Scott[26] and Hovorka and Rodebush[27] indicates that the use of the extended theory:

(1) leads only to positive values of a[3] whereas the a[1] values are sometimes negative.

(3) gives more consistent values of a[3] than of a[1] and

(3) the experimental points fit the curve of the extended theory better than that for the first approximation as is apparent from a comparison of the columns(bj) ($\Delta t_t - \Delta t_o$) in both cases.

The other data on salts of 1-2 type, namely, potassium sulphate, barium chloride (Table IX) and xantho-cobaltic chloride (Table X) all show that some negative and some impossibly small a[1] values are postulated, and that the a[3] values are again more consistent throughout. The fit of the curve (shown by $\Delta t_t - \Delta t_o$) in every case is slightly better when a comparison is made with the extended theory. For barium nitrate and xantho cobaltic chloride the probable a[3] is definitely more plausible in the light of the physical significance that has been attached to it, i.e., the distance of closest approach of two ions.

The only freezing point data for 1:3 salts which have been employed for comparison are those of Robertson on potassium cobalti-cyanide.[28] These (Table X) also indicate that the a[3] values are all positive whereas some of the a[1] values are negative and that the a[3] values are more consistent throughout the range of concentrations considered in this paper.

As is apparent from the curves, Figs. (12, 13) small differences in freezing point depression cause so great a change in the value of the osmotic deviation, for both 1:2 and 1:3 valence types, that until more accurate methods of measuring these at low concentrations are developed, the most that can be said is that freezing point depressions indicate better agreement with the extended theory than with the first approximation.

III. Solubility of Difficultly Soluble Salts in Solvent Salt Solutions.

1. Application of the Potential Functions to Free Energy of a Ternary Mixture (Two Electrolytes and Solvent).

When there is only one electrolyte present, consisting of but two ionic species ($s = 2$) $n_1 = \nu_1 n$; $n_2 = \nu_2 n$(bl) and since therefore(bm)

(bj) Δt_t = theoretical freezing point depression.
Δt_o = observed freezing point depression.

(bl) Nomenclature given in I^9 p. 359. (bm) 1-6.

$$q_\nu = \frac{z_1^\nu - z_2^\nu}{z_1 - z_2} \tag{12}$$

(i.e., q_ν is independent of n_1) the differentiation of the general expression for the free energy F_e with respect to the concentration of the solute (n_1) is comparatively simple. This has already been done(6a).

In the solubility case, if n denotes the number of mols of solute salt (consisting of ν_1 cations of valence z_1 and ν_2 anions of valence z_2), and n' the number of mols of solvent salt (ν_3 cations of valence z_3 and ν_4 anions of valence z_4), then

$$\begin{aligned} \nu_1:\nu_2 &= -z_2:z_1, \\ \nu_3:\nu_4 &= -z_4:z_3; \end{aligned} \tag{13}$$

the numbers of the four kinds of ions present are

$$n_1 = \nu_1 n,\ n_2 = \nu_2 n,\ n_3 = \nu_3 n',\ n_4 = \nu_4 n'; \tag{14}$$

according to (1-6), q_ν now takes the form

$$q_\nu = \frac{n\left(\nu_1 z_1^{\nu+1} + \nu_2 z_2^{\nu+1}\right) + n'\left(\nu_3 z_3^{\nu+1} + \nu_4 z_4^{\nu+1}\right)}{n(\nu_1 z_1^2 + \nu_2 z_2^2) \quad + n'(\nu_3 z_3^2 + \nu_4 z_4^2)}, \tag{15}$$

and in differentiating F_e with respect to n in order to obtain $\log f$ for the solute salt, account must be taken of the dependence of the various q_ν's on n. This makes the formula for $\log f$ more complicated than in the case of a single electrolyte.

In one case only, the formula becomes as simple as before, viz. when q_ν is independent of n for $\nu = 2,3, \ldots\ldots$ The condition for this is, by (15)

$$q_\nu = \frac{\nu_1 z_1^{\nu+1} + \nu_2 z_2^{\nu+1}}{\nu_1 z_1^2 + \nu_2 z_2^2} = \frac{\nu_3 z_3^{\nu+1} + \nu_4 z_4^{\nu+1}}{\nu_3 z_3^2 + \nu_4 z_4^2} \tag{16}$$

for $\nu = 2,3,\ldots$: eliminating ν_1, ν_2, ν_3 and ν_4 by means of (13); this reduces to

$$q_\nu = \frac{z_2^\nu - z_1^\nu}{z_2 - z_1} = \frac{z_4^\nu - z_3^\nu}{z_4 - z_3} \quad (\nu = 2,3,\ldots\ ).$$

Writing these equations out for $\nu = 2$ and 3, we obtain

$$\begin{aligned} z_2 + z_1 &= z_4 + z_3, \\ z_2^2 + z_2 z_1 + z_1^2 &= z_4^2 + z_4 z_3 + z_3^2, \end{aligned}$$

and solving for z_3 and z_4, it is seen that $z_3 = z_1$, $z_4 = z_2$ (the other solution $z_3 = z_2$, $z_4 = z_1$, is to be discarded, since z_1 and z_3 are positive, z_2 and z_4 negative). Consequently:

When solute and solvent salt are of the same valence type ($z_1 = z_3$, $z_2 = z_4$) and in this case only, every q_ν is independent of n and takes the form (12), so that the formula for log f established for a binary solution remains applicable with the only difference that κ depends now also on n'.

(6a) 1-34.

The general case requires that the differentiation of F_e with respect to *n* include terms due to the variation of q_ν with *n*. As a result of this differentiation, Gronwall[32] has arrived at the expression

$$\begin{aligned}-\ln f = & - z_1z_2\{\tfrac{1}{2}\beta[1-X_1(x)]+\beta^2q_2^2[\tfrac{1}{2}X_2(x)-Y_2(x)]\\ & + 2\beta^2q_2(z_1+z_2-q_2)Y_2(x)\\ & - \beta^3q_2^2q_3[\tfrac{1}{2}X_3^*(x)-2Y_3^*(x)]\\ & - \beta^3q_3^2[\tfrac{1}{2}X_3(x)-2Y_3(x)]\\ & - \beta^3q_2[2(z_1+z_2)q_3+(z_1^2+z_1z_2+z_2^2)q_2-3q_2q_3]Y_3^*(x) \qquad (17)\\ & - 2\beta^3q_3[(z_1^2+z_1z_2+z_2^2)-q_3]Y_3(x)\}, \text{ where}\end{aligned}$$

$$\beta = \frac{\epsilon^2}{akTD}.$$

correct to terms of the third order inclusive.

In the symmetrical case of course, $q_2 = 0$ and the formula simplifies accordingly.

Introducing numerical values for the constants and converting to Briggsian logarithms, (17) becomes at 25°C.

$$\begin{aligned}-\log f_s = & - z_1z_2\Big\{1.53636\frac{1}{10^8a}\cdot\frac{x}{1+x}\\ & + 0.21740\frac{q_2^2}{(10^8a)^2}[\tfrac{1}{2}X_2(x)-Y_2(x)]\\ & + 0.43480\frac{q_2}{(10^8a)^2}(z_1+z_2-q_2)Y_2(x)\\ & - 0.15382\frac{q_2^2q_3}{(10^8a)^3}[\tfrac{1}{2}X_3^*(x)-2Y_3^*(x)] \qquad (18)\\ & - 0.15382\frac{q_3^2}{(10^8a)^3}[\tfrac{1}{2}X_3(x)-2Y_3(x)]\\ & - 0.15382\frac{q_2}{(10^8a)^3}[2(z_1+z_2)q_3+(z_1^2+z_1z_2+z_2^2)q_2-3q_2q_3]Y_3^*(x)\\ & - 0.30764\frac{q_2}{(10^8a)^3}[(z_1^2+z_1z_2+z_2^2)-q_3]Y_3(x)\Big\}\end{aligned}$$

the form suitable for direct evaluation. Introducing the functions $B_1(x)$ $B_2(x)$, $B_3^*(x)$ and $B_3(x)$ already evaluated, this has been further simplified, for purposes of comparison, into

$$-\log f_s = - z_1z_2\Big\{\frac{B_1(x)}{10^8a} + \frac{q_2^2B_2(x)}{(10^8a)^2} + 0.43480\frac{q_2(z_1+z_2-q_2)Y_2(x)}{(10^8a)^2}$$

$$- \frac{q_2^2 q_3 B_3^*(x)}{(10^8 a)^3} - \frac{q_3^2 B_3(x)}{(10^8 a)^3} \qquad (19)$$

$$- 0.15382 \frac{q_2[2(z_1+z_2)q_3+(z_1^2+z_1z_2+z_2^2)q_2-3q_2q_3]Y_3^*(x)}{(10^8 a)^3}$$

$$- 0.30764 \frac{q_3[(z_1^2+z_1z_2+z_2^2)-q_3]Y_3(x)}{(10^8 a)^3} \Bigg\}.$$

2. Comparison of Experimental Values with the Theory

The outstanding discrepancy between existing theory and experimental results has been the solubility relations of the highly unsymmetrical 3:1 cobaltammine salts, luteo cobaltic diammino tetra nitro cobaltiate (LN_3) and luteo cobaltic diammino dinitro oxalo cobaltiate, (LOn_3) in potassium sulphate (1:2) solutions.[2,4] LaMer and his co-workers have shown that in dilutions even as low as 0.0002 M potassium sulphate, there is no evidence of fusion of the curve $\log S/S_0$ vs $\sqrt{\mu}$ with the limiting law. The first approximation (Debye) would obviously yield absurdly high negative values for a[1]. Consequently it was most interesting to examine these data in the light of the extended development. The complete development as given for the unsymmetrical case above is required.

The data of LaMer and Cook and those of LaMer and Mason on the solubility of LOn_3 in K_2SO_4 solutions have been used. If n_1 = the solubility of LOn_3 in mols per liter, and n_2 = concentration of K_2SO_4 in mols per liter, then for these salts,

$$q_2 = \frac{27n_1-3n_1+2n_2-8n_2}{9n_1+3n_1+2n_2+4n_2} = \frac{4n_1-n_2}{2n_1+n_2}$$

$$q_3 = \frac{81n_1+3n_1+2n_2+16n_2}{9n_1+3n_1+2n_2+4n_2} = \frac{14n_1+3n_2}{2n_1+n_2}$$

For each concentration there is a value of $10^{-8}\kappa(=0.327\sqrt{\mu})$, so that any assumed value of "a" in Å units leads to a series of x values (κa), one for each point, for which values of the functions $Y_2(x)$, $Y_3(x)$, $B_1(x)$, $B_2(x)$ etc., may be obtained by interpolation on the tables already computed. Using equation (19) a value of $-\log f_s$ has been computed for each of several experimental concentrations assuming various values of a[3]. From the relationship $-\log f_s = \log S/S_0 - \log f_0$, it is apparent that a theoretical value of $\log S/S_0$ for each concentration, may be obtained from that of $-\log f_s$, if $\log f_0$ the activity coefficient of the solute in the pure solvent be known. In this work $-\log f_0$ was taken as .034, the value calculated by the experimenters through application of the Debye limiting law, $-\log f = \alpha'(-z_1z_2)\sqrt{\mu}$.

As can be seen from Table XI and more readily, from Fig. 14 the theoretical points for the three lowest concentrations where a[3] is taken equal to 1.6Å are in good agreement with the experimental points i.e., up to a concention of .001 M of K_2SO_4 and 1.17×10^{-4}M of the solute salt, if the theoretical curve is assumed to join the Debye limiting law line at the same point[bs] as does the experimental curve.

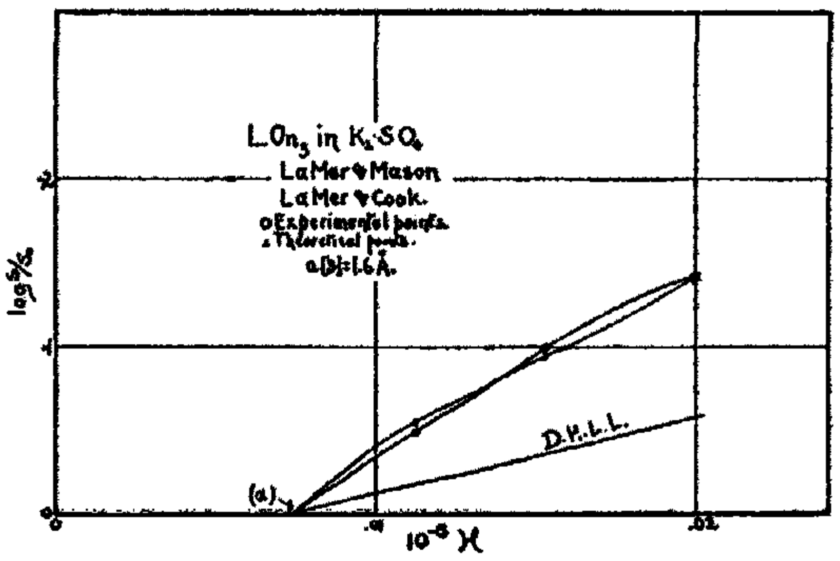


FIG. 14

TABLE XI

LOn_3 in K_2SO_4[2,4]

(a)

Pt.	K_2SO_4 M	Soly. in mols per liter $\times 10^4$	$\sqrt{\mu}$	$10^{-8}\kappa$
1	0.000 2	0.923 6[bu]	.033 97	.011 15
2	0.000 5	1.036	.046 07	.015 12
3	0.001 0	1.170 1	.060 83	.019 97
4	0.003 0	1.484 0	.099 45	.032 65

(b)

a[3] = 1.6Å

Pt.	x	$-\log f$ *theor.*	log S/S_0 *theor.*	log S/S_0 *exp.*	log S/S_0 *theor.-exp.*
1	1.8×10^{-2}	0.088 7	0.055	0.049	+0.006
2	2.4	0.128 1	0.094	0.099	−0.005
3	3.2	0.183 6	0.150	0.151	−0.001
4	5.2	0.343 2	0.309	0.254	+0.055

(c)

Effect of Various Errors

a[3] = 1.6Å

Pt.	log S/S_0 *theor.* [Table XI. (b)]	log S/S_0 *theor.* Δn_1 = 10%; κ unchanged	log S/S_0 *theor.* Δn_2 = 10%; κ unchanged
1.	0.055	0.053	0.056
2.	0.094	0.092	0.098
3.	0.150	0.150	0.157

[bs] At (*a*) in Fig. 14.

[bu] Given in original as 0.902 36 should be 0.923 6.

To ascertain whether a small error in the measured solubility might be responsible for the inflection in the theoretical curve near the origin, the effect of various changes in the solubilities have been investigated. A difference of 10% in the solubility of the solute salt if the solubility of the solvent salt is so changed as to keep κ constant is not sufficient to account for this inflection, whereas the probable error in the measurements is given by the investigators as of the order of 0.1%. If the solubility of both salts changed by the same amount (10%) q_ν would, of course, remain the same but κ would change. This change in κ would not be sufficient to smooth the curve. The effect of incomplete dissociation is the same as that of a reduction in solubility of the salts. This has been calculated assuming (*1*) the number of ions (n_i) of the solute salt to be decreased by 10% in the lowest concentration. (2) a similar reduction in the dissociation of the solvent salt. It has been found that neither of these changes corrected the divergence noted.

It is quite possible that introduction of terms higher than the third in the power series will smooth the curve as well as make it return more rapidly. This would, we believe, also give a higher, therefore more probable, "a" value.

Assumptions which have been made in applying the theory to this very complicated case are:

(1) that $a_1 = a_2 = a_3 = a_4 = a$ in the solutions considered

(2) that $\log f_0[3] = \log f_0[1]$(bd)

(3) that there is no specific interaction between the ions of the two salts such as would result in a change in the number of ions from that required by the theory of complete dissociation.

This comparison has shown that under the assumptions given, a not impossible "a" value has been found which in this extremely complicated case yields a theoretical curve

(1) joining the limiting law line at an angle comparable with that of the experimental curve

(2) showing fair agreement with the experimental curve over a region from .0002M — .0010M K_2SO_4 including three points.

Summary

I. Numerical evaluation of the second and third order terms in Gronwall's solution of the Poisson-Boltzmann equation has been completed from values of $x = 0.00$ to $x = 0.40$ in steps of 0.01, including $x = 0.005$.

II. Comparison of the appropriate resulting theoretical curves has been made with

  1. E.M.F. data for salts of types 2, — 1 and 3, — 1. It has been found that the extension is in better agreement with experiment

---

(bd) $\log f_0[3]$ = $\log f_0$ obtained in accordance with third approximation.
$\log f_0[1]$ = $\log f_0$ obtained by calculation in accordance with the limiting law.

to concentrations of 0.01 M than is the first approximation in that
(a) more plausible values for "a" are required
(b) it gives more consistent values for "a" throughout the range of concentrations considered

(c) the E_0 value so calculated for each experimental determination shows a constancy of the same order of magnitude as the experimental error and is not subject to personal interpretation as is that E_0 obtained by the graphical method.

2. Freezing point data for 1, −2 and 1, − 3 salts. Better agreement (to concentrations of 0.01 M) of experiment with the extended theory than with the first approximation has been found, in that more plausible and consistent "a" values are required.

3. The solubility of a difficultly soluble salt in a solvent salt solution in the case of luteo-cobaltic diammino dinitro oxalo cobaltiate in potassium sulphate solutions. It has been shown in this very complicated case that

   (a) a not impossible value for "a" is required

   (b) the theoretical curve joins the limiting law line at an angle comparable with the abrupt change in slope exhibited by the experimental curve. No existing theory has thus far been able to account for this anomaly.[bu]
   (c) fairly good agreement has been obtained with the experimental curve over a region from 0.0002 M to 0.001 M potassium sulphate including three points.

Conclusion

The numerical agreement between the theory extended in this paper to include unsymmetric valence types of electrolytes, and the data furnished by the simplest and most convincing experimental method, namely electromotive force, as well as the more than qualitative agreement with the most complicated case of solubility relationships of ternary mixtures furnishes confirmation of the validity of the Debye-Hückel Theory.

[bu] See Davies: J. Chem. Soc. Nov. 1930 p. 2421, a paper which has come to our attention since this paper was submitted for publication.

Bibliography

[1] Debye and Hückel: Physik. Z., 24, 185 (1923).
[2] LaMer and Mason: J. Am. Chem. Soc., 49, 410 (1927).
[3] Brönsted and LaMer: J. Am. Chem. Soc., 46, 555 (1924).
[4] LaMer and Cook: J. Am. Chem. Soc., 51, 2622 (1927).
[5] LaMer and Goldman: J. Am. Chem. Soc., 51, 2632 (1929).
[6] Lange: Fortschritte de Chemie, Physik und physikalische Chemie, 19, No. 6 (1928).
[7] Scatchard and Tefft: J. Am. Chem. Soc., 52, 2272 (1930).

[8] Eucken, Jette and LaMer: "Fundamentals of Physical Chemistry;" footnote p. 326 (1925).

[9] Gronwall, LaMer and Sandved: Physik. Z., **29**, 558 (1928).

[10] Bjerrum: Det. Kgl. Danske. Vidensk. Math-fysik. Medd., VII No. 9 (1926).

[11] H. Müller: Physik. Z., **28**, 324 (1927); **29**, 78 (a correction).

[12] Lange and Meixner: Physik. Z., **30**, 670 (1929).

[13] Lucasse: J. Am. Chem. Soc., **51**, 2601 (1929).

[14] Hansen and Williams: J. Am. Chem. Soc., **52**, 2766 (1930).

[15] Courant-Hilbert: "Methoden der Mathematischen Physik," **1**, pp. 273-275 (1925).

[16] Debye: Physik. Z., **25**, 97 (1924).

[17] Darmois: "Réunion Internationale de Chimie physique," pp. 25-40, (1928).

[18] Gronwall and LaMer: unpublished—See Reference [9].

[19] Gronwall with LaMer and Greiff: not yet published.

[20] Lewis and Randall: "Thermodynamics," pp. 254-255, 332-334 (1923).

[21] Fowler: "Statistical Mechanics," (1929).

[22] Horsch: J. Am. Chem. Soc., **41**, 1787 (1919).

[23] Cohen: Z. physik. Chem., **34**, 612 (1900).

[24] Carmody: J. Am. Chem. Soc., **51**, 2905 (1929).

[25] Hakomori: J. Am. Chem. Soc., **52**, 2372 (1930).

[26] Randall and Scott: J. Am. Chem. Soc., **49**, 649 (1927).

[27] Hovorka and Rodebush: J. Am. Chem. Soc., **47**, 1614 (1925).

[28] Robertson: Dissertation—Columbia University (1930)—J. Phys. Chem., **35**, 1953, (1931).

[29] Hall and Harkins: J. Am. Chem. Soc., **38**, 2674 (1916).

[30] Bedford: Proc. Roy. Soc., **83A**, 460 (1925).

[31] Harkins, Hall and Roberts: J. Am. Chem. Soc., **38**, 2652 (1916).

[32] Gronwall: not yet published.

[33] Wyman: Phys. Rev., (2) **35**, 623-34 (1930).

ELECTROLYSIS OF PERCHLORATES IN NON-AQUEOUS SOLUTIONS*

BY ALBERT L. CHANEY[1] AND CHARLES A. MANN[2]

Introduction

The use of perchlorates in non-aqueous solvents for electro-chemical work offers interesting possibilities on account of their exceptional solubility, and because of their chemical stability. The investigation of electro-deposition from non-aqueous solutions has been limited because of the lack of suitable inorganic salts with sufficient solubility. A number of investigations have been made with pyridin as a solvent for the purpose of depositing electrolytically the more active metals which cannot successfully be deposited from aqueous solutions. Müller et al. in particular have studied the deposition of metals such as the alkali and alkaline earth metals, aluminum, cerium, zinc, and cadmium, as well as the heavy metals. Solutions of halides and nitrates were used as electrolytes. They were able to obtain indications of deposits of several of the active metals, but the deposited metals interacted rapidly with the pyridin when the depositing current was stopped. These authors showed the importance of a knowledge of the polarization which takes place at the electrode during electrolysis.

Other organic solvents besides pyridin show good ionizing ability. In particular, furfural has a very high dielectric constant, and good conductances may be obtained in furfural solutions. The conductances of the iodides of lithium, sodium, potassium, rubidium, and ammonium were studied by Getman.[2] It was found that these salts showed a high degree of ionization.

Experiments on deposition of metals from furfural solutions were carried out by McKee[3] in this laboratory. He found that solutions of the pure heavy metal iodides were not generally soluble in furfural, but that double salts of these iodides with ammonium iodide could be successfully used. He was able to plate copper and silver from such solutions, but could not deposit zinc because of the instability of the furfural. He also tried the corrosion of a tungsten anode in ammonium iodide, but found no evidence that corrosion took place. Later, Haugsrud[4] found that the perchlorates were very soluble in furfural. He obtained successful electrodeposits of cadmium, copper, and lead, but was unsuccessful in plating cobalt, nickel, manganese, zinc, and aluminum. By allowing silver perchlorate to interact with tungsten hexa-

---

* Contribution from the Division of Chemical Engineering, School of Chemistry, University of Minnesota.

[1] The material presented in this paper is from part of a thesis submitted by Albert L. Chaney to the Graduate School of the University of Minnesota in partial fulfilment of requirements for the degree of Doctor of Philosophy, 1930.

[2] Chief, Division of Chemical Engineering, School of Chemistry, University of Minnesota.

chloride in furfural, a solution was obtained in which the tungsten anode was electrolytically corroded. However, no deposit of tungsten was obtained on the cathode. The perchlorates used by Haugsrud contained water of crystallization so that water was not entirely absent from these solutions. This water no doubt prevented the deposition of the metal.

The results indicated the desirability of obtaining more information concerning the electrochemical behavior of the perchlorates in organic solvents. Experiments were undertaken to determine the conductances shown by the perchlorates in organic solvents, particularly furfural, pyridin, ethylene glycol, and its monoethyl ether, cellosolve, and to determine the electrode potentials assumed by these metals in solutions of their perchlorates, and to measure the polarization occurring at the electrodes during the electrolysis.

Preparation, Purification, and Properties of Materials

Perchlorates

Comparatively little information is available in chemical literature on the preparation or properties of the perchlorates, except those of the alkali and alkaline earth metals.

The perchlorates of the alkali and alkaline earth metals have been studied extensively by G. F. Smith.[5] The perchlorates of potassium, rubidium, and caesium are quite insoluble in water, alcohols, acetone, ethyl ether, and ethyl acetate.

The alkaline earth perchlorates, and in general the perchlorates of most other metals, are on the contrary very soluble in water and organic solvents, and in some cases extremely so.

The perchlorates used in this investigation were very kindly supplied by Dr. G. F. Smith, of the University of Illinois. These perchlorates were the hydrated compounds which normally crystallize from water solutions. The barium and silver perchlorates were, however, anhydrous.

Methods of Analysis. Since experiments on conductance and electrodeposition were to be carried out in non-aqueous solvents, it was desirable to obtain the different perchlorates in the anhydrous state.

At the beginning of this investigation, a number of experiments were carried out to determine the loss in weight when these hydrated compounds were dehydrated under a number of conditions. At a later time, a method of analysis was worked out based on the determination of the perchlorate ion in any metallic perchlorate as potassium perchlorate. The results are conveniently expressed as the percentage of ClO_4 in the compound. This method of analysis is very similar to that described by Arndt and Nachtwey[6] for the analysis of organic perchlorates.

With slight modifications for the various salts, the method is as follows. From one fourth to one half gram of the perchlorate in question was weighed out and dissolved in about 5 cc. of absolute alcohol. To this was added about 20 cc. of a saturated solution of potassium acetate in absolute alcohol, which furnished an excess of potassium for the precipitation of the perchlorate ion. The solution was then heated nearly to the boiling point of alcohol for a few minutes and allowed to stand for two or three hours. This, however, was not permissible in the case of copper because the acetate of this metal decomposes if the solution is heated. The potassium perchlorate was then filtered off in a sintered glass crucible and then washed with absolute alcohol. The precipitate was dried and weighed at 110°C. The acetates of the metals were soluble in absolute alcohol, with the exception of silver acetate. Silver perchlorate could therefore not be analyzed at all by this method.

The perchlorates were dehydrated in a vacuum desiccator using P_2O_6 as the drying agent, or they were dried in a vacuum oven at a pressure of less than one cm. The vacuum oven could be maintained at any temperature from 25° to 140°C.

The following results were obtained on the metallic perchlorates. First

Aluminum Perchlorate

Four hydrates of aluminum perchlorate are recorded in the literature: $Al(ClO_4)_3.15H_2O$, $Al(ClO_4)_3.12H_2O$, $Al(ClO_4)_3.9H_2O$, and $Al(ClO_4)_3.6H_2O$.[7,8] The salt used in these experiments proved to be the hydrate containing nine molecules of water, and was very hygroscopic. This salt readily loses three molecules of water in a vacuum desiccator corresponding to a loss in weight of 11%, or in a vacuum oven at temperatures up to 100°C. At temperatures above 140°, decomposition occurs, with the oxide as probably the final product. Analysis of the salt after drying in a vacuum desiccator gave 68.5% to 68.9% ClO_4 compared to a calculated percentage of 68.84% for the hexahydrate. Some additional aluminum perchlorate was prepared by dissolving aluminum metal in 20% perchloric acid at a temperature of 70°C. After purification, the salt recrystallized from water proved to be the hydrate containing nine molecules of water, and behaved in a manner identical with that indicated above for the original material.

Barium Perchlorate

The properties and preparation of this salt have been studied extensively by G. F. Smith.[5,9] The anhydrous salt may be prepared by heating to 140°C. in a vacuum. Analyses gave 59.1% to 59.2% ClO_4 compared with 59.15 ClO_4 in anhydrous barium perchlorate.

Cadmium Perchlorate

Cadmium perchlorate is stated to form the hexahydrate by Salvadori.[10] He states that it melts at 105° and loses $2H_2O$ at that temperature, and the resulting tetrahydrate decomposes at 290°C. This salt may be prepared in the anhydrous state by first drying in a vacuum desiccator at temperatures of from 25° to 30°C. when a loss of weight of from 17% to 18% takes place. This corresponds to a loss of four molecules of water. If the resulting dihydrate is heated to a temperature of 120°C. in a vacuum, the anhydrous salt may be obtained. It is not possible to dry the hexahydrate in a vacuum at high temperatures, because the salt fuses at 60°C. Analysis of the dihydrate gave 57.7% ClO_4 compared to 57.26% for the calculated value. Analysis of an incompletely dried sample of the anhydrous salt gave 61% ClO_4 compared to a calculated value of 63.9% ClO_4.

Copper Perchlorate

Two hydrates of copper perchlorate, $Cu(ClO_4)_2.6H_2O$ and $Cu(ClO_4)_2.4H_2O$, are mentioned by Salvadori.[10] He gives its decomposition temperature as 180°C. On standing over P_2O_5 in a vacuum desiccator, a loss of from 9.5% to 10% in weight occurs, corresponding to the tetrahydrate. In a vacuum oven at the temperature of 100°C. the hexahydrate loses from 19.1% to 19.6% corresponding to the formation of the dihydrate. At a temperature of 110°C. the dihydrate decomposes with the formation of oxide. Accordingly, the anhydrous salt was not obtained in any of these experiments.

Cobalt Perchlorate

Salvadori,[10,11] gives the formula for cobalt perchlorate as $Co(ClO_4)_2.6H_2O$ and states that a tetrahydrate, $Co(ClO_4)_2.4H_2O$ is formed at 153°C. with decomposition at 180°C. Goldblum and Terliowski,[12] give the formula for cobalt perchlorate as $Co(ClO_4)_2.5H_2O$. In the vacuum oven at temperatures up to 120° C. a loss of 19% in weight occurs corresponding to the formation of the dihydrate. On further heating at 150° in a vacuum, decomposition to cobaltic oxide took place rapidly. This compound could be dehydrated only as far as the dihydrate.

Nickel Perchlorate

The behavior of nickel perchlorate is very similar to that of cobalt perchlorate, the same formula being given by Salvadori,[10,11] and Goldblum, and Terliowski.[12] In a vacuum oven at temperatures of 100° to 140°C., the dihydrate is obtained, the color of the salt changing from green to a pale yellow.

Analyses of nickel perchlorate by the potassium perchlorate method were not very satisfactory, the value of 64.7% ClO_4 being obtained for the dihydrate compared to a calculated value of 67.7%. Similarly the hexahydrate gave 53.3% compared to 54.4% calculated. However, analyses for the nickel content by dimethyl glyoxime gave 16.03% compared to a calculated value of 16.05%.

Lead Perchlorate

The formula for lead perchlorate as given in Gmelin-Kraut[13] is $Pb(ClO_4)_2.3H_2O$. In the vacuum desiccator, or in a vacuum oven at temperatures below 100°C. a loss of from 10% to 13% in weight occurs, giving the anhydrous salt. Analysis of the anhydrous lead perchlorate gave 48.5% ClO_4 compared to a calculated value of 48.98%. Lead perchlorate, both hydrated and anhydrous is extremely hygroscopic.

Silver Perchlorate

Silver perchlorate has been extensively studied by Hill,[14,15,16] and Macey,[17,18] and by Gomberg,[19] and it has been shown to be moderately soluble in many organic liquids, including benzene, toluene, nitrobenzene, chlorobenzene, glycerine and glacial acetic acid. Silver perchlorate may be obtained in the anhydrous state by heating to 120°C. in a vacuum oven. Silver perchlorate is slowly affected by light. When freshly prepared, silver perchlorate dissolves in furfural and forms stable, non-darkening solutions. If silver perchlorate has been exposed to light for some time, it reacts with furfural very rapidly with the formation of a jet black, pitch-like product.

Zinc Perchlorate

The following formulas are given for zinc perchlorate by Salvadori:[10] $Zn(ClO_4)_2.6H_2O$ and $Zn(ClO_4)_2.4H_2O$. In a vacuum oven at a temperature of 90° to 100°C. a loss of weight of 19% to 20% occurs which corresponds to the formation of the dihydrate. At 130°C., decomposition with the formation of zinc oxide took place. Analysis of the dihydrate gave 66.2% ClO_4 compared with the calculated value of 66.3% ClO_4.

General Conclusions. It may be seen from the above data that anhydrous perchlorates of the following metals may be obtained: alkali metals, magnesium, calcium, strontium, barium, silver, and lead. The following metals: copper, cadmium, cobalt, nickel, and zinc form perchlorates which normally crystallize from water solutions as the hexahydrates. On heating in the vacuum oven, all of these salts may be dehydrated to the dihydrate which is stable without further loss of water at temperatures up to 100°C. These dihydrates have not been previously described. Aluminum perchlorate forms the hexahydrate as the lowest stable hydrate at temperatures up to 100°C., and with this compound decomposition occurs at slightly higher temperatures.

Solvents

Purification and Properties of Furfural

Furfural when pure is a nearly colorless liquid, but readily undergoes auto-oxidation. Traces of acid and alkali cause a very rapid darkening, and aluminum chloride causes the furfural to change to black tar almost immediately. On the other hand, pyrogallol[3] and hydroquinone[20] act as negative catalysts, and furfural may be preserved by their use for several months. The furfural was purified from crude furfural manufactured by the Miner Laboratories of Chicago. It was purified by a method similar to that described by Evans and Aylesworth.[21] This method consisted of repeated distillations under reduced pressure, discarding the first and last portions of the distillate. The distillation was carried out over metallic calcium turnings to remove all traces of water. The pressure used was about 25 mm., and the temperature of distillation was approximately 65° to 70°C. A fractionating column was used filled with iron chain to a height of about 20 cm. Metallic calcium was found to have no reaction on the pure furfural. The principle guide to the purity of the product was a measurement of the conductance of a sample, since very small traces of water affect the conductance considerably. The furfural purified in this way gradually acquired a yellow color on standing, but remained entirely transparent for a month or two. All measurements of conductance were made with furfural which had been distilled less than a week. No stabilizer such as pyrogallol or hydroquinone was used.

This method of purification resulted in a furfural which had a specific conductance very much less than that previously reported in the literature. The specific conductances of the various samples used were not uniform, but only those samples of furfural were used which had specific conductances of from 35.10^{-8} to $7.3.10^{-8}$. The specific conductance of furfural as recorded by Getman[2] varied from $1.38.10^{-6}$ to $4.77.10^{-6}$. Lincoln[22] records the specific conductance of furfural used by him as being $25.6.10^{-6}$, and Walden[23] gives the specific conductance as being $1.45.10^{-6}$. Probably water affects this specific conductance more than any other substance. It was found that one or two drops of water added to a few cc. of furfural so that a saturated solution of water in furfural resulted, gave a specific conductance of approximately 7.10^{-5}.

The specific gravity was found to be 1.15505, calculated to the basis of 25°/4°. The value given by Mains[24] is 1.1545. The dielectric constant is stated by Walden[25] to be 41.9 at 20°C. The index of refraction was found to be 1.5271 compared to a value of 1.52608 given by Evans and Aylesworth.[21]

Cellosolve

Preliminary experiments had shown that the perchlorates gave conducting solutions in cellosolve (monoethyl ether of ethylene glycol). Cellosolve manufactured by the Eastman Kodak Company was fractionated by vacuum distillation over metallic calcium in a manner similar for that of furfural until a sample had a specific conductance between 5.10^{-8} and 10.10^{-8} reciprocal ohms. The temperature of distillation under vacuum was approximately 48°C. After the removal of water it reacted very slowly if at all with metallic calcium at room temperatures. The specific gravity 25°/4° of the purified cellosolve was 0.9270 compared to a value of 0.930 at 20°/20° given by Reid and Hofmann.[26] No information could be obtained from the literature on the dielectric constant of cellosolve.

Ethylene Glycol

Ethylene glycol could not be distilled over calcium due to the rather rapid reaction with evolution of hydrogen. A commercial sample of ethylene glycol was redistilled under reduced pressure at a temperature of about 80°C. The specific conductance of the fraction used was about 35.10^{-8}. Its vigorous reaction with calcium indicates that it probably would be of very little use for the electro-deposition of the more active metals. Its high viscosity is also a disadvantage. The dielectric constant as given by Walden[25] is 41.2

Pyridin

Mallinckrodt's chemically pure pyridin was redistilled and the fraction having a boiling point of 114.7° to 115° C. uncorrected, was used. The specific conductance was 23.10^{-8} and specific gravity, 25°/4° was 0.9771. The specific conductance given by Hantzsch and Caldwell[27] is $6.8.10^{-8}$ and the specific gravity 0.9776.[28]

Solubilities of Perchlorates

The perchlorates are in general very soluble in water, and in the common organic solvents. The solubilities of the alkali and alkaline earth perchlorates have been determined by Smith[5] in water, methyl, ethyl, propyl, and butyl alcohol, ether, acetone, and ethyl acetate. The solubility of $AgClO_4$ in a number of organic solvents has been determined by *Hill and Macy*[14,15,16,17,18]. Serullas[29] noted that the perchlorates of cadmium, cobalt, nickel, manganese, zinc, were very soluble in alcohol. Haugsrud[4] found that the perchlorates of nickel, cobalt, manganese, copper, cadmium, aluminum, zinc, and silver which he prepared were very soluble in furfural.

Approximate measurements of solubility were made for the various salts in the following manner. Samples of from one to three grams were weighed into a small bottle and small amounts of solvent added by means of a graduated pipette, until the perchlorate was just dissolved. The salt and solvent were shaken vigorously between additions of solvent so that an estimate could be made of the additional quantity of solvent necessary.

More accurate determinations were not feasible because of the large quantities of salts necessary which were not available. In the case of furfural, the rather rapid darkening of the more concentrated solutions makes it necessary that the determination be carried out rapidly.

In cellosolve, solutions were very viscous due to great solubility, and several hours were required for the solvent to become saturated, even though considerable excess of solute was present.

Table I gives the solubilities measured by the above method, together with the data on solubilities already published in chemical literature. The results are stated in grams of solute per hundred cubic centimeters of solvent throughout, unless otherwise stated. References in brackets are given after those values obtained from the literature.

TABLE I

Solubility of Metallic Perchlorates in Various Solvents
Grams of solute per 100 cc. of solvent

Salt	Solvent			
	Furfural	Cellosolve	Water	
$Ba(ClO_4)_2$	50 g	100+ g		
$Cd(ClO_4)_2.6H_2O$	80 g	145 g	478 g	(10)
$Cu(ClO_4)_2.6H_2O$	70 g	100+ g		
$Cu(ClO_4)_2.2H_2O$	20+ g		259 g	(10)
$Co(ClO_4)_2.6H_2O$	60 g	110 g	292 g	(10)
$Mn(ClO_4)_2.6H_2O$	90 g	130 g	268 g	(10)
$Ni(ClO_4)_2.6H_2O$	60 g	100+ g	267 g	(10)
$Ni(ClO_4)_2.2H_2O$	20 g	35 g		
$AgClO_4$	40 g	125 g	540 g	(14)
$Pb(ClO_4)_2$	25 g	105 g		
$Zn(ClO_4)_2.6H_2O$	85 g	130 g		

Conductance Measurements

Description of Apparatus. Measurements of conductance were made with a Leeds and Northrop Wheatstone bridge of the post office, dial type. The arrangement of apparatus is shown in Fig. 1. This bridge allowed measurements to be made to one tenth of one percent accuracy.

The vacuum tube oscillator is similar to that described by Jones and Josephs.[29] A UX171 tube with a plate voltage of 22.5 volts was used instead of the 201 A type used by them. It was found that a voltage of about five volts was obtained from the oscillator with a plate voltage of only 22.5 volts. For the tuned circuit a 0.1 mfd. paper condenser, C_1, was used in parallel with an iron cored coil, L_1, of approximately seven hundred turns. The number of turns on the plate coil L_2 was varied to give maximum voltage output. The coupling coil, L_3, to the bridge contained about one hundred turns.

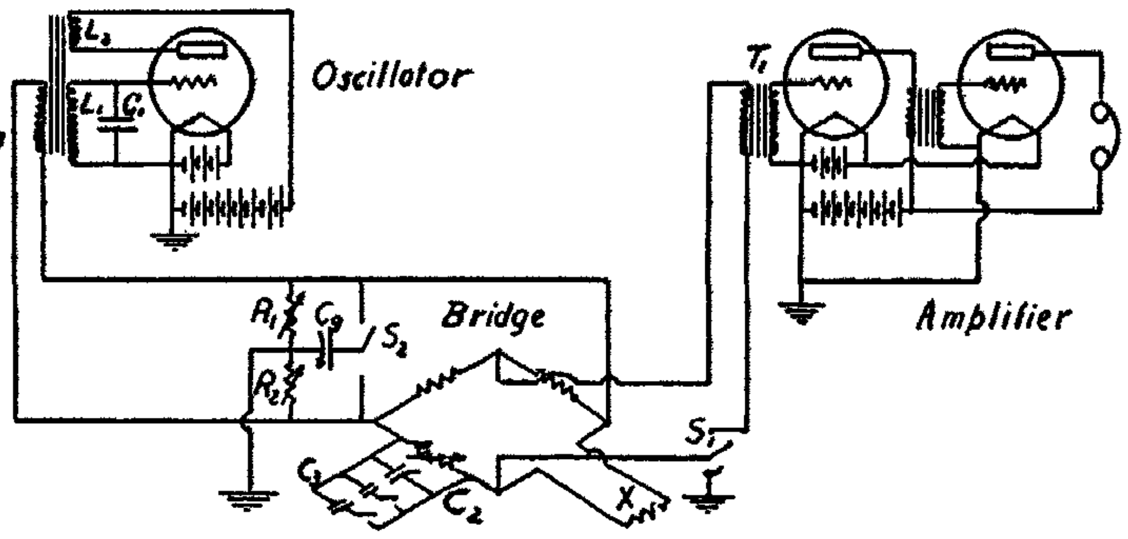


Fig. 1
Apparatus for Conductance

The whole set of coils, and the condenser for the tuned circuit, were shielded by enclosing them in a copper box approximately four by four by two and half inches (not shown). This shielding box was grounded to the negative side of the A battery. The use of an iron core makes the oscillator much more compact, and decreases the external magnetic field very considerably, so that the oscillator could be placed within four feet of the bridge proper without encountering any difficulties due to induced currents in any part of the bridge. Effective shielding is an absolute necessity for measurements of any accuracy.

The output was not entirely free from harmonics, but these did not create any difficulty in carrying out measurements to the degree of accuracy available with this type of bridge.

The method of grounding was similar to that described by Jones and Josephs.[29] This method of grounding was found to give very good results. The resistances marked R_1 and R_2 in Fig. 1 consisted of four-dial resistance boxes furnishing resistances up to 9,999 ohms; and a General Radio variable air condenser having a maximum capacity of 1500 mmfd. was used for the variable capacitance ground connection, shown in Fig. 1 as Cg.

The effective capacity across the cell was balanced out by means of a variable air condenser, C_2, of 1500 mmfd. capacity connected across the variable resistance arm of the bridge. With the more concentrated solutions, quite large capacities across the cell were encountered, as is usually the case in conductance measurements. A set of mica condensers, C_3, with switches attached, could be connected in parallel with the variable air condenser, C_2, and permitted capacities up to .02 mfd. to be used.

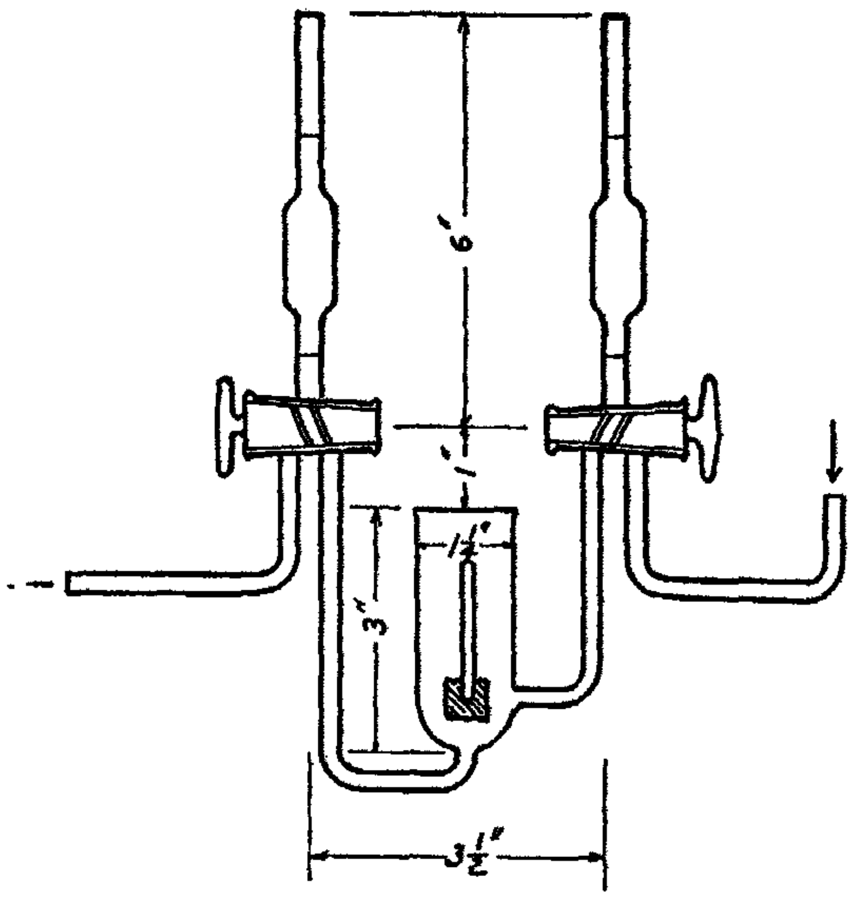


Fig. 2
Conductance Cell

In order to obtain accurate measurements of very high resistances, the phones were replaced by a two-stage audio amplifier. This amplifier consisted of two transformer coupled 201A tubes connected to the bridge by means of an audio transformer, T_1, with the phones in the plate circuit of the second tube, and with a 22.5 volt B battery for the plate supply. This enabled all four dials on the bridge to be set accurately at all resistances from 1,000 to 100,000 ohms, and with an estimation of the fourth figure on measurements from 100,000 up to 5,000,000.

A diagram of the cell with dimensions is shown in Fig. 2. It was made of pyrex glass, and the electrodes of smooth platinum were each about a centimeter square, and a little over one centimeter apart. The pipettes at the sides of the cell, for introduction and removal of solvent and solution, were of 5 cc. capacity, and also served as a convenient means of stirring and agitation for the solutions. In the earlier experiments, a weighed amount of salt was introduced into the cleaned and dried cell, and 20 cc. of pure solvent introduced. In the later experiments, a concentrated solution was first prepared, and by means of the pipette, 20 cc. were introduced into the cell. After a measurement of resistance had been made, 15 cc. was removed by the other pipette, and 15 cc. of fresh solvent introduced. This gave a concentration of one quarter of the previous solution. This could be repeated to as many dilutions as desirable.

The conductivity cell was filled with 20 cc. of the solution measured by the pipette attached to the cell, or in some cases dried salt was introduced into the cell, and 20 cc. of pure solvent introduced by means of the side pipette. In the latter case, the exact concentration of the solution was calculated from the total weight of the material introduced and the specific gravity of a solution of like concentration. This concentrated solution was used for conductance measurement and then a series of dilutions made by withdrawing 15 cc. of solution from the cell and introducing 20 cc. of pure solvent. Measurements of conductance were made after each dilution. At the end of the series of dilutions, the cell was rinsed out with pure solvent, and the conductances of the pure solvent for that particular series measured. In very dilute solutions, the conductance of the pure solvent becomes a very appreciable fraction of the conductance of the solution. It is usual in conductance measurements to subtract the conductance of the pure solvent from the measured conductance, and to call the resulting difference the conductance of the solution.[30] The cell constant was measured by means of .01 normal aqueous KCl solution, as given in the International Critical Tables.[31] In some cases, especially with furfural solutions, the readings for conductance did not remain constant, but slowly changed, due to reactions taking place in the solution. This was also evidenced by the darkening of the furfural solution. The data on the conductances of the various salts in furfural, cellosolve, ethylene glycol and pyridin are shown in Figs. 3 to 17 in which the equivalent conductance has been plotted against the square root of the concentration. Due to the rather rapid change in conductance for the lower concentrations and the fact that these conductances are not much greater than the equivalent conductance of the pure solvent, the graphs do not permit the determination of the equivalent conductances at infinite dilutions with any great accuracy, except in a few cases.

General Conclusions. Of the four solvents studied, furfural proved to be the best ionizing medium, and good conductances were obtained over the entire range of concentrations studied, as shown in Figs. 3 to 9. It will be also seen that the perchlorates of the divalent metals barium, nickel, cobalt, cadmium, manganese and copper show very similar values for conductance. In the case of nickel perchlorate, Fig. 5, the data for the hexahydrate, in Run 1, and the dihydrate, in Runs 3 to 5, have been plotted on the same curve. From this it may be seen that the degree of hydration of the salt in this case has no significant effect upon the conductances obtained. Cellosolve shows values for conductances which are rather small for the higher concentrations. At concentrations below 0.01 normal, however, the equivalent conductances increase rapidly as the solutions are made more dilute. As an ionizing medium, cellosolve is distinctly inferior to furfural. The solutions of the

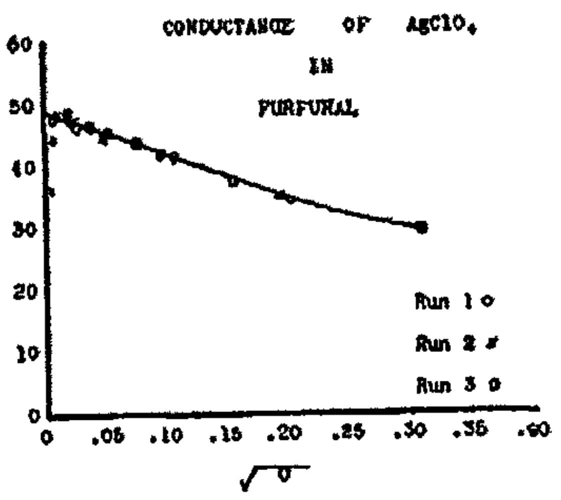


FIG. 3

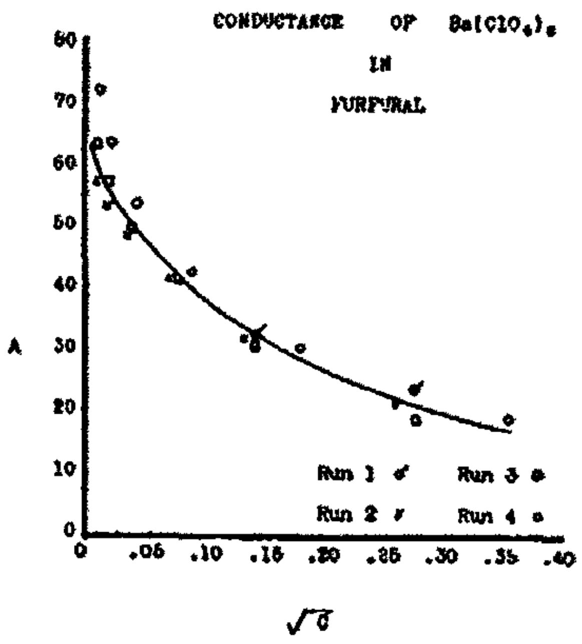


FIG. 4

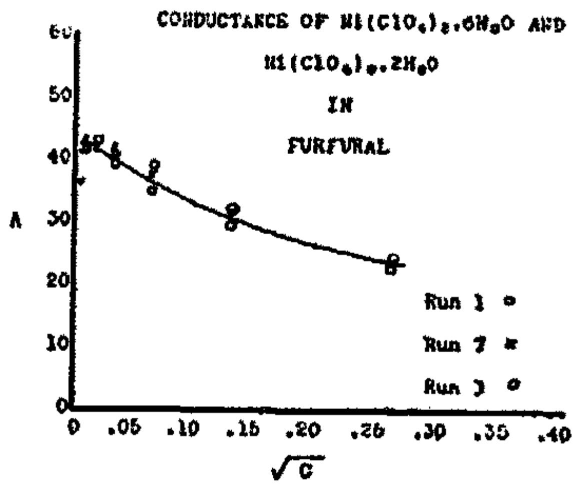


FIG. 5

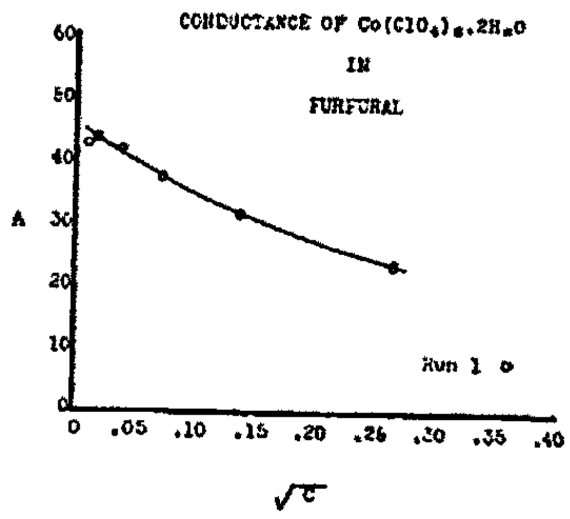


FIG. 6

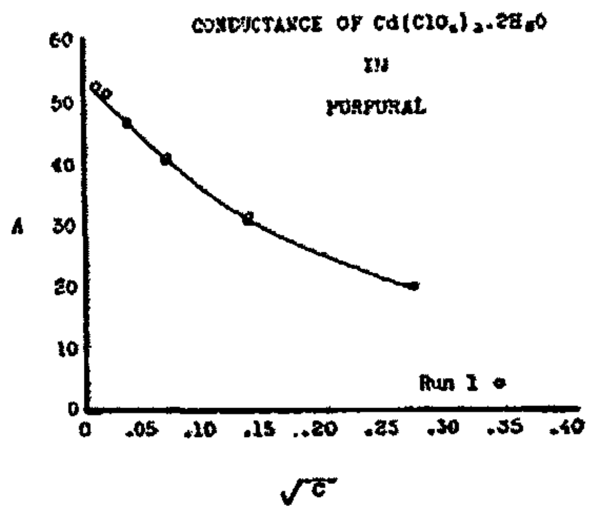


FIG. 7

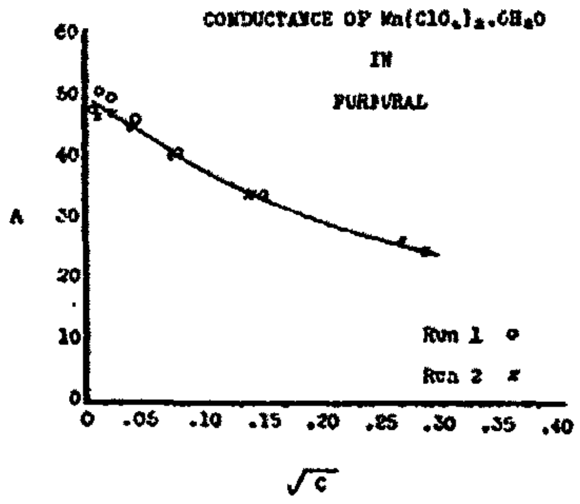


FIG. 8

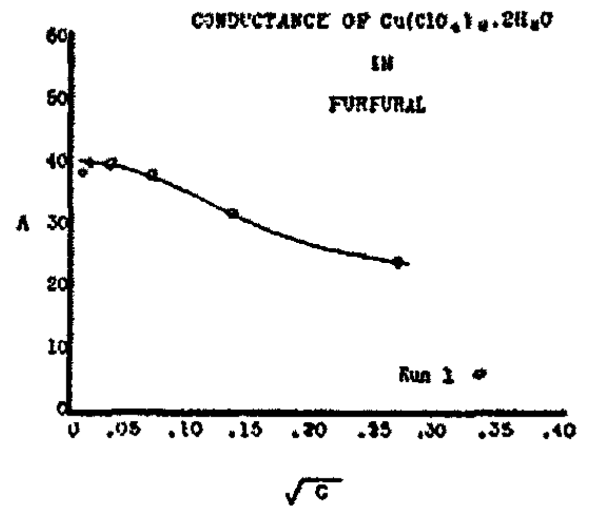


FIG. 9

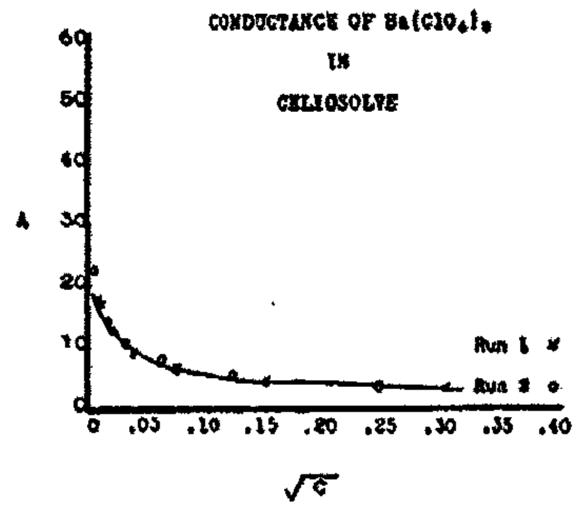


FIG. 10

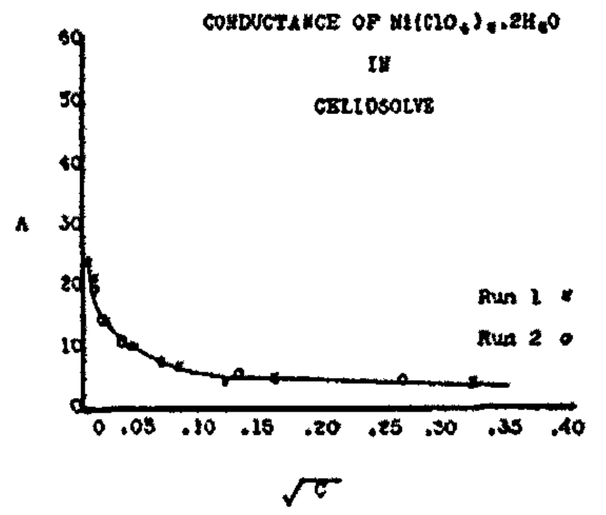


FIG. 11

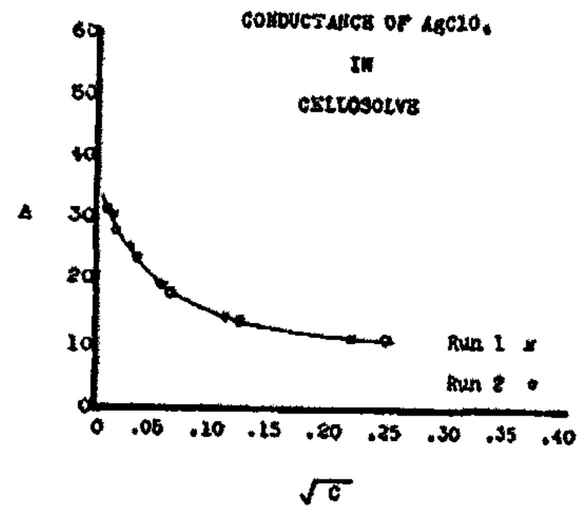


FIG. 12

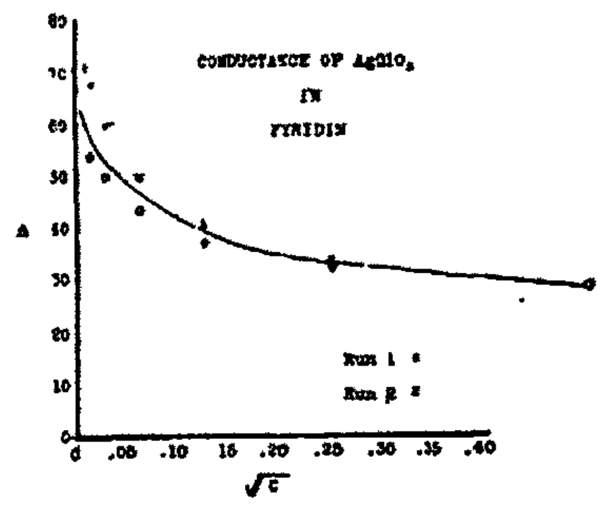


FIG. 13

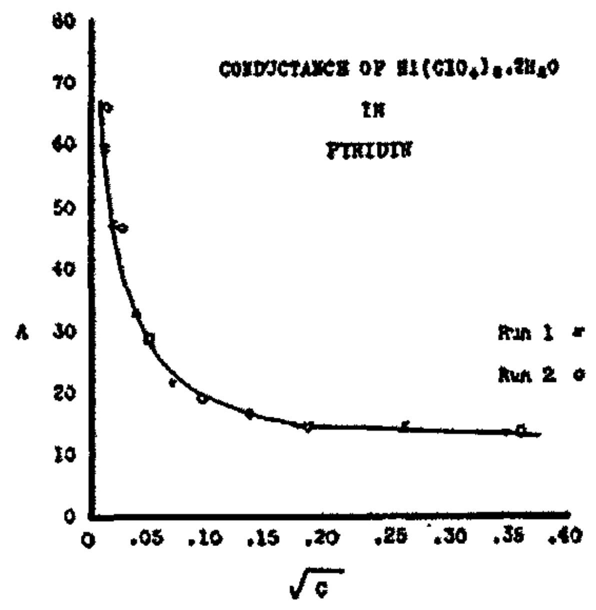


FIG. 14

perchlorates in pyridin show conductances of the same order of magnitude of those in furfural, although giving somewhat lower values in the more concentrated solutions. Ethylene glycol, in spite of its high dielectric constant, gives solutions which show very small conductances, and these conductances are also anomalous since they show a region of maximum equivalent conductance. This maximum occurs in solutions having a concentration of approximately .1 normal. It is distinctly inferior to cellosolve as an ionizing medium, and is not likely to be very useful in electrolytic work, as it is readily acted upon by the more active metals, such as calcium.

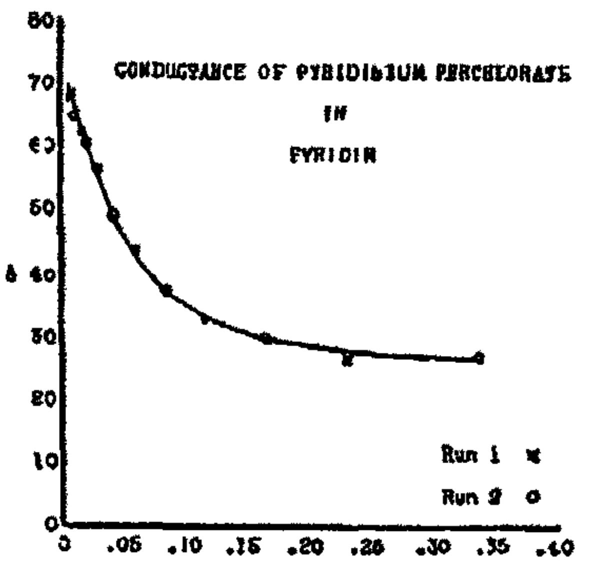


Fig. 15

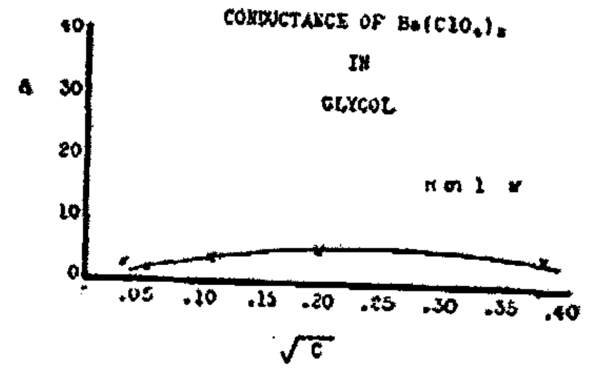


Fig. 16

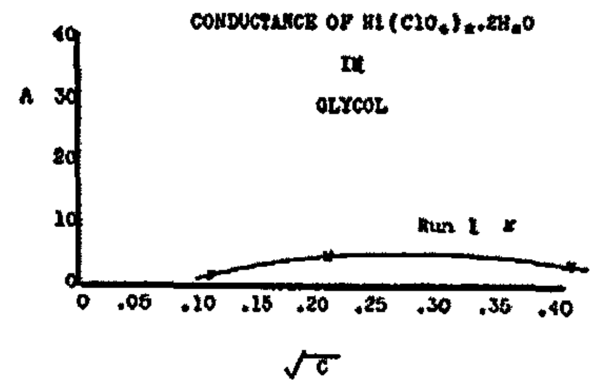


Fig. 17

Experiments on Electrodeposition

The E.M.F. across the cell while electrolysis is taking place may be considered as made up of three parts: the anode polarization, or difference in potential between the anode and the solution; the drop in voltage in the solution itself, due to the resistance of the solution; and the cathodic polarization, or difference in potential between the solution and the cathode.

Conductance measurements furnish information regarding the magnitude of the second of these E.M.F.'s, while the others may be measured with reference to some standard or reference electrode.

In non-aqueous solutions, the polarization potentials are difficult to determine, first because of the lack of suitable standard or reference electrodes, and secondly, because of the very high resistances of the cell and reference electrode. The reference electrode is usually connected to the anode or cathode by means of a long siphon tube, and this long column of poorly conducting liquid introduces a large electrical resistance.

The use of a vacuum tube potentiometer overcomes the difficulty with regards to resistance, since the potential of the system may be measured even though the internal resistance is several megohms. As an additional advantage, the vacuum tube potentiometer may be arranged to be direct reading so that changes in potentials may be followed as rapidly as they occur. Vacuum tube potentiometers of the direct reading type have been described by Goode.[32,33]

A second form of vacuum tube potentiometer in which the unknown voltage is compensated by an equal known voltage supplied from a standard potentiometer has been described by Partridge,[34] Morton,[35] and Elder.[36]

The requirements for an instrument to measure polarization potentials for electrodeposition are somewhat different than those encountered in ordinary potentiometric work, due to the difference in magnitude of the voltages involved. Constancy in calibration of the order of one millivolt is more than sufficient, and a much greater range of voltage is required. A simple type of vacuum tube potentiometer which used only one vacuum tube, and was direct reading, was accordingly devised which gave very satisfactory results for the purpose for which it was designed. The sensitivity of this instrument was such that 2.5 millivolts produced a change approximately of one microampere in the plate circuit. With a microammeter having a maximum range of 500 microamperes, voltages up to 1.25 volts may be read, or with a suitable shunting of the microammeter, larger voltages may be measured.

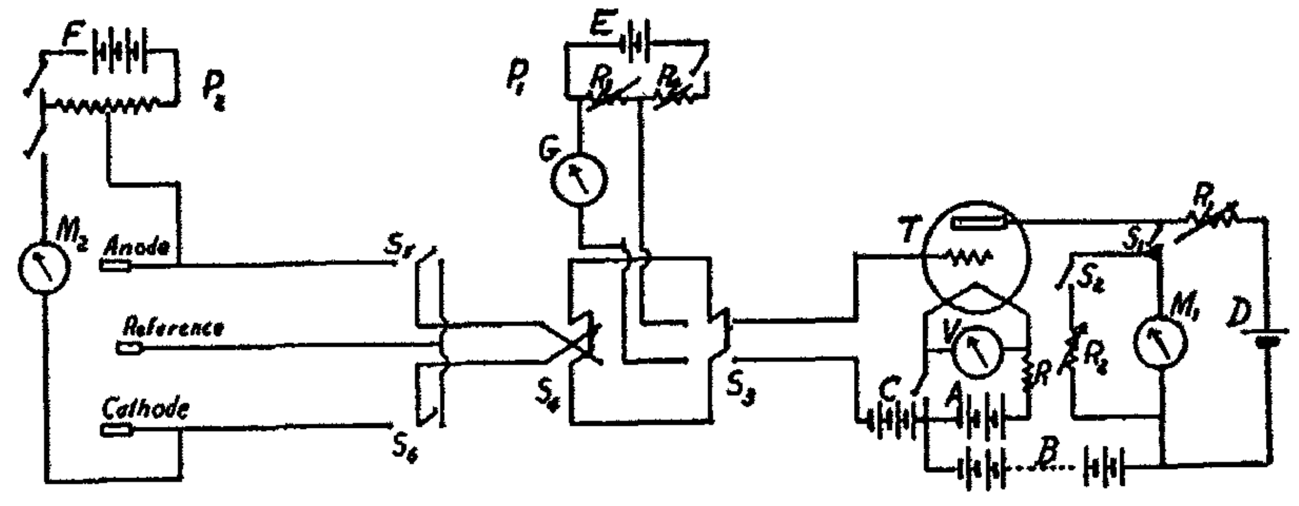


Fig. 18

Apparatus for Electrolysis and Vacuum Tube Potentiometer

Description of Apparatus. In Fig. 18 is shown a diagram of the apparatus and connections used for measurements of electrode and polarization potentials. The vacuum tube, T, is of the 201A type, requiring .25 amperes at five volts for its filament current. V is a filament voltmeter, and A is a storage battery. The B battery with a total voltage of 67.5 volts supplies the plate voltage. The meter, M_1, in the plate circuit is a microammeter having a maximum range of 500 microamperes, and estimates may be made to the nearest microampere. The C battery which fixes the operating potential of the grid consists of three dry cells giving a voltage of 4.5 volts. The battery designated as D is a single dry cell, and is the bucking-out battery which balances the normal plate current by an equal and opposite current. The value of this current is adjusted by means of the four-dial resistance box, R_1, having a maximum resistance of 9,999 ohms. R_2 is an adjustable shunt for the microammeter in order to increase the range of voltages which may be measured. The switch, S_1, serves to connect the meter in the circuit only when readings are desired, to avoid damage to the meter by any excessive plate current. S_2 is a switch which serves to shunt the meter when desired. The voltage to be measured is applied between the grid and the negative side of the C battery. A double-pole double-throw switch, S_3, permits this voltage to be applied either to the tube, or to an ordinary form of potentiometer, P_1. This potentiometer was used for comparison purposes, and also for calibrating the tube circuit. S_4 is a reversing switch which is required in order that the plate current may always be increased when voltages are applied in the grid circuit. By means of the two single-pole double-throw switches, S_5 and S_6, the voltage between the reference electrode and either the anode or cathode may be applied to the tube. By throwing both S_5 and S_6 to the left, the total voltage across the cell may be measured. By throwing both these switches to the right, the grid is directly connected to the C battery which reduces the plate current to the zero point, and the drift, if any has taken place, may be corrected by adjusting R_1. The battery, F, is used to supply the current for electrolysis. The voltage applied to the cell may be varied by means of the low resistance potentiometer, P_2. The current through the cell is read on the milliammeter, M_2.

A reference electrode which is easily reproducible, and gives constant voltages, is necessary for making any measurements on potentials. In aqueous solutions, the calomel electrode fulfills these requirements admirably. The use of such an electrode would have serious disadvantages, however, if used in connection with a non-aqueous system. There would be large and perhaps variable liquid junction potentials, and in addition there would be a continual diffusion of one solvent into the other, and this would introduce water into the non-aqueous system which it is particularly desired to keep anhydrous. Müller[1] has used in electrodeposition work from pyridin, a reference electrode of silver metal in contact with a .1 normal solution of silver nitrate in pyridin. Since silver perchlorate may be prepared in the anhydrous condition, and is very soluble in all of the solvents used, it was decided to try the use of a reference electrode consisting of silver metal in contact with a .1 normal solution of silver perchlorate in the solvent desired. The electrode consisted of a small tube with a side arm which could be closed by a stop-cock, and with silver wire inserted through the stopper of the tube. The side arm was bent so as to dip into the electrolysis cell, and this was drawn out to a fine capillary which dipped into the solution. After the electrode had been filled with a .1 normal silver perchlorate solution, the electrode was used with the stop-cock closed, since sufficient contact was made by the fluid around the stop-cock. Later a similar electrode was made from lead, in a .1 normal lead perchlorate solution. This electrode was more stable in furfural solutions than the silver electrode, and since lead is higher in the E.M.F. series than silver, the voltages impressed on the tube potentiometer were smaller.

The electrolysis cell was a small glass jar with a tight-fitting bakelite cover through which projected the two electrode holders and the side arm of the reference electrode. A diagram of the cell and reference electrode are shown in Fig. 19. With such a set-up using furfural solutions throughout, the resistance between either the anode or cathode and the reference electrode was approximately 1,000,000 ohms. In cellosolve the resistances were somewhat greater.

The vacuum tube potentiometer was calibrated by means of the potentiometer, P_1, using a Weston standard cell as the original standards of voltage. The leads from the potentiometer, P_1, were directly connected to the input of the potentiometer. The calibration curves obtained both with and without a shunt across the microammeter are shown in Fig. 20. It was found that a variation of filament current plus or minus 10% from the rated value did not produce an appreciable effect on the plate current readings, provided the zero point was correctly adjusted for each reading by means of the resistances R_1. It was also found that no appreciable error was caused by the internal resistance of the cell whose potential was being measured, provided the resistance was less than 100 megohms.

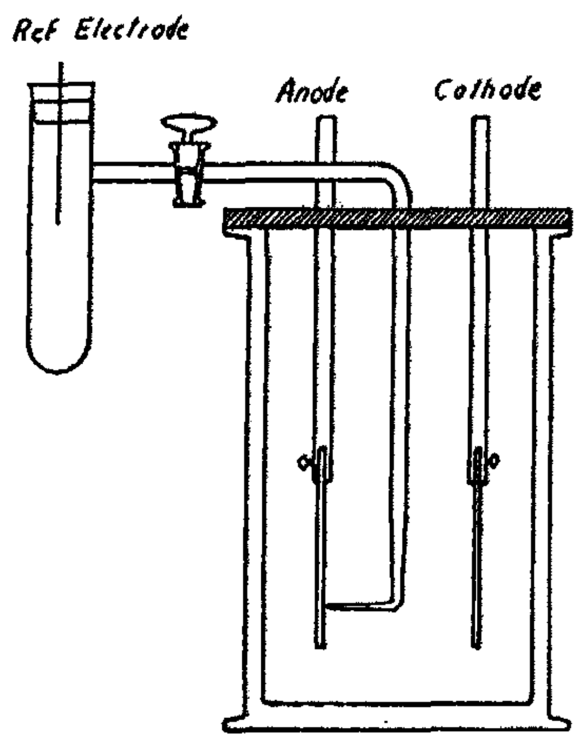


FIG. 19
Electrolysis Cell

Electrode Potentials. It was desirable to know the potentials assumed by the different metals in contact with their perchlorate solutions in order to interpret the measurements on polarization during electrolysis. Accordingly, a number of cells were set up using the reference electrode as half-cell, and the metals in contact with approximately a .1 normal solution of their perchlorate salts as the other half cell. Measurements were made in furfural, cellosolve, and aqueous solutions. The measurements in aqueous solutions were made for comparison purposes. Both lead and silver reference electrodes were used. Liquid junction potentials will exist between the two solutions in the reference half cell and the electrodes being measured; but these will probably be slight between solutions of metals containing similar ions, such as lead and cadmium The metallic electrodes were ground with emery to remove tarnish and oxide film, and were then scrubbed with soap and water. After rinsing in distilled water, the electrodes were finally dipped into pure 99% alcohol and allowed to dry.

Chemically pure metallic electrodes were used in each case. In order to insure that the surface of the electrode was in proper contact with the solution after the initial measurement had been made, this electrode was used as anode, and electrolysis carried out for a short time. This caused anodic corrosion to take place and thus expose a free surface of the metal to the solution. A measurement was made of the potentials between the anode and the reference electrode during electrolysis, to obtain some idea of the magnitude of polarization occurring. With some metals very little polarization occurred, and after electrolysis was stopped, the metal quickly returned to its original potential. With nickel and cobalt, however, very large polarization occurred, and the return to the original potential took a long time. This took place in water solutions as well as in the non-aqueous solutions, and is to be expected in view of the tendency of the cobalt and nickel to become passive. Table II shows the E.M.F. obtained from the different combinations in each solvent. Reference electrodes of both silver and lead were used in making these measurements. The perchlorate solutions used were .1 normal throughout.

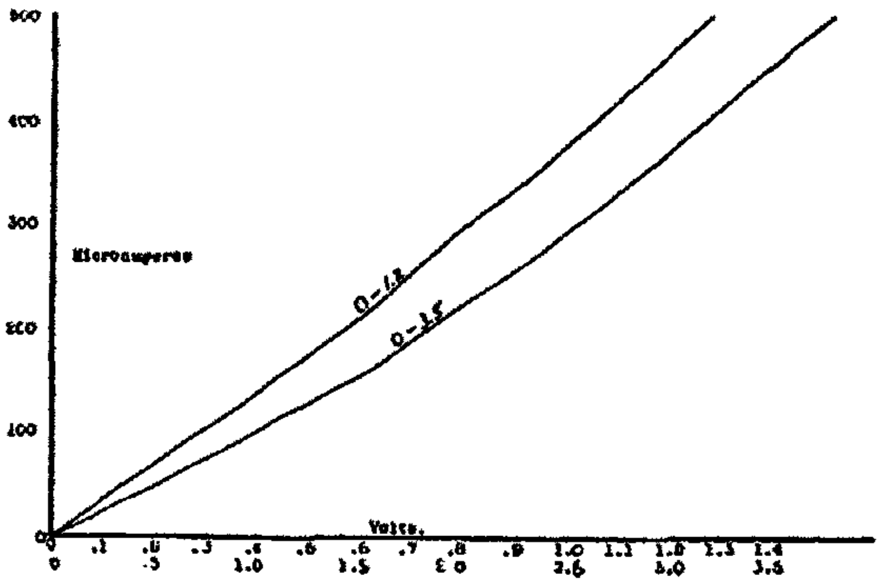


Fig. 20
Voltmeter Calibration Curve

Table II

E. M. F. Measurements

Cell Ref. El. Metal	E.M.F. in Volts Furfural	 Cellosolve	 Water
Ag–Zn	+1.239	+1.110	+1.485
Ag–Cd	+ .967	+ .845	+1.120
Ag–Co	+ .972	Irreg.	+ .875
Ag–Ni	+ .871	Irreg.	+ .547
Ag–Pb	+ .830	+ .825	+ .870
Ag–Cu	+ .251	+ .285	+ .332
Pb–Zn	+ .445	+ .434	
Pb–Cd	+ .138	+ .175	
Pb–Co	+ .123	Irreg.	
Pb–Ni	− .320	Irreg.	
Pb–Cu	− .547	− .720	
Pb–Ag	− .830	− .825	

In order to interpret the results shown in Table II, it is convenient to assume an arbitrary value for some single electrode and then to refer all other electrodes to that. In this manner it is possible to draw up a table of so-called single electrode potentials, and the values for different liquids may conveniently be compared.

For the purposes of comparison, therefore, it will be assumed that in each liquid the value of the lead in .1 normal lead perchlorate has the value ordinarily assigned to it in aqueous solutions, that is, −.122 volts.[37] With this assumption, Table III has been drawn up. Lead was chosen because it was a satisfactory reference electrode, and because it has a potential nearest to hydrogen of any metal used.

TABLE III

Single Electrode Potentials

Metal	Furfural		Cellosolve		Water	Standard Potentials[37]
	(1)	(2)	(1)	(2)		
Zn	−.531	−.567	−.407	−.556	−.689	−.7581
Cd	−.259	−.260	−.142	−.297		−.3976
Co	−.264	−.245	Irreg.	Irreg.	−.127	
Ni	−.163	+.198	Irreg.	Irreg.	+.201	
Pb	*−.122*	*−.122*	*−.122*	*−.122*	*−.122*	*−.122*
Cu	+.457	+.425	+.418	+.598	+.358	+.3448
Ag	+.708	+.708	+.703	+.703	+.748	+.7995

In series (1), silver was used as reference, while in series (2), lead was used.

It may be seen from this table that the values obtained by the use of the lead reference electrode are similar to those obtained from the silver reference electrode, but not identical with them. These differences are undoubtedly due to the liquid junction potentials involved in measuring the E.M.F. of the combinations.

In the last column of the table, the standard normal electrode potentials are given. These values are taken from the International Critical Tables.[37]

The values measured in water are not directly comparable with the standard *potentials, since the concentration is .1 normal instead of normal, but they* are given in this form for comparison between the different liquids.

It will be noted that the potentials, both positive and negative are smaller in furfural than in water, and still smaller in cellosolve than in furfural.

Electrodeposition from Furfural. Both McKee[3] and Haugsrud[4] found that it was possible to produce metallic deposits from furfural solutions. By using the iodides of copper and silver with ammonium iodide, McKee obtained deposits of each of these metals. Haugsrud, using hydrated perchlorates in

TABLE IV

Exper.	Conc. of Solution *Grams per liter*	Voltage *Volts*	Current *Milli-amp.*	Current Density *Amps. per sq. dm.*	Results
1	60 g. $Ba(ClO_4)_2$ 30 g. $Pb(ClO_4)_2$	2.5	43	.43	Coarse crystalline deposit
2	60 g. $Ba(ClO_4)_2$ 6 g. $Pb(ClO_4)_2$	4.0	22	.22	Loose, brown deposit
3	40 g $Pb(ClO_4)_2$	3.0	35	.35	Bright adherent deposit

furfural solutions obtained deposits of copper, cadmium, and lead. Experiments on cobalt, nickel, manganese, zinc, and aluminum did not yield deposits of these metals.

In the following experiments on furfural, attention was directed mainly to the deposition of the metals nickel and aluminum. Some results obtained in preliminary experiments on deposition of lead are also significant and will be described first. The conditions for electrolysis are shown in Table IV.

In each case the anode and cathode were lead plates, and the volume of solution was 30 cc. of furfural. The presence of the additional barium perchlorate in the first two experiments might be expected to decrease the resistance of the solution, and in the second experiment the concentration of the lead ion is very small. In deposition from aqueous solutions it is sometimes advantageous to keep the concentration of the metallic ion small, as in the deposition of silver from complex cyanides.

A deposit of lead was obtained in the first experiment, this deposit showing marked tendency to grow in the form of needle-like crystals. In the second experiment no deposit of lead metal as such was obtained. The deposit was very loose and flaky, and only a brown film similar to lead peroxide remained. The third experiment yielded the best plating of lead, which was dense and adherent. In this case the original lead cathode was further replaced during the course of the experiment by one of copper, and a successful deposit of lead was again obtained. The anode lost during the run 0.218 grams in weight, while the cathode gained 0.200 grams. This indicates very good current efficiency.

The influence of barium perchlorate in these experiments is apparently detrimental, since the best plate was obtained when no barium perchlorate was present, and when the solution contained a high concentration of lead ion.

The furfural solution showed no tendency to form tar during these experiments, though a slight film of lead peroxide was obtained on the anode in each case. The lead anodes were accordingly not insoluble under these conditions. It was observed, however, that a voltage of from three to four volts was required to start a current of more than one milliampere. After the current had once started, the voltage could be lowered to a volt and a half, and a current of more than ten milliamperes could be obtained. Steady currents were, however, only obtainable with voltages above two and a half volts.

Experiments on Deposition of Nickel. As has been mentioned, Haugsrud[4] did not obtain a deposit of nickel on electrolysis of nickel perchlorate solutions. Instead, deposits were obtained which were soluble in water and which gave test for the perchlorate ion. Haugsrud's conclusions were that the nickel perchlorate was deposited as such on the cathode, and that the solution of nickel perchlorate in furfural was colloidal in character.

Due to these rather unexpected results, a considerable number of experiments were carried out on the deposition of nickel. The nickel perchlorate used by Haugsrud was hydrated, probably the hexahydrate. In these experiments the dihydrate of nickel perchlorate was used. The experiments on conductivity indicate that furfural solutions of nickel perchlorate were true solutions and not colloidal, since the conductivities were of the same order of magnitude as the conductivities of the other perchlorates, both hydrated and anhydrous.

Experiment 1. Electrolysis of furfural containing the dihydrated nickel perchlorate yielded only a deposit of insoluble tar on the cathode, and the furfural itself rapidly darkened. An anode of nickel and a cathode of copper were used and the solution contained 50 grams $Ni(ClO_4)_2 \cdot 2H_2O$ per liter. This result differs from that obtained by Haugsrud[4] since the deposit described by him was soluble in water.

Experiment 2. This was an attempt to introduce nickel into the solution by anodic corrosion, and thus obtain a solution of nickel perchlorate which contained no water of hydration. The solution containing 120 grams of $Ba(ClO_4)_2$ per liter, and 5 grams $Pb(ClO_4)_2$ per liter was electrolysed with a voltage of 3.5 volts for a period of an hour, after which the electrodes were examined and then replaced, and the electrolysis continued for twelve hours. The anode was of nickel and the cathode of copper. During the first hour a deposit of lead was obtained. After replacing with a new cathode, no further deposit was obtained. The solution remained clear, and the current, which was approximately five milliamperes, caused a total loss of weight in the anode of about one hundred milligrams, whereas the increase in weight on the cathode was only about one milligram. Whenever nickel anodes were used in furfural solutions, marked anodic polarization was noted, and small amounts of insoluble tar were formed on the anode. This tar prevented calculation of the exact anodic efficiency, but this efficiency was found to be approximately 90%. Absence of any deposit on the cathode indicates a cathodic efficiency of zero, and some reaction other than deposition must have occurred at the cathode. No gas was liberated at any time. This was to be expected, since the materials were all anhydrous.

A possible reaction is the conversion of furfural into furyl alcohol with perhaps the simultaneous production of pyromucic acid. Furyl alcohol when treated with a concentrated hydrochloric acid polymerizes rapidly and gives a green color.[38] Under the same circumstances, furfural, in the absence of furyl alcohol, polymerizes slowly, but without the formation of the green color. Some crude furyl alcohol was purified by distillation, and it was found by experiment that furyl alcohol could be detected in the presence of furfural by this color test.

This test was then made on the solution which had been electrolysed for a period of twelve hours, and a positive test for furyl alcohol was obtained. This accordingly may be taken as an explanation of the absence of metallic deposition during electrolysis.

Experiment 3. The object of this experiment was to ascertain if furyl alcohol would be produced using nickel perchlorate solutions. The solution contained 120 grams $Ba(ClO_4)_2$ per liter and 15 grams $Ni(ClO_4)_2 \cdot 2H_2O$ per liter. The anode was of nickel and the cathode of copper, as in Experiment 2. In this case a tarry deposit was obtained on the cathode initially. After replacing the cathode with a fresh copper strip, no further deposition took place on continued electrolysis. On testing the furfural solution, a positive test was obtained for furyl alcohol. Thus this experiment gave the same results as Experiment 2.

Experiment 4. Anodic corrosion was again resorted to, this time using anhydrous lead perchlorate only in the furfural solution. The concentration was 40 grams $Pb(ClO_4)_2$ per liter. A copper cathode and nickel anode were used as in the previous experiments. An initial plate of lead was obtained on the copper cathode. This was a dense adherent deposit. Electrolysis was continued for twenty-four hours at a voltage of four volts and with a current of twenty milliamperes at a current density of .2 amperes per square decimeter. At the end of the electrolysis, the deposit on the cathode was dissolved in nitric acid, and tested for both nickel and lead. The deposit contained a considerable percentage of metallic nickel. The final deposit was non-adherent, and quite spongy, and was readily scraped off the cathode. A new cathode was then placed in the solution, but the solution failed to give further deposit, producing furyl alcohol instead. No deposit was obtained when this copper cathode was replaced by a silver cathode. The silver cathode was used to ascertain if the nature of the electrode influenced the formation of furyl alcohol.

Experiment 5. A similar experiment on the replacement of cadmium ion by nickel in furfural solutions was carried out. In this case two grams of cadmium perchlorate were dissolved in 30 cc. of furfural, and electrolysed with a nickel anode and copper cathode. The initial deposit of cadmium was bright and adherent. Continued electrolysis produced a considerable amount of tar and a spongy deposit on the cathode. On testing, it was found that this deposit contained considerable nickel. It was found later on analysis that the cadmium perchlorate used was not entirely anhydrous, and this may possibly account for the formation of tar. These experiments are typical of those performed on the deposition of nickel.

The following conclusions may be drawn from these experiments. No entirely satisfactory deposits of nickel were obtained from any of these solutions. However, deposits of metallic nickel were obtained along with lead, by replacing the lead ion by nickel ion by means of anodic corrosion. Similar results were obtained in replacing cadmium ion by nickel. The secondary reactions which take place in furfural solutions, that is, the formation of tar and of furyl alcohol, constitute a serious disadvantage in the use of furfural for the deposition of metals from furfural solutions.

Experiments on Deposition of Aluminum. Solutions of hydrated aluminum perchlorate in furfural were so unstable that no attempts were made at electrolysis. The solution polymerizes to a black tar very quickly. There remains the possibility of anodic corrosion with the subsequent deposition of aluminum from the solution.

For anodic corrosion experiments, solutions of anhydrous perchlorates are desirable. Anhydrous perchlorates of barium, cadmium, lead, and silver were considered as possibilities. Silver perchlorate is undesirable, on account of its reduction by furfural under the influence of light. Experiments were carried out using barium and cadmium perchlorates. The following experiments are typical of the results obtained.

Experiment 1. A solution containing 150 grams of $Ba(ClO_4)_2$ per liter was electrolysed with an aluminum anode and a copper cathode. Though the resistance of this solution is very low, the large polarization encountered at the electrodes necessitates the use of high voltages in order to obtain useful currents through the solutions. At a voltage of 8.8 volts, the current is about three milliamperes, or .03 amperes per square decimeter. In this case the solution around both the anode and cathode rapidly became darkened with considerable tar formation. No evolution of gas was observed, and no appreciable deposition occurred on the cathode after electrolysing for three hours. These results are perhaps not unexpected since the barium ion is the only positive ion in the solution and barium must be deposited or some secondary reaction must take place at the cathode before aluminum ion can be introduced into the solution.

Experiment 2. A solution containing 100 grams of cadmium perchlorate per liter of furfural was electrolysed with an aluminum anode and copper cathode. The cadmium perchlorate used was not absolutely anhydrous, but contained a much smaller percentage of water than is found in the dihydrate. The initial deposit of cadmium was bright and adherent, but tar formation at the anode took place rapidly. The voltages required to produce appreciable currents in the solution were less than in the previous experiments, since 5.5 volts produced an initial current of twenty milliamperes. This current rapidly dropped off as the cadmium was deposited, and electrolysis was continued for about ten hours. The deposit of cadmium was finally dissolved in hydrochloric acid. On addition of ammonium hydroxide, traces of aluminum hydroxide estimated at one or two milligrams were obtained. The total time of electrolysis was insufficient in this experiment to deposit all of the cadmium from the solution, but the rapid formation of tar around the anode prevented further electrolysis.

It will be noted that in the anodic corrosion of both nickel and aluminum, considerable formation of tar occurred at the anode, even though the materials used in making up the solutions were all anhydrous. The tendency toward the formation of tar is a serious disadvantage in the use of furfural. In these replacement experiments, electrolysis must be carried on over a considerable length of time, which requires a stable electrolyte. Furfural does not fulfill these conditions.

Electrodeposition from Cellosolve. Cellosolve proved to be a suitable medium for deposition, in many respects superior to furfural. Although conductances in this solvent are not nearly so great as those in furfural or pyridin, the very great solubility of the perchlorates in this solvent permits solutions of fairly low resistances to be prepared. The solvent itself is much more stable under conditions of electrolysis than is furfural. In no case was any tar formed, or was there any evidence of decomposition. Preliminary experiments indicated that metals could be successfully deposited from cellosolve solutions of their respective perchlorates. The results of these experiments are shown in Table V.

TABLE V

	Deposit	Cathode	Solution, gr./liter	Voltage	Current Density	Results
1.	Copper	Silver	100 g. $Ba(ClO_4)_2$ 25 g. $Cu(ClO_4)_2{\cdot}2H_2O$	2.0	.025	Good plate
2.	Lead	Copper	100 g. $Pb(ClO_4)_2$	4.0	.08	Good plate
3.	Zinc	Copper	100 g. $Ba(ClO_4)_2$ 25 g. $Zn(ClO_4)_2{\cdot}2H_2O$	2.5	.04	Gas evolved No metal deposited

With these metals good results were obtained except in the case of zinc. The evolution of gas, which took place at both anode and cathode, may be due to the water present in the hydrated zinc perchlorate.

Electrodeposition of Nickel and Cobalt. In contrast to the results obtained in attempting to deposit nickel from furfural solutions, bright deposits of both nickel and cobalt were readily obtained in cellosolve solutions. The following table shows the results obtained with different concentrations of salts and different current densities. The current densities in the column headed C. D. are given in amperes per square decimeter.

TABLE VI

Deposit		Solution, gr./liter	Voltage	C.D.	Results
1.	Nickel	100 g. $Ba(ClO_4)_2$ 25 g. $Ni(ClO_4)_2{\cdot}2H_2O$	2.00	.01	Black deposit Slight gas
2.	Nickel	100 g. $Ba(ClO_4)_2$ 25 g. $Ni(ClO_4)_2{\cdot}2H_2O$	3.00	.025	Black deposit
3.	Nickel	50 g. $Ni(ClO_4)_2{\cdot}2H_2O$	5.00	.18	Bright deposit
4.	Cobalt	60 g. $Co(ClO_4)_2{\cdot}2H_2O$	4.00	.20	Deposit black, spongy
5.	Cobalt	60 g. $Co(ClO_4)_2{\cdot}2H_2O$	5.00	.30	Black, brittle deposit
6.	Cobalt	60 g. $Co(ClO_4)_2{\cdot}2H_2O$	2.00	.07	Black, brittle deposit
7.	Cobalt	120 g. $Co(ClO_4)_2{\cdot}2H_2O$ 60 g. $Ba(ClO_4)_2$	2.00	.10	Good deposit, black

Although bright nickel plates were readily obtainable, those of cobalt were black, similar to burnt deposits in aqueous electroplating. Copper was the cathode material used for all these experiments. The plates of nickel and cobalt both showed a marked tendency to crack and peel off the underlying metal. The best deposits were obtained with the use of low voltages and high salt concentrations. However the use of $Ba(ClO_4)_2$ for this purpose as in Experiments 1 and 2, Table VI, shows only detrimental results.

Electrodeposition of Aluminum. This experiment on deposition of aluminum was carried out in a manner similar to the experiments on aluminum deposition from furfural. Anodic corrosion was resorted to for production of a solution containing aluminum ion.

This experiment was carried out as follows. A solution of anhydrous lead perchlorate containing 60 grams $Pb(ClO_4)_2$ per liter of solution was prepared, and this solution was electrolysed at a voltage of four volts. The anode was of aluminum and the cathode of copper. The cathode was removed at intervals and the deposit was qualitatively analysed for the presence of aluminum and lead. This was done by dissolving the deposit in nitric acid and evaporation with sulfuric acid to precipitate the lead as lead sulfate. Ammonium hydroxide was then added to the filtrate for the detection of aluminum as aluminum hydroxide. The cathode was first replaced at the end of one hour. The current density was .08 amperes per square decimeter. A good adherent plate of lead had been deposited on the cathode. Continuing the electrolysis, the lead was deposited on the cathode as long needle-like crystals. The cathode was replaced at intervals of six hours. After about twenty-four hours of electrolysis, the character of the deposit gradually changed to a loose, gray, spongy deposit. This deposit contained traces of aluminum. After the electrolysis had been continued about forty-eight hours, the final deposit contained very little lead, and was apparently composed of finely divided aluminum metal. This deposit dissolved in acid with the evolution of hydrogen, and gave a precipitate of aluminum hydroxide on the addition of ammonium hydroxide. This experiment gave the most successful results of any tried for the deposition of aluminum.

General Conclusions on Deposition. The perchlorates of the heavy metals, especially those which can be obtained in the anhydrous state, are well adapted for electrodeposition from non-aqueous solutions. All anodes tried, including aluminum, lead and nickel, were readily corroded by the passage of current through the cell. The great solubility of the perchlorates permits solutions of low specific resistance to be prepared.

Comparing the solvents cellosolve and furfural, cellosolve was found to be superior, due to its chemical stability, though the conductances in cellosolve solutions were considerably smaller than those in furfural.

The current densities employed in these experiments were of the same order of magnitude as those used in aqueous electroplating.

We wish to express our appreciation to Doctor G. F. Smith for the preparation of the metallic perchlorates used in this investigation.

Summary

1. The hydrates of various metallic perchlorates have been subjected to dehydration in the vacuum oven, and the extent of dehydration determined. By this method, lead perchlorate and cadmium perchlorate have been prepared in the anhydrous state. The dihydrates of cobalt, copper, manganese, nickel, and zinc have been prepared from the corresponding hexahydrated perchlorates.

2. Furfural and cellosolve have been purified by distillation over metallic calcium, and their specific conductances determined.

3. The approximate solubility of the metallic perchlorates have been determined in furfural and cellosolve, and these salts have been found to be very soluble in nearly all cases.

4. Measurements of conductances for a series of metallic perchlorates have been made in furfural, cellosolve, ethylene glycol, and pyridin over a range of concentration from .1 normal to .00001 normal.

5. A modified form of vacuum tube potentiometer has been described, suitable for the determination of electrode potentials and for measurement of polarization.

6. The electrode potentials of zinc, cadmium, cobalt, nickel, lead, copper and silver have been measured in their perchlorate solutions in furfural and cellosolve.

7. The deposition of several of these metals from perchlorate solutions in furfural has been studied.

8. The metals copper, lead, nickel, and cobalt have been successfully deposited from cellosolve solutions of their perchlorates.

9. A deposit containing aluminum metal has been obtained from a cellosolve solution of the aluminum perchlorate prepared by anodic corrosion.

Bibliography of References

[1] Müller et al.: Monatsheft, 43, 67-74, 75-80, 419-437, (1922); 44, 219-236, 237-246, (1923).
[2] Getman: J. Phys. Chem., 28, 212, (1924).
[3] McKee: Master's Thesis 1926, University of Minnesota.
[4] Hausgrud: Master's Thesis 1928, University of Minnesota.
[5] Smith: J. Am. Chem. Soc., 45, 286 (1923).
[6] Arndt and Nachtwey: Ber., 59B, 446-448 (1926).
[7] Weinland and Ensgraber: Z. anorg. Chem., 84, 368-72 (1913).
[8] Dobroserdov and Pshenichni: Chem. Zentr., 1926 II, 2404.
[9] Smith: Ind. Eng. Chem. 19, 411 (1927).
[10] Salvadori: Gazz., 42 I, 458-494, (1912).
[11] Salvadori: Gazz., 40 II, 19-21.
[12] Goldblum and Terliowski: Bull., 11, 146-159 (Series 9 Vol. 2).
[13] Gmelin-Kraut: "Handbuch der anorg. Chemie," IV II, 356-357.
[14] Hill: J. Am. Chem. Soc., 43, 254 (1921).
[15] Hill: J. Am. Chem. Soc., 44, 1164-1193 (1922).
[16] Hill and Miller: J. Am. Chem. Soc., 47, 2702-2712 (1925).
[17] Hill and Macy: J. Am. Chem. Soc., 46, 1132 (1924).
[18] Macy: J. Am. Chem. Soc., 47, 1031 (1925).
[19] Gomberg: J. Am. Chem. Soc., 45, 398 (1923).
[20] Moureu and Dufraisse: J. Soc. Chem. Ind., 47, 819-828 (1928).
[21] Evans and Aylesworth: Ind. Eng. Chem., 18, 24-27 (1926).
[22] Lincoln: J. Phys. Chem., 3, 464 (1899).
[23] Walden: Z. physik. Chem., 54, 150 (1905).
[24] Mains: Chem. Met. Eng., 26, 779 (1922).

[25] Walden: Z. physik. Chem., **70**, 569 (1910).
[26] Reid and Hofmann: Ind. Eng. Chem., **20**, 497 (1928).
[27] Hantzsch and Cladwell: Z. physik. Chem., **61**, 227.
[28] Heap, Jones and Speakman: J. Am. Chem. Soc., **43**, 1936-40 (1921).
[29] Jones and Josephs: J. Am. Chem. Soc., **50**, 1055 (1928).
[30] Taylor: "Treatise on Physical Chemistry," **I**, 513.
[31] Int. Critical Tables, **6**, 230.
[32] Goode:'J. Am. Chem. Soc., **44**, 26 (1922).
[33] Goode: J. Opt. Soc. America, **17**, 62 (1928).
[34] Partridge: J. Am. Chem. Soc., **51**, 1 (1929).
[35] Morton: Trans. Faraday Soc., **24**, 14 (1928).
[36] Elder: J. Am. Chem. Soc., **51**, 3266 (1929).
[37] Int. Critical Tables: **6**, 332.
[38] Richter: "Organic Chemistry" Vol. III, p. 15.

THE APPARENT VOLUMES OF SALTS IN SOLUTION

I. A Test of the Empirical Rule of Masson

BY ARTHUR F. SCOTT

The apparent molal volume φ of a salt in an aqueous solution is defined as

$$\varphi = \frac{v - n_1 v_1}{n_2} \tag{1}$$

where v is the volume of a solution containing n_2 mols of electrolyte and n_1 mols of water; v_1 is the volume of one mol of pure water at the temperature of the solution. Although there have been many studies of the apparent molal volume, very little is known regarding this characteristic property of solutions, especially with respect to its bearing on the nature of the solution state. However, the empirical relationship, recently put forward by Masson,[1] appears to offer some interesting possibilities in this connection.

Masson's empirical rule may be expressed in the following form:

$$\varphi = a\, m^{\frac{1}{2}} + b \tag{2}$$

Here m is the molarity (gram-mols per liter); a and b are constants, characteristic of the salt involved and also dependent on temperature. Masson examined the validity of the above equation for solutions of twenty-eight salts with the following results: Of the twenty-four strong electrolytes in this group, the solutions of only two (magnesium nitrate and sodium acetate) were found not to conform to the above rule. The solutions of the four so-called weak electrolytes were found to be abnormal in that they apparently require the five-fourths power of the molarity instead of the square-root. Finally, in five instances (sulfuric acid, lithium chloride, nitric acid, and ammonium nitrate) the plotted points for a given solution exhibited an abrupt transition from the straight line, generally, at relatively high concentrations.

While the evidence in support of equation (2), which we have only partially summarized above, does indicate that the linear relationship is valid for the simple type of strong electrolytes, it appears desirable to extend the examination of the equation in a more systematic manner. In this way it should be possible not only to make a more thorough test of the equation but also to gain some insight into its significance. Therefore, in the present preliminary paper we shall examine the general applicability of equation (2) to solutions of the alkali halides (1) by testing its ability to represent the experimental variation of φ with concentration; (2) by checking the expected additive properties of the constant b; and (3) by comparing experimental and computed values of φ in saturated solutions. The data employed in this examination are from the careful measurements of Baxter and Wallace[2] and

---

[1] Masson: Phil. Mag., (7) **8**, 218 (1929).

[2] Baxter and Wallace: J. Am. Chem. Soc., **38**, 70 (1916).

are well suited for the purpose. From them it is possible to compute for the halogen salts of the five alkali metals values of φ at concentrations ranging from nearly saturated to about three-tenths molar for at least three different temperatures.

Before presenting the results of the present study it is important to call attention to certain matters affecting precision. In the first place φ is the difference of two volume terms and consequently is of a much lower order of precision than the basic quantities. Indeed, according to Baxter and Wallace, the values of φ, as determined by them, are about ten times more precise for concentrated solutions than for dilute solutions, despite the fact that the basic quantities involved in the latter are the more precise. Moreover, it should be noted that the probable precision of φ at a given concentration is not identical for each salt. Hence, only a very general statement regarding the precision of the φ values calculated from the experimental measurements is permissible: The uncertainty in φ is less than 0.01 cc. in concentrated solutions but in very dilute solutions it probably amounts to several hundredths of a cubic centimeter. In considering the applicability of equation (2) to the experimentally determined data it will be necessary to keep a second item in mind. Any error in a basic measurement of density or weight of salt per unit weight of solution which would act to increase φ would act to decrease the magnitude of $m^{\frac{1}{2}}$. Thus, any errors in the experimental data are magnified when represented by equation (2).

In carrying out the first test of equation (2), namely, that of determining how closely the linear relationship describes the variations of φ with $m^{\frac{1}{2}}$, it is necessary to know the values of the constants a and b for each case. These quantities, which are given in columns 3 and 4 of Table I, have been computed from the experimental points (φ, $m^{\frac{1}{2}}$ values) by the method of "zero sum."[1] In calculating these constants it became apparent that, because of the limited number of experimental points available (usually five), an error in the data of one point can introduce a serious error in the values of the constants, especially in a. Since it was desired to obtain the most representative values of the constants, it was considered advisable in applying the method of "zero sum" to disregard any point which deviates very markedly from a straight line drawn through the remaining points. Information on this matter is also presented in Table I. In column 5 are listed the total number of concentrations (points) for which Baxter and Wallace have measurements, and in column 6 are given the number of points omitted in determining the constants. In this same column are also the letters h, i, and l to indicate whether the rejected points are at highest, intermediate, or lowest concentrations, respectively.

We are now in position to compute the value of φ at each concentration using the values of the constants given in Table I, and thus find the difference between the φ value found experimentally and that calculated from the equation. For the sake of brevity only the average of the differences for each

---

[1] N. Campbell: Phil. Mag., (7) 47, 816 (1924).

TABLE I

Data bearing on the Constants of Equation 2

Salt	Temp.	a	b	No. of points	No. of points rejected	Average differences between expt. and calc. values in c.c.
LiCl	0.00	1.990	15.30	6	1h	0.02
	25.00	1.488	17.00	6	2h	0.01
	50.04	1.446	16.96	6	2h	0.02
	70.19	1.663	16.14	5	1h	0.05
	100.0	1.606	15.95	5	2h	0.06
LiBr	0.00	1.673	21.94	5	1h	0.02
	25.00	1.159	24.08	6	2h	0.01
	50.04	1.145	24.37	6	2h	0.02
	70.19	1.312	23.88	6	2h	0.04
LiI	0.00	1.425	32.50	9	3h	0.07
	25.00	0.841	35.50	9	4h	0.06
	50.04	0.569	36.81	5	2h	0.00
	70.19	0.708	36.85	5	2h	0.02
NaCl	0.00	3.240	12.36	5	0	0.05
	25.00	2.153	16.40	5	2l	0.01
	50.04	1.804	17.96	5	1i	0.05
NaBr	0.00	2.976	18.86	5	0	0.02
	25.00	1.760	23.51	5	0	0.02
	50.04	1.398	25.34	5	0	0.03
	70.19	1.377	25.80	5	1l	0.02
NaI	0.00	2.886	29.34	5	0	0.02
	25.00	1.346	35.10	5	0	0.03
	50.04	0.826	37.68	5	0	0.05
KCl	0.00	3.291	23.00	7	1l	0.05
	25.00	2.327	26.52	8	0	0.03
	50.04	2.087	27.66	5	1l	0.01
	70.19	1.982	27.95	14	1l, 2i	0.05
	100.0	2.574	26.49	4	1l	0.00
KBr	0.00	3.219	29.38	4	2l	0.01
	25.00	1.939	33.73	5	0	0.03
	50.04	1.640	35.32	5	0	0.05

Table I (Continued)

Data bearing on the Constants of Equation 2

Salt	Temp.	a	b	No. of points	No. of points rejected	Average differences between expt. and calc. values in c.c.
KI	0.00	3.133	40.05	5	1l	0.03
	25.00	1.556	45.36	5	1h	0.01
	50.04	1.168	47.58	5	0	0.03
RbCl	0.00	3.287	28.11	4	0	0.03
	25.00	2.219	31.87	15	1i	0.04
	50.04	2.047	32.95	5	0	0.02
RbBr	0.00	3.112	34.61	4	0	0.03
	25.00	2.038	38.71	5	0	0.03
	50.04	1.757	40.28	5	0	0.03
RbI	0.00	3.158	45.15	4	0	0.07
	25.00	1.607	50.31	4	0	0.05
	50.04	1.224	52.75	5	0	0.02
CsCl	0.00	3.293	35.23	5	2l	0.02
	25.00	2.172	39.15	6	0	0.02
	50.04	1.958	40.39	6	0	0.02
	70.19	2.053	40.45	6	0	0.03
CsBr	0.00	3.046	41.95	5	0	0.02
	25.00	1.901	46.19	6	2l	0.01
	50.04	1.632	47.81	6	2l	0.01
	70.19	1.646	48.24	6	1l	0.02
CsI	0.00	2.885	52.74	4	1l	0.00
	25.00	1.579	57.74	5	1h, 1i	0.05
	50.04	1.084	60.32	5	0	0.04
	70.19	1.160	61.06	5	2l	0.04

case is included in the last column of Table I. It should be mentioned that these average differences or deviations do not include the deviations of the rejected points which will be considered separately. In analyzing these figures it is probably best to deal first only with the unequivocal cases, those in which no i or l points have been rejected. Altogether 41 out of the 56 cases tabulated belong in this class and involve over two hundred points: the mean of their average differences is just a little more than 0.02 cc. In view of the difficulty in determining φ experimentally the magnitude of this uncertainty is all that can be expected. Furthermore, in those cases where *i* or *l* points were rejected in determining the constants the mean of the deviations of the accepted points is essentially the same as in the other cases, 0.02 cc.

The deviations of the rejected points will be considered in some detail, for it is important to ascertain as far as possible whether the deviations in question result from experimental error or from the inapplicability of equation (2):

h points: The marked deviations of the calculated from observed values of φ at high concentrations occur, with two exceptions, with all the lithium salts. They resemble the case of lithium chloride described by Masson in that they deviate very definitely and uniformly from the linear relationship. Therefore, since these deviations occur at concentrations where the linear relationship is presumably not valid, they have no bearing on the applicability of equation (2). The deviation between calculated and observed values of φ is 0.15 cc. for the high concentration points rejected in the cases of KI and CsI. Since the deviation is in the same direction in both instances and opposite to that found with the lithium salts, the cause cannot be the same as in the latter case. It is not unreasonable to suppose that the extreme deviation arises from an uncertainty in the basic measurements because it is evident at only one temperature.

i points: The average deviation of the five points at intermediate concentrations which deviate most decidedly from the linear relationship is 0.26 cc. The deviations in these cases are not only irregular in direction but appear only at one, high temperature. From these facts it may be concluded that here also the basic measurements involve a slight but definite error.

l points: An analysis of these rejected points is especially important because an incorrectness of equation might be expected to make itself most evident at low concentrations. It is found, however, that the mean of the deviations of the twenty points in this class is 0.24 cc. and that the deviations are not consistently in one direction. Since this mean figure is approximately ten times that obtained for the other points, it may be concluded that these deviations are no greater than what might result from the greater uncertainty in determining φ at low concentrations. Indeed, practically all that was gained by the omission of these points in the determination of the equation constants was to give more weight to the points at higher concentrations which are the more accurate.

In summarizing the results of the foregoing test we may state that with few exceptions the linear relationship describes within the limits of experimental error the variation of φ with concentration. A scrutiny of the few exceptions reveals no clear-cut evidence of the failure of the equation. On the contrary, there is evidence to indicate that most of the unusual deviations arise from exceptionally large errors in the basic measurements.

An objection to the above test is that, since it covers only a limited range of concentration, a discrepancy between the calculated and experimental variation of φ is not likely to be very evident. We can, however, test the equation further at the extreme limit where the molal concentration is zero.

At this concentration the apparent molal volume is, of course, equal to b. Furthermore, if the constant a is assumed to be correct, a measure of the uncertainty attached to b in each case is the average deviation given in the last column of Table I.

In infinitely dilute solution the apparent molal volume becomes identical with the partial molal volume of the salt. We are therefore able to compare the values of b (Table I) with the corresponding partial molal volumes, calculated by LaMer and Gronwall[1] who, it may be remarked, also based their computations on the measurements of Baxter and Wallace. A comparison of these two quantities shows, however, that the partial molal volumes are consistently larger than the values of b, the difference being greater than the estimated uncertainty of either quantity. As a matter of fact, the difference appears to be directly proportional to the constant a, the proportionality factor being roughly 0.3. Since this discrepancy may appear at first glance to be evidence of a defect in Masson's equation, it is important to show that its origin does not necessarily reside entirely in equation (2).

The apparent molal volume as well as the partial molal volume at infinite dilution can be regarded as the sum of the corresponding volumes of the ions. Since the latter quantities are presumably independent of the other ions present, we may, on the principle of additivity, expect the differences between any two ions to be the same regardless of the other ion present in the salt. Some of the possible combinations whereby this expected additivity can be tested are given in Table II.

A scrutiny of Table II shows that with exception of those differences which involve KCl at 25° and 50°, and CsI at 0°, the values of various combinations check very well with each other. The average deviation of the values of a given combination from the mean is given in brackets and is of the order of magnitude to be expected from the estimated uncertainty of the different values of b.

For the purpose of comparison there are included in the above table the corresponding mean values and average deviations obtained by La Mer and Gronwall. If the two sets of average deviations are compared, it is seen at once that the checks obtained for the different combinations are appreciably better with the b values than with the partial molal volumes: the mean of all the average deviations in the first case is 0.07 cc. and in the second, 0.15 cc. Moreover, it should be noted that, in addition to those differences (bracketed in Table II) which exhibit a somewhat marked divergence from the mean value of a given combination, La Mer and Gronwall found others which involve KCl at 0° and RbCl at 0°. The average amount of these extreme divergences is only 0.25 cc. in the case of the b values but is 1.11 cc. in the case of the partial molal volumes. These facts may be taken to indicate that the method employed by La Mer and Gronwall to find the partial molal volumes at infinite dilution is rather more susceptible to slight experimental errors in the basic measurements than is equation (2). On the other

---

[1] LaMer and Gronwall: J. Phys. Chem., 31, 393 (1927).

TABLE II
Differences between the Values of the Constant b

M	$b_{MBr} - b_{MCl}$			$b_{MI} - b_{MBr}$		
	0.00°C	25.00°C	50.04°C	0.00°C	25.00°C	50.04°C
Li	6.66	7.08	7.41	10.56	11.42	12.44
Na	6.50	7.11	7.38	10.48	11.59	12.34
K	6.38	7.21	(7.66)	10.67	11.63	12.26
Rb	6.50	(6.84)	7.33	10.54	11.69	12.47
Cs	6.72	7.04	7.42	(10.79)	11.55	12.51
Aver.	6.55(0.11)	7.11(0.05)	7.39(0.03)	10.56(0.05)	11.58(0.07)	12.40(0.08)
L. & G.	6.35(0.12)	6.95(0.15)	7.47(0.23)	10.52(0.05)	11.44(0.12)	12.01(0.25)
Diff.	0.20	0.16	−0.08	0.04	0.14	0.39
X	$b_{NaX} - b_{LiX}$			$b_{KX} - b_{NaX}$		
Cl	−2.94	−0.60	1.00	10.64	(10.12)	(9.70)
Br	−3.08	−0.57	0.97	10.52	10.22	9.98
I	−3.16	−0.40	0.87	10.71	10.26	9.90
Aver.	−3.06(0.08)	−0.52(0.08)	0.98(0.05)	10.62(0.07)	10.24(0.02)	9.94(0.04)
L. & G.	−2.58(0.03)	−0.31(0.05)	1.17(0.16)	11.00(0.06)	10.35(0.01)	9.87(0.13
Diff.	0.48	0.21	−0.19	− 0.38	−0.11	0.07
	$b_{RbX} - b_{KX}$			$b_{CsX} - b_{RbX}$		
Cl	5.11	5.35	5.29	7.12	7.28	7.44
Br	5.23	4.98	4.96	7.34	7.48	7.53
I	5.10	5.04	5.17	(7.59)	7.43	7.57
Aver.	5.15(0.05)	5.12(0.15)	5.14(0.12)	7.23(0.11)	7.37(0.08)	7.51(0.05)
L. & G.	4.43(0.04)	5.25(0.20)	5.05(0.26)	6.47(0.10)	6.76(0.35)	7.45(0.38)
Diff	0.72	−0.13	0.09	0.71	0.61	0.06

hand, the actual difference between the two sets of mean values of the various combinations is not very great. The average difference is 0.27 cc.; but, if the two combinations which show the greatest divergence are omitted, this difference drops to 0.20 cc., a figure not much greater than the average deviations of the partial molal volume differences.

Since the foregoing discussion suggests that the disagreement between the b values and the partial molal volumes at infinite dilution may arise from an uncertainty inherent in the procedure employed by La Mer and Gronwall as well as from a defect in equation (2), it is interesting to note corroborating evidence. From very precise measurements Lamb and Lee[1] have determined the apparent molal volumes of a number of salts in extremely dilute solutions at 20°C. The apparent molal volumes of three salts at infinite dilution, derived by these authors from their data, are given below in column 2. These figures, it should be remarked, are quite reliable because of the short range of extrapolation. The corresponding figures for the partial molal volumes and the b values are given in columns 1 and 3, respectively. These latter quantities are all for 20° and were obtained by graphical interpolation.

	1.	Diff.	2.	Diff.	3.
LiCl	17.5	−0.4	17.13	0.2	16.9
NaCl	16.7	−1.0	15.71	−0.1	15.9
KCl	26.6 (27.3)	−0.5 (−1.2)	26.10	0.0	26.1

The second, bracketed value given for the partial molal volume of KCl is a corrected value, calculated on the basis of the additivity principle. From the above data it appears that equation (2) yields results which are in better agreement with the measurements of Lamb and Lee than are those obtained by the method of La Mer and Gronwall.

We may now summarize the conclusions of this second way of testing equation (2) as follows. The b values satisfy excellently the requirements of the principle of additivity. They do not, however, agree very well with the partial molal volumes calculated from the same basic data by La Mer and Gronwall. Although this disagreement may be the consequence of a defect in equation (2), there is some evidence which points to the possibility that the method employed in the determination of the partial molal volumes at infinite dilution is at fault.

As the third and final means of testing the equation under discussion we can calculate the apparent molal volumes of salts in saturated solutions and compare them with the values obtained experimentally. The essential data for such a comparison are assembled in Table III. In the second, fourth, and fifth columns are given the temperatures, molarity, and φ values of the experimental measurements. The figures contained in column 6 are the φ values computed by use of the constants given in Table I and the molarity

---

[1] Lamb and Lee: J. Am. Chem. Soc., 35, 1683 (1913).

in column 4. It will be noted that some of the measurements are not exactly at 50.04° for which temperature the constants are valid. The difference, however, is practically negligible. In order to show to what extent the calculated values lie beyond the concentration range employed in determining the constants of equation (2), the maximum value of $m^{1/2}$ involved in each determination is given in column 3. Even though the concentrations of the saturated solutions are not much greater than these maximum values, the excellent agreement between calculated and observed values of φ is additional evidence in support of the applicability of equation (2). In order to reduce

Table III

Comparison of Observed and Calculated Values of φ in Saturated Solutions

Salt	Temp.	$m^{1/2}$ max.	$m^{1/2}$	obs.	calc.	Percent Difference
NaCl	0.00[1]	2.268	2.332	19.8	19.9	0.05
	25.00[4]	2.268	2.331	21.6	21.4	0.10
	50.00[1]	2.267	2.336	21.9	22.2	0.15
NaBr	0.00[2]	2.341	2.542	26.3	26.1	0.07
	25.00[3]	2.344	2.699	28.2	28.3	0.05
	50.31[2]	2.339	2.902	29.3	29.4	0.08
NaI	0.00[2]	2.634	2.764	37.2	37.3	0.08
	25.00[3]	2.633	2.879	38.8	39.0	0.16
	50.02[2]	2.633	3.056	40.2	40.2	—
KCl	0.00[4]	1.831	1.840	29.3	29.1	0.10
	25.00[3]	1.830	2.043	31.3	31.3	—
	50.02[2]	1.514	2.190	32.2	32.2	—
KBr	0.00[2]	1.515	1.975	36.0	35.6	0.15
	25.00[3]	2.145	2.119	37.8	37.8	—
	50.21[2]	2.144	2.313	39.5	39.1	0.20
KI	0.00[2]	2.360	2.375	47.7	47.5	0.10
	25.00[3]	2.360	2.489	49.3	49.2	0.06
	50.13[2]	2.359	2.581	50.8	50.6	0.10
RbCl	0.00[4]	1.805	2.301	36.1	35.7	0.20
	25.00[4]	2.468	2.474	37.7	37.4	0.18
	50.00[4]	2.554	2.582	38.3	38.0	0.20
CsCl	0.00[4]	2.076	2.603	43.9	43.8	0.06
	25.00[4]	2.744	2.741	45.1	45.1	—
	50.00[4]	2.743	2.843	46.0	46.0	—

[1] Tschernaj: Taken from Comey: "Dictionary of Chemical Solubility."
[2] Scott and Durham: J. Phys. Chem., 34, 1424 (1930).
[3] Scott and Frazier: J. Phys. Chem., 31, 459 (1927).
[4] International Critical Tables; 25° values are interpolated.

the differences between observed and calculated values of φ to a common basis, the calculated values of φ have been assumed to be correct and the error in the experimental determination of φ, necessary to cause the difference, has been computed. This error expressed in per cent is given in the last column of Table III, and is well within the known limits of experimental error. Incidentally, the values of $m^{\frac{1}{2}}$ are expressed in four significant figures to indicate the experimental precision required in order to calculate φ to three significant figures.

We have completed the examination of the applicability of equation (2). The conclusion to be drawn from the evidence considered is that the equation is valid within the limits of experimental error. This conclusion, however, cannot be generalized because the data which have been employed in testing the equation are not sufficiently complete or varied. On the other hand, it must not be forgotten that Masson found the equation to be applicable to solutions of electrolytes which are much more diverse in type than those which we have considered, a fact which strengthens our present conclusion. Whether the square-root function of m is the correct function or whether it is merely a good approximation[1] of this function is a question which possibly cannot be decided by the method of analysis which we have employed so far. A partial decision can be reached, however, by a consideration of the theoretical implications of the equation, a matter which will be taken up in the following paragraphs.

Attempts to interpret the variation of apparent molal volume with concentration have been based, as rule, on the assumption that the change in the ionization of the solute with concentration is the primary factor. The difficulty encountered in developing a theory along these lines is that the concept of apparent molal volume is by no means clear. According to one view the change in φ is a change in the volume of the solute itself. The following extracts from Masson's paper will suffice to illustrate this interpretation. "Where water is mixed with a soluble substance the change in volume that occurs is the sum of two changes. One is that due to the formation of a hydrate from its constituent molecules; the other is caused by the dilution of that hydrate with excess of water or with excess of the other component. The former may be called the 'chemical effect' . . . the latter may be distinguished as the 'physical effect'." Regarding the change in φ with $m^{\frac{1}{2}}$ in terms of hydrates, Masson states: ". . . and the suggestion is as inevitable that the hydrate exists in two forms, a greater and a smaller, and that φ as measured, belongs always to a mixture of the two in a proportion determined by concentration. The smaller form could exist by itself only if it were possible for the hydrate to exist at all in the complete absence of solute, i.e., at infinite dilution. The larger form could exist by itself only if it were possible for the hydrate to exist all in the complete absence of water." Apart from the change in volume which the water undergoes in forming the hydrate

---

[1] For example, Jablczynski [Roczniski Chemji, 3, 362 (1923).] has employed the cube-root of the molarity which holds very well for the solutions he deals with but is obviously incorrect when tested by the data employed in this paper.

it is assumed "that any excess of water which remains as solvent . . . retains its original specific volume practically unchanged."

The alternative concept attributes the change in φ to a change in the volume of the solvent molecules rather than to a change in the volume of the solute. Webb[1] offers an adequate picture of this mechanism in his mathematical theory of electrostriction. In very dilute solutions the ions are considered to be within a cavity which is free from water molecules and which represents the effective volume of the ion. Since the radius of the cavity is considerably larger than the radius of the ion proper, it is assumed that the cavity approximates a sphere with considerable exactness. About this spherical cavity the water molecules are compressed, the amount of contraction depending on the field strength of the ion involved, i.e., on the radius and charge of the ion. In terms of this mechanism the apparent molecular volume of an ion becomes equal to its effective volume (the spherical cavity) minus the total contraction suffered by the solvent.

Neither of the two concepts of φ, outlined above, offers obvious grounds for an interpretation of the square-root function. Nevertheless, by means of certain postulates it appears possible to indicate a connection between Masson's equation and the electrostriction concept of φ. According to this theory the change in φ with concentration is the direct result of a change in the amount of total contraction of the solvent molecules and probably also a change in the dimensions of the ion cavities. Even though the factors which control these changes are exceedingly complex, it may be assumed that they have their ultimate origin in the interaction of the ions of the solute. Consequently, if solutions of electrolytes of the same concentrations are compared, it may be supposed that differences in the rates of change of φ with concentration arise from differences in the effect of the inter-ionic forces involved. This very general assumption would lead us to expect the relative magnitude of the constant a (equation 2) to be a measure of the inter-ionic forces because this constant is a relative measure of the rate of change of φ with concentration when solutions are compared under conditions of identical concentration. This argument can be supported only indirectly by showing that the constant a is related to other properties of electrolytes which are dependent on the inter-ionic forces.

One factor which appears in the treatment of ionic interaction problems[2] is the so-called valence factor which is determined by the number and valence charges of the ions constituting the electrolyte. That this valence factor affects the magnitude of the constant a can be seen from the following values for uni-bivalent and bi-bivalent salts, taken from Masson's paper:

Salt:	$MgCl_2$	$CaCl_2$	$CdCl_2$	$(NH_4)_2SO_4$	K_2CO_3	$MgSO_4$	$ZnSO_4$
a :	6.17	7.10	5.72	10.13	13.60	11.12	10.71

---

[1] Webb: J. Am. Chem. Soc., 48, 2589 (1926).

[2] For example, the Debye-Hückel theory of solutions. It is of interest to note that in the mathematical elaboration of this theory a quantity is obtained which is defined as the "characteristic or probability" distance between ions in solution and which varies inversely as the square-root of the molal concentration.

These values are all considerably larger than the values of a for the uni-univalent electrolytes given in Table I and, with the exceptions of the values of $(NH_4)_2SO_4$ and K_2CO_3, fall into two distinct groups according to valence type.

This valence factor is, of course, not the only one which determines the value a as can be seen at a glance from the data in Table I. Since the positions of the water molecules about each ion and also the positions of ions about the oppositely charged ions are determined by electrostatic forces of attraction and repulsion, and since these latter forces depend on the ionic dimensions[1] it may be surmised that the ionic dimensions are of considerable importance in determining the rate of change of φ with concentration (a). One property which, on the basis of electrostatic theory, is also a function of ionic dimensions is the interionic distance in a crystal lattice. In a preliminary trial to see whether the differences in the a values corresponded in any way with the differences in lattice distances, it was observed for the alkali halides that, when log a is plotted against lattice distance, the plotted points exhibit distinct regularities. These regularities become more definite, if, instead of the lattice distances, the inter-ionic distances corrected for the radius ratio effect[2] are used, and they may be summarized briefly: The plotted points for the three halogen salts of each cation fall closely on straight lines which are sensibly parallel; analogous lines cannot be drawn through the points of salts with a common anion apparently because of a fairly uniform displacement of the points of the lithium and cesium salts.

The above-mentioned graphs are not presented because the possibility of a relationship between the constant a and the forces involved in determining the lattice distances is evidenced more clearly in a slightly different form. The actual inter-ionic distances in crystals, according to Pauling, can be represented as the consequence of two factors: (1) the radius sum $r_+ + r_-$ and (2) the radius ratio $\rho = r_+/r_-$. The corrected inter-ionic distances R_c are those of hypothetical substances in which the radius ratio effect has a standard value but whose other ionic properties are unchanged. Therefore, the fact that the log a relationships, described above, are more regular with R_c than with the actual lattice distances may mean that the effect of the radius ratio on lattice distance is quite different from its effect on the complex forces which determine φ. An empirical function of ρ which appears to represent approximately the effect of the radius ratio so far as log a is concerned is $(1 + 1/\rho)$. To show this possibility Fig. 1 has been constructed by plotting values of log a against the values of the expression $R_c\ (1 + 1/\rho)$. The former quantities are obtained from the data in Table I and the latter are computed from the figures given by Pauling.

To avoid misunderstanding it should be stated that the relationships portrayed in Fig. 1 are important only insofar as they call attention to a possible

---

[1] Garrick: Phil. Mag., (7) 9, 130 (1930); 10, 76, 77 (1930), has treated the problem of co-ordination numbers of ion hydrates and amino-compounds from this viewpoint, and has obtained results in agreement with Sidgwick's co-valency rule.

[2] Pauling: Z. Krystallographie, 67, 377 (1928).

functional dependence of the constant a on the same ionic factors which are involved in determining the lattice distances. The linearity of these relationships, indicated by the drawn straight lines, is, to be sure, open to question because of the uncertainty in the basic data but it will be a convenient

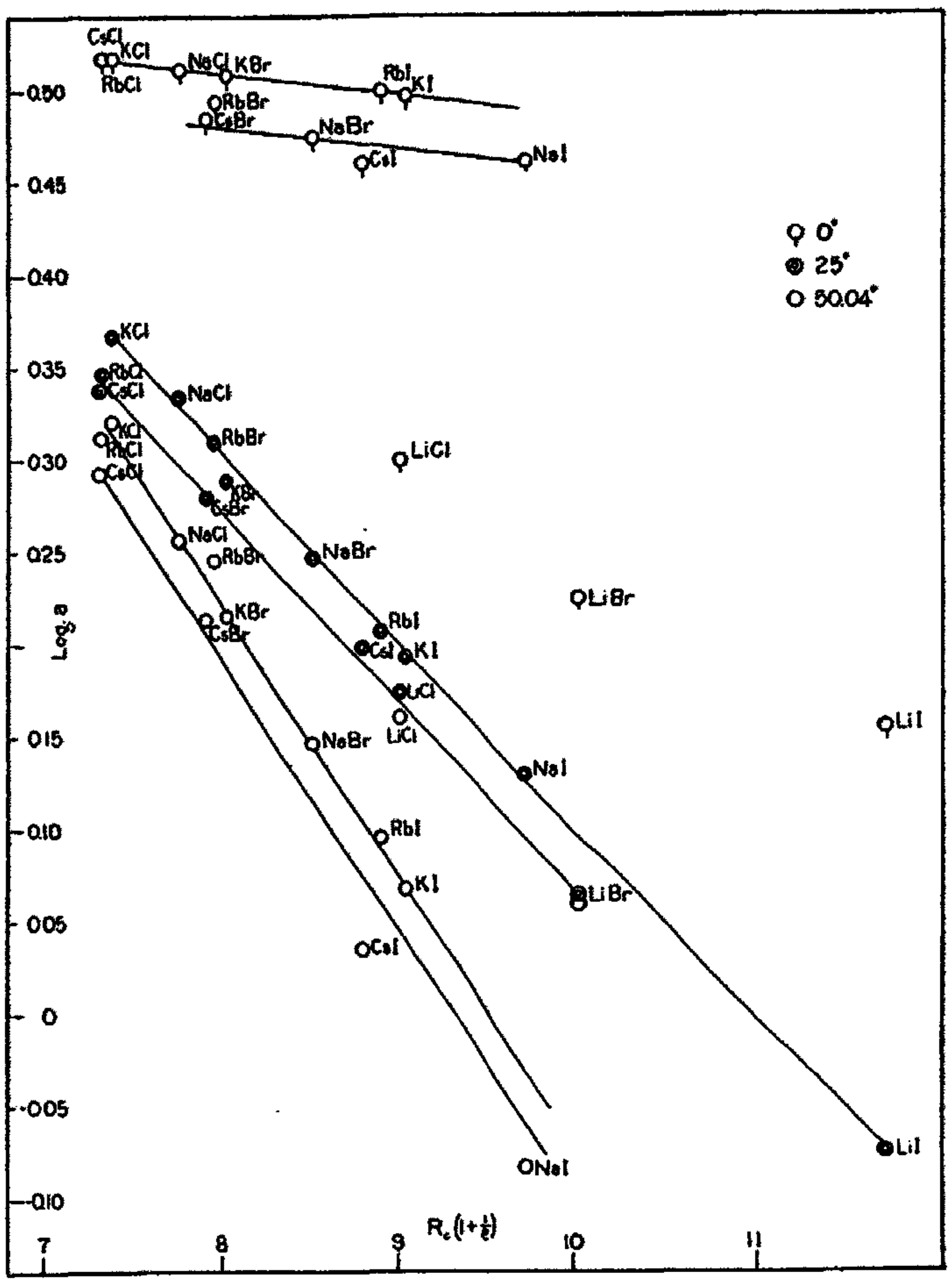


Fig. 1

The Variation of log a with the Function $R_c\ (1 + \frac{1}{c})$

assumption in discussing a number of interesting points. In the first place there is a marked difference in the linear constants for the three different temperatures, a difference which most probably originates in the changes produced by temperature in the electrical properties of the water molecule. Probably the most striking feature of the graph is the existence of at least two sets of points at each temperature with practically a constant difference of 0.02

in the values of log a. Thus, the a values of the lower set of points at any temperature are approximately 0.93 of the values necessary to agree with the upper set of points. An examination of the figure discloses that the points for the cesium salts are the ones which occur most consistently in this "lower" group. Since the R_c values employed in plotting these points are those of the non-existent rock-salt structure, the cause of the above division into two groups which suggests itself is the co-ordination number of the ions. In this connection it is interesting to note the following co-ordination numbers found by Garrick for ion-hydrates: Li = 4 or 6; Na and K = 6; Rb and Cs = 8. Finally, we may call attention to the fact that the plotted points of the lithium salts show little in common with those of the other salts except at 25°. In considering these exceptional points it should be recalled that the values of the constant a are for dilute solutions only because, as has already been pointed out, the linear relationships for these salts exhibit marked discontinuities at moderately high concentrations. In view of our present argument that the relative values of the constant a are dependent on inter-ionic forces, such a discontinuity suggests that a marked change in these forces takes place in solutions of lithium salts. We could account for these changes by postulating the existence of a "chemical" hydrate[1] of the lithium ion whose stability is dependent on concentration and possibly also on temperature; for the properties of such an aggregate would be quite different from those of the simple ion. This same postulate, furthermore, would be sufficient to account for the irregularities of the points plotted for the lithium salts in Fig. 1 because a hydrated ion would not be comparable to the other simple ions.

In the foregoing discussion it is shown that the constant a is dependent on the valence factor and that it is also related to the interionic distances in crystals. Although we are unable to derive any direct evidence in substantiation of equation (2) from these connections, we have implied a theoretical basis for the empirical rule. A further confirmation of this argument is found in the consideration of the maximum value of φ, that is, the hypothetical value when no water is present. This problem will be dealt with in a subsequent article.

Summary

The present paper is a study of the linear relationship $\varphi = am^{\frac{1}{2}} + b$, put forward by Masson. In the first part of the paper the applicability of the equation is tested (1) by examining its ability to reproduce the experimental data of Baxter and Wallace; (2) by examining the values of b on the basis of the principle of additivity; and (3) by computing φ values in saturated solutions and comparing them with experimental values. Although the test is not conclusive, the evidence, with few exceptions, tends to support the validity of the empirical relationship.

---

[1] A rather suggestive fact bearing on this matter is that, according to Masson, with lithium chloride solutions at 15°, the abrupt break in the linear relationship occurs when the composition of the solution is $LiCl + 10\ H_2O$.

In the second part of the paper the theoretical significance of the equation is considered briefly. The fact that the constant a is dependent on the valence factor and is likewise related to inter-ionic distances affords grounds for the suggestion that a basis for the equation may be found in the interaction of ionic forces.

Since the completion of this article two notes bearing on the present subject have been published. Redlich [Naturwissenchaften, **15**, 251 (1931)] finds that, according to the Debye-Hückel theory, the partial molal volumes of salts in solution should vary linearly with the square-root of the concentration. Geffcken [Naturwissenschaften, **15**, 321 (1931)] states that in connection with a study of the refractivity of solutions he has established a linear relationship between the apparent molal volumes of salts in solution and the square-root of the concentration. This relationship is identical with that proposed by Masson. Since Geffcken's conclusion is based chiefly on new measurements in very dilute solutions (less than 0.3M), it may be taken as additional evidence in support of the empirical rule of Masson.

The Rice Institute,
Houston, Texas.

THE TRANSFORMATION FROM ROSE TO GREEN MANGANOUS SULFIDE

BY HARRY B. WEISER AND W. O. MILLIGAN

Manganous sulfide in the form of a rose or flesh colored floc is thrown down from a solution of a manganous salt by the hydrosulfides and monosulfides of the alkali metals and ammonium. Under suitable conditions the flocculent rose sulfide which always precipitates first, becomes more granular and assumes a green color. Favorable conditions for obtaining the green sulfide have been described by a number of people.[1] The experimental procedures were summarized and analyzed critically a few years ago by Mickwitz and Landesen.[2] As a result of this analysis and some observations of their own *the following conclusions were reached: (1) The transformation from rose to* green MnS never takes place when the precipitation is effected with alkali sulfides. (2) The transformation from rose to green MnS never takes place except in the presence of free ammonia. (3) There are two rose sulfides of manganese. One, which will not turn green, is precipitated by NH_4HS in the absence of free ammonia. Its composition may be represented by the formula $H_2Mn_3S_4$ or $3MnS.H_2S$. A second rose sulfide which turns green spontaneously, is precipitated in the presence of free ammonia. Its composition may be expressed by the formula $NH_4HMn_3S_4$ or $3\ MnS.NH_4HS$.

The experiments to be described in this paper indicate that all three of the above conclusions are incorrect. After considering the conditions favorable for the transformation from the rose to the green sulfide, the relationship between the two preparations will be discussed in the light of their X-ray diffraction patterns.

Transformation from Rose to Green MnS in the Presence of Na_2S

Although it is generally stated that the rose sulfide of manganese thrown down by excess alkali sulfide will not change to green, experiments were begun with the sulfide formed in this way in an attempt to refute or to confirm the conclusion of Mickwitz and Landesen that free ammonia is necessary for the rose to green transformation. Early in the study, it was found that the change took place at the boiling temperature in a reasonable time when the amount of alkali sulfide exceeded a critical concentration. The following experiments were then carried out:

---

[1] Fresenius: J. prakt. Chem., **82**, 267 (1861); Muck: Z. Chem., **12**, 580, 629 (1869); Classen: Z. anal. Chem., **8**, 370 (1869); **16**, 319 (1877); DeClermont and Guiot: Bull., (2) **27**, 353 (1877); Meineke: Z. angew. Chem., **7**, 4 (1888); Mourlot: Compt. rend., **121**, 202 (1895); Raab and Wessley: Z. anal. Chem., **42**, 433 (1903); Olsen, Clowes, and Weidmann: J. Am. Chem. Soc., **26**, 1622; Olsen and Rapalje: 1615 (1904); Villiers: Compt. rend., **159**, 67 (1914); Fischer: J. Russ. Phys.-Chem. Soc., **46**, 1481 (1914); Seeligmann: Z. anal. Chem., **53**, 594 (1914); **54**, 104 (1915); Hahn: Z. anorg. Chem., **121**, 209 (1922).

[2] Z. anorg. Chem., **131**, 101 (1923).

Standard solutions of manganous chloride and sodium sulfide were prepared from salts which were found to be free from ammonium compounds by distilling samples with excess NaOH and testing the distillate with Nessler's reagent. Definite amounts of sodium sulfide diluted to 20 cc were placed in a 200 cc Pyrex flask supplied with a reflux condenser. After heating the sulfide solution to boiling, 5 cc of manganous chloride solution was pipetted in through the condenser. In every case the rose sulfide which precipitated first, became green in the presence of sufficient excess of Na_2S. Some observations are reported in Table I and shown in Fig. 1. The observations disclose that under the conditions of the experiment the rose sulfide is transformed into green in a short time, only in case the Na_2S concentration is greater than approximately 0.5 molar. Since it will be shown in a later section that the color change results from a molecular transformation, it is probable that the solvent action[1] of the Na_2S on the rose form is an important factor in initiating and hastening the change.

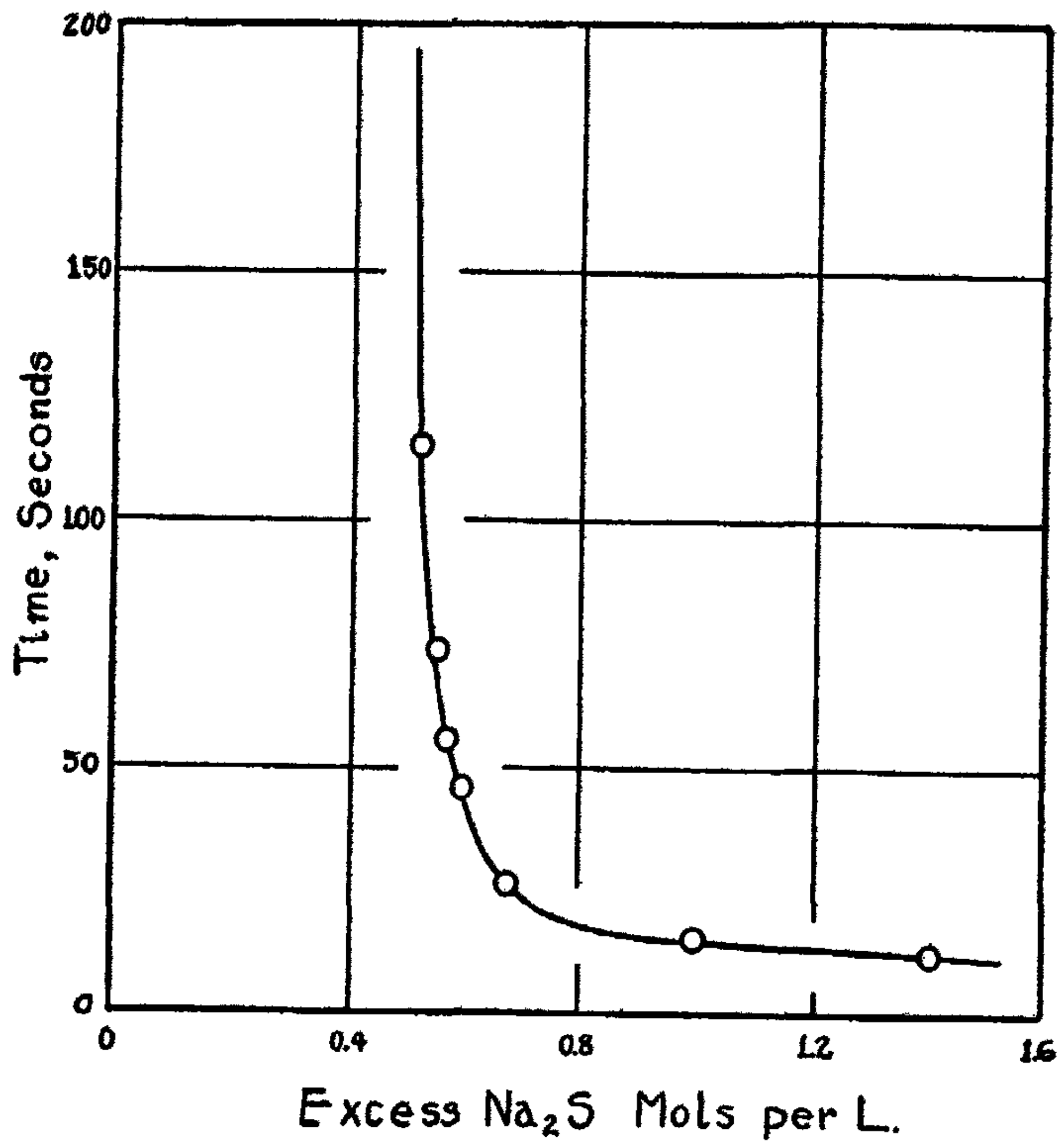


FIG. 1
Effect of Concentration of Na_2S on the Rate of Transformation from Rose to Green MnS

---

[1] Classen: Am. Chem. J., 8, 436 (1880).

Table I

Transformation from Rose to Green MnS in the Presence of Excess Na_2S

Cc solutions mixed			Excess Na_2S Mols per l.	Time for first appearance of green color seconds
$MnCl_2$ M	Na_2S 2M	H_2O		
5	20	0	1.40	13
5	15	5	1.00	16
5	11	9	0.68	25
5	10	10	0.60	46
5	9.6	10.4	0.57	56
5	9.4	10.6	0.55	74
5	9.0	11.0	0.52	115
5	8.75	11.25	0.50	No change in 5 minutes
5	8.50	11.50	0.48	No change in 5 minutes
5	8.00	12.00	0.44	No change in 5 minutes

It is of interest to record that the green color of the sulfide is of a distinctly lighter shade than that obtained when the precipitation is carried out with $(NH_4)_2S$ and NH_4OH.

The Transformation from Rose to Green MnS in the Presence of $(NH_4)_2S$ and NH_4OH

The transformation from rose to green MnS takes place quite rapidly at room temperature when the precipitation is carried out with $(NH_4)_2S$ in the presence of NH_4OH, provided the concentrations of the reacting solutions lie within a rather narrow range and provided the mixing of the manganous salt with the sulfide solution is done in a suitable way.

Effect of Concentration of NH_4OH. In order to determine the effect of NH_4OH on the rate of transformation from the rose to the green sulfide, varying amounts of a standard solution of NH_4OH were added to a standard solution of NH_4HS, free from ammonia. To prepare the latter 50 cc of concentrated NH_4OH was diluted to 500 cc, the solution cooled by surrounding it with crushed ice, and saturated with H_2S. The resulting solution was colorless and contained no free ammonia.[1] To analyze the solution it was oxidized to sulfate with 30 percent H_2O_2 after making alkaline with ammonia, and was precipitated and weighed as $BaSO_4$.

Since preliminary experiments disclosed that the manner of mixing affected greatly the rate of transformation, the following procedure was adopted. To 2 cc of 1.35 M NH_4HS in a 30 cc test tube were added varying amounts of 5.24 M NH_4OH and water to make a total volume of 12 cc. Molar $MnCl_2$ was then added from a 2 cc pipette, the tip of which was allowed to touch the top of the test tube so that the solution ran down the sides instead of dropping in. The tube was stoppered, inverted slowly and then replaced in the rack. The time of flow of the pipette was 8 seconds and inverting the tube

---

[1] Bloxam: J. Chem. Soc., 67, 277 (1895).

required 6 seconds more. This procedure is referred to in Table II as "slow mixing." The stopwatch was started when the solution began to flow from the pipette and was stopped when the first sign of change to the green color was noted. The results are given in Table II and shown graphically in Fig. 2. The U-shaped curve signifies that there is an optimum concentration of ammonia which is most favorable for rapid transformation. With too little ammonia there is no change in color in a reasonable time and with too much ammonia the rate of transformation is greatly retarded. The rate is increased by raising the temperature but this results in decomposition of the $(NH_4)_2S$ and loss of NH_3 and H_2S. Accordingly the observations were confined to room temperature.

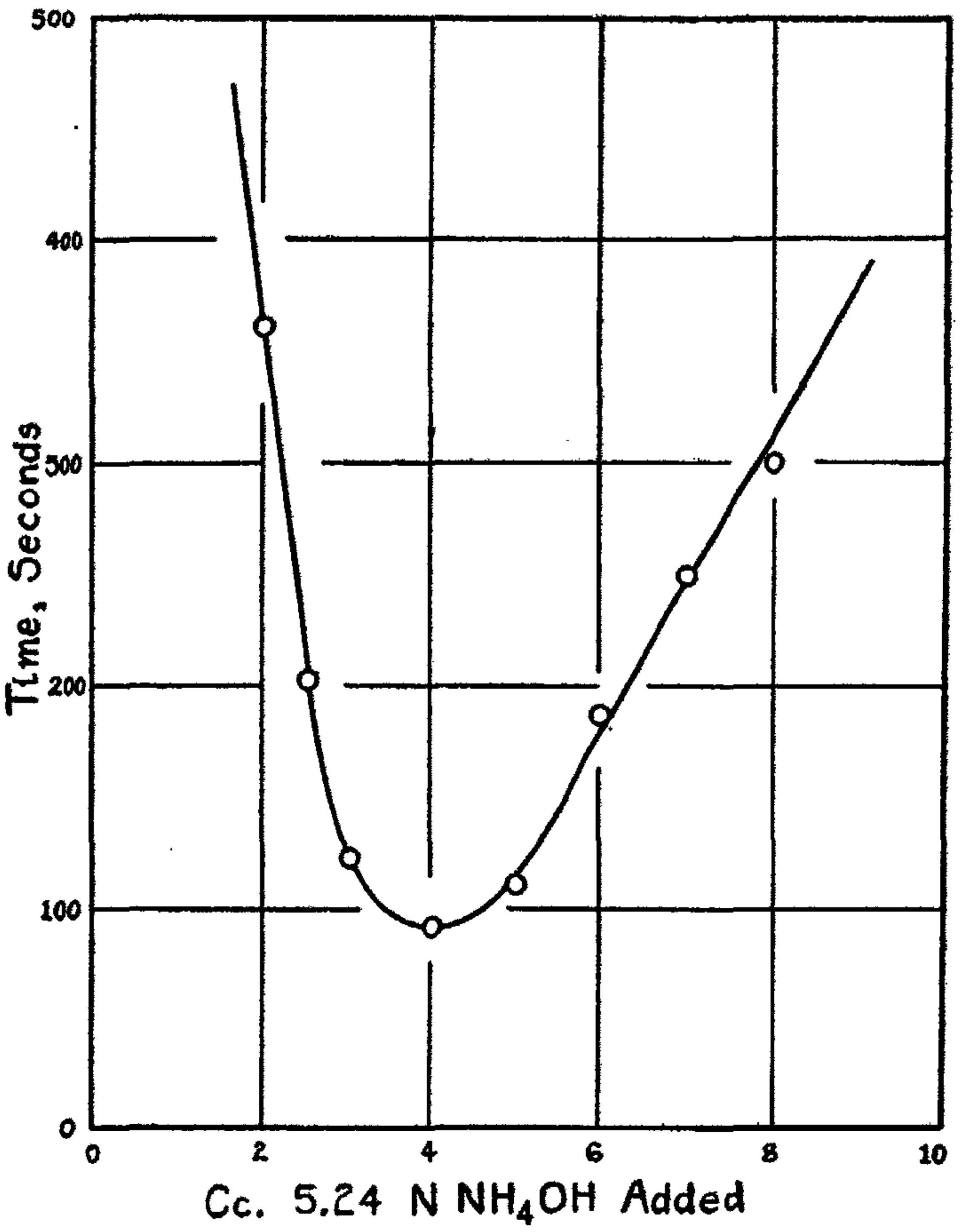


Fig. 2
Effect of Concentration of NH_4OH on the Rate of Transformation from Rose to Green MnS

In the experiments summarized in Table II it will be noted that the amount of NH_4HS in excess of that necessary for precipitation of all the

TABLE II

Effect of Free NH_4OH on the Transformation from Rose to Green MnS

Cc solutions mixed				Time for first appearance of green color	
NH_4HS 1.35 M	NH_4OH 5.24 M	H_2O	$MnCl_2$ M	Slow mixing	Fast mixing
2	0	0	2	No change	No change
2	1	7	2	No change in 15 min.	24 minutes
2	1	6	2	360 seconds	20 minutes
2	2.5	2.5	2	200 seconds	———
2	3	5	2	125 seconds	8 minutes
2	4	4	2	92 seconds	7 minutes
2	5	3	2	110 seconds	12.5 minutes
2	6	2	2	———	42 minutes
2	7	1	2	245 seconds	No change in 1 hour
2	8	0	2	300 seconds	No change in 1 hour

TABLE III

Effect of free NH_4OH on the Transformation from Rose to Green MnS (b)

Cc solution mixed				Excess NH_4HS added	Time for first appearance of green color
NH_4HS 1.35 M	NH_4OH 4 M	H_2O	$MnCl_2$ M	Mols per l.	
1.5	0	8.5	2	small	No change in 14 hours
1.5	1	7.5	2	"	"
1.5	2	6.5	2	"	Few specks of grayish green after 14 hours
1.5	3	5.5	2	"	
1.5	4	4.5	2	"	No change in 14 hours
1.5	5	3.5	2	"	"
1.5	6	2.5	2	"	"
1.5	7	1.5	2	"	"
1.5	8	0.5	2	"	"
	11.6 M				
3	1	6	2	0.17	645 seconds
3	2	5	2	"	180 "
3	2.5	4.5	2	"	85 "
3	3	4	2	"	150 "
3	4	3	2	"	210 "
3	5	2	2	"	260 "
5	1	4	2	0.40	No change in 10 minutes
5	2	3	2	"	480 seconds
5	3	2	2	"	105 "
5	3.5	1.5	2	"	80 "
5	4	1	2	"	110 "
5	5	0	2	"	215 "

manganese was a little less than 0.05 mol per liter. Observations were next made of the effect of varying the ammonia concentration when the NH_4HS added in excess of that necessary for precipitation was very small, 0.17 molar and 0.40 molar. The results are given in Table III.

It will be noted that free ammonia has little or no effect on the transformation from rose to green MnS when but little excess NH_4HS is added. Moreover, the greater the excess of NH_4HS, the greater the amount of ammonia which must be added to give the critical mixture for the most rapid rate of transformation. Finally, the greater the excess NH_4OH, the higher must be the concentration of ammonia to inhibit or prevent the transformation.

Effect of Rate of Mixing. As already noted, the rate of mixing the reacting solutions influences the velocity of transformation from the rose to the green sulfide. This was recognized by Fischer[1] but was denied by Mickwitz and Landesen.[2] The following experiments indicate the magnitude of the effect: The mixture of NH_4HS and NH_4OH was placed in the outside compartment of a mixing apparatus previously described[3] and the manganous chloride solution in the inside compartment. By vigorous shaking, rapid uniform mixing was accomplished and a finely divided semi-colloidal precipitate was obtained. Observations of time for the first indication of green coloration was noted as previously described. The results are given in the last column of Table II and shown graphically in the upper curve of Fig. 3. When the results with "slow mixing" are plotted on the same scale, for purpose of comparison, the lower curve of Fig. 3 is obtained. It is obvious that the flocculent precipitate formed by slow mixing changes to green much more quickly than the more highly dispersed precipitate thrown down by rapid mixing.

A probable explanation of the behavior described in this section is as follows: As already noted, the change from the flocculent rose precipitate consisting of aggregates of finely divided particles, to the denser green granules appears to be favored by dissolution of the rose and reprecipitation of the more insoluble green form.[4] The rose sulfide appears to be almost insoluble in an excess of NH_4HS and in view of the lower solubility of MnS than of $Mn(OH)_2$, the former is probably but very slightly soluble in NH_4OH. On the other hand, rose MnS is somewhat soluble in $(NH_4)_2S$.[5] Accordingly the addition of NH_4OH to a given excess of NH_4HS gives an optimum concentration of $(NH_4)_2S$ which is most favorable for the transformation. With too little ammonia the change is very slow and with too much ammonia the adsorption of the latter is sufficiently great to form a film around the particles and so to inhibit the transformation. The rate of mixing is important since it determines the form of the precipitate. The precipitate obtained by

---

[1] J. Russ. Phys.-Chem. Soc., **46**, 1481 (1914).

[2] Z. anorg. Chem., **131**, 102 (1923).

[3] Weiser and Middleton: J. Phys. Chem., **24**, 480 (1920).

[4] Weigel: Z. physik. Chem., **58**, 294 (1907).

[5] Abegg: "Handbuch anorg. Chemie," 4 (2), 724 (1913).

slow mixing is a fairly dense floc that is not greatly protected by adsorbed ammonia at least when the concentration of the latter is not too high. On the other hand, rapid mixing gives a highly dispersed precipitate, the individual particles of which adsorb ammonia and are protected thereby so that the rate of change is greatly retarded.

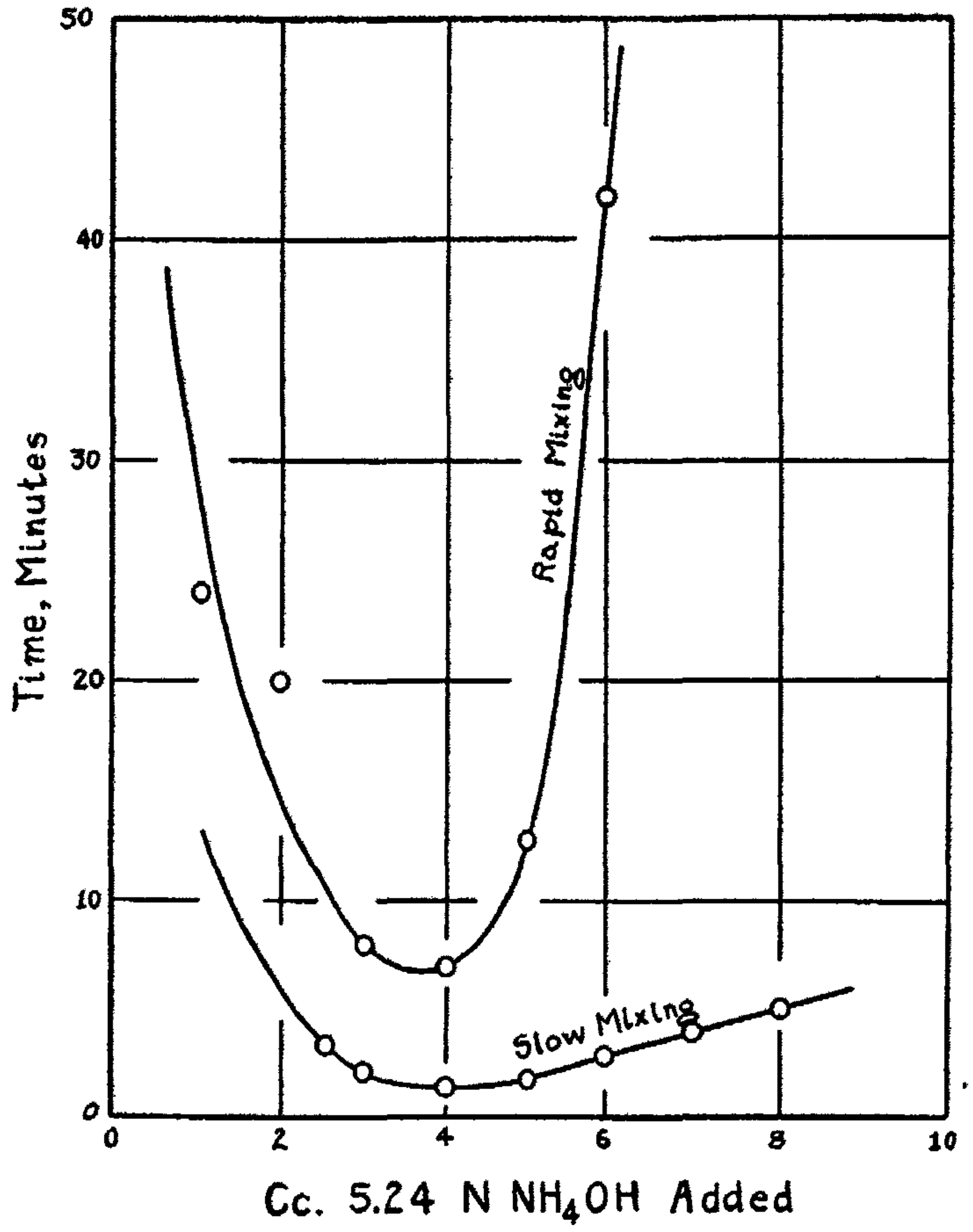


FIG. 3
Effect of Method of Precipitation on the Rate of Transformation from Rose to Green MnS

The Transformation from Rose to Green MnS in the Presence of NH_4HS

Fisher[1] claimed to have obtained a green manganese sulfide with NH_4HS in the absence of free ammonia but this was attributed to experimental error by Mickwitz and Landesen.[2] Two possible sources of error were pointed out. In the first place the ammonia from which the NH_4HS was prepared may have

---

[1] J. Russ. Phys.-Chem. Soc., 46, 1481 (1914).

[2] Z. anorg. Chem., 131, 101 (1923).

been above the limit of strength to give NH_4HS alone.[1] Secondly the observed transformation was accomplished by boiling the rose sulfide with excess of NH_4HS. Since this procedure would cause the loss of more H_2S than of NH_4OH from solution,[2] the observed change really took place in the presence of free ammonia.

The observations reported in the previous section indicate that the transformation from rose to green sulfide takes place very slowly if at all under ordinary conditions in the presence of pure NH_4HS. Since the transformation takes place so readily when a suitable mixture of $(NH_4)_2S$ and NH_4OH is present, it seemed likely that it would go in the hydrosulfide solution alone provided the rose sulfide were seeded with some of the green form. This proved to be the case as the following experiment shows: Twenty cubic centimeters of 0.1 molar manganous chloride in which was suspended varying small amounts of thoroughly washed green MnS, were precipitated with NH_4HS solution free from ammonia. The test tubes were filled almost to the top, stoppered tightly and kept in a box from which all light was excluded. Observations at intervals revealed a gradual change from the rose to the green form in the seeded samples, the rate being more rapid the greater the amount of green sulfide originally present. Some observations are reported in Table IV.

TABLE IV

Transformation of Rose to Green MnS in NH_4HS Solution

Sample	Green MnS added mg.	Observations after 4 weeks
1	0	No change
2	4	Trace of green
3	20	Mostly green
4	40	All green
5	100	All green

The Composition of Precipitated Manganous Sulfide

Precipitated rose manganous sulfide like the precipitated sulfides of arsenic, copper,[3] etc., contains adsorbed sulfide in greater or lesser amounts depending on the conditions of precipitation.[4] On the other hand the more granular green sulfide is said to be free from adsorbed sulfide. The presence of excess sulfur in the precipitated rose sulfide and the belief that the rose form changes to green only when precipitated in the presence of ammonia, led Mickwitz and Landesen to conclude that there were but two rose sulfides, one precipitated in the presence of free ammonia which will turn green, and one precipitated in the absence of free ammonia which will not turn green.

---

[1] Bloxam: J. Chem. Soc., 67, 277 (1895).

[2] Gmelin-Kraut: "Handbuch anorg. Chemie," I, 1627 (1907).

[3] Linder and Picton: J. Chem. Soc., 61, 114 (1892).

[4] Jordis and Schweitzer: Z. angew. Chem., 23, 588 (1910).

They attempted to prove this by the following experiments: 10 cc of N $MnCl_2$, 25 cc of 0.895 N NH_4HS free from ammonia, 5 cc of 5 N NH_4Cl (to prevent sol formation) were mixed in a 100 cc flask and diluted to the mark with water. The supernatant solution was filtered and an aliquot part taken for analysis. Their observations are given in Table V.

TABLE V

(From Mickwitz and Landesen)

Cc N/10 solution for			$\frac{\text{Mn}}{\text{bound NH}_3}$
Every 10 cc. of 10 cc. NH_4HS + 90 cc. H_2O	Every 10 cc of filtrate		
	calculated	found	
8.96	14.16	13.82	$\frac{1.00}{0.09}$
8.95		13.80	
Mean 8.95		Mean 13.91	

The calculated result in the second and fourth column do not follow from the reported observations. Since 10 cc of N $MnCl_2$ reacted, 10 cc of N NH_4HS would be used up. From the recorded data it would appear that the NH_4HS solution employed was 0.895 N so that the 25 cc of solution added is equivalent to 22.37 cc of N NH_4HS. Hence after precipitation the supernatant solution should contain 12.37 cc of N NH_4HS or 12.37 cc of 0.1 N HCl would be required to titrate 10 cc. Mickwitz and Landesen calculated that 14.16 cc. of 0.1 N HCl would be necessary to titrate 10 cc of supernatant solution. This value can not be deduced from the reported data; but even if one takes their own figures, these show that 0.35 cc of N NH_3 is carried down by the Mn corresponding to 10 cc of normal or 5 cc of molar Mn. The ratio $\frac{\text{Mn}}{\text{bound NH}_3}$ is thus $\frac{5.00}{0.35}$ or $\frac{1.00}{0.07}$ instead of $\frac{1.00}{0.09}$ as given in the last column of Table V.

Similar observations were carried out with the addition of 5 cc of 17.7 percent NH_4OH to the reaction mixture. In this case the ratio of $\frac{\text{Mn}}{\text{bound NH}_3}$ was found to be $\frac{1.00}{0.30}$. Here again the results reported cannot be calculated from the data given.

But even granting the presence of typographical errors that would account for the discrepancies noted above, the errors inherent in the experimental procedure of Mickwitz and Landesen are too great to enable one to conclude that there is one rose sulfide having the formula $H_2Mn_3S_4$ and one having the formula $(NH_4)HMn_3S_4$. In the first place, we have found that analysis of an NH_4HS solution by titration with HCl using methyl orange as an indicator is not sufficiently reliable for precise work. Moreover the pipetting, pouring, filtering,[1] etc. of the relatively strong ammoniacal solutions will

---

[1] Mickwitz and Landesen attempted to minimize loss during filtration by a special enclosed filter.

result in the loss of ammonia. Finally, if the analytical conditions were ideal, the procedure ignores the presence of the ammonium as ammonium chloride and, without evidence to the contrary, there is no justification for assuming that this is without influence on the amount of ammonium carried down by the precipitate.

In an attempt to determine the extent of contamination by ammonium salts, of manganese sulfide precipitated under varying conditions, the following experiments were carried out. Definite amounts of solutions of NH_4HS alone or of NH_4HS and NH_4OH were diluted to 150 or 175 cc in a 250 cc wide mouth bottle and 50 cc or 25 cc of $MnCl_2$ solution corresponding to 2 g MnS were added. For each set a control was prepared in which water was substituted for the $MnCl_2$ solution. It was found unnecessary to add NH_4Cl to prevent sol formation. The bottles were stoppered tightly and centrifuged to throw down the precipitate. An aliquot part was then pipetted off and analyzed for NH_3 by the Kjeldahl method. From the difference in concentration of ammonium in the bottle containing the precipitate and in the one without precipitate, the amount of ammonium carried down was calculated. The results of a series of observations are given in Table VI.

Table VI

Adsorption of NH_4 by Rose MnS

	Cc solutions mixed					
	$MnCl_2$ equivalent to 2 g MnS	NH_4HS 1.35 N	NH_4OH approx. 5.5 N	H_2O	Equilibrium concn. of NH_4 by Kjeldahl Millimols per l.	NH_4 adsorbed Millimols per gram
a	0	35	0	165	236	—
b	20	35	0	145	232	2.0
a	0	40	0	160	269	
b	20	40	0	140	266	1.5
a	0	50	0	150	337	
b	20	50	0	130	333	2.0
a	0	50	10	140	505	
b	50	50	10	90	496	4.5
a	0	50	15	135	592	
b	50	50	15	85	582	5.0
a	0	50	25	130	771	
b	50	50	25	8	756	7.5

No great accuracy is claimed for these experiments although the procedure corrects most of the errors inherent in the method of Mickwitz and Landesen. It is however too much to hope that the loss of ammonia during the handling of (b) the solutions which give a precipitate and (a) the control, would be identical. Moreover, the amount of ammonium carried down is so very small in all cases compared to the total amount of ammonium present that any small error in measuring the aliquot part of the strong solutions to be analyzed would show up as a large percent of the total adsorption. The experiments do show however that the amount of ammonium carried down by the precipitate increases gradually with increasing concentration of ammonium in the supernatant solution and that there is no indication of the formation of a compound between the MnS and NH_4HS such as Mickwitz and Landesen assumed.

X-Ray Examination of Manganous Sulfides

Rose and green manganous sulfide are identical in composition[1] but the difference in color, density and particle size of the two preparations is so marked that they are usually assumed to represent two isomeric forms of the same substance. As numerous cases are known where differences in color, density, etc., are due to differences in physical state of the same substance, it becomes a question of fact whether the transformation from rose to green manganous sulfide is due to a change in physical character or in molecular structure. This question was settled definitely by X-ray examination of the following preparations by the powder method using the General Electric X-ray Diffraction Apparatus. The numbers correspond with the numbers on the X-radiograms reproduced in Fig. 4.

1. *Pure sodium chloride.* This was used to calibrate the film.

2. *Green MnS precipitated with* $(NH_4)_2S$ *in the presence of* NH_4OH. One-half gram of the sulfide was precipitated and, after the transformation to green, it was washed by the aid of the centrifuge until the supernatant solution was free from chloride, with water containing a little H_2S to prevent oxidation. It was then washed 6 times with 20 cc portions of alcohol, twice with carbon disulfide and finally 3 more times with alcohol. The product was dried at 60° in an atmosphere of H_2S.

3. *Rose MnS formed in the absence of* NH_4OH. The precipitate was washed and dried as in 2. When dried in this way the sulfide has a reddish appearance and does not oxidize readily.

4. *Rose MnS precipitated with* NH_4HS *in the presence of* NH_4OH. This precipitate was prepared under such conditions that it would turn green if allowed to stand. The washing with water and alcohol was carried out promptly before any change took place.

5. *Green MnS formed in the presence of excess* Na_2S. This sample was prepared as described in the first section of this paper and was washed very thoroughly to remove the excess sodium sulfide.

In every case the dried samples were ground in an agate mortar and sealed in a small capillary tube for X-ray examination. The X-radiograms reproduced in Fig. 4 were obtained by exposure for 12 hours. A diagram of the

---

[1] Antony and Donnini: Gazz., 23, 560 (1893).

lines and their relative intensities for the rose and green MnS and for NaCl is given in Fig. 5. The lengths of the vertical lines give the estimated relative intensities of the lines on the film.

A comparison of X-radiograms 2 and 3 shows conclusively that both rose and green sulfides are crystalline, and that the two are isomers with a distinctly different structure. A comparison of 3 and 4 discloses that the rose precipitates formed in the absence and in the presence of ammonia are identical in structure. There is no indication that the rose precipitate which readily turns green is an ammonium sulfo-salt. The X-radiogram of the light green sulfide obtained in the presence of excess Na_2S, preparation 5,

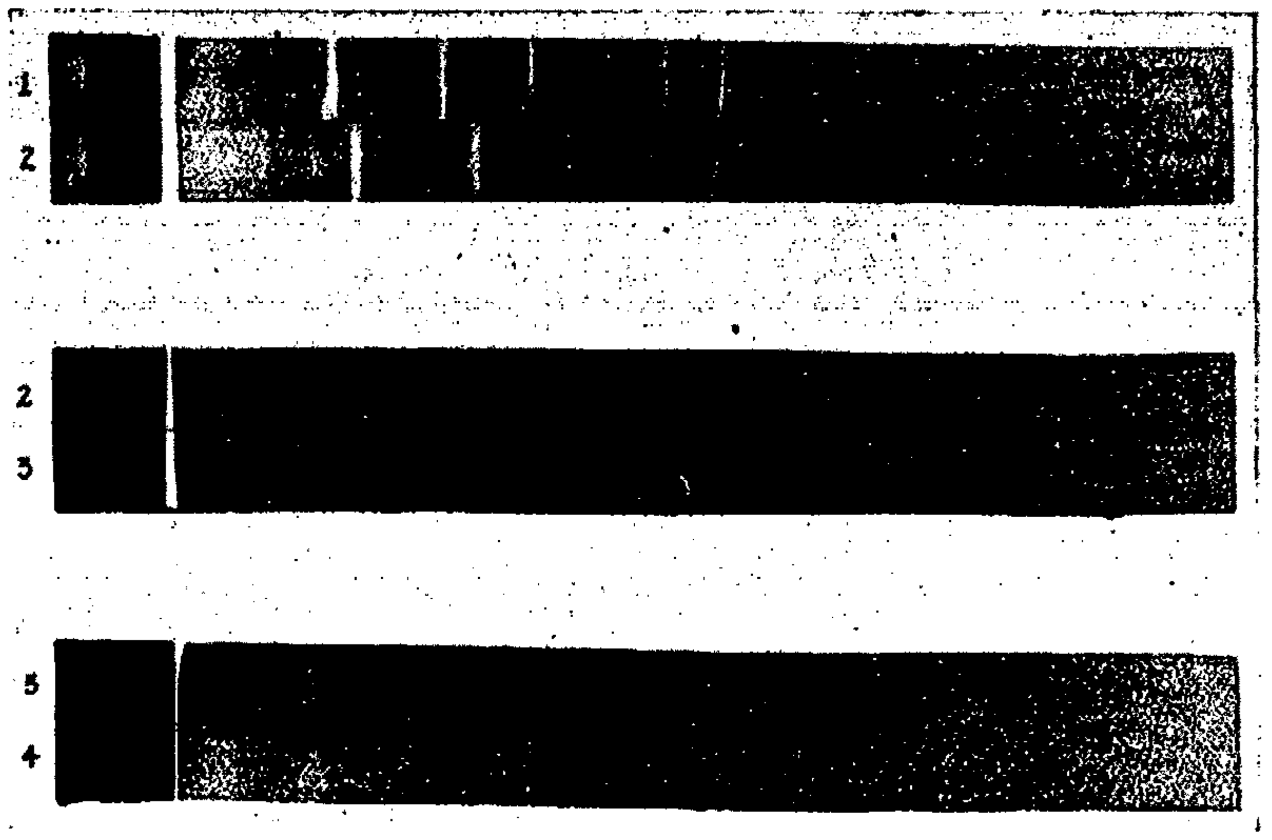


Fig. 4

X-ray Diffraction Patterns of (1) NaCl, (2) Green MnS formed in the presence of NH_4OH, (3) Rose MnS formed in the absence of NH_4OH, (4) Rose MnS formed in the presence of NH_4OH.

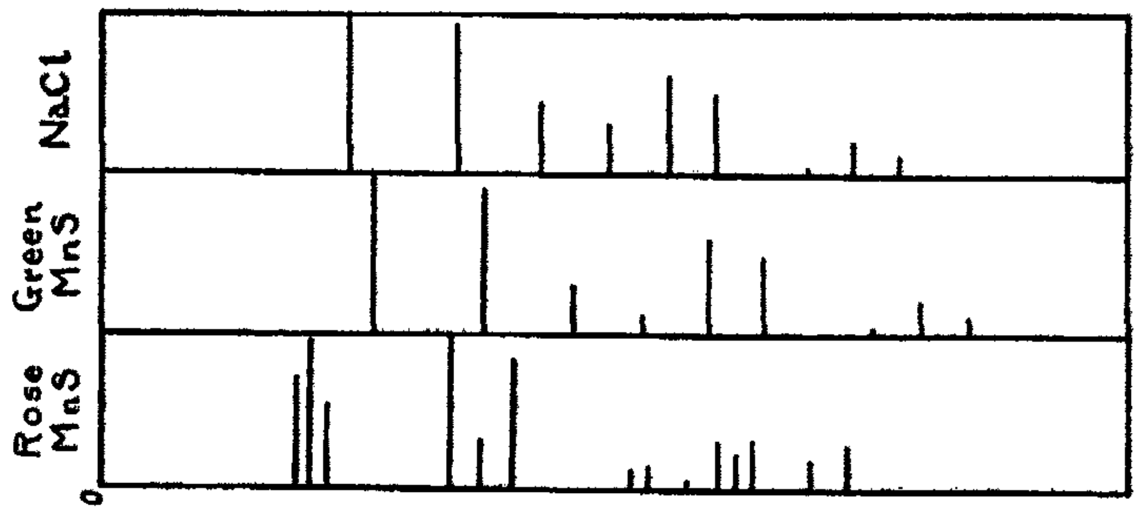


Fig. 5

Spacings and Intensities of Lines in the X-radiograms of NaCl, Green MnS and Rose MnS was identical with that of the dark green, preparation 2, and so the former was not reproduced. Apparently the difference in the shade of green is due to a difference in particle size. In this connection it should be pointed out that a gray sulfide described by Olsen and Rapalje[1] as a third manganous sulfide was found to be merely a mixture of the rose and green forms in suitable proportions.

The Crystal Structure of Green MnS. The lines in the X-radiogram of green MnS are what would be expected from a cubic crystal. Assuming this to be the case, the spacings corresponding to the observed lines were calculated, with the results given in Table VII. The MnS X-radiogram was calibrated by comparison with that of NaCl, the spacings of which are known. It will be observed that the values agree closely with those recorded by Wyckoff[2] for the mineral alabandite.

Since the observed and calculated values agree, it follows that the crystals are cubic and that a_0 the side of the unit cube is n × 2.60 Å where *n* is the order of reflection.

TABLE VII

Spacings and Intensities of Lines in the X-radiogram of Green Precipitated MnS

Indices d n k l	Spacing			Intensity	
	Observed	Calculated	Wyckoff's values	Observed	Wyckoff's values
100 (2)	2.600	2.600	2.61	10	10
100 (2)	1.835	1.839	1.84	9	8
111 (2)	1.501	1.501	1.50	3	3
100 (4)	1.300	1.300	1.31	1	2
120 (2)	1.162	1.163	1.17	6	6
112 (2)	1.062	1.061	1.06	5	5.5
110 (4)	0.917	0.920	—	0.1	—
110 (4)	0.862	0.867	0.87	2	2
100 (6)	0.818	0.822	0.83	1	1

The density ρ of the sulfide may be calculated[3] from the equation

$$\rho = \frac{m \times 86.99 \times 1.649 \times 10^{-24}}{(d_{100}.n \times 10^{-8})^3}$$

if *m* and *n* are known. In this equation *n* represents the order of reflection and *m* the points associated with the unit cell. The value of *m* is 1 for the simple cubic arrangement; 2, for body centered cubic; 4 for face centered cubic; and 8 for diamond cubic. Substituting different values for *m* and *n* in the above equation, it was found that when $m = 4$ and $n = 2$, the calculated density comes out to be 4.08 compared with the observed density of

---

[1] J. Am. Chem. Soc., 26, 615 (1904).

[2] Am. J. Sci., (5), 2, 239 (1921).

[3] Cf. Wyckoff: "The Structure of Crystals," 203 (1924).

3.99.[1] The results indicate that the crystals are probably of the face centered cubic type. The value of a_0 is 5.20 Å which agrees well with the value 5.24 Å reported by Ott.[2]

The Crystal Structure of Rose MnS. The spacings and intensities of the lines in the X-radiogram of rose MnS are given in Table VIII. No attempt was made to determine the structure but it is obvious that it cannot be cubic. It should be noted that the lines occur in triplets.

TABLE VIII

Spacings and Intensities of Lines in the X-radiogram of Rose MnS

Spacing	Intensity	Spacing	Intensity
3.57	7	1.294	1
3.35	9	1.210	0.1
3.11	5	1.148	3
2.04	10	1.113	2
1.861	3	0.990	1.6
1.709	8	0.946	2.5
1.338	1		

Summary of Results

1. The conditions which favor the transformation of the flocculent precipitate of rose MnS to the denser green form are given and the nature of the transformation is described.

2. The transformation from rose to green MnS takes place at the boiling point in the presence of a suitable excess of Na_2S.

3. The transformation from the rose to green sulfide takes place quite readily even at room temperature when precipitated and allowed to stand in the presence of suitable mixtures of NH_4HS and NH_4OH. If the NH_4OH concentration is too low or too high the rate of change is greatly retarded. The critical concentration of reactants for most rapid transformation is quite sharply defined.

4. The rose sulfide changes to green slowly at room temperature in the presence of NH_4HS solution free from ammonia provided the rose precipitate is seeded with some of the green crystals by mixing a small amount of the latter with the reactants before precipitation.

5. The rate of mixing the reactants has a decided effect on the rate of transformation from rose to green MnS. The flocculent rose precipitate formed by slow mixing changes to green much more rapidly than the highly dispersed semi-colloidal precipitate formed by rapid mixing.

6. The conclusion of Mickwitz and Landesen that free ammonia is essential for the transformation from rose to green MnS has been disproven.

7. The solvent action of Na_2S and $(NH_4)_2S$ on the rose sulfide is an important factor in initiating and hastening the transformation to green.

---

[1] International Critical Tables, 1, 127 (1926).

[2] Z. Krist, 63, 22 (1926).

On the other hand, the adsorption of ammonia by the rose particles acts protectively and slows down the rate of transformation. This accounts for the existence of a critical concentration of NH_4HS and NH_4OH for the most rapid rate of transformation and for the influence of the form of the precipitate, as affected by the rate of mixing, on the velocity of change.

8. The rose sulfide adsorbs ammonium and hydrosulfide ions in varying amounts depending on the form of the precipitate and the concentration of the supernatant solution. There is no indication that the rose sulfide which turns green spontaneously is an ammonium sulfo-salt of the composition $(NH_4)HMn_3S_4$ as assumed by Mickwitz and Landesen.

9. X-ray analysis of precipitated rose and green MnS shows that both are crystalline and that they differ in molecular structure.

10. The crystals of precipitated green MnS are probably cubic of the face-centered type. The structure is identical with that of the mineral alabandite. The value of a_0 for the crystals was found to be 5.20 Å.

11. The rose sulfides formed in the presence and in the absence of free ammonia are identical in structure.

12. The light green sulfide formed in the presence of Na_2S is identical in crystal structure with the dark green sulfide formed in the presence of $(NH_4)_2S$. The difference in color is due to variation in particle size.

13. A gray manganous sulfide described by Olsen and Rapalje is not a definite chemical individual but a mixture of the rose and green modifications.

The Rice Institute,
Houston, Texas.

AN ACCURATE FORM OF COPPER COULOMETER

BY HAROLD PFLAUM MATTHEWS AND IAN WILLIAM WARK

There has not hitherto been described any accurate and easily manipulated form of coulometer, suitable for the measurement of currents greater than those that can be passed through the standard silver coulometer—that is, greater than one ampere. Even where it is applicable, the silver coulometer is not easily manipulated. Consequently a more rapid and yet reliable form of coulometer would be welcome, especially should it be capable of dealing with currents greater than one ampere. Marshall[1] has described a copper coulometer for which he claims a high order of accuracy for currents over ten amperes. His claims are not, however, supported by adequate experimental work, and his method (the best available at the time) of checking the coulometer against a standard Weston ammeter is, perhaps, not the most satisfactory.

While engaged on some electrochemical work extending over a period of three years, we have had the opportunity of studying the practical performance of the Marshall type copper coulometer. The work performed had to be kept subservient to the main problem under investigation and therefore no ordered study along theoretical lines was possible. At the outset it was hoped that the instrument, as described by Marshall, would prove sufficiently accurate for our purposes. It soon became apparent, however, that though the instrument was satisfactory for the high currents for which it was designed, it failed for lower ones. It was retained in circuit in the hope that when the causes of failure had been ascertained and eliminated it would be possible to rely exclusively on it; it is satisfactory to be able to report that this position has now been reached. In all, some three hundred tests have been made on its accuracy under various conditions; not least important are a number of tests over a period of twenty-four hours.

Under the conditions recommended later, current can be measured with a maximum error of one or two parts per thousand. The best results have been obtained with the simplest running conditions. Thus it is unnecessary generally to rotate the cathode; no depolariser is necessary in the electrolyte nor is any accurate temperature control necessary. It is strange that Oettel's artifice of adding alcohol to the coulometer electrolyte has been followed so closely by later experimenters, seeing that it now appears unnecessary except in certain well-defined cases.

It will be advisable to outline the method used in checking the coulometer. In the same circuit was placed a standard 1/10 ohm resistance,[2] the volt drop

---

[1] Trans. Faraday Soc., 21, 297 (1925).

[2] This was certified by the makers, Leeds and Northrup, to be correct to within 1/40%. It was checked in Melbourne against the University Sub-Standard of the Natural Philosophy Dept. and found to differ by 0.06%. The makers' value was accepted.

across which was measured at frequent intervals by a calibrated potentiometer. The duration of the passage of current was estimated by means of a calibrated stopwatch.

In tests of one hour's duration, at least fifteen current measurements were recorded. In the longer tests the period between readings was increased to a maximum of fifteen minutes. If the current varied, especially at the beginning of the test, the frequency of measurement was increased. By drawing current from the battery through an auxiliary circuit for a few minutes prior to the test, the familiar irregularities on closing circuit were largely eliminated. In no case was the variation in current between readings sufficient to lead to any significant error. The current determinations by these means are certainly correct to within 0.1% and probably to within 0.05%.

Description of Coulometer

Construction: The anode was a sheet of 1/16 inch electrolytic copper bent to form a cylinder 12 cm. diameter by 12 cm. high, with suitable lugs. It was thickened by electrodeposition of copper to the extent of over 200 ampere hours, and re-plated whenever necessary. It was hung by the lugs mentioned above in a 3-litre beaker, which formed the cell; from 2 to 2.5 litres of electrolyte were required. The cathode was a cylinder of platinum gauze of 2.5 cm. diameter by 5 cms. high. It could be rotated about a vertical axis, also of platinum.

Electrolyte: At first Oettel's solution was used. This consists of

150 grms copper sulphate crystals	50 grms alcohol
50 grms sulphuric acid	1 litre water

Subsequently variations were introduced. Dissolved alcohol was replaced, where specified, by the passage of hydrogen during the test and later both were dispensed with. The acidity was reduced by one half in some tests and even to zero during two tests. The effects of these variations are discussed later.

Operation: The cathode was freed from copper by immersion in concentrated nitric acid. It was washed in distilled water, dried by heating in a blowpipe flame (which treatment detects any undissolved copper) and cooled in a desiccator before weighing. It was placed in position with the cell on open circuit and, where necessary, was set in rotation before the circuit was closed. Approximately one minute elapsed after the circuit was broken before the cathode could be removed from the cell. It was then washed in distilled water and finally in alcohol, the adhering film of which was ignited to dry the deposit, which was cooled in a desiccator before weighing.

Experimental Results

The first series of tests was undertaken with an electrolyte of the composition of Oettel's solution; no record of the temperature is available as the usual procedure of running at room temperature was followed. The cathode was rotated at 200-300 r.p.m. (The higher speed, 1000 r.p.m., recommended by Marshall caused a vortex to penetrate the hollow cylinder of the electrode, offering facilities for the aeration of the electrolyte). Currents were lower than those for which Marshall designed the instrument, and it is to be emphasized that the errors reported under these conditions do not in any way condemn the instrument for higher currents.

TABLE I

Tests in Oettel's Solution. Rotating Cathode

Test No.	Time Hours	Current	Coulometer Error
1	1	1 amp	+0.3%
2	1	1	Nil
3	1	1	+0.1
4	1	1	+0.6
6	1	1	+0.2
7	1	1	Nil
8	1	1	+0.2
9	0.8	1.5	+0.1
12	1	1	+0.9
13	1	1	Nil
14	1.05	1	+0.6
16	1	1	+0.8
17	1	1	−1.0
5	1	0.5	−1.5
11	1	0.25	−1.5

The low values indicated by the coulometer in Nos. 5 and 11 are to be attributed to the low current. With the exception of No. 17, all other results are high. Some recent results of Fuseya and Murata[1] indicate that the alcohol may have been responsible for these high results. These authors have shown that citric and other hydroxy-acids may be deposited with copper up to the extent of 6% of the weight of the copper. It was suspected that the hydroxyl group of alcohol might be responsible for its co-deposition with copper also. Accordingly, in another series of tests, no alcohol was added but as the literature is insistent on the use of some depolariser, hydrogen was bubbled through the solution instead. Between 4 and 7 litres of hydrogen per hour were used.

---

[1] Trans. Am. Electrochem. Soc., 50, 235 (1926).

TABLE II

Preliminary Tests in Alcohol-free Solution
Hydrogen bubbled. Cathode rotated

Test No.	Time	Current	Coulometer Error
20	1 hour	1	−0.2
21	1 "	1	−0.2
29	1 "	1	−0.1
30	1 "	1	−0.1
31	1 "	1	−0.1
22	0.25	4	−0.1
23	0.25	4	Nil
25	0.25	4	+0.2
26	0.25	4	+0.35
27	0.25	4	Nil
28	0.25	4	+0.2

Although high errors had been eliminated at currents of 1 ampere, with higher currents they were still sometimes encountered. Further tests were therefore undertaken with currents of 4 amperes but the errors now disappeared.

TABLE III

Summary of Tests at 4 Amperes {Alcohol absent
Hydrogen bubbled
Cathode rotated}

Test No.	Time	Current	Coulometer Error	Remarks
22	0.25 hrs	4 amps.	−0.1%	
23	"	"	Nil	
25	"	"	+0.2	
26	"	"	+0.03	
27	"	"	Nil	
28	"	"	+0.2	
33	"	"	Nil	
38	"	"	Nil	
39	"	"	+0.1	
40	"	"	+0.1	
93	"	"	−0.15	Fresh solution tests were conducted at about 25°C
94	"	"	−0.13	
95	"	"	−0.13	
96	"	"	−0.11	
97	"	"	−0.10	
98	"	"	−0.16	
110	"	"	+0.06	A fresh solution of one half normal acidity now used
111	"	"	Nil	
112	"	"	−0.04	

The acidity of the solution was reduced at Test No. 110 because it was thought that, if re-solution of copper was responsible for low results, they might thereby be partly eliminated. Though the three different solutions seemed to give slightly different results,[1] it was concluded that at this current density the Marshall coulometer is a trustworthy instrument.

The instrument was then tested further with lower currents. After giving fairly consistent results for twenty tests, the performance became erratic and errors up to 2% were not uncommon. It was some considerable time before the cause of the variations was discovered; meantime, fifty tests were made in which the error was sometimes high, sometimes low. The period of good results coincided with the winter season, and ultimately the variations were shown to be due to fluctuations in room temperature. It was ascertained later that the actual temperature was the important factor and not fluctuations during or immediately prior to the test. The results during this period are set out in Table IV.

TABLE IV

Summary of Early Results at 1 Ampere {Cathode rotated, Alcohol absent, Hydrogen bubbled, Temp. uncontrolled, 1 Hour Tests}

Month	Number of Tests	Mean Error	Mean Max. Daily Temp. of Weather Bureau	Maximum Error
Sept. 1927	17	+0.1%	18° C.	+0.5 (twice)
Oct. 1927	14	−0.45%	21°	−1.8%
Nov. 1927	15	−1.6%	25°	−2.1%
Dec. (First half)	8	−0.7%	24°	−0.9%

During September almost all errors were on the high side; after September all were on the low side. As it now appeared probable that temperature had an influence on the performance of the coulometer, direct tests were undertaken to test this theory, the cell being arranged to function as a thermostat. It became desirable to extend the testing to include other variables and work has now to be reported covering the effects of

(a) Rotation of cathode or stirring of solution

(b) Temperature

(c) Bubbling of hydrogen

and, over more restricted ranges, of

(d) Acidity of solution

(e) Filtering the solution

---

[1] Later work has failed to reveal any differences between different solutions provided that they be given a short preliminary electrolysis to remove impurities.

(f) Duration of deposition up to 24 hours

(g) Current density variations.

(a), (b) and (c) were considered together, as illustrated in Table V.

TABLE V

Current 1 Ampere Standard Marshall Coulometer
(Tests from ½ to 12 hours duration)

	Hydrogen bubbled		Hydrogen not bubbled	
	Cathode rotated	Cathode stationary	Cathode rotated	Cathode stationary
Room Temp. (below 30°)	Low Results (18 tests)	Good Results (5 tests)	High Results (7 tests)	Good results (40 tests)
Higher Temp. (above 30°)	High results (6 tests)	Slightly high results (5 tests)	Very high results (7 tests)	High results (8 tests)

This compilation represents average results only, full experimental details are given later. The following deductions may be drawn:—

Effect of Rotation: With this current, rotation leads to incorrect results; rotation in conjunction with high temperatures leads at times to very high errors; these can be reduced by passing hydrogen through the cell.

With a stationary cathode, variations, though in the same direction, become much smaller.

At higher current densities, rotation might become essential, but it has already been shown that rotation is then no longer sufficiently detrimental to vitiate results. The range of the coulometer would therefore be increased if facilities were provided to rotate the cathode.

Effect of Temperature: Below 20° results are generally good, but if the cathode be rotated, errors mount with the temperature until, above 30°, they reach 5%.

With stationary cathode, results are reliable at room temperature, even up to 30°C. Room temperature seldom exceeds this value in Melbourne.

Effect of Hydrogen: With stationary cathode, hydrogen is unnecessary at room temperature. If the cathode be rotated or the temperature be raised hydrogen exerts a corrective influence. In extending the use of the instrument to higher current densities at intermediate values—where rotation has just become necessary—it would be advisable to bubble hydrogen past the cathode.

Table VI-XIII show in detail the effects of these factors:

Table VI

Hydrogen bubbled, Cathode rotated, Room Temperature
(Current 1 Ampere)

No. of Test	144	145	146	147	151	152	154	155	165	166	168	169
Temp.	> 20	29	23	24	21	24	27	22	25	24	20	22
Hours	7	12	11	6	6	6	1	1	½	½	1	1
Error %	−2.3	−1.4	−0.8	−0.7	−0.8	−0.8	−0.5	−0.3	−0.6	−0.2	−0.4	−0.1

Above 20°

No. of Test	148	149	150	156	157	213
Temp.	17	19	19	15	16	17
Hours	1	½	6	4	1	1
Error %	−0.1	−0.2	−0.3	−0.1	−0.2	−0.05

Below 20°

Table VII

Hydrogen bubbled, Cathode not rotated, Room Temperature
(Current 1 Ampere)

Test No.	212	221	232	233	234
Temp.	16	14	14	14	14
Hours	1	1	5	5	5
Error %	Nil	Nil	−0.1	Nil	−0.2

Table VIII

Hydrogen not bubbled, Cathode rotated, Room Temperature
(Current 1 Ampere)

Test No.	173*	174	175	176	207	209	211
Temp.	24	24	23	19	17	17	17
Hours	½	½	½	½	½	1	1
Error %	(−2.0)	−0.6	−0.2	Nil	+1.2	+0.8	+1.4

* Fresh solution, not previously electrolysed.

Table IX

Hydrogen bubbled, Cathode rotated, Temperature above 30°
(Current 1 Ampere)

Test No.	153	160	161	170	171	172
Temp.	36	33	33	33	33	33
Hours	1	6	¾	1	1	1
Error %	−0.8	+0.4	+0.3	+1.3	+0.4	+1.7

Table X

Hydrogen bubbled, Cathode not rotated, Temperature above 30°
(Current 1 Ampere)

Test No.	235	236	237	238	239
Temp.	40–26	28–36	34–37	53–36	34–30
Hours	5	5	5	5	5
Error %	−0.1	−0.1	+0.15	+0.2	+0.1

Table XI

Hydrogen not bubbled, Cathode rotated, Temperature above 30°
(Current 1 Ampere)

Test No.	189	190	205	241	243	244	258*
Temp.	32	35	30	31	42	32	34
Hours	1	5	1	5	1	1	6
Error %	+2.6	+2.1	+4.4	+2.7	+3.4	+4.9	+0.5

* Solution stirred by hand every 15 minutes instead of cathode being rotated.

TABLE XIII

Hydrogen not bubbled, Cathode not rotated, Room Temperature

Test No.	179	180	195	196	197	198	269	274	275	293
Temp.	21	21	22	20.2	21	21	23	24	24	30
Hours	½	1	1	1	1	1	5	24	24	12
Current	1	1	1	1.5	1.5	1	1	1	1	1
Error %	−0.05	Nil	Nil	+0.1	Nil	+0.05	−0.1	Nil	Nil	+0.1

Above 20°

Test No.	177	178	181	194	199	200	201	202	206	208	210	217	220	223	224
Temp.	20	20	19	19	18	18	19	19	16	17	16	14	15	16	13
Hours	½	½	5	1	1	1	1	1	1	1	1	5	5	5	5
Current	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Error %	+0.1	−0.1	Nil	Nil	−0.1	+0.05	−0.05	+0.1	Nil	−0.05	−0.05	Nil	Nil	Nil	Nil

Test No.	245	246	247	248	249	250	251	259	261*	262*	265	266	267	268	271	272
Temp.	13	13	16	16	17	18	18	18	18	18	19	20	—	20	19	20
Hours	24	24	12	5	1	1	1½	24	24	23	24	24	24	5	24	24
Current	1	1	1	1	1	1	3	1	1	1	1	1	1	1	1	1
Error %	Nil	+0.2	−0.2	+0.15	−0.15	+0.15	−0.15	−0.1	Nil	Nil	−0.2	Nil	−0.1	−0.2	Nil	Nil

* New solution, not acidified; acidified before 265.

TABLE XII

Hydrogen not bubbled, Cathode not rotated, Temperature above 30°
(Current 1 Ampere)

Test No.	186	187	188	191	192	193	203	204
Temp.	39	35	35	35	36	37	35	33
Hours	5	1	1	3	1	1	1	1
Error %	−0.15	+0.15	+0.15	Nil	+0.65	+0.4	+0.1	+0.1

Acidity of Solution: Even when no free acid was present—in Tests Nos. 261 and 262 of Table XIII—results were quite satisfactory. Previously no difference was observed when the acidity was reduced by one half. Evidently the acidity has little if any influence on results.

As almost a minute elapses before the cathode can be removed from the electrolyte after the circuit is broken, it was thought that there might be introduced an error due to slow re-solution of copper in the acid electrolyte. Therefore the rate of re-solution was measured for several deposits; the cathode was rotated during each estimation of re-solution rate.

TABLE XIV

Rate of Re-solution on Open Circuit

Test No.	Rate of re-solution	Coulometer Error
87	0.6 mg./min	−4.5%
91	0.8	−3.0
93	0.7	−0.1
137	0.8	−1.7
138	0.9	−1.6
139	0.7	−1.2

There is no connection between error and rate of re-solution. With the cathode stationary the re-solution loss would be much less than in these tests. Even with rotation the error due to re-solution need not amount to more than 0.05% for a deposit corresponding to 1 ampere hour.

Filtration: Filtration of the electrolyte made no difference to results. Owing to the formation of an anode slime, filtration is necessary from time to time, especially if the cathode be rotated. (Filtration does influence the form of the deposit, however.)

Duration: From Table XIII it follows that duration, up to 24 hours, has no effect on the reliability of the coulometer.

Current Density: Current density is difficult to estimate for a gauze cathode. We have therefore reported our results in terms of the current passing and the size of the cathode. Results for four and one amperes respectively have been reported above. Results for lower currents are set out in the following graph—

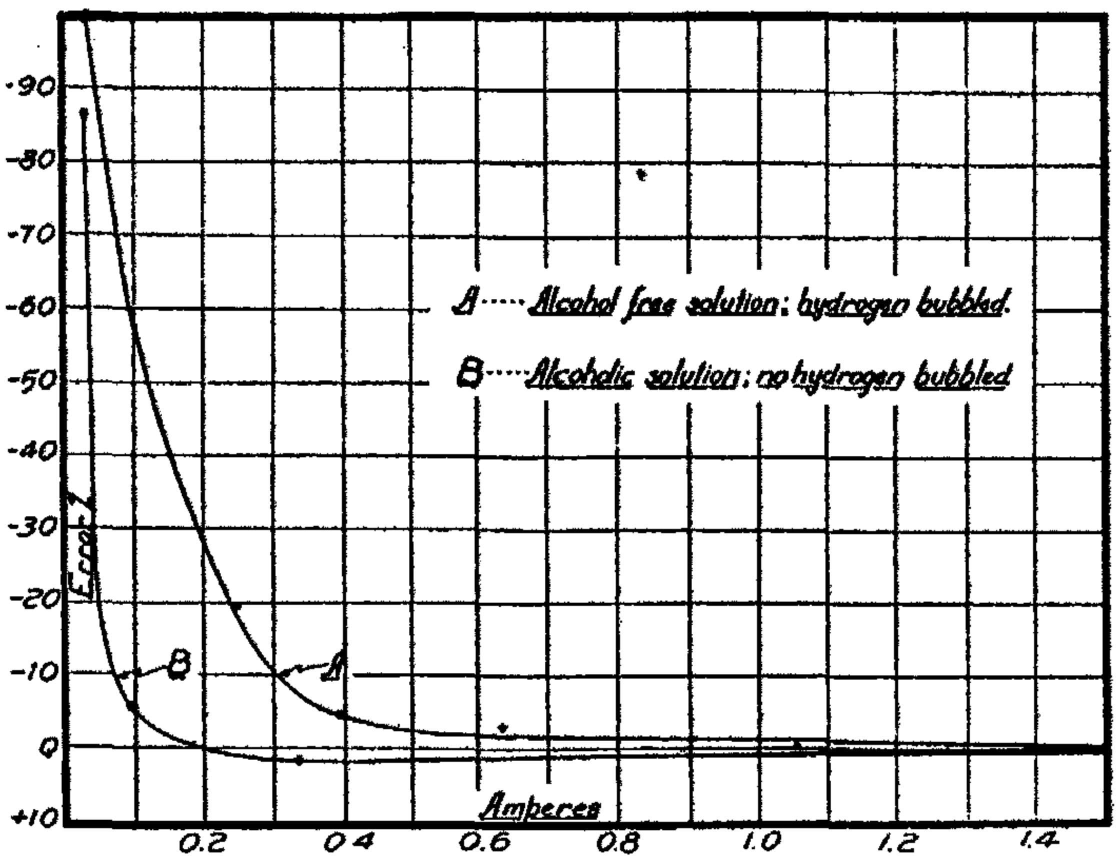


Fig. 1

Procedure now recommended: The conditions of Table XIII are recommended for currents of from one to three amperes and a cathode of the specified size. The cathode should not be rotated, there is no need to pass hydrogen, though it does no harm. (Tables VII and X) and results are equally satisfactory for all room temperatures between 13 and 30°. The mean error of 41 determinations under these conditions was zero. The maximum error of 0.2% occurred only on three occasions and on two of these, the tests having extended over 24 hours, the comparison method of current measurement may have been slightly in error, as the variation between readings was greater than usual.

For higher currents it is advisable to rotate the cathode, but in this case hydrogen should be bubbled past the cathode. High temperatures are to be avoided and in hot weather cooling would perhaps be necessary. Marshall's results indicate that the coulometer would be applicable for currents of 15 amperes, but further testing is desirable above 4 amperes.

For lower currents the addition of alcohol would increase the range of the instrument (See Fig. 1). A more satisfactory procedure would be to decrease proportionally the size of the cathode and cell. It is to be emphasised that the results reported above apply only for a cell of the given size; variations are to be expected with variation in the cell dimensions.

Explanation of Results: Low results might be occasioned either

(i) by liberation of hydrogen at the cathode, or

(ii) by an increase in the cuprous ion concentration at the cathode, caused by the action,

$$Cu^{++} + e = Cu^{+}$$

High results might be occasioned by precipitation of cuprous ions. This implies either

(i) a decrease in the Cu^+/Cu^{++} ratio in solution (which appears unlikely), or

(ii) Cu^+ ions forming at the anode in compensating amounts.

The proper working of the coulometer demands firstly that the Cu^+/Cu^{++} equilibrium should not be upset by electrolysis, and secondly that only cupric ions should be dissolved at the anode and precipitated on the cathode. A complete study of the working of the coulometer would necessitate weighing of both anode and cathode and carefully following the changes in composition of the electrolyte. The anode sludge should also be weighed and analysed. For the reasons cited earlier we were unable to do this.

Summary

The Marshall copper coulometer has been subjected to more than three hundred tests over a wide range of current density. For high (see text) current density it is satisfactory as described by Marshall. For lower current densities certain specified modifications in procedure are necessary to keep the error below 0.2%.

Temperatures higher than 30° cannot be tolerated and it is unwise to rotate the cathode with low current densities; but the errors resulting from either of these causes may be considerably reduced by bubbling hydrogen through the electrolyte. Alcohol additions are not generally necessary, though they are helpful in extending the range of the instrument on the low current density side.

Comparatively large variations in the acidity and lengthy periods of electrolysis—up to 24 hours in fact—are without effect on the performance of the coulometer.

We are much indebted to Sir David Masson, under whose direction this work was carried out, for his stimulating interest and helpful advice. To Dr. A. L. Marshall our thanks are due for his help in obtaining for us a cathode similar to that used by him in his earlier work. We have also to thank Professor E. J. Hartung for having made available the University laboratory for this research, which was carried out while we were in the service of the Electrolytic Zinc Company of Australasia, Ltd.

Department of Chemistry,
The University,
Melbourne.

THE GENERAL THEORY OF SOLUTIONS

BY R. C. CANTELO*

A fundamental treatment of the general theory of solutions must find its beginning in the First and Second Laws of Thermodynamics. Clausius had combined theses two laws for a system of constant mass by writing $dU = TdS - pdV$, where U, S, T, p, V are the energy, entropy, temperature, pressure and volume respectively of the system. Milne[1] says, "But it was left to Willard Gibbs to import a genuinely mathematical idea and so make thermodynamics applicable to chemistry. Willard Gibbs simply introduced partial differential coefficients into a situation in which the ordinary 'physical' notion of a partial differential coefficient is physically not realizable. He considered the increase in energy of a system which occurs when its volume and entropy remain fixed but the mass of a chemical constituent is altered. How on earth (or in physics, which is the same thing) one can experimentally import matter into a system without importing or exporting entropy, or indeed knowing what entropy has been imported or exported I have never been able to see; . . . The fact is the idea is a purely mathematical one."

Since U is a function of S, V, m, where m is the mass of the system, mathematics tells us that $dU = \frac{\partial U}{\partial S} dS + \frac{\partial U}{\partial V} dV + \frac{\partial U}{\partial m} dm$. The coefficient of dm in the right hand member is actually $\left[\frac{\partial U}{\partial m}\right]_{S,V}$ and this is the partial differential coefficient introduced by Gibbs. To this partial differential coefficient Gibbs gave the name "chemical potential." From this viewpoint we have the following definition[2] of the chemical potential of a substance:

"If to any homogeneous mass we suppose an infinitesimal quantity of any substance to be added, the mass remaining homogeneous, and its entropy and volume remaining unchanged, the increase of the energy of the mass divided by the quantity of the substance added is the *potential* for that substance in the mass considered."

It is, however, possible to admit that the importation of the mass dm into a homogeneous mixture of mass, m, produces a simultaneous increase in the energy, volume and entropy of the system, and it is easy to show then, that dU expressed as an exact differential becomes $dU = TdS - pdV + \frac{\partial}{\partial m}(U - TS + pV)_{T,p}dm$ or $dU = TdS - pdV + \bar{F}dm$, where $\bar{F}$ is written for the partial differential coefficient $\frac{\partial}{\partial m}(U - TS + pV)_{T,p}$ It is this potential or chemical potential that is of particular importance in the treatment of solutions.

---

* Assistant Professor of Chemistry, College of Liberal Arts, University of Cincinnati.

The chemical potential of a constituent A in a mixture of (perfect) gases can be expressed as a function of its partial pressure. Thus the molar chemical potential $\bar{F}_A$ is given by $\bar{F}_A = RT\ln p_A + \text{const.}$ Similarly, the molar chemical potential of a solute present in very small amount in a solution is given by $\bar{F}_A = RT\ln C_A + \text{const.}$ Such a solution in which the solute is present in very small amount, we shall call a perfect solution. Since in an infinitely dilute solution, the molar concentration of solute is directly proportional to its mole fraction x, $\bar{F}_A$ becomes for the perfect solution $\bar{F}_A = RT\ln x + \text{const.}$ This equation is a fundamental one for the theory of solutions.

At this point it becomes necessary to acquire a new viewpoint as regards the meaning of $\bar{F}$. For a homogeneous system consisting of masses m_1, m_2, m_3, ... we write for dU,

$$dU = TdS - pdV + \bar{F}_1dm_1, + \bar{F}_2dm_2 + ----$$

or $$dU - TdS + PdV = \Sigma\, \bar{F}_1dm_1.$$

or $$d(U - TS + pV)_{T,p} = \Sigma\, \bar{F}_1dm_1$$

or $$(dF)_{T,p} = \Sigma\, \bar{F}_1dm_1.$$

so that we can write for $\bar{F}_K$,

$$\bar{F}_K = \frac{(\partial F)}{(\partial m_K)_{T,p,m_1,----}}$$

The function $F = U - TS + pV$ is the well known Free Energy Function for the system. Then the chemical potential of a constituent K, is the partial differential coefficient of the Free Energy Function with respect to the mass m_K, the temperature and pressure as well as the masses of the other constituents being held constant.

If we substitute moles for grams,

$$\bar{F}_K = \frac{(\partial F)}{(\partial n_K)_{T,p,n_1,n_2---}}$$

or for a binary mixture

$$\bar{F}_1 = \frac{(\partial F)}{(\partial n_1)_{T,p,n_2}}$$

$\bar{F}_1$ is the molar chemical potential or as it is now usually called, the partial molal free energy of the constituent indicated by the subscript 1.

For a solute in a perfect solution $\bar{F}_1 = RT\ln x + \text{const.}$ This equation may be replaced by the equivalent expression

$$d\bar{F}_1 = RTd\ln x$$

whence $$\bar{F}_1 - F_1 = RT\ln x \qquad (1)$$

F_1 is the molal free energy of pure solute. Similarly,

$$\bar{F}_2 - F_2 = RT\ln(1 - x) \qquad (2)$$

F_2 is the molal free energy of pure solvent. x is the mole fraction of solute.

If equations (1) and (2) hold, all the additional equations for dilute (perfect) solutions follow as well. For example, we may find the relation between the vapor pressure of a volatile solute from a dilute solution and its mole fraction. Let K_1 be the solute, K_2 the solvent. Then for the partial molal free energy of K_1 in the vapor phase we can write:

$$dF_1 = RTd\ln p_1$$

and for the partial molal free energy of K_1 in the solution, we have

$$d\bar{F}_1 = RTd\ln x,$$

and $dF_1 = d\bar{F}_1$ (this is easily shown)

Hence $d\ln p_1 = d\ln x$

or $p_1 = kx$, the familiar expression for Henry's Law.

Equations (1) and (2) apply to ideal dilute solutions. Actual solutions, especially solutions of strong electrolytes, deviate greatly from the laws of dilute solutions. For such actual solutions, we can substitute no longer mole fractions in our formulas because substitution of such values gives results which do not agree with those obtained experimentally. The quantities which when substituted in our thermodynamic formulas, do give results which agree with the experimental values are known as *activities*. Activities correct for deviation from the ideal state of the infinitely dilute solution; and the extent of the deviation is expressed by $f = a/x$ where f is the activity coefficient, a is the activity and x is the mole fraction of a given component.

For actual solutions we have to write

$$\bar{F}_1 - \bar{F}_{1,0} = RT\ln a_1 \qquad (3)$$

$$\bar{F}_2 - \bar{F}_{2,0} = RT\ln a_2 \qquad (4)$$

$\bar{F}_{1,0}$ and $\bar{F}_{2,0}$ are the partial molal free energies of solute and solvent respectively in some standard reference state of unit activity. Thus, in general, the activity is defined mathematically by

$$\bar{F} - \bar{F}_0 = RT\ln a$$

Since the activity expresses a deviation from the ideal state of the infinitely dilute solution, we can write $a_1 = x$ and $a_2 = 1 - x$ for the ideal solution.

This additional information regarding the values of a_1 and a_2 as x approaches zero enables us to write equations (3) and (4) as follows,

$$\bar{F}_1 - \bar{F}_{1,0} = RT\ln f_1 x; \qquad (5)$$

$$f_1 = \frac{a_1}{x} \text{ and } f_1 = 1 \text{ when } x \rightarrow 0.$$

$$\bar{F}_2 - \bar{F}_{2,0} = RT\ln f_2(1-x); \qquad (6)$$

$$f_2 = \frac{a_2}{1-x} \text{ and } f_2 = 1 \text{ when } x \rightarrow 0.$$

It is evident from (5) and (6) that the standard state of unit activity is a hypothetical one for the solute; but for the solvent, this standard state is simply pure solvent. For solvent we can write

$$\bar{F}_2 - F_2 = RT\ln f_2(1-x) \qquad (7)$$

Activities and activity coefficients have been introduced to correct for deviation in the behavior of a component from its behavior in infinitely dilute solution. Bjerrum[3] has done this in another way for the solvent.

For the ideal state $\bar{F}_2 - F_2 = RT\ln(1-x)$ and since x is very small, we can write this $\bar{F}_2 - F_2 = -RTx$.

For actual solutions we write this

$$\bar{F}_2 - F_2 = -RTxG \qquad (8)$$

where G is the osmotic coefficient. We can define G by the equation

$$G = \frac{P}{P_i} \qquad (9)$$

P is the osmotic pressure of the given solution, and P_i is the osmotic pressure for the ideal state, calculated by $P_i = CRT$.

Equation (8) applies to a solution of two components. For several solutes this becomes

$$\bar{F}_2 - F_2 = RT(x_1 + x_2 + \cdots)G \qquad (10)$$

where $x_1, x_2 \cdots$ are the mole fractions of the several solutes calculated on the assumption that their behavior is the same in the given solution as in infinitely dilute solution. For an electrolyte, this means that $x_1, x_2, \cdots$ are the mole fractions of the ions calculated on the assumption that the electrolyte is completely ionized.

It is especially in the treatment of solutions of strong electrolytes that the concepts of activity and osmotic coefficients have been most useful. Let us examine what we mean when we speak of the "mean" activity or "mean" activity coefficient of the ions of an electrolyte.

Suppose that the salt $MgCl_2$ is in solution. Then according to the Arrhenius theory of solutions of electrolytes, an equilibrium exists thus

$$MgCl_2 \rightleftarrows \overset{++}{Mg} + 2\,\bar{Cl}.$$

Hence $$a_{Mg^{++}}\ a^2_{Cl^-} = Ka_{MgCl_2}$$

The activities of the ions may be determined by electromotive force measurements; but the only method that might be used to determine the activity of unionized $MgCl_2$ is that of vapor pressure measurements. Unfortunately, few strong electrolytes possess an appreciable vapor pressure, so that we are unable to determine the value of K. Accordingly, we shall find it convenient to *define* the activity of a strong electrolyte in the following way:

If one mole of an electrolyte on complete dissociation furnishes n_+ moles of positive ion and n_- moles of negative ion, then the activity of the electrolyte is defined by the equation:

$$a = a_+^{n_+}\, a_-^{n_-} \qquad (10)$$

Note that this is equivalent to placing K = 1 in the mass action expression.

Then the mean activity of the electrolyte, that is, the mean activity of the ions of the electrolyte, is defined by

$$a_{\pm} = [a_{+}^{n+} a_{-}^{n-}]^{\frac{1}{n}} \qquad (11)$$

where $n = n_{+} + n_{-}$. Similarly the mean activity coefficient of the ions is defined by

$$f_{\pm} = [f_{+}^{n+} f_{-}^{n-}]^{\frac{1}{n}}$$

A differential equation giving a relation between the mean activity coefficient of the ions and the osmotic coefficient of the solvent can be derived readily. This equation follows:

$$1 + x\frac{d \ln f_{\pm}}{dx} = x\frac{dG}{dx} + G$$

If we use the molar concentration, c, instead of mole fraction, we have

$$1 + c\,\frac{d\ln f_{\pm}}{dc} = c\,\frac{dG}{dc} + dG \qquad (12)$$

Here c is the stoichiometrical concentration of the electrolyte. Hence if either $f\pm$ or G can be determined experimentally as a function of c, equation (12) permits the calculation of the other also as a function of c. Thus Brönsted[4] found experimentally that the functional relationship between G and c for uni-univalent salts was given by $1 - G = a\sqrt{c} + bc$ where a is a universal constant and b is a coefficient peculiar to the individual salt. From equation (12) it can be shown that $\ln f_{\pm} = -3a\sqrt{c} - 2bc$.

Activity coefficients and osmotic coefficients may be determined experimentally; but the most interesting development of recent years is found in the theory of Debye and Hückel.[5] This theory permits of the theoretical calculation of activity and osmotic coefficients for solutions of strong electrolytes.

Debye and Hückel postulate that strong electrolytes are completely ionized; and that an ion consists of a point charge ZE—where Z is the valence of the ion, and E is the charge on a univalent positive ion—situated at the center of a sphere of diameter a, equal to the average distance of closest approach of the ions, the matter of sphere being that of the medium.

A potential exists at the surface of an ion sphere due not only to the point charge at its center, but due also to the distribution of point charges about the central ion. By an application of the Boltzmann Principle, Debye and Hückel calculate the density of electricity in the solution, and finally by substituting this density in the Poisson Equation for the variation of the potential with the radial distance, they obtain an equation for the potential due to the ion atmosphere; and hence an expression for U_e, the potential energy of solution. From U_e, the *Electrical* Free Energy of the solution can be calculated by an application of the Gibbs-Helmholtz equation. This electrical free energy, F_e is given for a *symmetrical* binary electrolyte forming a total of n ions, by the equation

$$F_e = -\frac{EKXnZ^2}{3D}$$

$K = \frac{4\pi E^2 n Z^2}{DkT}$, where D is the dielectric constant of the medium, k is the Boltzmann constant, and T is the absolute temperature. X is a function of Ka where a is an average diameter of the ions.

The partial differential coefficient of F_e with respect to n gives the partial electrical free energy of an ion. This value $\bar{F}_{1,e}$ is given by

$$\bar{F}_{1,e} = -\frac{E^2 Z^2 K}{2D(1 + Ka)} \tag{14}$$

In an infinitely dilute solution the potential due to the ion atmosphere does not exist. For such a solution $\bar{F}_{1,e} = 0$.

The difference between the free energies of the ions in a given solution and in an infinitely dilute solution is given by the relation

$$F - F_0 = NRT \ln \frac{a_1}{a_0}$$

where F_0 and a_0 are the free energy and the activity respectively of the *ions* in the infinitely dilute solution, and N is the number of ion-moles in the solution. Using n the number of *ion-molecules*, we have

$$F - F_0 = nkT \ln \frac{c_1}{c_0} + nkT \ln \frac{f_1}{f_0};$$

where f_1 and f_0 are the activity coefficients of an ion in the given solution and in the infinitely dilute solution, respectively. Since $c_0 \rightarrow 0$,

$$F - F_0 = nkT \ln \frac{c_1}{c_0} = nkT \ln f,$$

where f represents the activity coefficient of an ion in the given solution.

If the ions were uncharged we should have for F

$$F = F_0 + nkT \ln \frac{c_1}{c_0},$$

and the ions act as perfect solutes in infinitely dilute solution. Hence the term nkTlnf must represent the electrical free energy of the ions in the solution. Then kTlnf must be equal to $\bar{F}_{1,e}$. Hence we can obtain the relation

$$-\ln f = \frac{E^2 Z^2 K}{2\,DkT(1 + Ka)}, \tag{15}$$

a theorectical equation for the calculation of the activity coefficient of an ion. Again since $f_{\pm} = [f_{+}^{n+} f_{-}^{n-}]^{\frac{1}{n}}$, it is a simple matter to obtain the corresponding equation for $f_{\pm}$. By a somewhat similar method, it is possible to calculate G, the osmotic coefficient, also.

The calculated values of $f \pm$ and of G are in excellent agreement with the experimental ones in the region of great dilution, in the absence of high-valence ions. With more concentrated solutions and even with the dilute solutions when high valence ions are present, discrepancies arise, but, nevertheless this theory represents a remarkable contribution to the theory of solutions of strong electrolytes.

It is beyond the scope of this brief paper to discuss the modifications of this theory due to Hückel[6] to Gronwall, LaMer, and Sandved[7] and to Guntelberg.[8] Neither can we discuss some of the interesting applications of the theory. We must, however, mention the fact that Brönsted's application of the original Debye-Hückel theory to the velocity of ionic reactions[9] has furnished an adequate explanation of the linear and exponential salt effects which have been observed in so many ionic reactions.

This paper has given a brief review of the development of the theory of solutions. The advances in the theory of solutions and application of these advances have been remarkable in the last few years. Yet these advances have been possible because Gibbs introduced a purely mathematical idea into thermodynamics over half a century ago.

References

[1] Milne: "The Aims of Mathematical Physics," p. 9 (1929).
[2] Gibbs: "Scientific Papers," Vol. I, p. 93 (1906).
[3] Bjerrum: Z. Elektrochemie, **24**, 321 (1918).
[4] Brönsted: J. Am. Chem. Soc., **44**, 938 (1922).
[5] Debye and Hückel: Physik. Z., **24**, 185, 344 (1923).
[6] Hückel: Physik. Z., **26**, 93 (1925).
[7] Gronwall, LaMer and Sandved: Physik. Z., **29**, 258 (1928).
[8] Guntelberg: Z. physik. Chem., **123**, 241 (1926).
[9] Brönsted: Z. physik. Chem., **102**, 169 (1922).

ON THE MECHANISM OF INVERSION OF SUGAR IN MIXED SOLVENTS*

BY A. GANGULI AND A. B. MALKANI

Although the mechanism of inversion of sucrose has been studied for the last fifty years, no satisfactory explanation has been offered as yet. Scatchard[1] and others regard this as uni-molecular reaction, while W. C. McC. Lewis and co-workers[2] have indicated that the part played by water molecules in the formation of sucrose hydrate and its subsequent decomposition, should also be taken into account. This is really a pseudo-uni-molecular reaction. Again Brönsted[3] regards the inversion of sucrose as a so-called 'zero type' reaction, which should show slight neutral salt effect, a fact experimentally verified by Kautz and Robinson[4]. The rate of inversion is represented by him by the following equation:

$$h = k_1 C_S C_{H^\cdot} \times f_0$$

where K_1, is the velocity coefficient, C_S and $C_{H^\cdot}$ the concentration of sucrose and the hydrogen ion respectively and f_0 another additional term representing the activity of the neutral molecule. Thus in studying the effect of neutral electrolytes, and non-electrolytes, the change in the hydrogen ion activity thereby produced, is a fundamental factor in determining the rate of reaction. Now the relation between the hydrogen ion activity f and the dielectric constant D is expression by the following equation of Debye and Hückel,[5]

$$\log f = \frac{z_i^2 e^2}{2DkT} \sqrt{\frac{4\pi\epsilon^2}{DkT} \Sigma z_i^2 n_i^2}$$

where the other factors have their usual significance. Since sugar itself lowers the dielectric constant of water, it follows from the above equation that the activity of hydrogen ion increases with the addition of sugar and more so by the addition of neutral salts and non-electrolytes.[6] Not only the activity of the hydrogen ion but also that of sucrose is affected by the addition of neutral salts, as has been shown by Debye and McAulay[7] from theoretical considerations.

The variation in the rate of catalysed reaction by changing the solvent is far from regular. Cohen[8] observed that the inversion of sucrose is sensitized by alcohols. Caldwell[9] on the other hand, observed an increase in the

---

* Contribution from the Chemical Laboratory. Benares Hindu University, Benares.

[1] Scatchard: J. Am. Chem. Soc., **48**, 2259 (1926).

[2] W. C. McC. Lewis and Moran: J. Chem. Soc., **121**, 1613 (1922).

[3] Brönsted: Z. physik. Chem., **103**, 169 (1922).

[4] Kautz and Robinson: J. Am. Chem. Soc., **50**, 1022 (1928).

[5] Debye and Hückel: Physik. Z., **24**, 185 (1923).

[6] Hückel: Physik. Z., **26**, 93 (1925).

[7] Debye and McAulay: Physik. Z., **26**, 22 (1925).

[8] Cohen: Z. physik. Chem., **38**, 145 (1899).

[9] Caldwell: Proc. Roy. Soc., **178A**, 272 (1906).

rate of inversion of a semi-normal sugar solution by normal hydrochloric acid, by the addition of glycerol, while, alcohol had no effect; for weight normal solutions of sugar, these had a retarding effect, which might be due to increase in total volume or in other words, decrease in H ion concentration. A survey of the literature on the other reactions[10] in mixed solvents lead us to no definite conclusion. It may be simply stated that solvents have specific effect, in some case retardation and in other cases acceleration. In this connection the work of Cashmore and others[11] on hydrolysis of esters in alcohol-water mixture may be mentioned. They obtain breaks in the composition-mixture velocity, at points which correspond to complex hydrate formation. At higher temperature, breaks were obtained at different points, corresponding to the complexes at that temperature.

The present investigation has been undertaken in order to study the effect of mixed solvents on the rate of inversion of sugar at different temperatures that may lead to the elucidation of the mechanism of the reaction. The hydrogen ion activity is simultaneously determined by electrometric methods in some cases.

Experimental

Materials: Saccharose and other chemicals used were Merck's extra pure material taken from freshly opened bottles. Standard hydrochloric acid was prepared by distilling twice Merck's extra pure acid, the middle portion of the distillate having constant boiling point was taken. The solutions were all prepared in conductivity water.

Apparatus: The saccharimeter used in this work was Adam Hilger's Triple Field Polarimeter. The polarimeter tubes were 220 mm. long and provided with a metal jacket through which water was circulated from a thermostat. The temperature of the solution was maintained constant within 0.5°C. The source of light was the ordinary gas mantle, the light being filtered through solutions of potassium dichromate and permanganate.

Experimental Procedure: For each experiment 20 gms. of sugar were weighed out, dissolved in the least quantity of water and transferred to a carefully cleaned and steam washed 100 c.c. flask. The requisite quantity of the non-electrolyte and 10 c.c. normal HCl were added and the volume quickly made up to 100 c.c. by adding water. In some cases the quantity of water added was measured. The mixture was shaken thoroughly and transfered with the least delay to the polarimeter tube which was washed thoroughly before with the solution. The instrument was adjusted every time and the readings were taken at definite intervals. The final reading was taken after 48 hrs., the completion of the reaction being ascertained in each case.

---

[10] See in this connection, Dawson and Powis: J. Chem. Soc., **103**, 2135, (1913); Bohnson: J. Phys. Chem., **24**, 677 (1930); Kappana J. Indian Chem. Soc., **6**, 419 (1929); Prasad and others: **7**, 21, 59 (1930).

[11] Cashmore, McCombie and Others: J. Chem. Soc., **119**, 970 (1921); **121**, 2241, 2301 (1922).

Method of Calculation: The reaction velocity constants are calculated according to the usual formula can be expressed

$$k = \frac{1}{t}\left\{\log\left(r_0 - r_\infty\right) - \log\left(r_t - r_\infty\right)\right)$$

where r_t is the rotation at a time t, r_∞ the final rotation, and r_0 is the initial rotation extrapolated from the graph t, $\log(r_t - r_\infty)$ according to the methods of Rosanoff, Clarke and Sibley.[12] It may be mentioned that the initial rotation is modified by the addition of non-electrolytes.

Electrometric Method: The hydrogen ion activity was obtained from the E.M.F. of the cell

H_2 (Pt)	N/10 HCl in Reaction Mixture	Saturated KCl	N/10 KCl Saturated with Hg_2Cl_2	Hg_2Cl_2,Hg

The electrolytic hydrogen was passed through a series of washes containing the same solution before letting it into the Clarke Hydrogen Cell, that was used for the purpose. The electrodes were platinised by a very low current from solution of 1% chloroplatinic acid. E.M.F. was measured by a K-type potentiometer reading up to millivolts made by Baird and Tatlock, null point was determined by a Weston galvanometer using Weston Cadmium Standard Cell.

Results.

TABLE I

Temperature 31°C

$k \times 10^4$

Percentage of Alcohol	0	5	10	20	25
1. Methyl Alcohol	10.16	7.625	8.26	6.84	8.26
2. Ethyl Alcohol	10.16	10.56	11.54	8.485	7.183
3. Isopropyl Alcohol	10.16	7.137	7.146	6.11	5.975
4. Glycol	10.16	9.0	9.33	9.475	10.1
5. Glycerol	10.16	8.18	8.375	9.32	11.23
6. Acetone	10.16	8.8	8.24	8.7	10.00

TABLE II

Temperature 44.5°C.

$k \times 10^3$

1. Methyl Alcohol	4.61	5.1	6.0	5.13	5.25
2. Ethyl Alcohol	4.61	6.62	6.91	7.3	5.45
3. Isoproypl Alcohol	4.61	4.53	5.17	4.88	4.98
4. Glycerol	4.61	5.27	7.1	6.05	7.8

---

[12] Rosanoff, Clarke and Sibley: J. Am. Chem. Soc., 33, 1911 (1911).

TABLE III

Temperature 25°C.

$k \times 10^4$

	Percentage of non-electrolyte	0	5	12.5	25
1.	Methyl Alcohol	4.73	—	6.1	7.6
2.	Ethyl Alcohol	4.73	8.9	9.6	5.25
3.	Isopropyl Alcohol	4.73	7.0	9.4	6.20
4.	Glycerol	4.73	—	5.80	8.20

TABLE IV

Strength of Acid 0.1 N.

Sugar added—20 grms. per 100 c.c. of the mixture

Percentage of non-electrolyte added	Time	E.m.f.	
0 0% Sugar		0.4045	1.13
0 Ethyl Alcohol	5 hrs.	0.3920	0.922
10 " "	6 hrs. 8 hrs.	0.3990	1.05*
20 " "	7 hrs.	0.4030	1.11*
25 " "	5 hrs.	0.3994	1.052*
25 Glycerol	7 hrs.	0.3686	0.866
20 Glycol	4 hrs.	0.3782	0.69

* These readings may not be quite correct on account of the liquid-junction potential.

Discussion of Results

From Tables I and II and Figs. 1 and 2 it will be seen that both methyl and ethyl alcohols have retarding action at low concentration, which is followed by sensitizing action with increasing concentration of the alcohols. The curves however show no regularity; there are definite indications of maxima and minima. Isopropyl alcohol has more or less retarding effect (Table III). There is however no definite relationship between the number of hydroxyl groups in the alcohols and their effect. Thus although ethyl alcohol and glycerol have marked influence on the reaction rate, glycol has got practically no effect although the hydrogen ion concentration is markedly changed. Acetone also like glycol has but little effect. The effect of temperature in most cases is to modify the curves, which however retain the general characteristics. The effect of neutral bodies on the hydrogen ion activity is again very peculiar. With alcohols an increased activity is accorded which however falls off with time the same phenomenon was observed by W. C. McC. Lewis[2] and also by Scatchard[13] who accounted for this being due to liquid junction potential. With glycerol and glycol however a definite increase in the hydrogen ion activity is obtained.

---

[13] Scatchard: J. Am. Chem. Soc., **48**, 2026 (1926).

In order to explain the anomalous behaviour of solvents in the case of inversion of sucrose, three factors are to be taken into consideration: (a) Hydration; (b) Polarisability of ions and neutral molecules, which is manifested in the lowering of dielectric constant of the medium; (c) Viscosity, which affects the mobility of ions. Some authors rule out the last two. That hydration is an important factor in the catalysed reaction has been pointed out by several authors. Bjerrum, Goldschmidt and others postulate that the catalysing acid forms ion hydrates which are the actual catalysts. Now in presence of non-electrolytes the probability of the formation of hydrated ion and hydrated sugar molecule will be diminished: (a) with the decrease of water content; (b) with the removal of water by the non-electrolyte. The formation of hydrates with the non-electrolytes then causes two opposing effects. Firstly since it removes water it increases the relative concentration of the hydrogen ion or in other words it decreases the water concentration. Secondly, as it has been pointed out by Harned[14] that the water molecules enter into reaction in the hydrolysis of esters and by an addition of salts (and so also the non-electrolyte) to the catalysing acid, the concentration of water and hence its activity will be decreased. Thus the reaction may be retarded. Lewis and coworkers suggest the following scheme for sucrose inversion:

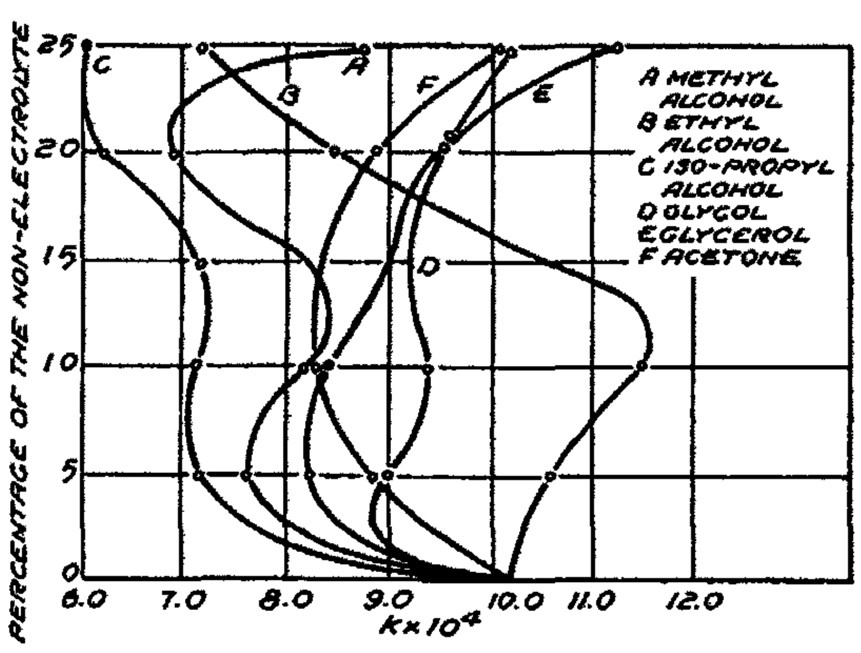


FIG. 1

$$(S.2H_2O) + H^{\cdot} \rightarrow (S.2H_2O.H^{\cdot}) \quad \text{(measurable speed)} \ldots \qquad (1)$$

$$S.2H_2O.H^{\cdot} + y\,H_2O \rightarrow \text{Glucose}, 2H_2O + \text{fructose} + H^{\cdot} + (y-1)\,H_2O \ldots (2)$$

Here inversion of sucrose is preceded by the hydration of sucrose, and hence the removal of water by non-electrolytes forming the hydrates, will cause a retardation of the velocity. The observed result would be a cumulative effect of these two factors.

---

[14] Harned: J. Am. Chem. Soc., 40, 1461 (1918).

It may, however, be suggested that the inflexions in the curves may be due to the formation of hydrates. If we make correction for the volume of water in the dissolution of sugar, we find from the breaks in the curve the existence of hydrates of alcohol and water.

Since in most cases maximum is obtained at the region of hydrate formation, the first effect mentioned above predominates.

The second factor is the dielectric constant of the medium. Now, although Debye's theory has been confirmed in a very satisfactory manner by the experiments of Brönsted and LaMer[15] with aqueous solutions, the agreement between theory and experimental results with non-aqueous or mixed solvents is however far from satisfactory. The effect of the lowering of dielectric constant is to increase the hydrogen ion activity and consequently to accelerate the reaction. But with alcoholic mixtures the experimental results of Danner[16] and Harned[17] do not agree with theoretical value. Again the hydrogen ion conc. of HCl in sucrose solutions presents some difficulties owing to liquid juncture potential as pointed out by Scatchard and there is also a time factor, the e.m.f. changing with time due to the presence of glucose. Further the dielectric constant of the mixtures of sugar solution and alcohols may not be a linear function of their concentrations. Some changes may take place owing to hydration.

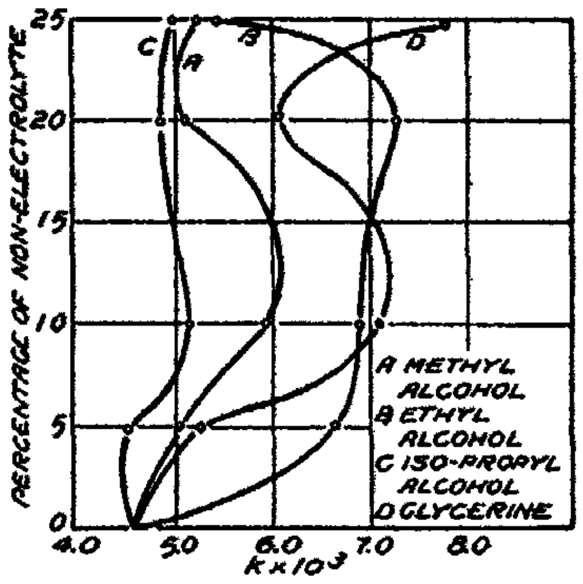


FIG. 2

With the change in the dielectric constant, the activity of sucrose itself may be changed. Incidentally, it may be mentioned that Debye and McAulay theoretically accounted for about 17% increase of activity of sugar in presence of 0.4 N KCl. Since the activity of sugar plays an important role in the process of inversion, it is natural to expect changes in the velocity coefficient of inversion.

As inversion depends upon the hydrogen ion activity it may be expected that the ion mobility of the latter is affected by changes in the viscosity of the medium. The rate of reaction may be an inverse function of the viscosity, i.e. it will be greater in a less viscous medium and conversely will be retarded with increase in viscosity. This has also been pointed out by W. McC. Lewis as well.

Besides the above factors, the solubility effects should also be taken into consideration. It has been pointed out by Bhide[18] that the solubility of the

---

[15] Brönsted and LaMer: J. Am. Chem. Soc., **46**, 555 (1924).

[16] Danner: J. Am. Chem. Soc., **44**, 2832 (1922).

[17] Harned and Fleysher: J. Am. Chem. Soc., **47**, 82 (1925); also Lucasse: **48**, 626 (1926).

[18] Bhide: J. Indian Chem. Soc., **7**, 575 (1930).

catalyst in the solvent is an important factor. Thus since HCl is as much soluble in water as in the alcohols, the velocity of inversion is retarded in presence of alcohols as some of it passes into the alcohol. An alcohol causes a decrease in the velocity of hydrolysis of ester in presence of acetone and isoamyl alcohol as was observed by Bhide. Similar argument may be advanced in this case as well.

Summary

(1) The velocity of inversion of cane sugar by 0.1 N HCl has been studied in mixtures of water with methyl, ethyl, isopropyl alcohols and glycol, glycerol and acetone, at different temperatures.

(2) It has been found that the rate of the reaction is first retarded and then accelerated as the percentage of the non-electrolyte is varied. The curve-mixture composition-velocity constant goes through minima and maxima. Glycol and acetone have little effect on the reaction velocity. No relationship between the number of hydroxyl groups of the alcohols and the effect on the velocity of reaction has been found.

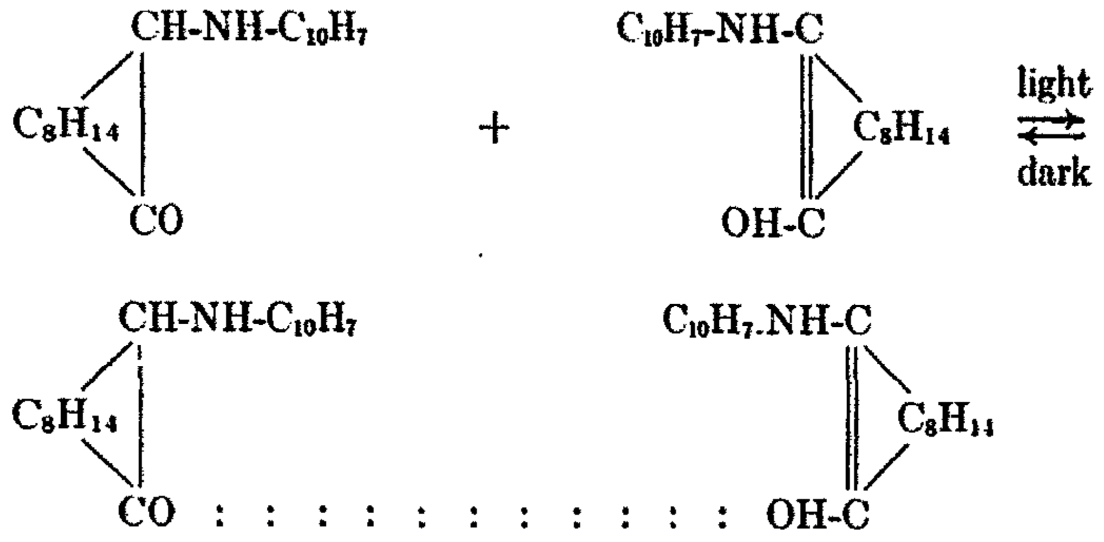
(3) It has been found that the effect of temperature is to modify the effect of the non-electrolyte, but the nature of the composition velocity constant curves is similar at different temperatures.

(4) These results have been explained as due to three factors: (a) Hydration; (b) Lowering of the Dielectric constant; (c) Viscosity.

AN INVESTIGATION ON THE ACTION OF LIGHT ON A CHLOROFORM SOLUTION OF α-NAPHTHYL-AMINO-CAMPHOR

BY BHUPENDRA NATH MITRA

Singh[1] described a few camphor-quinone derivatives which exhibit phototropy in solution. He investigated particularly α-naphthyl-amino-camphor in chloroform solution, which on exposure to sunlight, turns green in a minute or two, and reverses in the dark in about 24 hours. Singh explained the phenomenon on the assumption that α-naphthyl-amino-camphor in chloroform solution exists in both ketonic and enolic modifications,—which probably combine to give a compound of quinhydrone type, thus—



According to him, "the phototropic change occurs only when both the modifications are present together in solution and is accompanied by the formation of a green substance and by a marked increase in the rotatory power of the solution." He also stated that "such change is also noticed only in chloroform solution while in other solvents such as ether, alcohol, acetone, etc., the solution turns yellow on long standing."

It occurred to the author that the phenomenon was of sufficient interest to warrant a quantitative investigation and the present research was undertaken. A few preliminary experiments, however, showed that the reaction was not so simple as pointed out by Singh, probably arising out of various side-reactions. It was therefore decided that in the first instance the identification of the reaction products was more important and the present paper is an account of experiments carried out with that end in view.

Experimental

The chloroform solution of α-naphthyl-amino-camphor, on exposure to sunlight, turns green almost instantaneously; but, on standing, the colour deepens with the separation of a crystalline solid, and on long standing the

---

[1] J. Am. Chem. Soc., 43, 333 (1921); J. Indian Chem. Soc., 1, 45 (1924-25).

colour becomes dark brown. The green colour of the solution, obtained on long exposure, does not change even on standing for several days in the dark, but gradually turns brown. Tables I-III will illustrate the changes observed under different experimental conditions.

TABLE I

Exposure to direct sun of a dilute solution (0.5%) in presence of air

Exposure for	Colour	Followed by 20 hours darkness	40 hrs.	60 hrs.	100 hrs.
1 min.	Bluish green	Faint yellow	Yellow	Yellow with a reddish tint	Orange red
5 min.	Bottle-green	Greenish yellow	Yellow	Yellow	Yellow with a reddish tint.
15 min.	Green	Greenish yellow with a scanty ppt.	Yellow	Yellow	Yellow (reddish)
75 min.	Deep green	Dull green with a heavy ppt.	Dull green	Turbid green	Brown

TABLE II

Exposure to direct sun of a dilute solution (0.5%) in an atmosphere of hydrogen

Exposure for	Colour	Followed by 20 hours darkness	100 hours darkness
1 min.	Bluish green	Colourless	Colourless
5 min.	Bottle-green	Slightly greenish	Slightly reddish
15 min.	Green	Greenish with a scanty precipitate	Orange red with a scanty precipitate
75 min.	Deep green	Dull green with a heavy ppt.	Orange red with a heavy ppt

TABLE III

Exposure to direct sun of a solution (about 4%) for—

½ hr.	1 hr.	2 hrs.	4 hrs.	Followed by 20 hrs. in darkness
Very deep green	Deeper	Dark green with a ppt.	Dark green with an increasing amount of ppt.	The colour is too deep to distinguish and the ppt. settles down

Analysis

The following analytical experiments were carried out with the residual products:

(1) The light green solution on evaporation, gave an almost colourless solid with a slightly green tint. The green tint was dissolved out with alkali; and the remaining portion, on purification, was entirely colourless α-naphthyl-amino-camphor.

(2) The brown solution was evaporated. The residue was a tarry brown mass,—the major portion of which was found to be unchanged α-naphthyl-amino-camphor, and the remaining portion was a tar in which the presence of free α-naphthyl-amine was detected by diazotisation.

(3) The intensely deep green solution, on evaporation, gave a black mass resembling coal-tar in which the parent substance formed the major portion, the rest being uncombined free α-naphthyl-amine and camphor-quinone.

An account of the examination of the precipitate will be given later. It will be sufficient to mention here that the precipitate contains halogen.

Discussion

(A) According to Singh, the role of chloroform is merely that of a solvent, having no part to play in the reaction. This view seems to be untenable, firstly because the solution, which is neutral before exposure, becomes distinctly acid the moment the solution turns green, and secondly because on long exposure a precipitate is formed which also contains halogen.

Effect of moisture and temperature on the green solution:

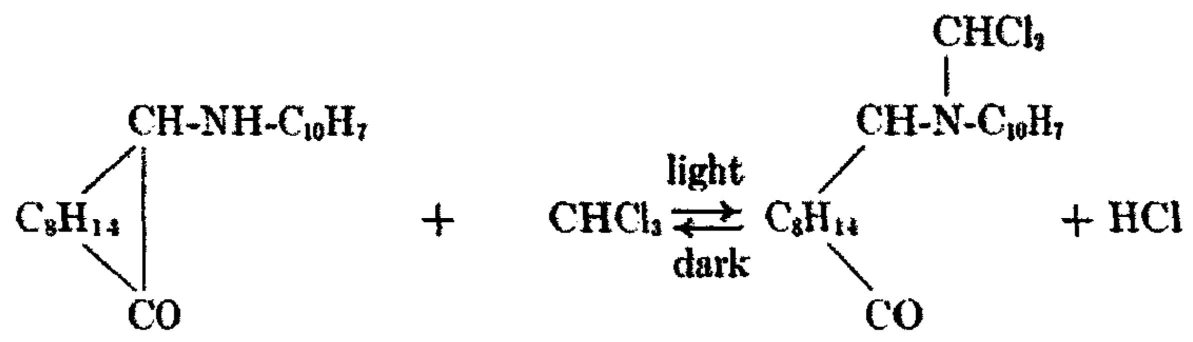
(a) The addition of a drop of water to a green solution, obtained on short exposure, destroys the green colour all at once.

(b) The heating in the dark of a far deeper green solution with a drop of water or two in it at about 60°C accelerates the reversal of the green product.

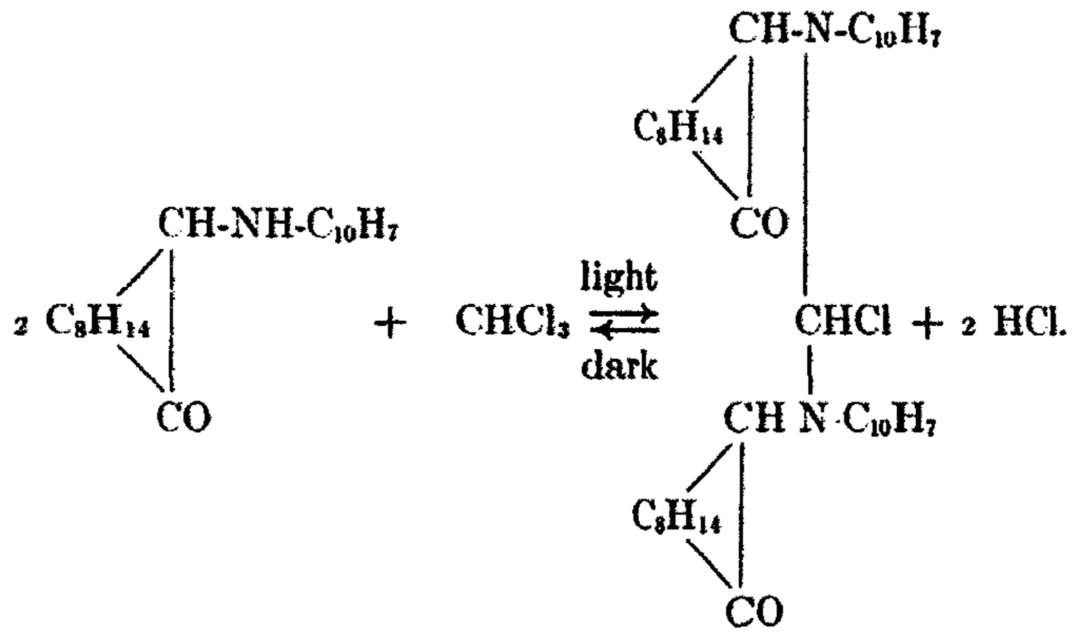
(c) The presence of moisture in a colourless solution is found inhibitive to the formation of the green compound on exposure to light.

From the fact that the solution is acid the moment the green compound is formed, it is evident that the solvent chloroform undoubtedly takes part in the reaction; and the formation of the green product may probably be attributed to the interaction between chloroform and α-naphthyl-amino-camphor according to the following equations:

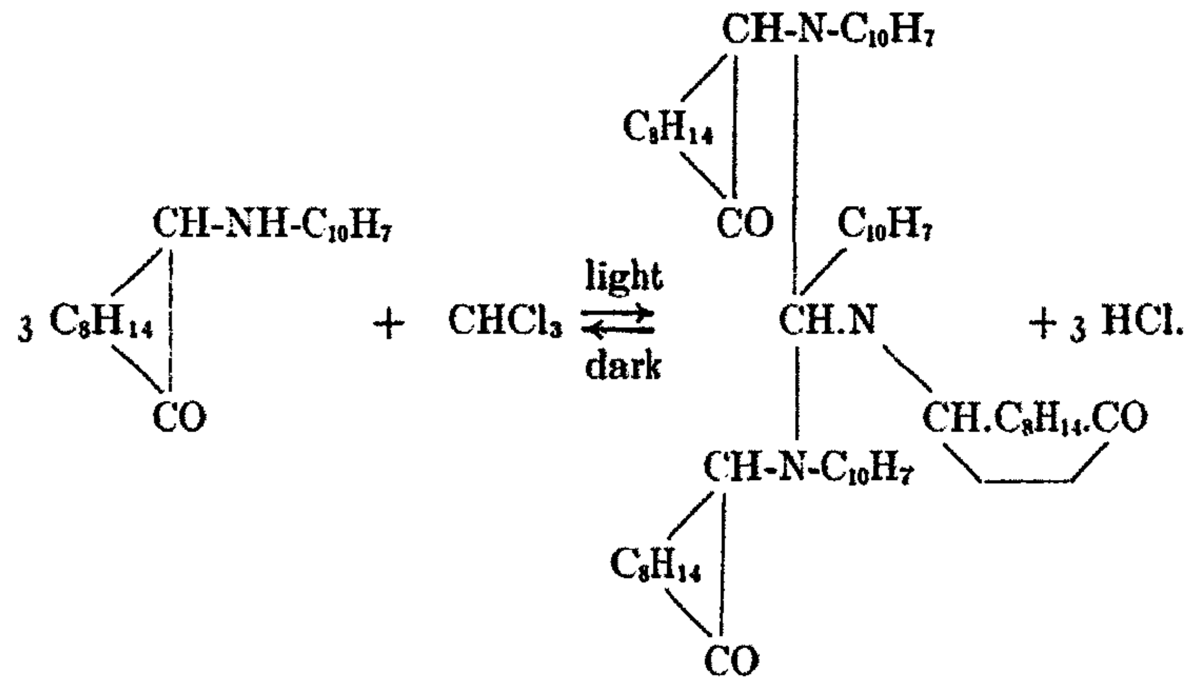
(i)



(ii)



(iii)



Why compounds of such constitution should exhibit such a deep colour is, however, difficult to explain. It is also very difficult to examine the green product systematically, as it exists only in solution and cannot be isolated in the free state.

(B) It has already been mentioned that the green colour of the solution disappears in the dark, but the solution assumes a faint yellow tint. That this yellow colour is due to the simultaneous oxidation of the substance to the corresponding imino-compound is best corroborated by the fact that (1) the yellow solution is reducible by 10% KOH and zinc dust, yielding a colourless compound having the same melting point as α-naphthyl-amino-camphor

(165°C), and that (2) if a fresh solution be exposed for a short time in an atmosphere of hydrogen and kept in the dark, the green solution undergoes reversion and the solution becomes colourless.

The above experiments were repeated with other solvents, such as ether, alcohol, acetone, etc., and it was found that the substance is oxidised in these solvents as well, when exposed to sunlight. The formation of yellow colour in other solvents on insolation, as noticed by Singh, is thus due to the formation of the oxidation product, namely α-naphthyl-imino-camphor.

It has, however, been found that α-naphthyl-imino-camphor decomposes in solution on standing. Thus the gradual transformation of yellow colour of the solution to red colour in the dark may be accounted for.

In all the above reactions, the rate of change is very slow, in no case does the reaction proceed in one direction completely. The analytical results show that in all these reactions the major portion of α-naphthyl-amino-camphor remains unchanged.

(C) A systematic examination of the halogen-containing precipitate is a difficult affair, since the yield of the ppt. is very small. Various isolated reactions, such as the action of $COCl_2$, free chlorine, gaseous hydrochloric acid, etc., on α-naphthyl-amino-camphor dissolved in a different solvent (other than $CHCl_3$) were tried in presence of light, but no precipitate was obtained. The halogen containing precipitate has the following properties:

(1) White, (2) crystalline, (3) soluble in water, alcohol and ether, (4) contains a primary amino group, (5) the substance has not got any definite melting point; at about 220°C the colour changes; when heated to about 300°C no further change is noticed.

Combustion results:

0.0440 gms. gave 3 c.c. of N_2 at 29°C & 753 mm.

$$N = 7.485\%.$$

0.0423 gms. gave 0.0348 gms. of AgCl

$$Cl = 20.35\%$$

Thus the ratio of N:Cl = 1:1

From the properties of the precipitate and its percentage composition of nitrogen and chlorine, the substance is identified to α-naphthyl-amine-hydrochloride ($C_{10}H_7NH_2.HCl$).

$$\text{Theoretical } N = 7.821\%;\ Cl = 19.55\%.$$

The formation of the precipitate then clearly points to show that chloroform essentially takes part in the reaction. The hydrochloric acid that is formed in course of the reaction reacts with free α-naphthyl-amine which is set free by the decomposition of the parent substance, and we get α-naphthyl-amine-hydrochloride ($C_{10}H_7NH_2.HCl$) as a precipitate. It is really very peculiar to observe that the agency of light alone brings about the decomposition of the substance into its component parts, namely α-naphthyl-amine and camphor-quinone, which have on the other hand got so great an affinity for each other to combine together to form α-naphthyl-imino-camphor under ordinary conditions[1]. The solvent-effect is indeed so very pronounced.

Summary

α-naphthyl-amino-camphor in chloroform solution, on exposure to sunlight, probably forms substituted green compounds with the solvent which reactions are reversible in the dark. The substance is also oxidised in solution in presence of light. The further effect of sunlight is to precipitate from the chloroform solution α-naphthyl-amine-hydrochloride formed by the action of HCl and $C_{10}H_7NH_2$, liberated in course of the reaction.

In conclusion, I would like to express my sincerest thanks to Prof. J. G. Ghosh of Dacca University for his very kind help and much valued suggestions on this research.

Chemical Laboratory,
University of Dacca,
March 5, 1931.

---

[1] J. Chem. Soc., 115, I, 573 (1919).

THE DECOMPOSITION OF OXALIC ACID BY ARSENIC ACID*

BY G. BROOKS KING AND JAMES H. WALTON

The study of the decomposition of oxalic acid by arsenic acid was made in order to compare the dehydrating properties of arsenic acid with those of sulfuric and phosphoric acids. The decomposition of oxalic acid by sulfuric and phosphoric acids has been studied by Lichty[1] and Walton and Weber[2] respectively, who have shown that the reactions follow the unimolecular reaction law, and are strongly inhibited by water. It was of interest to determine whether or not arsenic acid would decompose oxalic acid similarly.

Menzies and Potter[3] have shown from a phase rule study of the two component system, As_2O_5 and H_2O, that $As_2O_5.4H_2O$ and $3As_2O_5.5H_2O$ are the only hydrates of As_2O_5 which can be isolated. When heated, $As_2O_5.4H_2O$ fuses at 36.1° and rapidly changes to $3As_2O_5.5H_2O$. No indications of $As_2O_5.3H_2O$ (H_3AsO_4) were obtained. In the present work solutions of As_2O_5 in water were used for the decomposition of oxalic acid.

Experimental Part

Preparation and Purification of Materials—The arsenic acid used was the C.P. quality of General Chemical Co. Solutions of various concentrations were made by dissolving the solid in water, and the acid content determined by the titration method developed by Menzies and Potter.[3] This method was checked against a gravimetric analysis and found to be very satisfactory. C.P. sodium oxalate was dried in an oven at 140° for several days, and thereafter kept in a desiccator. Sodium oxalate was used rather than oxalic acid as it is easier to obtain in the anhydrous state and because at the temperatures used, the oxalic acid would sublime to an appreciable extent.

Apparatus and Method of Procedure—Preliminary experiments showed that CO and CO_2 were present in the reaction products from the decomposition of the sodium oxalate by arsenic acid. The rate of reaction was followed by measurement of the volume of gas evolved at various time intervals during a decomposition, the apparatus employed and the method of procedure being essentially that used by Wiig,[4] Whitford,[5] and Dittmar[6] in their studies on the decomposition of organic acids by sulfuric acid. 10 cc. of arsenic acid solution were taken for each decomposition, and at the time of adding the acid to the reaction flask, a sample was taken in a weighing

---

* Contribution from the Laboratory of General Chemistry of the University of Wisconsin.

[1] Lichty: J. Phys. Chem., 11, 225 (1907).

[2] Walton and Weber: Unpublished Results.

[3] Menzies and Potter: J. Am. Chem. Soc., 34, 1462 (1912).

[4] Wiig: J. Am. Chem. Soc., 52, 4729-4751 (1930).

[5] Whitford: J. Am. Chem. Soc., 47, 953 (1925).

[6] Dittmar: J. Am. Chem. Soc., 52, 2746 (1930); J. Phys. Chem., 33, 533 (1929).

pipette for subsequent analysis for arsenic content. A qualitative test on the decomposition products showed that no reduction had taken place in the reaction.

Results

Completeness and Order of Reaction—The decompositions were carried out at temperatures of 140° and 150°. The concentrations of arsenic acid which could be used were limited; with solutions containing less than 70% As_2O_5, water condensed in the upper part of the flask and in the capillary tubes, thereby concentrating the acid solution and hindering the flow of gas, thus making the results unreliable. At concentrations above 78% As_2O_5, a white solid separated on shaking, undoubtedly some of the arsenic acid precipitating from a supersaturated state.

The results given in Table I show that the reaction is a quantitative one.

TABLE I

Temperature of run	140°	150°	150°
Theoretical volume of gas	34.0	35.7	34.4
Volume of gas found	33.5	35.6	34.3

The decomposition of oxalic acid by arsenic acid follows the unimolecular reaction law, as shown by the following velocity constants obtained when the data for any one decomposition were substituted in the equation for a reaction of the first order: 31.0; 33.6; 32.2; 30.4; 32.0; 31.3; 30.8; 31.1. That the true speed of decomposition and not the speed of solution was measured was shown by the fact that the velocity constants were not affected by the volume of arsenic acid solution. 5, 7, and 10 cc of the acid solution were used and the deviation from a constant value for k was within the limits of experimental error. The value of $k \times 10^3$ for any particular run was taken as the average value between 30 and 70 per cent decomposition in from two to four determinations.

The Effect of Water on the Reaction Rate—The data obtained at the temperatures 140° and 150° are summarized in Table II, and represented graphically in the curves, Fig. 1.

TABLE II

Effect of Water on Reaction Velocity

At 140°			At 150°		
% Water	Mol of H_2O	$k \times 10^3$	% Water	Mol of H_2O	$k \times 10^3$
9.54	5.85	30.2	10.34	6.39	116
6.64	3.95	63.2	10.22	6.33	123
5.58	3.28	71.0	8.60	5.22	144
5.16	3.02	85.2	7.75	4.67	174
4.90*	2.86	84.1	4.03	3.64	220
			1.2*	0.67	320

* Some separation of solid.

From the curves in Fig. 1, the temperature coefficients of the reaction have been calculated and are given in Table III.

TABLE III

Molality of water	2.0	3.0	4.0	5.0
Temperature coefficient	2.7	3.06	3.48	3.90

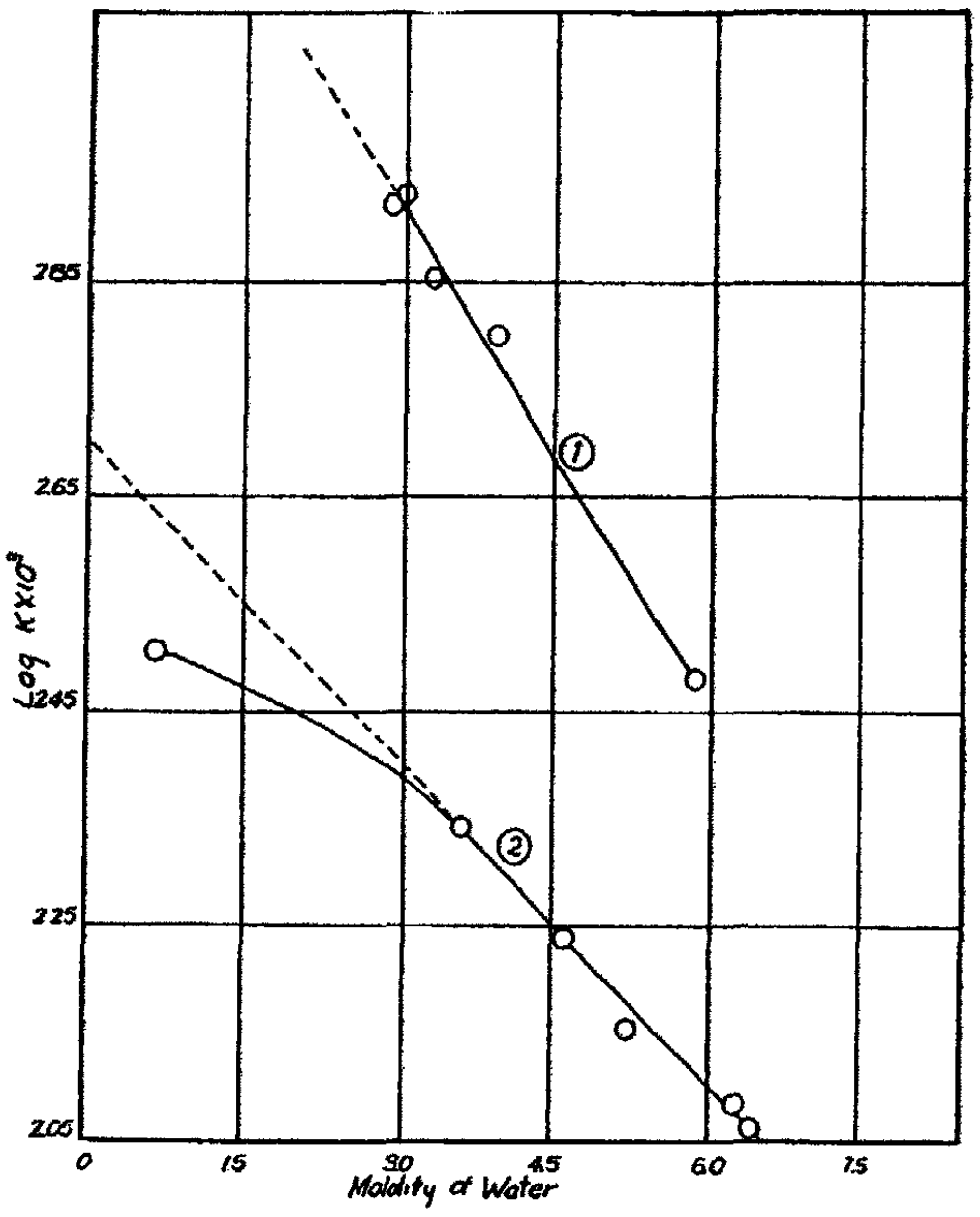


FIG. 1
Effect of water on reaction rate at
1. 140° Subtract 1.00 from log K × 10³ scale
2. 150°

Although the effect of the addition of very small amounts of water can not be ascertained from these data, it is evident that water has a marked retarding effect on the velocity of reaction. Similar results were obtained by Wiig,[4] Whitford,[5] Dittmar,[6] and Lichty[1] in their studies on the decomposition of organic acids by sulfuric acid, also by Walton and Weber[2] in the study of the decomposition of sodium oxalate with phosphoric acid.

The temperature coefficients vary considerably with change in molality of water, however the change is regular and in accord with results obtained by other investigators in similar decompositions, showing an increase as the concentration of water increases which is in accord with Dhar's[7] statement that a negative catalyst increases the temperature coefficient of a reaction.

Solubility of Oxalic Acid in Solutions of Arsenic Acid—It has been shown by Dittmar,[6] Wiig[4] and others that the decomposition of organic acids with sulfuric acid may take place as a result of a preliminary reaction between the two components to form an oxonium salt. If the decomposition of oxalic acid with arsenic acid is similar to that with sulfuric acid, then indications of compound formation between arsenic acid and oxalic acid might be obtainable. Knox and Richards[8] have shown that solubility determinations furnish a convenient method for such a study. Their method consists in determining the solubility of one acid at a particular temperature in solutions of increasing concentration of the second acid. Indications of compound formation are obtained by a minimum in the solubility curve.

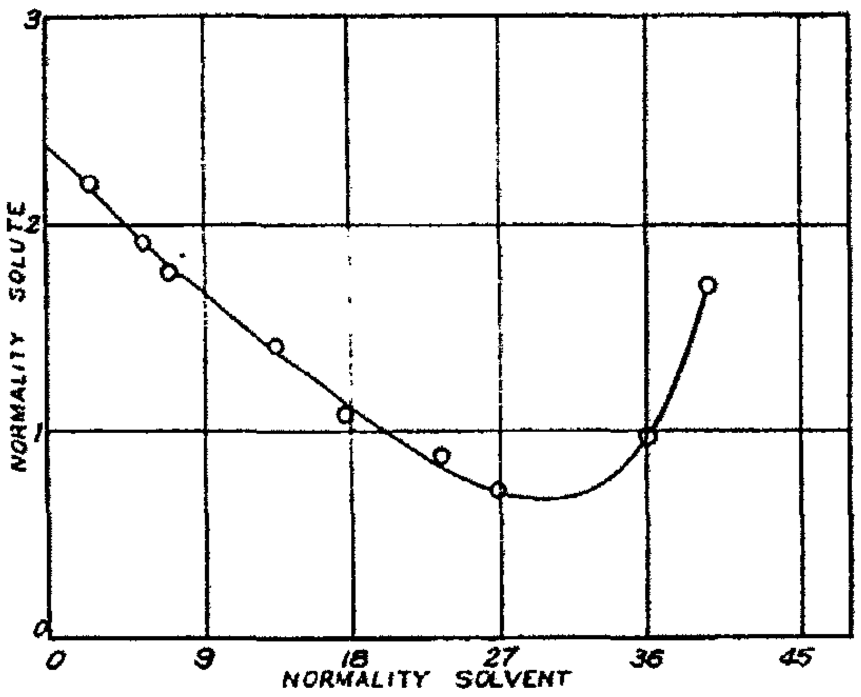


FIG. 2
Solubility of $H_2C_2O_4$ in solutions of H_3AsO_4 at 25°.

In the present study, several solutions of arsenic acid of various concentrations were prepared. An excess of oxalic acid was added to each solution which was then kept in a thermostat for several days to reach equilibrium. Samples were then withdrawn, the oxalic acid titrated with standard potassium permanganate, and the total acidity determined by titration with standard alkali. The difference between the total acidity and that due to oxalic acid gave the acidity due to arsenic acid. The results obtained are summarized in Table IV and the curve for these data is plotted in Fig. 2.

---

[7] Dhar: J. Phys. Chem., 28, 951 (1924).

[8] Knox and Richards: J. Chem. Soc., 115, 508 (1919).

TABLE IV

Solubility of Oxalic Acid in Arsenic Acid

Normality of solvent	Normality of solute
0.0	2.412
2.2	2.20
5.41	1.92
7.05	1.77
13.6	1.44
17.7	1.08
23.8	0.878
27.0	0.716
36.3	0.967
39.7	1.72

The data are expressed in normalities of solute ($H_2C_2O_4$) and solvent (H_3AsO_4). A distinct minimum appears in the curve, indicating compound formation between the arsenic and oxalic acids.

Discussion

Mechanism of the Decomposition and Inhibition—The decomposition of oxalic acid by arsenic acid is probably best explained by assuming the formation of an unstable oxalic acid-arsenic acid complex, the concentration of which will govern the speed of reaction. The inhibiting effect of water on the reaction may be explained on the basis of Taylor's[9] theory of negative catalysis in which it is postulated that the added substance decreases the concentration or the active mass of one or more of the reactants through compound formation. In the present case, water would be assumed to form molecular complexes with either arsenic acid or oxalic acid or with both. The hydrates of these acids are, of course, well known.

Comparison of Arsenic, Sulfuric and Phosphoric Acids—By extrapolation to 0 concentration of water in the oxalic acid decomposition by arsenic acid at 150°, a value of approximately 500 is obtained for $k \times 10^3$. Walton and Weber[2] obtained 307 as a value for $k \times 10^3$ using pure ortho phosphoric acid at 150°. A much higher value than either of the above is obtained for pure sulfuric acid at 25°. The acid strength of the acids as measured by their dissociation constants follow: Oxalic 3.8×10^{-2}; Phosphoric 1.1×10^{-2}, Arsenic 0.5×10^{-2}. If the tendency for molecular compound formation governs the speed of reaction, then on the basis of Kendall's[10] rule, the rate of decomposition of oxalic acid with these acids should be in the order, sulfuric, arsenic, phosphoric. This is in the order found by experiment. Wiig[4] has given evidence to show that there is no relation between acidic strength

---

[9] Taylor: J. Phys. Chem., 27, 322 (1923).

[10] Kendall and Carpenter: J. Am. Chem. Soc., 36, 2506 (1914).

and rate of decomposition. It is doubtful, however that these acidic strengths which were determined in water solutions give a proper basis for comparison, since the relative acidic strengths might be very different in a solvent other than water. More data must be had before definite conclusions can be reached about any relationship between acidic strength and rate of reaction.

Summary

1. The decomposition of oxalic acid by arsenic acid is a reaction of the first order.

2. The velocity of reaction has been determined with various concentrations of acid at the temperatures, 140° and 150°.

3. Water is a marked inhibitor of the reaction.

4. The temperature coefficient is approximately 3.

5. Evidence of compound formation between oxalic and arsenic acids has been given.

6. The decomposition presumably takes place through the formation of an unstable molecular complex. Inhibition is explained on the basis of Taylor's theory of negative catalysis.

7. The decomposition of oxalic acid with arsenic acid seems to be similar to the decomposition with sulfuric and phosphoric acids.

Madison, Wisconsin.

COPPER SALTS AS LIGHT FILTERS. I

BY W. V. BHAGWAT AND N. R. DHAR

Part I.

Perhaps the copper salts are the only ones which are most extensively used either individually or in combination with other substances as light filters in photo-chemistry. Although a large number of investigators such as Winther,[1] Weigert-Kummerer,[2] Gray,[3], Eder[4], Lehmann[5] and others have worked with these salts, the exact knowledge regarding the absorption of radiations by copper salts is still lacking. It is essential in photo-chemistry to have a monochromatic source to study the effect of various wavelengths on any given photochemical reaction. The requirements for a satisfactory light to be used as a source of monochromatic radiation are: (1) it must have high intensity (2) it must be steady for relatively long periods (3) its spectrum should have a few very strong lines rather than a closely packed large number of lines of moderate intensity. It is very rare that we can get a monochromatic source of light by itself, such as the flame of the Bunsen burner fed with sodium salt. It is this that necessitates the study of suitable filters which will just transmit the required wavelength and will absorb the rest. Clearly, a light filter, in order that it may be used with maximum advantage, must satisfy the above-mentioned conditions for a satisfactory monochromatic light source. The filter must absorb as little as possible of the light to be transmitted and should be completely opaque to other regions. To ascertain the intensity of the transmitted light it is necessary to study the percentage transmission in various regions. To satisfy the second condition for a monochromatic source of light, that the light source should be steady for relatively long periods to secure comparable results, the filter should remain unchanged in composition for a very long time. That is, the filter should be photochemically inert. To get the knowledge of the third condition for a monochromatic light source the study of absorption is necessary. In this communication we have recorded our results of the experiments carried out in accordance with the necessity of getting exact knowledge of a filter and ascertaining the degree of accuracy with which it can be used in photochemical work. We have carried out experiments in the visible part of the spectrum and determined the extinction coefficient, light absorption and transmission with a Nutting's photo-spectrometer using various concentrations of the individual copper salts or their combination with other substances placed in a

---

[1] Z. physik. Chem., **41**, 169 (1902).
[2] Ber., **46**, 1210 (1913).
[3] J. Phys. Chem., **31**, 1732 (1927).
[4] Z. wiss. Phot., **26**, 373 (1929).
[5] Chem. Ztg., **33**, 1167 (1909); Physik. Z., **11**, 1039 (1910).

quartz vessel of one centimeter thickness. We have also determined the absorption in the ultraviolet photographically with a Hilger quartz spectrograph using a copper arc as a source of ultraviolet light.

Winther[1] reported that a solution of 25 gms. of cupric chloride in 100 c.cs with a solution of 0.25 gms. of violet yellow in 2 cm. thickness transmits 5332 Å. It is known that a two percent solution of cupric chloride absorbs infra-red. Copper salt solutions are largely used for cutting off heat rays. The following tables respresent our results regarding absorption, extinction coefficient, and percentage transmission for varying concentrations of copper chloride, copper nitrate, and copper sulphate.

The concentrations of the copper salts are expressed on the assumption that molar weight/2 = normal solution. The amount of copper in solutions was determined by adding potassium iodide to the solutions and titrating the liberated iodine by a standard thiosulphate solution.

Cupric chloride.

(1) Concentration = 9.285N.

λ = Wavelength in Å Units. e = extinction coefficient.

% T = percentage transmission.

λ	7000–5770	5680	5600	5520	5440	5360	5290
e	∞	2.1	1.85	1.48	1.20	1.06	1.00
%T	0	0.79	1.41	3.31	6.3	8.7	10
λ	5220	5150	5080	5020	4960	4900 – 4000	
e	1.06	1.20	1.38	1.70	2.25	∞	
%T	8.7	6.3	4.1	1.99	0.56	0	

Cupric chloride.

(2) Conc. 4.6425 N.

λ	7000–6060	5960	5680	5440	5220	5020	4840
e	∞	2.25	1.22	0.61	0.31	0.27	0.46
%T	0	0.56	6.02	24.5	48.9	53.7	34.6
λ	4700	4580	4540-4000				
e	0.84	1.85	∞				
%T	14.4	1.4	0				

Cupric chloride.

(3) Conc. 2.3262 N.

λ	7000–6280	5960	5680	5440	5220	5020
e	∞	1.55	0.63	0.33	0.18	0.18
%T	0	2.8	23.4	46.7	66.0	66.0
λ	4840	4700	4580	4460	4340	
e	0.13	0.20	0.26	0.48	0.52	
%T	74.1	63.1	54.9	33.1	30.2	

---

[1] Z. physik. Chem., 41, 169 (1902).

Cupric chloride.

(4) Conc 0.9285 N.

λ	7000–6480	6380	6280	5960	5680	5440	5220
e	∞	1.85	1.48	0.72	0.32	0.22	0.15
%T	0	1.41	3.3	16.9	47.8	60.2	70.7
λ	5020	4840	4700	4580	4460	4340	
e	0.12	0.11	0.08	0.11	0.20	0.20	
%T	75.8	77.6	83.1	77.6	63.1	63.1	

Cupric chloride.

(5) Conc. 0.09285 N.

λ	6600	6280	5960	5680	5440	5220–4000
e	0.25	0.20	0.12	0.08	0.06	0.04
%T	56.2	63.1	75.8	85.1	89.1	91.2

These results can be summarised as follows:—

Conc. of Cupric Chloride	Range of Transmission	%T(Maximum)
9.285 N	4900–5770 Å	10
4.6425 N	4540–6060	53.7
2.3262 N	4000–6280	74.1
0.9285 N	4000–6480	83.1
0.09285 N	4000–7000	91.2

Cupric nitrate.

(1) Conc. 11.054 N

λ	7000–5580	5510	5220	5020	4840	4700
e	∞	2.5	1.12	0.64	0.30	0.19
%T	0	0.31	7.5	22.9	50.1	64.5
λ	4580	4460	4340			
e	0.11	0.10	0.08			
%T	77.6	79.4	83.1			

Cupric nitrate.

(2) Conc. 5.527 N.

λ	7000–5960	5860	5770	5680	5440	5220	5020
e	∞	2.4	2.15	1.6	0.90	0.49	0.25
%T	0	0.39	0.70	2.5	12.5	32.3	56.2
λ	4840	4700	4580	4460	4340		
e	0.13	0.10	0.10	0.10	0.08		
%T	74.1	79.4	79.4	79.4	83.1		

Cupric nitrate.

(3) Conc. 2.763 N.

λ	7000–6280	6160	6060	5960	5680	5440
e	∞	2.20	1.97	1.67	0.82	0.42
%T	0	0.60	1.07	2.1	15.1	38.0
λ	5220	5020	4840	4700–4000		
e	0.22	0.16	0.12	0.08		
%T	60.2	69.1	75.8	83.1		

These results are summed up in the following table:—

Conc. of $Cu (NO_3)_2$—11.054 N, 5.527 N, 2.763 N.

Range of transmission—4000–5580 Å, 4000–5960 Å, 4000–6280 Å.

Cupric sulphate.

(1) Conc. 2.962 N.

λ	7000–6280	6170	6060	5960	5680	5440
e	∞	2.09	1.89	1.59	0.75	0.41
%T	0	0.81	1.2	2.5	17.0	38.9
λ	5220	5020	4840	4700–4300		
e	0.25	0.16	0.13	0.09		
%T	56.2	69.1	74.1	81.2		

We have determined the absorption in the ultraviolet region photographically for the various concentrations of the copper salts and the results are tabulated in the following tables:—

Ultraviolet Absorption

(1) Conc. of $CuCl_2$	Region of absorption	Region of transmission
9.782 N	absorbs all ultraviolet rays	Nil
9.285		
4.891	"	"
4.642	"	"
2.445	"	"
2.321	"	"
0.9782	absorbs up to 3602 Å	3602–4000 Å
0.09782	2767	2767–4000
0.04642	2618	2618–4000
0.009782	Nil	transmits all

(2) Conc. of $Cu(NO_3)_2$	Range of absorption	Range of transmission
12.174	Up to 3861 Å	3861–4000 Å
11.054	3861	"
6.087	3602	3602–4000
5.527	3602	"
3.043	3426	3426–4000
2.763	3274	3274–4000
1.2174	3248	3248–4000
0.1217	2618	2618–4000
0.01217	Nil	transmits all

(3) Conc. of $CuSO_4$	Range of absorption	Range of transmission
2.962	Up to 3200 Å	3200–4000 Å
2.716	3200	"
1.481	3036	3036–4000
1.358	3000	3000–4000
0.679	2961	2961–4000
0.2716	2825	2825–4000
0.1481	2767	2767–4000
0.02716	Nil	transmits all

It will be observed from the above results that cupric salts in concentrated solutions can cut off both ultraviolet and red regions of the visible spectrum and hence can be advantageously used to eliminate these regions. Moreover, copper salts are known to absorb infra-red radiations. Thus for the transmission of the visible region up to red, copper salts are the best filters. Cupric chloride has the advantage over cupric nitrate and cupric sulphate that it has strong absorption towards violet even in the visible region and hence a definite short range is available with cupric chloride for photo-chemical work. Thus a cupric chloride solution of conc. 9.285 N transmits only 4900–5770 Å, the maximum transmission being 10%. Cupric nitrate solution of conc. 11.054 N is also useful from the point of view that it absorbs a longer region towards red (up to 7000–5880) than cupric chloride, and therefore can be used to cut off that region where cupric chloride is unsuitable. Copper sulphate is no better than either cupric chloride or cupric nitrate. This is attributed to the fact that it is less soluble than the other two salts of copper. This will be clear from the concentrations that we have used. Although we could prepare a solution of cupric nitrate of as high a concentration as 11.054 N and cupric chloride of concentration 9.285 N, with copper sulphate solution we could not get a concentration higher than 2.962 N.

Many glass and gelatine filters of various makes such as Corning, Wallace, Wratten and others, which transmit all the visible radiations, appear to be less suitable for accurate photochemical work. The transmission of various kinds of gelatine and glass filters have been determined by Voege,[1] Coblentz,[2]

---

[1] Illuminating Engineer, 2, 543 (1909).

[2] J. Franklin Institute, 180, 255 (1920).

Gibson and McNicholas,[1] Gibson, Tyndall and McNicholas,[2] and others. Copper chloride solution of concentration 9.285 N as a light filter is comparable to the Wratten filters 53, 54, 58A, 60, 61, 62, 63, and 74. Of these 53, 58A, 60, 61, and 63 have a much longer range of transmission than the solution of cupric chloride. Wratten filter 54 has a transmission of only one percent. Thus copper chloride is equally good as a light filter for the region 4900-5770 as the Wratten filters 62 and 74. Copper nitrate solution of concentration 11.054 N is comparable to the Wratten filters 44 to 50. It has one great advantage over all these that its transmission is much greater although the range available with cupric nitrate is a little longer than that of the Wratten filters mentioned above.

Absorption results clearly point out one important fact, that cupric chloride behaves differently in comparison with the other copper salts, especially in concentrated solutions. Copper nitrate and copper sulphate behave similarly even in concentrated solutions. This abnormal behaviour of cupric chloride is not limited to the visible region only but is also seen in the ultra violet. For the same concentrations copper nitrate and copper sulphate have practically the same range of absorption in the ultra violet and similar values of extinction coefficient for the visible. These two salts have only one-sided absorption, that is, towards the red in the visible, while cupric chloride has absorption towards the violet also. With decreasing concentrations, cupric chloride behaves similarly to the other copper salts. It appears that the nature of the anion has some influence on the colour of the cupric salt solutions, and hence the light absorption depends on the anions as well. We believe that it is much more so when the anions are also coloured, and when the undissociated molecules exist in the solutions and in the vapour states. That is why the abnormality is more prominent in concentrated solutions where the salt is less dissociated than in dilute solutions where the salt is less dissociated than in dilute solutions, where there is greater ionisation. Chlorine in the gaseous state has an absorption maxima in the region 3800–3000 Å. The chlorine ion of cupric chloride appears to exert a marked influence on the absorption of cupric chloride. Even for the concentration 2.231 N of cupric chloride there is no ultra violet transmission although a cupric nitrate solution of concentration 12.174 N has the transmission from 3861-4000Å in the ultra violet. In the case of a molecule used as a light absorbent, the light has to pass through the complete structure of the molecule, and hence the absorption is the net result of the light absorbed both by cations and anions of the molecule. If the molecule is ionised, we have to take into account the influence of the individual ions, the net result may be due to the cation, which is the predominating factor in the case of cupric and other coloured salts. It will be observed that the coefficients of absorption are not proportional to their concentration, that is, Beer's law is not valid with solutions of cupric chloride. This discrepancy is attributed to the formation of complex ions such as $CuCl_4''$, $CuCl_3''$, etc. It is

---

[1] Bur. of Standards, Tech. Paper 119 (1919).

[2] Bur. of Standards, Tech. Paper 148 (1920).

assumed that electrolytic dissociation unaccompanied by change of structure does not change the optical absorption. The case of potassium permanganate is always cited as an example, for it follows Beer's law. Although the degree of dissociation increases with dilution, the absorption of these solutions is not changed by the addition of sulphuric acid, which decreases the permanganate ion concentration. The hypothesis of the formation of hydrates in place of complexes can as well explain the discrepancies. It is difficult to understand why light absorption should not change with ionisation of a salt. It should change provided a molecule of the salt and the ion have different absorptions. It is only when both the molecule and ion have the same absorption that ionisation should not have any effect on absorption. Perhaps this might be the case with potassium permanganate, and that is, why the change in ionisation does not change the absorption. Concentrated solutions of cupric chloride differ in colour from the solutions of cupric nitrate and sulphate in that they are green and not blue like the solutions of the copper salts. We attribute the green colour of cupric chloride solution to the undissociated cupric chloride molecules. In the cases of copper sulphate and copper nitrate, the molecules and the ions have practically the same absorption, as the anions from these salts appear to be colourless. Such is not the case with cupric chloride. Here both the ions appear to be coloured and therefore the molecule and the ion have different absorptions. When, however, the solutions are diluted, cupric ions, as in case of copper sulphate and copper nitrate, become responsible for the absorption. This view appears justified from the fact that for the same concentrations, the limit of complete absorption on the longer wavelength side is practically the same for all the three copper salts. We have chosen the longer wavelength side because the anion Cl′ of cupric chloride appear to exert a great influence on the shorter wavelength side and chlorine as a gas shows absorption towards violet and ultra violet.

Ostwald[1] found that 0.002 N solutions of different permanganates showed the same absorption bands. The spectrum was independent of the nature of the cation, except in few cases where deviations occurred and could be satisfactorily explained. Merton,[2] who photographed the absorption spectra of various permanganates in various solvents reported that the position of the bands in any single solvent is the same for permanganate of potassium, sodium, calcium, barium, zinc etc. Since some of the solvents employed have very slight ionising power, the light absorption was ascribed to the MnO_4 group and was not much influenced by ionisation. Thus Merton contradicts Ostwald's view on the subject. Unfortunately Ostwald and Merton have chosen salts with colourless cations and hence the molecules and ions may have the same absorption as we have stated above in the case of $CuSO_4$ and $Cu(NO_3)_2$.

The cause of absorption of light by cations which show selective absorption has been discussed by Miss Kato.[3] The selective absorption of the salt

---

[1] Z. physik. Chem., 9, 579 (1892).

[2] J. Chem. Soc., 99, 637 (1911).

[3] Sci. Papers Inst. Phys. Chem. Res. Tokyo, 12, 230; 13, 7 (1930).

solutions are attributed to the electrons in the incomplete d-shells of the cations, most of the transmission being traced to the intercombination between different multiples of the ionized atoms. This conclusion was arrived at by the comparison of her absorption frequencies with the spectral terms in gases investigated by Gibbs[1] and White.[2] She has studied the selective absorption of copper salts, which is found to be at 8500Å, the general absorption extending to 2450Å. The electronic configuration for the copper atom is

$$\begin{array}{ccccccccc} & 3 & & & \qquad & & 4 & & \\ S & p. & d. & & & S & p. & d & f \\ 2 & 6 & 10 & & & 1 & & & \end{array}$$

and hence the outermost electron of this atom is in the state 4 S′. Copper shows its maximum valency as two, but for solutions of cuprous salts no selective absorption was observed, because all S-electrons are removed and all the remaining shells are completed. From these observations she has come to the above conclusion as regards the cause of selective absorption by cations. This view is in agreement with the theory given out by M. N. Saha,[3] regarding the colour of inorganic salts.

Summary

(1) The absorption, extinction coefficient and percentage transmission of cupric chloride, cupric nitrate and cupric sulphate have been determined in the visible region.

(2) Ultra violet light transmission for the same salts solutions obtained photographically has been recorded.

(3) The use of copper salts as light filters has been discussed. It is shown that cupric chloride is a better filter than cupric nitrate or sulphate and is equally good as Wratten filters 62 and 74.

(4) Solutions of cupric sulphate are less suitable as light filters than solutions of cupric nitrate and chloride, because cupric sulphate is less soluble than cupric nitrate and chloride.

(5) The molecular and ionic absorptions have been distinguished. It is shown that the anion may have some effect on light absorption especially when it is coloured and when undissociated molecules exist. The green colour of concentrated cupric chloride solutions and the conflicting views of Ostwald and Merton regarding the absorption of permanganates can be explained on the above basis.

Chemistry Department,
University of Allahabad,
Allahabad, India.
March 12, 1931.

---

[1] Phys. Rev., **29**, 426, 655 (1927).

[2] Phys. Rev., **33**, 538, 672 (1929).

[3] Nature, **125**, 163 (1930).

COPPER SALTS AS LIGHT FILTERS. II

BY W. V. BHAGWAT AND N. R. DHAR

Part II

We have shown that copper salts can cut off the red side of the visible spectrum. The regions of transmission by copper salts can be shortened further, provided a suitable combination of light filters can be obtained which will partly cut off the rays transmitted by copper salts.

Winther[1] states that 0.0025 gms. of crystal violet in 100 c.cs with 25 grms. of $CuCl_2$ in 100 c.cs of water transmits 4665 Å in 2 c.ms thickness. Vanino[2] recommends 3 c.ms layer of 1% solution of aqueous tetrammino copper sulphate, combined with 1/2 cm. layer of 6% aqueous quinine hydrochloride solution. 0.4 grms. picric acid, 3.5 grs. copper sulphate crystals, 15 grs. didymium nitrate in 300 c.cs of water transmits the green mercury line 5460 Å. Picric acid solutions show strong absorptions in the region 4700–3500 Å. Landolt[3] reports that S.F.double green 0.02 grms. in 100 c.cs of water and 15 gms. of $CuSO_4.5H_2O$ in 100 c.cs transmit 4885 Å in 2 centimeters thickness. He also states that crystal violet 5 B.O. 0.005 grms. in 100 c.cs with 15 grms. of $CuSO_4.5H_2O$ transmits 4482 Å in two centimeters thickness. Lehmann[4] has recommended a vessel of Jena blue uviol glass filled with $CuSO_4$ solution and coated on the outside with gelatine containing nitroso dimethylaniline for the transmission of ultraviolet rays. More recently Eder[5] recommends a mixture of copper and cobalt salt solutions with Davis-Gibson light filter as suitable for removing heat rays. A solution of 1 grm. crystalline copper sulphate, 75 c.c. ammonium hydroxide (density 0.80) and 225 c.cs of water, is said to transmit blue light of wavelengths 4050-4360 Å.

We have studied the use of copper salts as light filters in combination with picric acid, didymium nitrate, ammonia methyl violet, and cobalt chloride. The absorption, extinction coefficient, and percentage transmission of various concentrations of these combinations have been determined for visible region. In every case, the thickness of the cell = 1 cm. Work on ultraviolet transmission has also been carried out photographically. The results are recorded in the following tables:

---

[1] Z. physik. Chem., 41, 169 (1902).

[2] Preparative chemistry, I, 500, (1921).

[3] "Das optische Drehungsvermögen," 2nd ed., p. 387.

[4] Chem. Ztg., 33, 1167 (1909); Physik. Z., 11, 1039 (1910).

[5] Z. wiss. Phot., 26, 373 (1929).

Picric Acid

λ = Wavelength in Å units; e = extinction coefficient; %T = percentage transmission.

(1) Picric acid Conc.—1.333 gms. in 100 c.cs of water.

λ	4000–4720	4850	5000	5180	5380–7000
e	∞	1.05	0.17	0.07	0.02
%T	0	8.9	67.6	85.1	95.5

(2) Picric acid Conc.—0.6666 gms. in 100 c.cs of water.

λ	4000–4720	4850	5000	5180–7000
e	∞	0.60	0.09	0.03
%T	0	25.1	81.2	93.3

(3) Picric acid Conc.—0.1333 gms. in 100 c.cs of water.

λ	4000–4590	4720	4850	5000	5180–7000
e	∞	2.05	0.70	0.13	0.02
%T	0	0.89	19.9	74.1	95.5

(1) Didymium nitrate Conc.—45.375 gms. in 100 c.cs of water.

λ	4370	4400	4470	4590	4640	4720	
e	0.35	1.19	0.40	0.58	0.72	0.49	
%T	44.6	6.4	39.8	26.3	19.05	32.3	
λ	4850	5000	5020	5100	5180	5380	5640
e	0.07	0.79	1.03	1.27	0.57	0.07	2.25
%T	85.1	16.2	9.3	5.3	26.9	85.1	.56
λ	5870	6160	6540				
e	0.03	—	0.18				
%T	93.3	—	66				

(2) Didymium nitrate Conc.—22.687 gms. in 100 c.cs of water.

λ	4370	4400	4470	4590	4640	4720
e	0.19	0.64	0.21	0.32	0.41	0.26
%T	64.5	22.9	61.6	47.8	38.9	54.9
λ	4850	5000	5020	5100	5180	5380
e	0.05	0.47	0.50	0.74	0.29	0.04
%T	89.1	33.8	31.6	18.2	51.2	91.2
λ	5640	5870	6160	6540		
e	1.65	0.02	—	0.11		
%T	2.2	95.5	—	77.6		

(3) Didymium nitrate Conc.—4.5375 gms. in 100 c.cs of water.

λ	4370	4400	4470	4590	4640	4720
e	0.05	—	0.05	0.07	—	0.06
%T	89.1	—	89.1	85.1	—	87.1
λ	4850	5000	5020	5100	5180	5380
e	0.02	0.10	—	—	0.07	—
%T	95.5	79.4	—	—	85.1	—
λ	5640	5870	6160	6540		
e	0.40	—	—	0.03		
%T	39.8	—	—	93.3		

It is clear from the foregoing results that didymium nitrate shows a peculiar type of absorption. The absorption is not continuous but shows maxima at various places, the centre of maximas being 4200 Å, 4640 Å, 5020 Å, 5100 Å, and 6540 Å. Hence it appears that it does not show general absorption but line absorption.

(1) Copper nitrate Conc.—5.527 N 10 c.cs + 10 c.cs picric acid Conc.—1.333 grms. in 100 c.cs of water in one centimetre thickness.

λ	4000–4720	4850	5000	5180	5380
e	∞	0.75	0.15	0.15	0.30
%T	0	17.7	70.7	70.7	50.1
λ	5600	5870	6050–7000		
e	0.66	1.41	∞		
%T	21.8	3.8	0		

(2) Copper nitrate Conc.—5.527 N 10 c.cs + 10 c.cs picric acid Conc.—1.333 gms. in 100 c.cs of water.

10 c.cs of Didymium nitrate Conc.—45.375 gms. in 100 c.cs of water.

λ	4000–4640	4720	4850	5000	5180	5380
e	∞	2.20	0.53	0.41	0.34	0.21
%T	0	0.63	29.5	38.9	45.7	61.6
λ	5600	5870	6160	6280		
e	1.70	1.05	2.05	∞		
%T	1.9	8.9	.89	0		

(3) Copper sulphate 1.05 N. 10 c.cs + picric acid 10 c.cs Conc.—1.333 grms. in 100 c.cs of H_2O + 6 c.cs of didymium nitrate Conc. —45.375 grms. in 100 c.cs.

λ	4000–4720	4850	5000	5180	5380	5600
e	∞	0.73	0.36	0.20	0.12	1.12
%T	0	23.4	43.6	63.1	75.8	7.5
λ	5870	6160	6540	7000		
e	0.38	0.87	1.75	∞		
%T	41.6	16.9	1.7	0		

Ultraviolet Absorption

(1) *Picric acid:* picric acid absorbs all ultraviolet rays for the concentrations examined (1.333 grms. to 0.1333 grms. in 100 c.cs of water).

(2) *Didymium nitrate.*

Conc.	Range of absorption.	Range of transmission.
45.375 grms. in 100 c.cs.	up to 3338 Å	3338–4000 Å
22.687 "	3338 Å	3338–4000 Å
4.5375 "	3248 Å	3248–4000 Å

Didymium nitrate shows line absorption in the ultraviolet as well as in the visible. In the ultraviolet region transmitted, the region from 3602-3470 Å is completely absorbed by a solution of didymium nitrate containing 45.375 gms. in 100 c.cs of water. A solution of didymium nitrate containing 22.687 grms. in 100 c.cs absorbs the region 3602–3536 Å, but the solution containing 4.5375 grms. in 100 c.cs does not absorb any line completely but shows marked absorption in these regions, which are completely absorbed by higher concentrations of didymium nitrate solution.

(3) *Didymium nitrate + Copper salt + Picric acid.*

A. Copper sulphate 10 c.cs Conc.—1.05N.
10 c.cs. Picric acid. 1.333 grms. in 100 c.cs
Didymium nitrate 6 c.cs. Conc. 45.375 grms. in 100 c.cs.

B. Copper nitrate 10 c.cs. Conc. 5.527 N.
Picric acid 10 c.cs. 1.333 grms. in 100 c.cs. of water.
Didymium nitrate 10 c.cs. Conc. 45.375 grms. in 100 c.cs.

Absorb all ultraviolet rays.

It will be seen that so far as ultraviolet light absorption is concerned, the combination of copper salts with didymium nitrate and picric acid possesses no advantage over picric acid alone. Our experimental results also indicate that due to the discontinuous absorption by didymium nitrate, its addition to the mixture of picric acid and copper salts does not improve the range of transmission by shortening it, but actually diminishes the intensity of the transmitted rays. The combination of picric acid with copper nitrate is the best and trasmits a long region extending from 4720–6160 Å. Wratten filters Nos. 53, 60, and 61 are comparable to the above combination. It is superior to Wratten Nos. 53 and 60, because its range is shorter and its transmission greater. It has a greater amount of transmission than Wratten 61, although the range is the same.

Our results clearly indicate that picric acid obeys Beer's law for the concentrations studied and Berr's law is partially applicable in case of didymium nitrate.

Copper Salts and Ammonia

(1) Cupric chloride Conc. 4.891 N 20 c.cs + 30 c.cs of 20% ammonia.

λ	4200	4280	4370	4470	4590–7000
e	1.32	1.6	1.8	2.2	∞
%T	4.78	2.5	1.5	0.63	0

(2) Copper nitrate Conc. 3.043 N 10 c.cs + 20% ammonia 20 c.cs

λ	4200	4280	4370	4470	4590	4270	4850–7000
e	0.32	0.35	0.54	0.70	1.18	1.7	∞
%T	47.8	44.6	28.8	19.9	6.6	1.9	0

(3) Copper sulphate Conc. 1.05 N, 20 c.cs + ammonia 20%. 10 c.c.

λ	4200	4280	4370	4470	4590	4720–7000
e	0.62	0.70	1.04	1.55	2.15	∞
%T	23.9	19.9	9.1	2.8	0.70	0

A combination of cupric chloride and ammonia is a very good filter for the transmission of violet only. However, it does not transmit violet only but also some of the ultraviolet.

Ultraviolet Absorption

(1) Conc. of the salt.	Range of transmission
10 c.cs $Cu(NO_3)_2$ Conc. 3.04 N + 20% ammonia 20 c.cs	3248–4000 Å
10 c.cs. $CuSO_4$ Conc. 1.05 N + 20% ammonia 10 c.cs.	3742–4000 Å
20 c.c. $CuCl_2$ 4.891 N + 20% ammonia 30 c.cs.	3883–4275 Å

Thus the ammoniacal complex of cupric chloride transmits the region 3883–4590 Å. By keeping this solution in a glass cell the ultraviolet portion is cut off and the range is shortened to 4000–4590 Å. There is no suitable Wratten filter which can be compared to the above cuprammonium solution. We, therefore, recommend its use in photochemical work when the effect of the violet side of the spectrum is to be studied. The transmission for wavelength 4470 is very small and hence the range of transmission may be stated to be 4000–4470 Å. A solution of 1 grm. crystalline $CuSO_4$, 75 c.cs of ammonium hydroxide (density—0.88) and 225 c.cs of water is said to transmit the wavelengths 4050–4360 Å. Our results with $CuSO_4$ and ammonia of concentrations very much higher than the above show a transmission of 4000–4620. The results obtained by other workers are either erroneous or represent mean region. Combinations of copper sulphate and copper nitrate with ammonia are also very useful for the ranges 4000–4720 and 4000–4850 Å respectively. Although Wratten filters Nos. 44 to 50 are comparable to the cuprammonium salts, all of them have the disadvantage of having longer regions of transmission and a smaller percentage of transmission.

Copper Sulphate and Methyl Violet

Methyl violet transmits both violet and red and hence can be combined with copper sulphate to eliminate red and transmit only violet. Our results of absorption with methyl violet alone and with copper sulphate both in the visible and ultraviolet are recorded below:

(1) Methyl violet Conc.—0.1000 grms. in 100 c.cs.

λ	6540	6160–4470	4370	4280
e	0.23	∞	1.95	1.5
%T	58.8	0	1.1	3.1

(2) Methyl violet Conc.—0.0500 grms. in 100 c.cs.

λ	6540	6160	6050–4590	4470	4370	4280
e	0.12	1.50	∞	1.85	1.22	0.76
%T	75.8	3.1	0	1.4	6.0	17.3

(3) Methyl violet Conc.—0.02500 grms. in 100 c.cs.

λ	6540	6160	6050	5960	5870–4850	4720	4590	4470	4370	4280
e	0.07	0.80	1.75	2.45	∞	1.85	1.85	1.12	0.75	0.50
%T	85.1	15.8	1.7	.35	0	1.4	1.4	7.5	17.7	31.6

(4) Methyl violet Conc.—0.0100 grms. in 100 c.cs of water.

λ	6540	6160	5870–5000	4850	4720	4590	4470	4370
e	0.03	0.44	∞	2.0	1.32	0.76	0.52	0.35
%T	93.3	36.3	0	1.0	4.7	17.3	30.2	44.6

(5) Methyl violet Conc.—0.0020 gms. in 100 c.cs of water.

λ	6540	6160	5870	5600	5380	5180	5000	4850	4720	4590	4470	4370
e	0.03	0.09	0.55	0.16	0.92	0.73	0.45	0.27	0.19	0.14	0.12	0.12
%T	93.3	81.2	28.1	6.9	12.0	18.6	35.4	33.7	64.5	72.4	75.8	75.8

(6) $CuSO_4$ Conc.—2.716 N + methyl violet 0.050 gms. in 100 c.cs, each in one centimeter quartz cell.

λ	4130	4200	4280	4370	4470	4590–7000
e	0.69	0.89	1.02	1.60	2.05	∞
%T	20.4	12.8	9.5	2.5	0.89	0

(7) $CuSO_4$ Conc. 2.716 + methyl violet 0.0100 gms. in 100 c.cs, each in one centimeter quartz cell.

λ	5000–7000	4850	4720	4590	4470	4370	4280	
e	∞	2.25	1.42	0.94	0.63	0.63	0.45	0.34
%T	0	0.56	3.8	11.4	23.4	35.4	45.7	

Ultraviolet Absorption

Conc. of Methyl violet	Range of absorption	Range of transmission
0.1000 grms. in 100 c.cs H_2O	Up to 3883 Å	3883-4000 Å
0.0500 "	3248 Å	3248–4000
0.0205 "	3248	3248–4000
0.0100 "	Nil	transmits all
0.0020 "	Nil	"

Although methyl violet is not a suitable filter by itself, its combination with copper sulphate gives such a short range of transmission as 4000–4590, when glass cells are used to cut off the ultra-violet portion. It is a better filter than the ammoniacal complex of cupric chloride studied above. It has the advantage of transmitting greater percentage of the incident light. The maximum transmission of ammoniacal complex of cupric chloride is only 5%, while the methyl violet combination of copper sulphate has the maximum transmission of 20% of the incident light. This filter, therefore, is recommended for the transmission of the region 4000–4590 Å.

Cobalt Chloride and Cupric Chloride

A cobalt chloride solution of concentration 8 N is found to absorb all the visible rays. The transmissions for other concentrations are recorded below:

(1) Cobalt chloride Conc. 4 N.

λ	6540	6160	5870	5600	5380–4370	4280
e	0.51	0.74	0.91	1.65	∞	2.5
%T	30.9	18.2	12.3	2.2	0	0.31

(2) Cobalt chloride Conc. 2 N.

λ	6540	6160	5870	5600	5380	5180–4720
e	0.26	0.38	0.46	0.38	1.90	∞
%T	54.9	41.6	34.6	14.7	1.2	0
λ	4590	4470	4370	4280		
e	2.5	2.2	1.7	1.22		
%T	0.31	0.63	1.9	6.0		

(3) Cobalt chloride Conc. 0.8 N.

λ	6540	6160	5870	5600	5380	5180	5000
e	0.11	0.16	0.19	0.34	0.78	1.50	1.75
%T	77.6	69.1	64.5	45.7	16.6	3.1	1.7
λ	4850	4720	4590	4470	4370	4280	
e	1.65	1.44	1.26	1.12	0.85	0.61	
%T	2.2	3.6	5.4	7.5	14.1	24.5	

(4) Cobalt chloride Conc. 0.08 N.

λ	6540	6160	5870	5600	5380	5180
e	0.07	0.09	0.14	0.23	0.29	0.32
%T	85.1	81.2	72.4	58.8	51.2	47.8
λ	5000	4850	4720	4590		
e	0.32	0.29	0.29	0.26		
%T	47.8	51.2	51.2	54.9		

Cobalt chloride, like methyl violet, shows transmission in the red as well as in the violet region, but the range of absorption is further towards violet side than in case of methyl violet. The range of absorption by a 4 N solution of cobalt chloride is 5380–4370 Å. To get the transmission towards red, no copper salt except cupric chloride can be used with cobalt chloride, for even the most concentrated solution of cupric nitrate (11.054 N) absorbs 7000–5580 Å. Hence, even if it combined with 4 N cobalt chloride solution, the transmission will be still on both sides of the spectrum. Our results with the combination of cupric chloride are represented below:

(a) Cupric chloride Conc.—9.782 N + $CoCl_2$ Conc.—4 N, each in one centimeter quartz cell, $CuCl_2$ Conc.—9.782 N + $CoCl_2$ Conc.—2 N and, $CuCl_2$ Conc.—4.89 N + $CoCl_2$ 4 N absorb all the visible regions.

(b) $CuCl_2$ Conc.—9.782N + $CoCl_2$ 0.8N. each in one centimeter cell.

λ	5600–7000	5520	5450	5380	5180	5120
e	∞	2.25	2	1.95	2.1	2.25
%T	0	0.56	1	1.1	.79	0.56
λ	5060	5000–4000				
e	2.4	∞				
%T	0.39	0				

(c) $CuCl_2$ Conc.—4.891 N + $CoCl_2$ 2N.

λ	7000–5870	5690	5600	5520	5380	5180–4000
e	∞	2.10	1.95	1.75	2.3	∞
%T	0	.79	1.1	1.7	0.50	0

(d) $CuCl_2$ Conc.—2.445 N + $CoCl_2$ 4N.

λ	6160–7000	5870	5780	5600	5380
e	∞	2.1	2.05	2.2	∞
%T	0	0.79	0.89	0.63	0

(e) $CuCl_2$ Conc.—2.445 N + $CoCl_2$ 2N.

λ	6160–7000	5870	5600	5380	5180–4000
e	∞	1.8	1.6	2.1	∞
%T	0	1.5	2.5	0.79	0

(f) $CuCl_2$ Conc.—0.9782 N + $CoCl_2$ 4N.

λ	7000–6400	6160	5870	5600	5380–4000
e	∞	1.8	1.6	2.1	∞
%T	0	1.5	2.5	0.79	0

(g) $CuCl_2$ Conc.—0.9782 N + $CoCl_2$ 2N.

λ	6400–7000	6160	5870	5600	5380	5180–4000
e	∞	1.9	1.3	1.3	2.05	∞
%T	0	1.2	5.0	5.0	0.89	0

Combination of cupric chloride of concentration 9.782 N, with cobalt chloride concentration 0.8 N, is the best among the above combinations. It transmits the visible region from 5000–5600 Å. Unfortunately the intensity of the transmitted light is very low. The ultraviolet absorption of cobalt chloride is recorded below.

Ultraviolet Absorption

Conc of $CoCl_2$	Range of absorption	Range of transmission
7.244 N	—	Transmits lines 3248–3274 and 2961 only
3.622 N	Up to 2618 Å	2618–4000 Å
1.811 N	2370 Å	2370–4000 Å
0.7244 N	Nil	Transmits all ultraviolet rays

Cupric chloride is known to absorb infra-red, while a concentration greater than 2.321 N absorbs all the ultraviolet. Also cobalt chloride of Conc. 7.244 N eliminates all the visible. Hence a combination of cobalt chloride of concentration 7.244 in combination with a solution of cupric chloride of very low concentration as N/10, will transmit only ultraviolet rays, especially the line 2961 Å and the region 3248–3274 Å. We, therefore, recommend its use for the transmission of ultraviolet rays. When a longer region of ultraviolet is desired, lower concentrations of cupric chloride should be used.

Summary

1. The absorption, extinction coefficient, and percentage transmission for various concentrations of picric acid, didymium nitrate, methyl violet and cobalt chloride has been determined in the visible region. The ultraviolet absorption for the same is obtained photographically.

2. The use of combinations of methyl violet, cobalt chloride, didymium nitrate, picric acid and ammonia with copper salts as light filters has been studied and discussed. It is shown that ammoniacal complex of cupric chloride is a good filter for the region 4000–4590 Å. The use of methyl violet and copper sulphate for the transmission of the same region has been recommended.

3. It has been shown that a combination of cupric chloride with cobalt chloride is very convenient for the transmission of ultraviolet region especially the lines 2961 Å and 3248-74 Å.

The solution must be placed in a quartz vessel.

4. Didymium nitrate does not show a continuous absorption but a type, which resembles line spectra. Its addition to the combination of copper salt and picric acid has practically no advantage, so far as visible and ultraviolet regions are concerned.

5. The filters studied by us have been compared with standard Wratten filters and some of the solution filters have been shown to be much better than the gelatine filters.

Chemistry Department,
University of Allahabad,
Allahabad, India.
March 12, 1931.

COPPER SALTS AS LIGHT FILTERS. III

BY W. V. BHAGWAT AND N. R. DHAR

Part III

Landolt[1] states that crystal violet 5 B.O. 0.005 grm. in 100 c.cs with 15 gms. of $CuSO_4.5H_2O$ transmits 4482 Å in two centimeters thickness. Potassium dichromate and $CuSO_4.5H_2O$ are known to transmit 5769–5790 Å. Winther[2] observed that a combination of cupric chloride with potassium chromate transmits 5400–5050 Å. Chromic acid with a saturated solution of copper nitrate is known to eliminate blue violet rays.

We have studied the combination of methylene blue, crystal violet, potassium chromate, potassium dichromate and chromic acid with copper salts as light filters both in the visible and ultra violet.

Methylene Blue

The methylene blue is found to absorb the visible portion of the spectrum on the side of the red, a property, which is similar to that of copper salts. Hence methylene blue cannot be advantageously used in combination with copper sulphate or copper nitrate, which has absorption only towards the red side of the visible spectrum. However, methylene blue can be combined with cupric chloride, which possesses absorption both in the red and violet ends of the spectrum.

λ = Wave length in Å units.
e = extinction coefficient.
%T = percentage transmission.

(1) Methylene blue Conc. —0.0232 grm. in 100 c.cs of water.
Cell one centimeter thick.

λ	5400–7000	5380	5310	5040	5180	5000
e	∞	2.6	2.3	2.15	2.05	1.70
%T	0	0.25	0.50	0.70	0.89	1.9
λ	4850	4720	4590	4470		
e	1.38	1.04	0.84	0.66		
%T	4.1	9.1	14.4	21.8		

(2) Methylene blue Conc.—0.0116 grm. in 100 c.cs of water.

λ	5600–7000	5520	5380	5180	5000	4850
e	∞	2.0	1.46	1.08	0.86	0.72
%T	0	1.0	3.4	8.3	13.8	19.05
λ	4720	4590	4470			
e	0.54	0.34	0.27			
%T	28.8	45.7	53.7			

---

[1] "Das optische Drehungsvermögen" 2nd. Ed., p. 387.

[2] Z. physik. Chem., **41**, 169 (1902).

(3) Cupric chloride Conc. 9.285 N + Methylene blue 0.0232 gms.
Thickness of each substance = 1 cm. in 100 c.cs.

λ	7000–5220	5150	5080	5020–4000
e	∞	2.5	2.5	∞
%T	0	0.31	0.31	0

(4) Cupric chloride Conc. 9.285 N + Methylene blue 0.0116 gms. in 100 c.cs.

λ	7000–5440	5220	5150	5080	5020	4980–7000
e	∞	1.9	1.90	2.0	2.15	∞
%T	0	1.2	1.2	1.0	0.70	0

(5) Cupric chloride Conc. 4.642 N + Methylene blue 0.0232 gms. in 100 c.cs.

λ	7000–5220	5020	4840	4700	4580–4000
e	∞	1.95	1.85	2.1	∞
%T	0	1.1	1.4	0.79	0

(6) Cupric chloride Conc. 4.642 N + Methylene blue 0.0116 gms. in 100 c.cs.

λ	7000–5440	5220	5020	4840	4700	4580–4000
e	∞	1.55	1.26	1.2	1.55	∞
%T	0	2.8	5.4	6.3	2.8	0

These results are summarised in the following tables:—

Conc. of methylene blue	Conc. of cupric chloride	Range of transmission	%T (Maximum)
0.0232 gms. in 100 c.cs of water	9.285 N	5220–5020 Å	0.31
0.0116 "	9.285 N	5440–4980 Å	1.2
0.0232 "	4.642 N	5220–4580 Å	1.4
0.0116 "	4.642 N	5440–4580 Å	6.3

These results clearly point out that, although the combination of cupric chloride and methylene blue, transmits short ranges, the amount of transmission is very low. This difficulty cannot be avoided by decreasing the concentration of any or both of the constituents, because the range of transmission is much widened on diluting the substances and even then the percentage transmission is less than that of 9.285 N cupric chloride alone. Although a concentrated solution of methylene blue shows only one-sided transmission, that is, towards the violet, when the solution contains 0.0058 grm. in 100 c.cs of water, it begins to transmit the red radiations. In other words, it has transmission in both the sides of the visible spectrum in dilute solutions like methyl violet. Concentrated solutions of methylene blue can be combined with potassium chromate, to give a short range of absorption on the violet side. Concentrated solutions of potassium dichromate have high absorption on the violet side extending as much as to absorb all the visible region transmitted by methylene blue and hence a combination of potassium dichromate and methylene blue has little advantage as a light filter. Dilute solutions of potassium dichromate with methylene blue transmit the regions similar to those transmitted by a combination of potassium chromate with methylene blue.

(1) Methylene blue Conc. 0.0232 grm. in 100 c.cs + K_2CrO_4. Conc. 3.68 N
Thickness of each substance = 1 cm.

λ	5020–4000	5080	5150	5220	5300	5370–7000
e	∞	2.4	2.3	2.2	2.4	∞
%T	0	0.39	0.50	0.63	0.39	0

(2) Methylene blue Conc. 0.0116 gms. in 100 c.cs—K_2CrO_4 Conc. 3.68 N.

λ	5020–4000	5080	5150	5220	5300	5370	5440	5520–7000
e	∞	1.70	1.50	1.40	1.44	1.55	1.95	∞
%T	0	1.9	3.1	3.9	3.6	2.8	1.12	0

Crystal Violet

Crystal violet has properties similar to those of methyl violet, transmitting both red and violet sides of the visible region and absorbing the intermediate portion. It can, therefore, be combined with cupric salts to transmit only the violet side or with potassium dichromate to transmit only the red end. Our results with crystal violet are recorded below:

(1) Crystal violet Conc. 0.0081 grm. in 10 c.cs of water.

λ	6600	6280	6180	6070–5020	4840	4700	4580	4460	4340
e	0.05	1.1	2.0	∞	1.75	1.18	0.65	0.43	0.20
%T	89.1	7.9	1.0	0	1.7	6.6	22.3	37.1	63.1

As cupric nitrate and copper sulphate have only one-sided transmission and that also in the same region as that of methyl violet or crystal violet, a combination of crystal violet and copper nitrate or sulphate will only decrease the intensity of the incident light without any gain. A combination of crystal violet with cupric chloride of concentration 9.285 N absorbs all the visible. Crystal violet containing 0.0040 grm. in 100 c.cs water transmits the regions from 5960–7000 Å and 5220–4000 Å. A solution of crystal violet having 0.0016 grm. in 100 c.cs water transmits all the region of visible spectrum without complete absorption anywhere and having maximum absorption in the yellow.

(1) Crystal violet—0.0016 grm. in 100 c.cs + cupric chloride—Conc. 9.285 N.
Thickness of each substance = 1 cm.

λ	7000–5520	5440	5360	5290	5220	5150	5020
e	∞	2.15	2.05	2.05	2.0	1.95	2.05
%T	0	0.70	0.89	0.89	1.0	1.1	0.89

λ	4960	4900–400
e	2.25	∞
%T	0.56	0

Thus the combination is not so suitable as cupric chloride alone.

(1) Crystal violet Conc. 0.0080 grm. in 100 c.cs + $K_2Cr_2O_7$ 1.165 N.
Thickness of each substance = 1 cm.

λ	4000–6070	6100	6280	6380	6490	6600
e	∞	2.05	1.34	0.72	0.29	0.10
%T	0	0.89	4.5	19.0	51.2	79.4

(2) Crystal violet Conc. 0.0080 grm. in 100 c.cs $K_2Cr_2O_7$ 0.582 N.

λ	6600	6490	6380	6280	6180	6070–4000
e	0.10	0.23	0.68	1.32	2.05	∞
%T	79.4	58.8	20.8	4.7	0.89	0

Thus for the transmssion of red from 6180–7000 Å, a combination of crystal violet with potassium dichromate is a suitable filter. However the range of transmission is rather long.

(1) Methyl violet 0.100 grm. in 100 c.cs + $K_2Cr_2O_7$ 1.165 N.
Thickness of each substance = 1 cm.

λ	4000–6280	6380	6490	6600	6730	6860
e	∞	1.50	0.98	0.52	0.25	0.23
%T	0	3.1	10.4	30.2	56.2	58.8

(2) Methyl violet 0.100 grm. in 100 c.cs + $K_2Cr_2O_7$ 0.1165 N.

λ	4000–6280	6380	6490	6600	6730	6860
e	∞	1.48	0.98	0.52	0.25	0.23
%T	0	33.1	10.4	30.2	56.2	58.8

(3) Methyl violet 0.100 grm. in 100 c.cs + K_2CrO_4 5.889 N

λ	4000–6280	6380	6490	6600	6730	6850
e	∞	0.48	0.98	0.50	0.25	0.25
%T	0	33.1	10.4	31.6	56.2	58.8

These results indicate one interesting fact that the methyl violet combination with potassium chromate and potassium dichromate of different concentrations transmit not only the same range but also the same amount of light.

This fact is also observed in case of crystal violet. We[1] have shown that potassium dichromate and potassium chromate have practically the same and very little absorption in the red and hence when combined with methyl violet or crystal violet exert the same influence. Wratten filters Nos. 89, 70, 71A, 89A, and 91 are comparable with the above combinations. Of these Wratten No. 71A has much less transmission and still longer range. Although filter Nos. 89A and 91 have very short ranges, they have very low percentage of transmission. Wratten filters Nos. 70 and 89 are decidedly superior both in respect to short range and high transmission.

Chromic Acid and Copper Salts

Chromic acid with a saturated solution of copper nitrate is known to eliminate blue-violet rays. Like potassium chromate and dichromate it has the absorption in the violet side of the visible spectrum. A pure sample of chromic acid was obtained by dissolving Merck's chromic acid in water and filtering through glass wool. The chromic acid was precipitated from the solution by adding fuming nitric acid, which was removed by slow evaporation on a water bath and finally by keeping it over solid caustic potash. The highly concentrated solutions (conc.—7.66 N) of chromic acid is found to absorb all visible and ultraviolet light rays. Dilute solutions of chromic acid transmit the same regions as those transmitted by potassium chromate and dichromate. The advantage of chromic acid over potassium chromate or dichromate consists in its greater solubility and hence in its greater power of absorption. When a concentrated solution of chromic acid is diluted, the change in complete absorption instead of being gradual is sudden and hence suitable alterations in its concentration does not offer much advantage over potassium dichromate. The following tables represent our results with chromic acid of various concentrations and its combination with cupric nitrate solutions of different strengths:

(1) Chromic acid Conc.—5.666 N.

λ	4000–5600	5870	6160	6540
e	∞	1.38	0.86	0.50
%T	0	4.1	13.8	31.6

(2) Chromic acid Conc.—2.833 N.

λ	4000–5080	5600	5870	6160	6540
e	∞	1.44	0.50	0.38	0.25
%T	0	3.6	31.6	41.6	56.2

(3) Chromic acid Conc.—1.416 N.

λ	4000–5310	5380	5600	5870	6160	6540
e	∞	2.25	0.58	0.27	0.23	0.15
%T	0	0.56	26.3	53.7	58.8	70.7

---

[1] Bhagwat and Dhar: J. Indian Chem. Soc., 7, 913 (1930).

(4) Chromic acid Conc.—0.2833 N.

λ	4000–5120	5180	5380	5600	5870	6160	6540
e	∞	2.0	0.56	0.11	0.10	0.09	0.07
%T	0	1.0	27.5	77.7	79.4	81.2	85.1

(5) Cupric nitrate 1.2174 N + Chromic acid 0.2833 N.
Thickness of each substance = 1 cm.

λ	7000–6540	6870	5870	5600	5380	5180	5120–4000
e	∞	1.48	0.75	0.46	0.74	2.10	∞
%T	0	3.3	17.7	34.6	18.2	0.79	0

(6) Cupric nitrate 1.2174 N + Chromic acid 1.416 N.

λ	7000–6540	6160	5870	5600	5380	5310–4000
e	∞	1.48	0.83	0.83	2.4	∞
%T	0	3.3	14.7	14.7	0.39	0

(7) Cupric nitrate 1.2174 N + Chromic acid 2.833 N.

λ	7000–6540	6160	5870	5600	5380–4000
e	∞	1.60	1.04	1.60	∞
%T	0	2.5	9.1	2.5	0

(8) Cupric nitrate 1.2174 N + Chromic acid 5.666 N.

λ	6540–7000	6160	5870	5600
e	∞	1.95	1.90	∞
%T	0	1.12	1.25	0

(9) Cupric nitrate 6.087 N + Chromic acid 0.2833 N.

λ	5870–7000	5600	5380	5180	5120–4000
e	∞	1.6	1.26	2.25	∞
%T	0	2.5	5.4	0.56	0

(10) Cupric nitrate 6.087 N + Chromic acid 1.416 N.

λ	5870–7000	5600	5380–4000
e	∞	1.9	∞
%T	0	1.2	0

These results may be summarised as follows:

Conc. of Chromic acid	Conc. of Cupric nitrate	Range of transmission	%T (Maximum)
5.666 N		5600-7000Å	31.6
2.833 N		5380-7000Å	56.2
1.416 N		5310-7000Å	70.7
0.2833 N		5120-7000Å	85.1
" +	1.2174 N.	5120-6540Å	34.6
1.416 N +	"	5310-6540Å	14.7
2.833 N +	"	5380-6540Å	9.1
5.666 N +	"	5600-6540Å	12.5
0.2833 N +	6.087 N.	5120-5870Å	5.4
1.416 N +	"	5380-5870Å	1.2

Ultraviolet Absorption

Photographic measurements show that chromic acid of concentrations greater than 0.0146 N absorbs all the ultraviolet while the concentration 0.00146 N is found to transmit from 3248Å-2883Å. It is of interest to note that transmission does not extend continuously from 4000-2883 Å, but shows absorption of the ultraviolet in the region 4000-3248 Å.

Potassium Dichlorate and Copper Salts

(1) Cupric chloride Conc.—9.285 N + Potassium dichromate Conc. 0.5825 N. Thickness of each substance = 1 cm.

λ	4000-5220	5290	5360	5440	5520	5600	5680	5770-7000
e	∞	2.3	2.15	2.0	1.85	1.93	2.15	∞
%T	0	0.50	0.70	1.0	1.41	1.12	0.70	0

(2) Cupric chloride Conc.—4.142 N + Potassium dichromate 0.5825 N.

λ	4000-5220	5290	5360	5440	5520	5600
e	∞	1.95	1.48	1.28	1.16	1.26
%T	0	0.70	1.4	3.8	5.4	6.9
λ	5680	5770	5870	5960		
e	1.42	1.85	2.15	∞		
%T	3.8	1.4	0.70	0		

(3) Cupric chloride Conc.—2.321 N + Potassium dichromate Conc. 0.5825 N.

λ	7000-6280	6170	6060	5960	5870	5770	5680
e	∞	2.20	1.90	1.70	1.29	1.09	0.88
%T	0	0.63	1.2	1.9	5.1	8.1	13.1
λ	5600	5520	5440	5360	5290	5220	
e	0.79	0.84	1.03	1.50	1.85	∞	
%T	16.2	14.4	9.3	3.1	1.4	0	

(4) Cupric chloride Conc.—0.9284 N + Potassium dichromate Conc. 0.5825 N.

λ	7000-6480	6380	6280	6170	6040	5960
e	∞	2.0	1.55	1.27	1.07	0.89
%T	0	1.0	2.8	5.3	8.5	12.8
λ	5870	5770	5680	5600	5520	5440
e	0.65	0.59	0.51	0.50	0.65	0.93
%T	22.3	25.7	30.9	31.6	22.3	11.7
λ	5360	5290	5220-7000			
e	1.31	1.90	∞			
%T	4.8	1.2	0			

(5) Cupric nitrate Conc.—5.527 N + Potassium dichromate 0.582 N

λ	7000-5870	5770	5680	5600	5520	5440
e	∞	2.2	2.0	1.75	1.75	2.0
%T	0	0.63	1.0	1.7	1.7	1.0
λ	5360	5290-4000				
e	2.4	∞				
%T	0.39	0				

(6) Cupric nitrate Conc.—11.054 N + Potassium dichromate 0.05825 N

λ	7000-5520	5440	5360	5290	5150	5080	5020-4000
e	∞	2.2	2.0	1.85	2.0	2.15	∞
%T	0	0.63	1.0	1.4	1.0	0.70	0

(7) Copper sulphate Conc.—2.962N + Potassium dichromate 0.5825 N.

λ	6280-7000	6060	5680	5440	5360	5290	5220-4000
e	∞	1.93	0.89	1.53	2.03	2.33	∞
%T	0	1.4	12.8	2.09	0.93	0.46	0

We have summarised these results in the table given below:—

Conc. of Copper salt	Conc. of Potassium dichromate	Range of transmission	(Maximum) %T.
Cupric chloride			
9.285 N	0.5825 N	5220-5770 Å	1.41
4.142 N	"	5220-5960 Å	6.9
2.321 N	"	5220-6280 Å	16.2
0.9285 N	"	5220-6480 Å	31.5
Cupric nitrate			
5.527 N	"	5290-5870 Å	1.7
11.054 N	0.05825 N	5020-5520 Å	1.4
Copper sulphate			
2.962 N	0.5825 N	5220-6280 Å	12.8.

It will be observed from these results that although by suitable increase of concentration of either salts the range can be shortened, yet this is done at the cost of percentage transmission, which decreases as the range is shortened. The higher transmitting combinations are unsuitable on account of their long range. However, the above combinations are useful for the transmission of the regions 5220-5770 Å, 5020-5520 Å and 5220-5960 Å. The usefulness of such combinations consists in the fact that potassium dichromate, potassium chromate and chromic acid cut off the violet side and the copper salts the red side of the visible spectrum, and hence suitable combinations of cupric salts and a chromate give us filters of convenient range in the visible spectrum. We can, however, control only one of the two factors, the transmission or the range. It is impossible to shorten the range without the loss of transmission.

Ultraviolet Absorption

Any concentration of potassium dichromate greater than 0.00942 N absorbs all the ultraviolet, while the concentration 0.000942 is found to transmit all the ultraviolet obtained from copper arc. Thus the combinations of potassium dichromate with copper salts transmit only the visible portion of the spectrum. Cupric nitrate combination transmitting 5020-5520 Å can be compared with Wratten filters Nos. 54, 62, and 74. All of them have a longer range extending from 5000-5800 Å although Wratten No. 62 and 74 are more useful on account of their greater transmission which is 15% (maximum) of the incident light.

Potassium Chromate and Copper Salts

The principle of combining potassium chromate with copper salts is the same as that of combining potassium dichromate and cupric salts and that is to cut off the violet side. From the measurements of absorption of potassium chromate and dichromate we[1] have shown that for the same concentrations potassium dichromate has a greater absorption limit than potassium chromate. Hence, potassium chromate has no advantage over potassium dichromate combinations. Even the concentrated solutions of potassium chromate do not shorten the range of transmission of cupric chloride (9.285 N) but diminishes the intensity of the transmitted light. This will be clear from the following results:—

(1) Cupric chloride Conc. 9.285 N + Potassium chromate 5.889 N.
Thickness of each substance = 1 cm.

λ	4000-5020	5220	5290	5360	5440
e	∞	1.26	1.14	1.14	1.32
%T	0	5·4	7·2	7·2	4·7
λ	5520	5600	5680	5770-7000	
e	1.50	1.80	2·1	∞	
%T	3·2	1·5	0·79	0	

The range of transmission of cupric chloride 9.285 N alone is 5020-5770 Å and the maximum percentage transmission is 10. Thus the combinations of potassium chromate with copper salts have no advantage over combinations of potassium dichromate and copper salts.

Ultraviolet Absorption

Concentrations of potassium chromate greater than 0.05889 N absorb all the ultraviolet. A concentration of 0.01178 N transmits only 3036-3248 Å of the ultraviolet. It is observed that a concentration of 0.001178 of potassium chromate transmits all the ultraviolet with a tendency of absorption in the region 3248-4000 Å. Thus potassium chromate seems to have a selective absorption in the region 3248-4000 Å.

It has been shown by Dhar[2] and by Bhagwat and Dhar[3] that chromic acid in dilute solutions appears to exist mainly as $HCrO_4'$ and CrO_4'' ions and as Cr_2O_7'' and HCr_2O_7' ions in concentrated solutions. This view is confirmed from the ultraviolet absorption of dilute solutions of chromic acid and potassium chromate, where they show a selective absorption in the region 3248-4000 Å.

---

[1] Bhagwat and Dhar: J. Indian Chem. Soc., 7, 913 (1930).

[2] Z. anorg. Chem., 121, 99 (1921); J. Indian Chem. Soc., 5, 585 (1928).

[3] J. Indian Chem. Soc., 6, 781 (1929); 7, 913 (1930).

Summary

1. Combinations of cupric salts with crystal violet, methylene blue, potassium chromate, potassium dichromate and chromic acid as light filters have been studied and the percentage transmission and extinction coefficients of these combinations have been determined. The ultraviolet absorption for the same has been obtained photographically.

2. The ultraviolet absorption by dilute solutions of potassium chromate, dichromate and chromic acid in the region 3248-4000 Å, is practically identical. This behaviour is satisfactorily explained on the view point that chromic acid exists as $H_2Cr_2O_7 \rightleftarrows H_2CrO_4$ and the equilibrium is shifted towards $H_2Cr_2O_7$ for concentrated solutions.

3. It has been shown that potassium chromate or dichromate exerts the same influence on the absorption when combined with methyl violet or crystal violet for the transmission of the red region. This is explained by the fact that both the salts have practically the same and very little absorption in the red.

4. Combinations of copper salts with potassium chromate, dichromate, chromic acid and other substances have been compared with Wratten filters and it is observed that copper sulphate has no advantage over either of the two copper salts, the cupric nitrate and cupric chloride.

5. From our investigation we find the following solution light filters very convenient for photochemical investigations:

Filter	Range of transmission	Percentage transmission (Maximum)
One. 9.285 N Cupric chloride in 1 cm. thickness.	4900–5770 Å	10
Two. 4.891 N Cupric chloride 20 c.cs + 30 c.cs of 20% ammonia in 1 cm. thickness.	4000–4590 Å	4.78
Three. 1.05 N Copper sulphate 20 c.cs + 10 c.cs of 20% ammonia in 1 cm. thickness.	4000–4720 Å	23.9
Four. 2.716 N Copper sulphate + 0.050 grm. methyl violet in 100 c.cs. of water, each in 1 cm. thickness.	4000–4590 Å	20.4
Five. 2.716 N Copper sulphate + 0.010 grm. methyl violet in 100 c.cs. of water, each in 1 cm. thickness.	4000–5000 Å	45.7

Six. 7.244 N Cobalt chloride + N/10 cupric chloride, each in 1 cm. thickness.	Line 2961 Å & the region 3248–74 Å	—
Seven. 0.0116 grm. Methylene blue in 100 c.cs. of water + 9.285 N cupric chloride, each in 1 cm. thickness.	4980–5440 Å	1.2
Eight. 0.0080 grm. Crystal violet in 100 c.cs. of water + 1.165 N potassium dichromate, each in 1 cm. thickness.	6070–7000 Å	79.4
Nine. 0.10 grm. Methyl violet in 100 c.cs. of water + 1.165 potassium dichromate, each in 1 cm. thickness.	6280–7000 Å	58.8
Ten. 6.087 N Cupric nitrate + 1.416 N chromic acid, each in 1 cm. thickness.	5380–5870 Å	1.2
Eleven. 5.527 N Cupric nitrate + 0.5825 N potassium dichromate, each in 1 cm. thickness.	5290–5870 Å	1.7
Twelve. 11.054 N Cupric nitrate + 0.5825 N potassium dichromate, each in 1 cm. thickness.	5020–5520 Å	1.4
Thirteen. 9.285 N Cupric chloride 0.5825 N potassium dichromate, each in 1 cm. thickness.	5220–5770 Å	1.41

Chemistry Department,
University of Allahabad,
Allahabad, India.
March 12, 1931.

AN INVESTIGATION OF THE DEGREES OF HYDRATION OF THE ALKYL AMINES IN AQUEOUS SOLUTION

BY WILLIAM CAMPBELL SOMERVILLE

Introduction

The state of combination of ammonia in aqueous solution has been the subject of much controversy in recent years, as may be seen from a series of papers by R. M. Caven, T. S. Moore, and A. E. C. Smith.[1] The point on which these writers disagreed was whether a hydroxide NH_4OH actually existed, which ionised directly into NH_4^+ and OH^-, or whether the observed ionisation was due to the fundamental reactions

$$H_2O \rightleftarrows H^+ + OH^-$$

$$NH_3 + H^+ \rightleftarrows NH_4^+.$$

It has been shown that a hydrate of ammonia, NH_3,H_2O, does exist at low temperatures by Rupert,[2] and Moore and Winmill[3] obtained results by means of distribution coefficient determinations which indicated that ammonia is hydrated in solution. It was shown by Caven[4] however that the ammonium ion is similar in some of its properties to the ions of the alkali metals. On these grounds NH_4OH would be expected to be a strong base, whereas it is a very weak one. Caven suggests therefore that there exists in solution a hydrate, say NH_3,nH_2O which is not *directly* ionisable, and that the ionising process might be represented by

$$NH_3,nH_2O + H^+ \rightleftarrows NH_4^+,nH_2O$$

Similar equations might be applied to the alkyl amines. Thus the hydrate formation on Caven's theory takes place as a side reaction, and the extent to which the amines are hydrated may have little connection with their relative tendency to give positive ions in solution. On Moore's hypothesis, while we cannot postulate definitely that the order of hydration will parallel the order in which the amines are ionised, there is a greater possibility of its doing so, since combination with water is a preliminary to ionisation. The results obtained by Moore and Winmill for the degrees of hydration of the various amines show very marked irregularity.

The present research was undertaken in an attempt to obtain results from various physical properties which might be correlated to establish the degrees of hydration of the amines. The first line of attack was through the

---

[1] J. Soc. Chem. Ind., 42 (1923).

[2] J. Am. Chem. Soc., 31, 866 (1909); 32, 148 (1910).

[3] J. Chem. Soc., 101, 1635 (1912).

[4] e.g. J. Chem. Soc., 121, 1406 (1922).

freezing point curves. These have been examined by Pickering.[1] It was felt advisable to check the compositions of the hydrates he obtained, and also to determine more accurately the part of each curve where the crystallising substance is ice. For this part of the curve, deviations are apparent from the *ideal* curve given by Washburn,[2]

$$\Delta T_f = 103.20(x + 0.428x^2)$$

where ΔT_f = depression of freezing point

x = mole fraction of solute.

If the solute combines with water, less water will be available in the free state. Thus the effective concentration of the solute, and hence the freezing point depression, will be increased.

Conductivity measurements (and with them density and viscosity measurements), were undertaken to correct for the ionisation of the amines in dilute solution. It was also thought it might be possible to deduce from the conductivity results directly, approximate values for the degree of hydration of each amine at 0°C and at 25°C. This is treated fully in the discussion.

Conductivities have been determined by Bredig[3] at 25°, Bruni and Sandonnini[4] at 25°, Moore and Winmill[5] at 18°, 25°, and 32.35°. None of these used solutions more concentrated than N/8. Further it was necessary to determine the degrees of ionisation at 0°C, as that temperature corresponds most nearly to the temperatures encountered in the freezing point determinations. Densities and viscosities of solutions of the methylamines have been determined at 25° by Kanitz,[6] but it was thought advisable to check his values.

Materials

Monomethylamine. The hydrochloride was freed from ammonium chloride by adding to the solution twice as much sodium hydroxide as was equivalent to the ammonia impurity (6%) and boiling until no more base came off. More caustic soda was added, and the amine distilled into water, precautions being taken to exclude carbon dioxide. On testing the amine as hydrochloride by titrating a weighed amount with silver nitrate solution, the percentage of ammonia was found to be zero.

When a sample was required to be used in very concentrated solution, the amine solution was boiled in a flask under a reflux condenser, the amine being passed down a spiral immersed in a cooling mixture of ether and carbon dioxide snow. It was collected directly in the freezing point tube, only the amount required in the experiment being distilled over.

---

[1] J. Chem. Soc., 63, 181 (1893).

[2] "Principles of Physical Chemistry," equation 54 (1915).

[3] Z. physik. Chem., 13, 289 (1894).

[4] Z. Electrochemie, 16, 223 (1910).

[5] loc. cit.

[6] Z. physik. Chem., 22, 236 (1897).

Di and tri methylamines, mono, di and tri ethylamines. These were prepared by the usual methods,[1] or bought from Hopkins and Williams, and purified.

Standard solutions of hydrochloric acid and sodium hydroxide. These were standardised using pure dry anhydrous sodium carbonate, or calcspar.

Determination of Concentration

The mole fraction of amine in a solution was found by weighing a flask containing a pipetted volume of standard hydrochloric acid (N or N/10 according to the concentration of the amine solution), running in a quantity of the solution, and reweighing the flask. The quantities of acid and of amine were taken so as to leave a slight excess of acid. This excess was titrated with standard sodium hydroxide. Provided the volume of acid was at least 25 cc. the titration was accurate to one in one thousand. Knowing the density of the solution, the normality could also be calculated.

Methyl orange was used as indicator throughout.

Densities of Amine Solutions

The pyknometers were of the usual Ostwald type, of 1.1-1.8 cc. capacity. The accuracy of the results was of the order of 3 in 10,000.

Density data at 0°C x_a = mole fraction of amine in solution
D_0^0 = relative density of solution at 0°C.

$MeNH_2$	x_a	.05218	.02793	.01503	.00789	.00423
	D_0^0	$.978_2$	$.987_7$	$.993_0$	$.996_0$	$.998_0$
Me_2NH	x_a	.03817	.02426	.01299	.00829	.00543
	D_0^0	$.978_2$	$.985_2$	$.991_0$	$.994_2$	$.996_2$
Me_3N	x_a	.02385	.02318	.01008	.00417	
	D_0^0	$.980_4$	$.980_7$	$.990_2$	$.996_3$	
$EtNH_2$	x_a	.02984	.01425	.00724	.00362	
	D_0^0	$.985_7$	$.991_4$	$.995_9$	$.998_3$	
Et_2NH	x_a	.01340	.00684	.00380	.00206	
	D_0^0	.991	$.994_7$	$.997_4$	$.998_9$	
Et_3N	x_a	.02530	.01258	.00772	.00397	.00208
	D_0^0	$.981_0$	$.992_0$	$.994_4$	$.997_4$	$.998_9$

---

[1] Ber., 12, 523, 38, 882; J. Chem. Soc., 109, 174.

Density data at 25°C

$MeNH_2$........	x_a	.02592	.01352	.00652	.00344
	D_{25}^{25}	$.987_7$	$.993_2$	$.997_0$	$.998_7$
Me_2NH........	x_a	.01850	.00837	.00426	.00180
	D_{25}^{25}	$.987_1$	$.993_9$	$.996_9$	$.998_9$
Me_3N.........	x	.04623	.01516	.00864	
	D_{25}^{25}	$.961_0$	$.984_7$	$.991_7$	
$EtNH_2$.........	x_a	.01837	.00795	.00348	.00152
	D_{25}^{25}	$.989_0$	$.994_7$	$.997_7$	$.999_0$
Et_2NH.........	x_a	.01511	.00609	.00293	
	D_{25}^{25}	$.998_5$	$.995_0$	$.998_0$	
Et_3N..........	x_a	.00998	.00518	.00261	
	D_{25}^{25}	$.991_2$	$.995_4$	$.998_0$	

Viscosities of Amine Solutions

The method used was that given by Findlay,[1] using a viscometer of the type shown in Fig. 1, taking 2 cc. of liquid. The thermostat at 25° was a large glass jar, stirred and regulated to 25.00 ± 0.01°C. At 0°C a large vacuum flask filled with distilled water, and ice prepared from distilled water, was used.

Accuracy obtainable. The stop watch was graduated in fifths of a second, and read to 0.1 sec. After some practice, and by repeating the timing until concordant results were obtained, the error in starting and stopping the watch was about 0.1 sec., equivalent to an error of slightly less than 2 in 1000, since the time of outflow at 25° was 1 min. 7 sec. At 0°C this error was less.

Some deviation from Poiseuille's law due to the construction of the viscometer was found when a 20% solution of sucrose was employed (compare Washburn and MacInnes[2]). It was noticed at 0° that the surface tension of pure water differed so much from that of a solution that an error was being introduced in the time taken by the liquid surface to sink down the part of the capillary between the bulb and the mark B. A new mark was accordingly etched at C. It was now found that the results obtained with the 20% sucrose solution obeyed Poiseuille's law to within 1 in 1000, less than the error due to the stop watch.

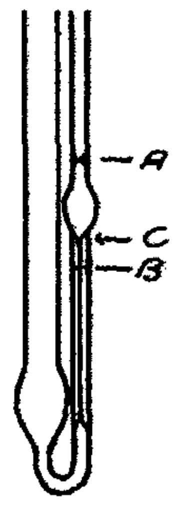


FIG. 1
Viscosity Apparatus

---

[1] "Practical Physical Chemistry," 4th ed., p. 35.

[2] J. Am. Chem. Soc., 33, 1692 (1911).

Viscosity data at 0°C. x_a = mole fraction of amine
η/η_w = viscosity of solution over viscosity of pure water.

$MeNH_2$	x_a	.04549	.02255	.00900	.003667	.001800
	η/η_w	1.525	1.239	1.095	1.040	1.019
Me_2NH	x_a	.04255	.01835	.00962	.004647	.002247
	η/η_w	1.734	1.373	1.186	1.084	1.039
Me_3N	x_a	.02395	.00971	.00693	.003747	.001771
	η/η_w	1.884	1.294	1.204	1.108	1.048
$EtNH_2$	x_a	.02269	.00836	.002958	.001538	
	η/η_w	1.427	1.138	1.043	1.021	
Et_2NH	x_a	.01888	.00993	.003854	.001701	
	η/η_w	1.818	1.374	1.133	1.055	
Et_4N	x_a	.02530	.01114	.005395	.001572	
	η/η_w	2.696	1.601	1.248	1.064	

Viscosity data at 25°C

$MeNH_2$	x_a	.02058	.01219	.00945	.00465	.002020	
	η/η_w	1.153	1.082	1.061	1.030	1.013	
Me_2NH	x_a	.02617	.01313	.004171	.001576		
	η/η_w	1.365	1.165	1.046	1.018		
Me_3N	x_a	.04672	.02537	.01079	.004685	.002225	.000951
	η/η_w	2.074	1.523	1.200	1.081	1.034	1.016
$EtNH_2$	x_a	.02318	.01114	.005030	.002574	.001064	
	η/η_w	1.281	1.128	1.051	1.022	1.007	
Et_2NH	x_a	.02654	.01171	.00590	.00264	.00140	
	η/η_w	1.727	1.278	1.126	1.049	1.023	
Et_3N	x_a	.01349	.005299	.002347	.001087		
	η/η_w	1.402	1.141	1.053	1.015		

Conductivities of Amine Solutions

Using a valve oscillator, headphones, and a three metre Kohlrausch slide wire bridge (Leeds and Northrup), an accuracy of 4 in 10,000 in the ratio of one side of the bridge to the other was obtained. A variable capacity was connected in parallel with the resistance box, balancing the capacity of the cell, giving a silent sound minimum. Platinum black electrodes were used. It is well known that the amines are catalytically decomposed by platinum black, but before each determination, the solution to be examined, a pipette, and the cell (previously dried with steam), were allowed to attain the thermostat temperature. Some solution was then transferred to the cell, and the conductivity determined after four minutes. On leaving the cell another four minutes, only very small changes of conductivity were recorded, so that no error was being introduced. The cell constants were determined after each run, and remained unchanged throughout. Good distilled water having a conductivity never greater than 2.0×10^{-6} mhos. at 25° was employed. As no high dilutions were being dealt with, this was satisfactory.

Thermostats. At 25° a large copper bath was used, protected by asbestos sheets, stirred and regulated to 25.00 ± 0.01°C. At 0°C a large Dewar vessel was employed as in the viscosity work.

The equivalent conductivities of the amines at infinite dilution. The mobilities of the amine ions have been determined accurately at 25° by Moore and Winmill,[1] who also found temperature coefficients for these mobilities. In the following table

Λ_{25} = value at 25° obtained by Moore and Winmill
Λ'_0 = value at 0° calculated from Λ_{25} using the temperature coefficients given
Λ_0 = value at 0° calculated from Λ_{25} by means of the equation given by Kohlrausch[2]

$$d\Lambda/dT_{18} = 0.01341 + 0.640/\Lambda_{18} - 6.94/(\Lambda_{18})^2$$

Ion	Λ_{25}	Λ'_0	Λ_0
$MeNH_3^+$	60.6	30.8	30.4
$Me_2NH_2^+$	53.5	26.0	26.0
Me_3NH^+	49.5	22.8	23.4
$EtNH_3^+$	47.7	19.6	22.3
$Et_2NH_2^+$	38.4	15.8	16.9
Et_3NH^+	34.7	15.1	14.9

The values finally adopted at 0° were those given by the Kohlrausch equation.

The values for the mobility of the OH^- ion were taken to be 196 at 25° and 118 at 0° as in the International Critical Tables.

Corrections. A correction was applied for the conductivity of the amine carbonate formed by the CO_2 in the water used. The data for the solubility of carbon dioxide in water were taken from Kendall.[3] As shown by Moore and Winmill,[4] practically all the carbon dioxide originally present in the water will be in the form of carbonate ion. At the concentrations considered here, it can be shown that this may be assumed without introducing error. The mobility of the carbonate ion was taken from the International Critical Tables.

---

[1] loc. cit.

[2] Z. Elektrochemie, 14, 129 (1908).

[3] J. Am. Chem. Soc., 38, 2460 (1916).

[4] loc. cit.

Amine	Conductivity correction for amine carbonate at 25°	at 0°
Monomethylamine	$3.0 \times {}^{-6}$mhos.	3.3×10^{-6}mhos.
Dimethylamine	2.8	3.0
Trimethylamine	2.7	2.9
Monoethylamine	2.6	2.8
Diethylamine	2.4	2.5
Triethylamine	2.3	2.4

The corrected conductivity of a solution was given by multiplying the experimental conductivity by η/η_w, adding the conductivity of carbon dioxide in pure water, and subtracting the above correction for the amine carbonate, and the conductivity of the water.

A correction was also applied to the experimental normality for the amine withdrawn in forming amine carbonate. This was equal to 2.8×10^{-5} moles /litre at 25°, and to 5.88×10^{-5} moles/litre at 0°.

Conductivity data. x_a = mole fraction of amine
N = normality of amine
α = degree of ionisation
K = ionisation constant of the amine.

Monomethylamine	0°				25°		
x_a	N	α	$K \times 10^4$	x_a	N	α	$K \times 10^4$
.04549	2.398	.00965	2.25	.01643	0.8914	.02100	4.02
.02255	1.219	.01625	3.28	.01331	0.7250	.02380	4.21
.00900	0.4940	.02797	3.97	.00999	0.5467	.02793	4.39
.003667	0.2026	.04406	4.11	.005755	0.3164	.03752	4.63
.001800	0.0997	.06224	4.12	.002678	0.1479	.05498	4.73
	0.06172	.07867	4.14		0.0997	.06675	4.76
	0.03086	.1079	4.02		0.04986	.0924	4.69
	0.01543	.1464	3.86		0.02493	.1269	4.63
Dimethylamine							
.04255	2.168	.00987	2.13	.01910	1.014	.02160	4.83
.01835	0.977	.01899	3.59	.00854	0.4639	.03537	6.02
.00962	0.5231	.02789	4.18	.004235	0.2322	.05080	6.31
.004647	0.2555	.04082	4.44		0.1196	.07080	6.45
.002247	0.1240	.05863	4.52	.001758	0.0970	.07834	6.46
	0.1108	.06200	4.54		0.05980	.0983	6.41
	0.05540	.08602	4.48		0.02990	.1342	6.21
	0.02770	.1176	4.33		0.01495	.1825	6.08

Trimethylamine

.02395	1.235	.003753	0.175	.02112	1.093	.005942	0.388
.02395	1.228	.003775	0.176	.00871	0.4690	.01058	0.531
.00971	0.5221	.006602	0.229	.004256	0.2323	.01569	0.581
.00693	0.3766	.00796	0.240	.002252	0.1237	.02205	0.615
.003747	0.2056	.01111	0.257		0.05411	.03375	0.637
.001771	0.0980	.01622	0.262		0.02706	.04763	0.644
	0.08268	.01778	0.266		0.01353	.06630	0.635
	0.04134	.02492	0.263		0.00677	.0922	0.631
	0.02067	.03482	0.259				

Monoethylamine

	0°				25°		
x_a	N	α	$K \times 10^4$	x_a	N	α	$K \times 10^4$
.02269	1.204	.01709	3.58	.01837	0.978	.01970	3.87
.00836	0.4560	.03060	4.40	.00795	0.4325	.03228	4.65
.002958	0.1632	.05227	4.70	.003476	0.1910	.04949	4.92
	0.09173	.06930	4.73	.001522	0.0839	.07405	4.97
	0.04586	.0967	4.74		0.08196	.07501	4.98
	0.02620	.1234	4.54		0.04098	.1038	4.92
	0.01263	.1706	4.41		0.02049	.1409	4.73

Diethylamine

.01888	0.978	.02702	7.34	.01511	0.7902	.03255	8.65
.00993	0.5308	.03860	8.23	.006091	0.3292	.05444	10.32
.003854	0.2109	.06225	8.71	.002924	0.1601	.07880	10.79
.001701	0.0938	.0917	8.67		0.07172	.1167	11.05
	0.05142	.1225	8.78		0.02586	.1600	10.92
	0.02571	.1663	8.51		0.01793	.2162	10.68
	0.01286	.2201	7.95		0.00897	.2860	10.01

Triethylamine

.02530	1.233	.01233	1.90	.00998	0.5231	.02801	4.22
.01114	0.5834	.02160	2.78	.005180	0.2787	.04166	5.04
.005395	0.2910	.03137	2.95	.002612	0.1426	.02990	5.44
.001572	0.0866	.05762	3.05		0.07534	.08235	5.57
	0.06910	.06443	3.06		0.03767	.1138	5.50
	0.03455	.08969	3.05		0.01884	.1559	5.42
	0.01728	.1231	2.98		0.00942	.2090	5.19

The observed values of the ionisation constant fall away as the concentration decreases, after attaining a constant value. This cannot be explained by the presence of traces of ammonia, since these would have caused a low value of K in concentrated solution, rising on dilution. Absorption of carbon dioxide previous to the experiment would have given a diminishing K, but the initial value would have been very high. A test was carried out with dimethylamine, runs being done with a solution which had been kept some months in a bottle from which portions were withdrawn from time to time, and also with a freshly distilled solution. No change in K was found. The most likely explanation is that the amine is adsorbed on the platinum black of the electrodes. The effect on the conductivity of a concentrated solution would be negligible, but would increase as the solution was diluted.

In the preceding tables, values are given down to N/64 solution only, as with still more dilute solutions the results become too uncertain.

Freezing Point Diagrams of the Amines and Water

Section 1. The crystallising substance is a hydrate. The apparatus used is shown in Fig. 2. The tube containing the solution was cooled in an air jacket surrounded by a mixture of ether and carbon dioxide snow, not shown in the drawing, and inoculated with a little previously frozen hydrate if possible. If not, it was further cooled and rubbed, until some solid separated. It was then placed as shown in the figure. Air was bubbled through the freezing mixture, the rate being adjusted by the screw clip so that the solution warmed up very gradually. Hand stirring was employed, and the temperature kept under observation. Around the maxima on the curves, the freezing point could be determined most conveniently by noting the temperature at which a sudden change in the value of $\delta T/\delta t$ (rate of change of temperature with time) occurred, since this indicated that practically all the hydrate had melted which had separated out. At points more remote from the maxima however, the change in composition in the liquid phase produced by the separation of the hydrate caused this value to be inaccurate. The method used in such cases, was to take the temperature at which the last traces of the solid disappeared. This was not generally easy, as Pickering found also, solutions of amines at such concentrations and at such temperatures being very viscous, while the hydrates are often gelatinous in character.

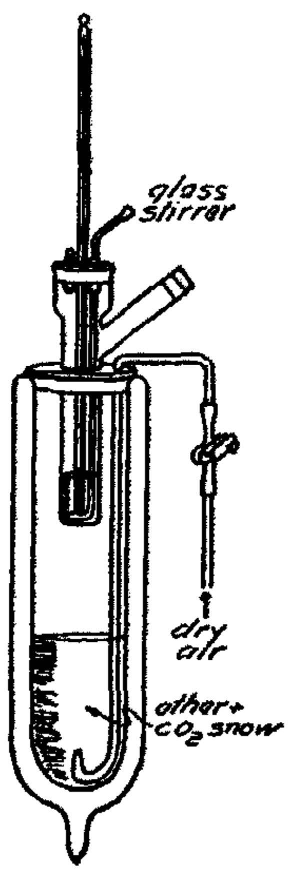


Fig. 2
Freezing-point Apparatus

Section 2. The crystallising substance is ice. The same apparatus was used as in section 1. The method however was different. Several were tried and the following was adopted.

The solution was cooled below the freezing point as before, inoculated with a little hoar-frost, and allowed to warm up gradually, observing the temperature every quarter or half minute. It was found that the temperature rose slowly at first. Then an increase in the rate of rise occurred, small at first, followed by a much more rapid increase. The point at which this second acceleration of the rise came was quite definite, was repeatable to 0.08° even when the freezing point was a low as -31°C, and was found to agree well with the correct freezing point when a few determinations were made using sodium chloride solutions made up in accordance with data given in the International Critical Tables.

Thermometers. Three thermometers were used in sections 1 and 2, a toluene one graduated in degrees, reading down to −150°, and two mercury thermometers. The first of these read from 0°C to −40°C in tenths of a degree, and was used whenever possible. The second was graduated in twentieths of a degree, from +15°C to −5°C. It was used only for part of the trimethylamine curve. All three were standardised at 0°C, and the first two at the melting point of mercury.

Each solution was made up by diluting the previous one. The concentration was determined after each freezing point had been taken.

Results obtained in sections 1 and 2

Monomethylamine x_a = mole fraction of amine

T_f = freezing point of solution (°C)

x_a	.0312	.0437	.0583	.0716	.0818	.0974	.1056	.1198	.1379
$-T_f$	3.39	4.94	6.96	8.97	10.65	13.58	15.36	18.69	23.68

x_a	.1623	ice	‖	.1843	.2040	.2387	.3075	.3732	$MeNH_2,3H_2O$
$-T_f$	31.61	cryst.	‖	42.6	39.8	37.8	40.5	47.6	cryst.

The value found by Pickering[1] for the melting point of the hydrate was −36°.

Dimethylamine

x_a	.0352	.0473	.0585	.0675	.0834	.0844	.1002	ice	‖	.1040
$-T_f$	3.94	5.61	7.50	9.14	12.62	12.90	17.35	cryst.	‖	17.33

x_a	.1099	.1186	.1205	.1295	.1336	.1393	.1453	.1644	.1784
$-T_f$	16.98	16.58	16.59	16.49	16.71	16.82	17.18	18.50	20.09

x_a	.1864	.2055	.2759	$Me_2NH,7H_2O$
$-T_s$	21.04	37	44	cryst.

Melting point of hydrate, Pickering −16.6°

Trimethylamine Run 1.

x_a	.0238	ice	‖	.0384	.0500	.0681	.0918	.1249	.1336	.1631
$+T_f$	−2.52	cryst.	‖	+0.1	2.8	4.8	5.4	4.8	4.1	1.7

x_a	.2039	.2663	.3266	.4070	hydrate
T_f	−2.0	−9.4	−17.3	−33	cryst.

Run 2.

x_a	.0588	.0829	.0877	.0902	.0991	.1139	.1713	hydrate
$+T_f$	3.77	5.09	5.16	5.27	5.18	4.78	1.69	cryst.

Run 3.

x_a	.0706	.0851	.0906	.0950	.1096	.1287	hydrate
$+T_f$	4.74	5.13	5.23	5.39	4.97	4.30	cryst.

---

[1] loc. cit.

Run 4.

x_a	.0639	.0808	.0867	.0882	.0908	.0949	.1235	hydrate
$+T_f$	4.30	5.02	5.10	5.15	5.19	5.15	4.50	cryst.

Run 5.

x_a	.0790	.0829	.0889	.0957	.0975	.0990	hydrate
$+T_f$	5.94	6.03	6.06	6.06	6.04	6.03	cryst.

Runs 1, 2, 3, 4, were done using the material first prepared. Run 5 was using material obtained from Hopkins and Williams. This sample was used in the density, viscosity and conductivity determinations.

The results from runs 2, 3, 4, and 5, when plotted, show that the formula of the hydrate is $Me_3N,10H_2O$, and not $Me_3N,11H_2O$ as found by Pickering.

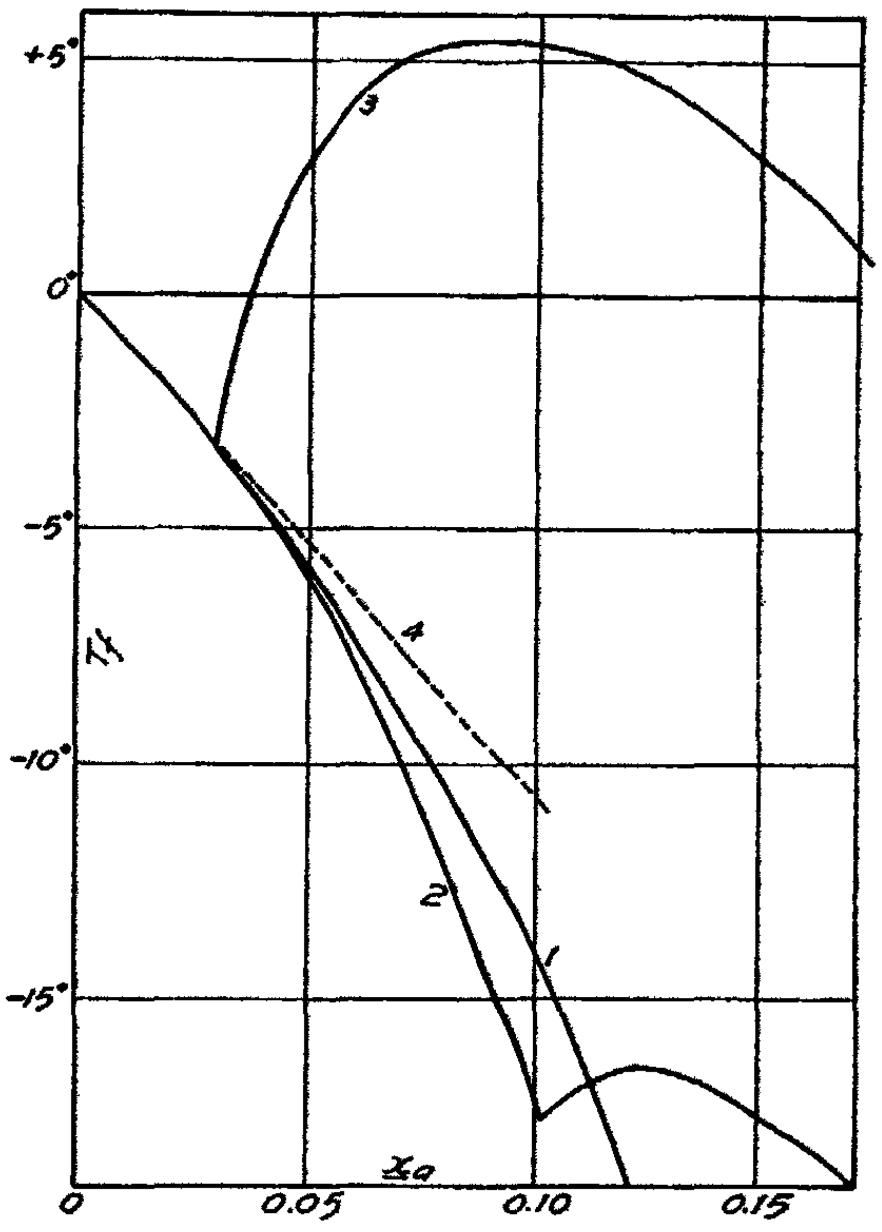


Fig. 3
The freezing-point curves of the three methylamines. (1) Monomethylamine, (2) Dimethylamine, (3) Trimethylamine, (4) *Ideal.*

Monoethylamine

x_a	.0153	.0299	.0440	.0533	.0604	.0687	.0761	.0808	.0855
$-T_f$	1.58	3.27	5.12	6.44	7.52	9.04	10.36	11.42	12.49

				‖						
x_a	.0865	.0870	ice	‖	.0907	.0931	.1074	.1423	.1583	.1671
$-T_f$	12.64	12.70	cryst.	‖	13.30	12.74	10.33	7.83	7.73	7.85

x_a	.1862	.2192	.2512	.2787	.2851	$2EtNH_2,11H_2O$
$-T_f$	8.54	10.38	13.02	17.5	18.5	cryst.

Melting point of hydrate, Pickering, $-7.5°$

Diethylamine

x_a	.0071	.0147	.0162	.0208	.0278	.0309	.0368	.0425	.0490
$-T_f$	0.68	1.48	1.69	2.19	3.15	3.54	4.52	5.49	6.77

					‖					
x_a	.0574	.0589	.0614	ice	‖	.0653	.0700	.0816	.0933	.1076
$-T_f$	8.44	8.99	9.51	cryst.	‖	9.12	8.43	7.73	7.44	7.32

x_a	.1367	.1789	.2296	.2365	$Et_2NH,8H_2O$
$-T_f$	7.58	9.14	11.83	12.33	cryst.

Indications of a hydrate unsuspected by Pickering were found in more concentrated solutions, the following points being determined,

x_a	.2450	.2452	.2460	.2480	.2677	.2838	.2858	.2931	.3503
$-T_f$	9.7	10.0	9.8	10.1	14	15	16	17	26

This hydrate was so gelatinous as to make the points obtained indefinite except for those at the maximum of the curve. The nearest simple composition for the hydrate is $Et_2NH,3H_2O$.

The following values were also determined,

x_a	.4153	.4522	.4954	.5827	.6318	.6335	.6855	.866	.881
$-T_f$	29.6	27.0	25.2	21.76	20.75	20.87	20.45	24.9	30

			‖		
x_a	.964	$2Et_2NH,H_2O$	‖	1.000	pure amine
$-T_f$	38	cryst.	‖	50.0	cryst.

Melting point of $Et_2NH,8H_2O$, Pickering, $\left.\begin{matrix}-7.3\\-6.5\end{matrix}\right)$

Triethylamine

x_a	.0083	.0143	.0270	.0354	.0409	.0470	.0542	.0679	.0855
$-T_f$	0.85	1.48	2.94	3.42	3.65	3.81	3.95	4.26	4.64

						‖				
x_a	.1218	.1877	.2861	.3055	ice	‖	.3321	.3760	.5397	$Et_3N,2H_2O$?
$-T_f$	5.53	8.00	14.1	15.3	cryst	‖	19.21	19.8	22.9	22.9 cryst

The peculiar character of this curve is accounted for since the amine and water become only partially miscible at temperatures above 18° (Rothmund[1]).

---

[1] J. Am. Chem. Soc., 38, 1472 (1916).

Two substances which are only partially miscible tend to give large positive deviations from Raoult's Law (Hildebrand[1]). At very low concentrations no immisicibility occurs, and the curve may be normal.

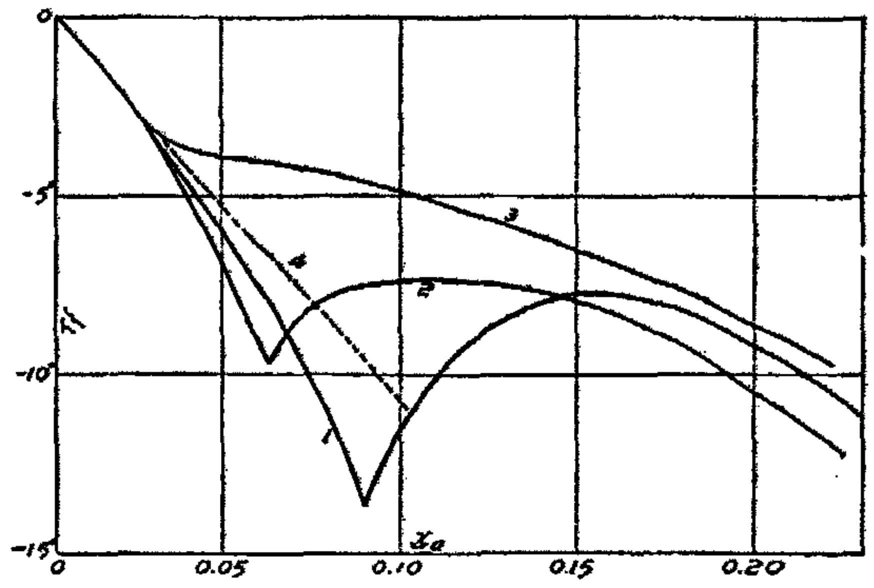


FIG. 4

The freezing-point curves of the three ethylamines. (1) Monoethylamine, (2) Diethylamine, (3) Triethylamine, (4) *Ideal.*

Section 3. Determinations using a Beckmann thermometer. The parts of the freezing point diagrams from 0° to −4° were required more accurately, since in that region the freezing points of all solutions are very near to the *ideal* values, and the differences which came up for consideration are relatively small. On this account the method had to be one in which the conditions could be repeated. That finally adopted was to supercool the tube and its contents about a degree below the freezing point, inoculate with a little hoar frost, and place in an air jacket which in turn was jacketed with ice and water. The temperature was read every quarter, half, or whole minute, according to the rate of rise. Regular mechanical stirring by an electric motor was used. For a space of at least five minutes, if the supercooling had been sufficient, these readings varied by equal increments. After some time the rate increased, a little at first, and then more rapidly. The temperature taken with each solution was that at which the rate of rise of temperature became double its original value. If there was a choice of two readings, the average was taken.

The absolute values of the freezing points were found by preparing a series of potassium chloride solutions from data in the International Critical Tables, and standardising the thermometer and the method thereby. The freezing points of these solutions were repeatable to 0.01° at −4°, the error decreasing to about 0.003° at −1°.

---

[1] J. Am. Chem. Soc., 39, 2303 (1917).

With solutions giving a freezing point depression of less than one degree, the temperature rose very slowly. In such cases the inoculated solution was stirred for two minutes, the temperature was read, and a sample pipetted out from which the mole fraction could be determined. In such cases only the zero correction was applied.

Thermometer. The thermometer used was of the usual Beckmann type, with a range of six degrees, graduated in hundredths of a degree, and read to 0.001° by means of a small lens. It was kept at 0° for a week before use, and not allowed to warm up throughout the experiments.

Stem correction. Variations in room temperature were allowed for by taking the zero after each run. The alteration in the zero from an arbitrary standard value gave the stem correction for the whole length of stem exposed, from which the correction for any fraction of the stem could be obtained. arbitrary value taken was that found when the potassium chloride solutions were investigated.

Results obtained in section 3.

x_a = mole fraction of amine corrected for ionisation

ΔT_f = freezing point depression (°C)

x_i = mole fraction calculated from the form of the *ideal* equation

$$x_t = 0.009690(\Delta T_f - 0.00425.\Delta T_f^2) \text{ (Washburn[1])}$$

Monomethylamine

x_t	ΔT_f	x_i	$x_t - x_i$
0.00344	0.346	0.00334	0.00010
.00400	0.407	.00393	.00007
.00675	0.700	.00676	−.00001
.01044	1.076	.01038	.00006
.01138	1.171	.01129	.00009
.01390	1.436	.01383	.00007
.01451	1.502	.01446	.00005
.01758	1.838	.01767	−.00009
0.01798	1.883	0.01810	−.00012
.02148	2.261	.02169	−.00021
.02148	2.263	.02171	−.00023
.02498	2.652	.02541	−.00043
.02852	3.066	.02932	−.00080
.03697	3.992	.03802	−.00105

Dimethylamine

x_t	ΔT_f	x_i	$x_t - x_i$
0.00240	0.235	0.00228	0.00012
.00336	0.342	.00331	.00005
.00587	0.602	.00581	.00006
.00734	0.755	.00730	.00004
.00926	0.955	.00922	.00004
.01239	1.287	.01240	−.00001
.01275	1.321	.01273	.00002
.01691	1.762	.01705	−.00014
0.01810	1.892	0.01819	−.00009
.02279	2.416	.02318	−.00039
.02575	2.747	.02631	−.00056
.03144	3.381	.03228	−.00084
.03796	4.153	.03954	−.00158

---

[1] loc. cit.

Trimethylamine			
x_t	ΔT_f	x_i	$x_t - x_i$
0.00424	0.415	0.00401	0.00023
.00666	0.658	.00636	.00030
.00790	0.785	.00758	.00032
.01018	1.017	.00981	.00037
.01364	1.368	.01318	.00046
.01542	1.561	.01503	.00039
.01688	1.731	.01665	.00023
.02108	2.193	.02106	.00002
.02451	2.578	.02471	−.00020
.02680	2.856	.02733	−.00053
.02694	2.870	.02747	−.00053
Diethylamine			
0.00237	0.240	0.00233	0.00004
.00430	0.437	.00423	.00007
.00736	0.747	.00722	.00014
.01027	1.045	.01008	.00019
.01054	1.072	.01034	.00020
.01173	1.193	.01150	.00023
.01674	1.734	.01667	.00007
.01824	1.918	.01843	−.00001
.01955	2.057	.01976	−.00021
.02254	2.406	.02308	−.00054
.02388	2.579	.02472	−.00084
.02581	2.817	.02696	−.00115
.02892	3.241	.03096	−.00204
.03066	3.461	.03305	−.00239
.03350	3.875	.03693	−.00343
.03911	4.694	.04457	−.00546

Monoethylamine			
x_t	ΔT_f	x_i	$x_t - x_i$
0.00405	0.405	0.00391	0.00014
.00751	0.762	.00736	.00015
.01034	1.065	.01027	.00007
.01126	1.161	.01119	.00007
.01595	1.653	.01590	.00005
.01688	1.758	.01690	−.00002
.02077	2.180	.02094	−.00017
.02330	2.454	.02352	−.00022
.02506	2.646	.02535	−.00029
.02900	3.084	.02950	−.00050
.03141	3.360	.03209	−.00068
.03329	3.565	.03402	−.00073
.03964	4.298	.04087	−.00123
.04213	4.598	.04368	−.00155
Triethylamine			
0.00276	0.278	0.00269	0.00007
.00423	0.429	.00415	.00008
.00756	0.763	.00737	.00019
.01203	1.247	.01202	.00001
.01475	1.542	.01484	−.00009
.01554	1.630	.01569	−.00015
.01837	1.962	.01885	−.00048
.02107	2.271	.02179	−.00072
.02205	2.381	.02284	−.00079
.02582	2.750	.02634	−.00052
.02764	2.928	.02802	−.00038

Values of $(x_t - x_i)$ are shown plotted against values of x_i instead of the actual freezing points of the solutions in order to greatly magnify deviations from the *ideal* curve.

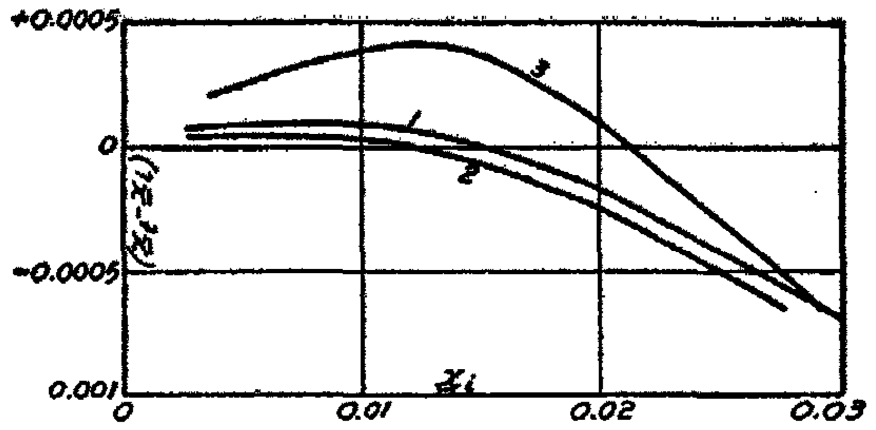


FIG. 5

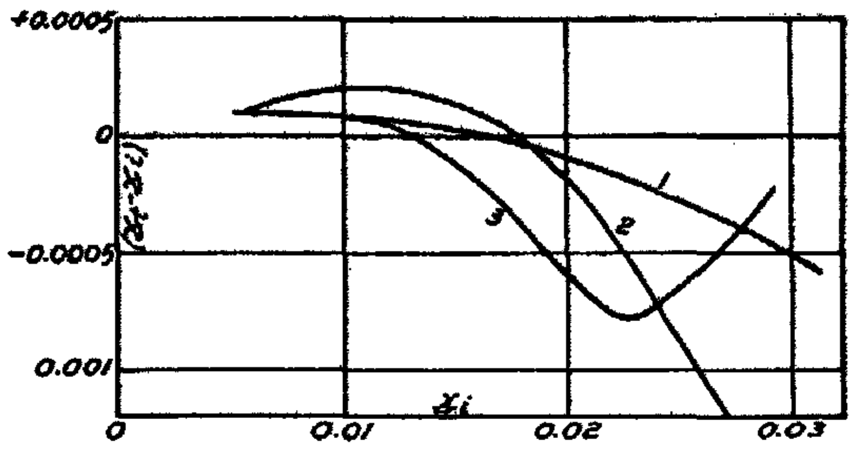


FIG. 6

Values of $(x_t - x_i)$ plotted against values of x_i. The *ideal* curve is given by the horizontal axis.

FIG. 5. (1) Monomethylamine, (2) Dimethylamine, (3) Trimethylamine.

FIG. 6. (1) Monoethylamine, (2) Diethylamine, (3) Triethylamine.

Discussion

Part 1. The relative hydration of the methyl and ethyl amines.

The formulae of the hydrates of each amine which contain the greatest proportion of water, and which give a definite maximum on the freezing point diagram are,

$MeNH_2,3H_2O$	$Me_2NH,7H_2O$	$Me_3N,10H_2O$
$2EtNH_2,11H_2O$	$Et_2NH,8H_2O$	$(Et_3N,2H_2O)$

This suggests that the order of hydration in the series of methylamines is Mono(Di(Tri. In the series of ethylamines it would seem that diethylamine is more highly hydrated than mono. The position of triethylamine is uncertain, as the curve does not follow the usual course.

When the part of each curve given when ice is the crystallising substance is examined, it is seen that the ideal curve is followed for some distance, after which each experimental curve lies below the ideal. Two main influences are at work, internal pressure differences tending to raise the experimental curve, and hydration of the amine tending to lower it (see Hildebrand[1], and Kendall[2]). In more concentrated solutions the latter effect more than counter-

---

[1] J. Am. Chem. Soc., 38, 1472 (1916).

[2] J. Am. Chem. Soc., 39, 2303 (1917).

balances the former, and we can calculate approximately the relative degrees of hydration of the amines as follows,

let x_a = mole fraction of amine by titration, neglecting ionisation, which is negligible at high concentrations

x_i = value of x corresponding to the observed value of ΔT_f from the *ideal* curve as before.

If the deviation from the *ideal* curve were *entirely* due to hydration, and if n molecules of water were combined with one of amine, the mole fraction of water would be $(1 - x_a - n.x_a)$

$$\text{So that } x_i = x_a \Big/ x_a + 1 - x_a - n.x_a = x_a \Big/ 1 - n.x_a$$

$$n = x_i - x_a \Big/ x_i . x_a$$

Values of n obtained in this way are as follows,

Monomethylamine	x_a	0.0600	0.1056	0.1623	
	n	1.85	2.28	2.39	compare $MeNH_2,3H_2O$

Dimethylamine	x_a	0.0600	0.1002	
	n	2.95	3.56	compare $Me_2NH,7H_2O$

Trimethylamine. The part of the curve in which ice crystallises is in this case too short to allow this calculated to be used. It is seen from the curve obtained with the Beckmann thermometer that if prolonged, it would very quickly come below those obtained with mono and di methylamines (Fig. 5).

Monoethylamine	x_a	0.0600	0.0870	
	n	2.34	2.90	compare $EtNH_2,5.5H_2O$

Diethylamine	x_a	0.0600	0.0614	
	n	4.88	4.99	compare $Et_2NH,8H_2O$

Triethylamine. The calculation is again impossible as the ice curve quickly deviates from a normal course. It does however show a large depression compared with the two other ethylamines at concentrations less than 0.0220 (Fig. 6)

The values of n increase as the influence of the internal pressure decreases. The increase is probably due in large measure to increasing hydrate stability as the temperature becomes lower, since the viscosity results show that a rise of temperature from 0° to 25° does significantly affect the relative viscosities. The viscosities at x_a = 0.0130 are found to be,

		$MeNH_2$	Me_2NH	Me_3N	$EtNH_2$	Et_2NH	Et_3N
η/η_w	at 0°C	1.138	1.225	1.410	1.228	1.510	1.725
η/η_w	at 25°C	1.088	1.163	1.248	1.151	1.315	1.385

The results with mono and di methylamines, mono and di ethylamines, therefore suggest that in dilute solution at 0°C each of the amines is hydrated to the same extent as in the first hydrate shown by a later maximum on the freezing point diagram, the stability of the hydrate in solution increasing as the temperature is lowered.

From all the above considerations, the order of hydration in the methylamines and ethylamines appears to be

$$\text{Mono} \langle \text{Di} \langle \text{Tri}.$$

This agrees not at all with the results obtained from the partition coefficients by Moore and Winmill,[1] and seems to show that the method is unsound. The assumptions made by them which appear most dubious are 1- the hydroxide (or hydrate) is insoluble in the nonaqueous layer, and 2- the solubilities in each layer are unaffected by the presence of a small amount of the second solvent (see Kendall[2])

The effect of hydration on the ionisation constant. At high concentrations the water withdrawn by the amine in forming hydrates will alter the effective concentration of the base. In the case of the weak acids, Kendall[3] showed that when account was taken of the water associated with the hydrion, constant values of the ionisation constant could be obtained from N/2 solution downwards.

In the case of the amines, the chemical equilibrium may be assumed to be either

$$M_3N,nH_2O + H_2O \rightleftarrows M_3N,nH_2O + H^+ + OH^- \rightleftarrows M_3NH^+,nH_2O + OH^- \quad \ldots\ldots\ldots\ldots\ldots\ldots(A)$$

or $M_3N,nH_2O + H_2O \rightleftarrows M_3NHOH,nH_2O \rightleftarrows M_3NH^+,nH_2O + OH^- \ldots(B)$

The same expression for the ionisation constant is obtained in either case, i.e.

$$K_n = \frac{[M_3NH^+nH_2O]\,[OH^-]}{[M_3N,nH_2O]\,[H_2O]}$$

If all concentrations are expressed as moles per litre, using

α = fraction ionised
N = normality of solute
M = molecular weight of solute
M_w = molecular weight of water
D^t_4 = specific gravity of solution

we have, from equation (A)

$$[M_3NH^+,nH_2O] = \alpha N \qquad [M_3N,nH_2O] = (1-\alpha).N$$

$$[OH^-] = \alpha N \qquad [H_2O] = \frac{1000.D^t_4 - NM}{M_w} - nN - \alpha N$$

If equation (B) were employed, the last term in the expression for $[H_2O]$ would be βN, where β = fraction of solute as hydroxide. But $\alpha < \beta < 1$, and may be neglected, compared with n. Putting v' = moles solvent dissolving one mole solute $= \dfrac{10000.D^t_1 - NM}{NM_w}$, then $K_n = \alpha^2 \Big/ (1-\alpha)\,(v'-n)$

---

[1] loc. cit.

[2] Proc. Roy. Soc., **85A**, 204 (1911).

[3] J. Am. Chem. Soc., 36, 1079 (1914).

If we now calculate values of K_n for different values of n, there may be a value of n which will give constant values of K_n from N/2 solution downwards. The equation used finally, bringing the values of K_n to the same order of magnitude as the usual K, was

$$K_n = \alpha^2 \times 55.5 \Big/ (1-\alpha)\,(v'-n)$$

The results obtained with two amines follow in detail, a summary is given of the others. In every case except that of trimethylamine at 25°, a constant was found.

Monomethylamine. 0°C

N	K(usual)	K_0	K_2	K_3	K_4
2.398	2.25	2.49	2.75	2.91	3.08
1.219	3.28	3.44	3.61	3.70	3.79
0.4939	3.79	4.05	4.13	4.17	4.21
0.2025	4.11	4.15	4.18	4.19	4.21
0.0996	4.12	4.13	4.15	4.16	4.16
0.06166	4.14	4.15	4.16	4.17	4.17

$n = 3$ gives the most constant values of K_n

Trimethylamine. 0°C

N	K(usual)	K_0	K_4	K_{10}	K_{11}	K_{12}
1.235	1.75	1.92	2.39	2.55	2.64	2.73
1.228	1.76	1.93	2.40	2.56	2.64	2.73
0.5220	2.29	2.39	2.59	2.65	2.68	2.70
0.3765	2.40	2.48	2.62	2.66	2.68	2.70
0.2055	2.57	2.61	2.69	2.71	2.72	2.73
0.0979	2.62	2.64	2.68	2.69	2.70	2.70
0.0826	2.66	2.68	2.71	2.72	2.72	2.73

$n = 12$ gives best agreement.

Summary of hydration values obtained

	n 0°C	n 25°C	compare
$MeNH_2$	3	6	$MeNH_2,3H_2O$
Me_2NH	7	7	$Me_2NH,7H_2O$
Me_3N	12	no const. value	$Me_3N,10H_2O$
$EtNH_2$	6 or 7	6 or 7	$EtNH_2,5.5H_2O$
Et_2NH	4	9 or 10	$Et_2NH,8H_2O$
Et_3N	3 or 4	23	$(Et_3N,2H_2O)$

These results show that this method, while giving values of the correct order in several cases, involves a very large error, especially at 25°, due to the interference of other factors. In the case of the methylamines, the order of hydration agrees with that deduced from other considerations. In the case of the ethylamines, no conclusion can be drawn.

Part 2. The internal pressures of the amines. If there is a large difference between the internal pressures of two substances, positive deviations from Raoult's Law are general in the properties of mixtures of the two. Thus since the internal pressure of water is large compared with that of most substances, we would expect the amine with the lowest internal pressure to give the largest deviation.[1]

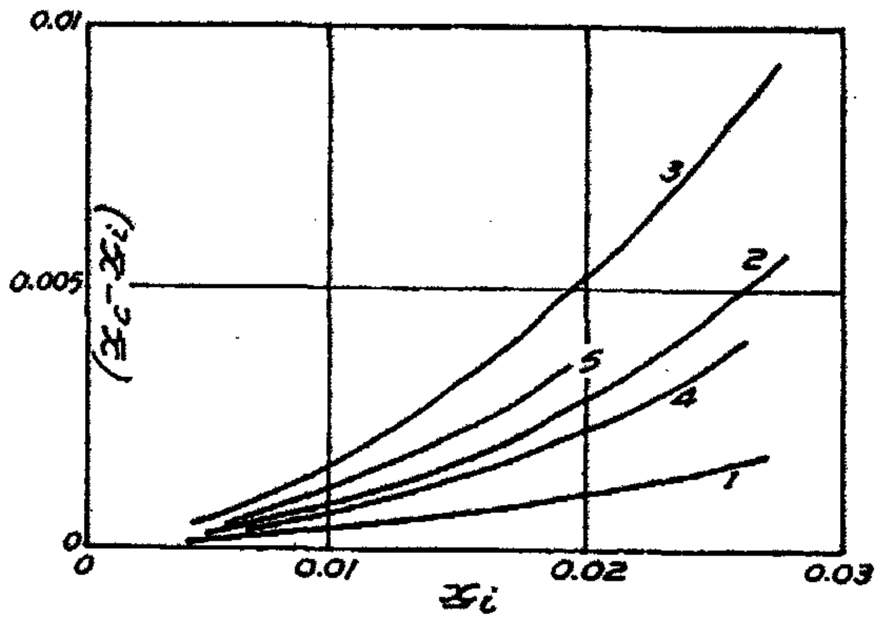


Fig. 7

Values of $(x_c - x_i)$ plotted against values of x_i.
The *ideal* curve is given by the horizontal axis.
(1) Monomethylamine, (2) Dimethylamine, (3) Trimethylamine, (4) Monethylamine, (5) Diethylamine.

The following approximate relative values for the internal pressures of the amines at 0°C were obtained by the method of van Laar.[2]

$MeNH_2$	Me_2NH	Me_3N	$EtNH_2$	Et_2NH	Et_3N
5850	4550	3750	4750	3900	3650

It is evident that at low concentrations the effects of hydration and internal pressure largely annul each other. For this to happen in all cases, the compound with the highest internal pressure must be the least hydrated, and vice versa. If we could correct for the hydration of the amines, curves could be drawn showing the internal pressure effect much more markedly. If we allow it to be qualitatively true that in dilute solution at 0°, the amines are hydrated to almost the same extent as in their first hydrates, except in the case of triethylamine, tables may be drawn up in which the concentration of amine has been corrected for the amount of water withdrawn to form hydrate.

---

[1] Hildebrand: J. Am. Chem. Soc., 41, 1067 (1919).

[2] J. Chim. phys., 14, 3 (1916); (also Hildebrand: ibid.)

The equation which may be used is

$$x_c = \frac{x_t}{1 - nx_t}$$

where x_c = corrected mole fraction
x_t = uncorrected mole fraction
n = number of molecules of water in one molecule of hydrate.
In the following table x_i = mole fraction calculated from the ideal equation corresponding to each value of x_t as before.

Monomethylamine as $\mathrm{MeNH_2,3H_2O}$

x_t	x_c	x_i	x_c-x_i
0.00400	0.00405	0.00393	0.00012
.01044	.01078	.01038	.00040
.01451	.01517	.01446	.00071
.02148	.02296	.02171	.00125
.02498	.02700	.02541	.00159

Dimethylamine as $\mathrm{Me_2NH,7H_2O}$

x_t	x_c	x_i	x_c-x_i
0.00587	0.00612	0.00581	0.00031
.01239	.01357	.01240	.00117
.01691	.01919	.01705	.00214
.02279	.02710	.02318	.00392
.02575	.03142	.02631	.00511

Trimethylamine as $\mathrm{Me_3,N,10H_2O}$

0.00666	0.00714	0.00636	0.00078
.01018	.01133	.00981	.00152
.01542	.01823	.01503	.00320
.02108	.02670	.02106	.00564
.02451	.03248	.02471	.00777
.02680	.03661	.02733	.00928

Monoethylamine as $\mathrm{EtNH_2,5.5H_2O}$

0.00751	0.00783	0.00736	0.00047
.01126	.01200	.01119	.00081
.01688	.01861	.01690	.00171
.02330	.02673	.02352	.00321
.02506	.02906	.02535	.00371

Diethylamine as $\mathrm{Et_2NH,8H_2O}$

x_t	x_c	x_i	x_c-x_i
0.00736	0.00782	0.00722	0.00060
.01173	.01294	.01150	.00144
.01674	.01933	.01667	.00266
.01842	.02160	.01843	.00317

Triethylamine. In this case the depression from the *ideal* curve is greatest of all down to −2°. The internal pressure appears to be a little less than that of trimethylamine. Since the curves obtained by correcting for the hydration of the other five amines are found to lie in the order of internal pressures, an approximate value for the degree of hydration of triethylamine in dilute solution should be obtainable by calculating how many molecules of water must be combined with one of base to bring the curve up to the trimethylamine curve. For each value of x_i corresponding to a freezing point obtained with triethylamine, the value of $x_c - x_i$ was found from the trimethylamine curve.

The equation used was as before $n = (x_c - x_t)/x_c.x_t$

x_t	x_i	$x_c - x_i$	x_c	n
0.00756	0.00737	0.00095	0.00832	12.1
.01203	.01202	.00217	.01419	12.7
.01554	.01569	.00344	.01913	12.1
.01837	.01885	.00470	.02355	12.0
.02107	.02179	.00601	.02780	11.5
.02582	.02634	.00864	.03498	10.2
.02764	.02802	.00976	.03778	9.7

n falls off at greater concentrations as the curve deviates from a normal course. The most probable value of n appears to be 12, that is, the degree of hydration of trimethylamine in dilute solution at 0°C appears to be not less than 12.

Conclusions

1. On repeating the work of Pickering on the freezing point curves of the amines, the hydrate of trimethylamine is found to be $Me_3N,10H_2O$ and not $Me_3N,11H_2O$. The existence of another hydrate of diethylamine, possibly $Et_2NH,3H_2O$, is indicated.

2. The degrees of hydration calculated from the curves obtained where ice is the crystallising substance agree as well as might be expected with the criterion that in dilute solution at 0°C, each amine is hydrated to approximately the same extent as in the first hydrate shown by a maximum in the freezing point diagram, except in the case of triethylamine.

It appears that the order of hydration in the series of methyl and ethyl amines is Mono $<$ Di $<$ Tri.

3. A method of deducing the degree of hydration of a solute directly from the conductivities of its solutions is suggested. While in a few cases the values agree with those from the freezing point data, in others discrepancies are found. The effect is thus liable to be masked by other factors, especially at 25°C.

4. When the results obtained with the Beckmann thermometer are corrected for hydration to the extent indicated, the positive deviation of the curve given by each amine from the *ideal* curve increases as the internal pressure decreases. From this consideration, the degree of hydration of triethylamine in dilute solution at 0°C is deduced.

The order of hydration of the amines is not the same as the order of basic strength, but appears to correspond exactly with the order of internal pressure. The greater the difference between the internal pressure of an amine and water, the greater is the degree of hydration.

I wish to acknowledge my indebtedness to the Moray Fund of the University for the purchase of the Kohlrausch slide wire used in this work. I wish also to record my thanks to Professor James Kendall for his helpful interest and encouragement.

Chemistry Department,
The University,
Edinburgh.
March 30, 1931.

5 - 4

REACTIONS OF SILK FIBROIN WITH SOLUTIONS OF STANNIC CHLORIDE AND DISODIUM PHOSPHATE*

BY WILLIAM EDWARD COUGHLIN

The study reported herein was undertaken to ascertain the type of reaction occurring during the process of increasing the weight of silk fibroin by alternate immersion in stannic chloride and disodium phosphate. This process, known as the weighting of silk, is extensively practiced in the silk finishing industry.

The study was divided into the following parts: (1) investigation of the effects of concentration, temperature, and pH on the gain in weight of fibroin when immersed in stannic chloride, including a determination of the comparative amounts of tin and chlorine removed from the bath during immersion; (2) determination of the amount of disodium phosphate taken up by fibroin which has had a previous treatment with stannic chloride; and (3) determination of the amount of stannic chloride taken up by fibroin which has had previous successive treatments with stannic chloride and disodium phosphate.

The fibroin used throughout the research consisted of woven silk taken from one bolt made from raw silk carefully selected for uniformity of grade, the finished piece having been passed upon by mill experts as uniform in mechanical details. Removal of sericin from the silk fibroin consisted in boiling the samples in 50 grams of a 2 per cent. solution of neutral soap per gram of silk for one hour, keeping the solution constant in volume after the boiling point was reached. After rinsing in distilled water, the samples were boiled for two successive half-hour periods in fresh distilled water. Of sixteen samples analyzed for loss of weight during the removal of sericin, losses ranged from 23.57 to 24.74 per cent. The average deviation of a single observation was 0.20, the average deviation from the mean was 0.05, or 0.20 per cent, of the mean.

First Treatment with Stannic Chloride

Preliminary determinations were made in which the time of immersion of fibroin in stannic chloride solution ranged between 10 minutes and 24 hours. Little variation in the quantity of stannic chloride taken up per gram of fibroin took place, the average increase being that obtained within 10 minutes. One hour was thereafter used as a safe immersion time.

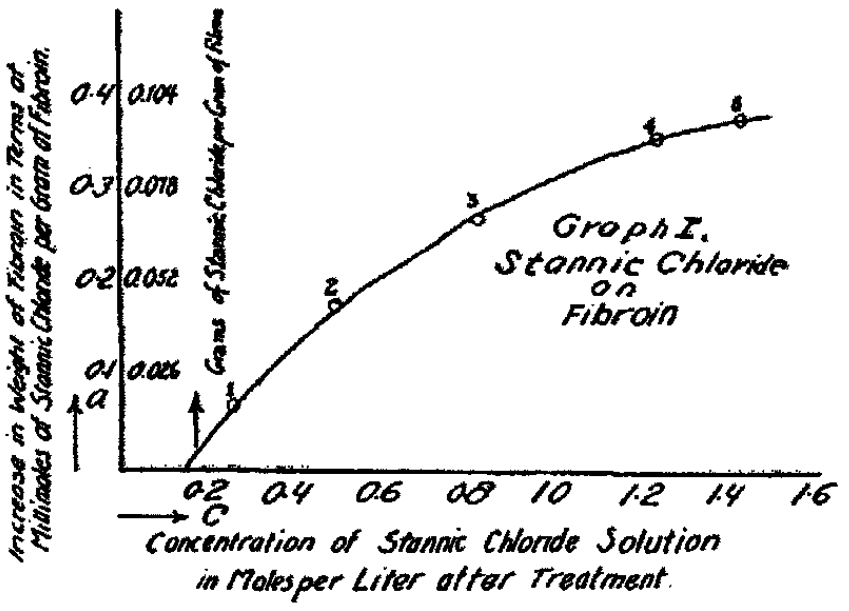
All samples of fibroin in which changes were recorded were heated until bone-dry, or to constant weight in a 98-102°C. oven. In all treatments of fibroin with stannic chloride solution, except those in the temperature studies, the temperature was held constant at 15°C.

---

* Submitted in partial fulfillment of the requirements for the Ph.D. degree, June, 1930.

The Effect of Concentration of Stannic Chloride Solution on Change in Weight of Fibroin.

A preliminary study was made in order to determine the weight of fibroin samples needed and the range of concentrations of the stannic chloride baths required to give measurable results. Fibroin samples varying from 0.2992 to 6.1378 grams were used, the concentrations of stannic chloride ranging from specific gravities of 1.037 to 1.250. When the concentrations of stannic chloride were plotted against the weights of stannic chloride taken up per unit weight of fibroin (as measured by the increase in the weight of the fibroin), a curve of the parabolic type was obtained. An analysis of the solutions was possible, however, only in the case of the larger samples.



In order to obtain changes in the concentration of the stannic chloride bath large enough for analytical investigation, a second study was made with fibroin samples weighing approximately 6 grams. Stannic chloride solutions with specific gravities varying from 1.048 (0.2467 moles per liter) to 1.3 (1.4218 moles per liter) were used. The data obtained in this case are given in Table I and are plotted in Fig. 1.

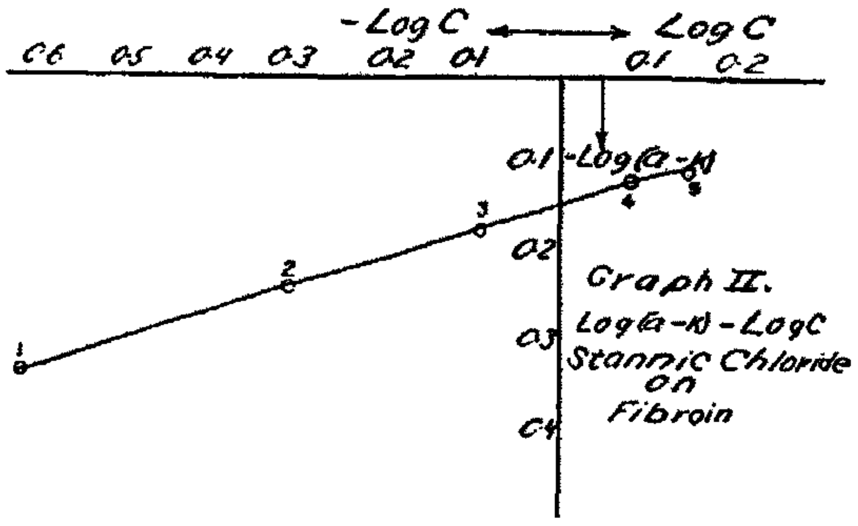
TABLE I

Relation of Concentration of Stannic Chloride Solution to Change in Weight of Fibroin

Point Number	Concentration of Stannic Chloride Solution in Moles per Liter after Treatment	Increase in Weight of Fibroin in Terms of Millimoles Stannic Chloride per gram of Fibroin (average of 3)	Increase in Weight of Fibroin in Terms of Grams of Stannic Chloride per gram of Fibroin
1	0.2467	0.0705	0.0183
2	0.4932	0.1807	0.0471
3	0.8172	0.2754	0.0717
4	1.2233	0.3652	0.0951
5	1.4218	0.3862	0.1006

Discussion of Graphs.

By visual inspection it appeared that the relation of the increase in weight per unit weight of silk to the concentration of the stannic chloride solution (as given in Table I and Fig. 1) conformed to the Freundlich adsorption equation, $a = \alpha c^{1/n}$. In order to determine whether or not this was a fact, it was necessary to introduce a third term to correct for the fact that the curve did not pass through the origin. This was done by a standard mathematical method, which consisted in the introduction of a constant term K, which is the intercept of the curve on the a axis. Introducing this term, the equation then became $a = \alpha c^{1/n} + K$.



This relationship was verified by changing to the logarithmic equation $\log (a - K) = \log \alpha + 1/n \log c$, and finding whether the plot $\log (a - K)$, $\log c$ gave a straight line. Trial showed (Fig. 2, Table II) that a straight line relationship existed if K was taken as -0.400.

Table II

Observed and Calculated Data from the Equation
$\log (a - K) = \log \alpha + 1/n \log c$.

$K = -0.400$; Average α (increase in weight in millimoles stannic chloride per gram of adsorbent at unit concentration) $= 0.716$; $1/n$ (slope of the curve) $= 0.292$

Point Number	Concentration of Stannic Chloride Solution in Moles per Liter after Treatment C	Log C	Increase in Weight of Fibroin in Terms of Millimoles Stannic Chloride per Gram of Fibroin a (Observed)	a (Calculated)	Log (a-K)	α Calculated
1	0.2467	−0.60801	0.071	0.070	−0.32698	0.717
2	0.4932	−0.30697	0.181	0.183	−0.23582	0.714
3	0.8172	−0.08767	0.275	0.275	−0.17070	0.716
4	1.2233	+0.08754	0.365	0.359	−0.11634	0.721
5	1.4218	+0.15283	0.386	0.388	−0.10458	0.714
					Average	0.716

When the values of log (a − K), log c were plotted, the average value for the constant $1/n$ obtained from the slope was 0.292. The average value of α was then obtained by substituting the five experimental values of log (a − K) and log c in 5 logarithmic equations containing the known values of $1/n$, k, a, and c. The values obtained for each point are given in Table II, together with other calculated and observed data:

The fact that the curve intercepts the c-axis at a certain definite value of c would seem to indicate that no adsorption took place until a certain definite concentration of the stannic chloride solution had been reached.

The fact that fibroin did not appear to adsorb stannic chloride at the lower concentrations may have been due to the possibility that most of the tin present at these concentrations was in the form of the a colloidally dispersed hydrous oxide, which would not be adsorbed because of its comparatively large particle size. The existence of colloidally dispersed hydrated stannic oxides in dilute solutions is discussed by Weiser in his book, "The Hydrous Oxides."

TABLE III

Results of Tin and Chloride Analyses, and Ratio of Tin to Chloride removed from Bath

Using Solutions in which Single Samples of Fibroin were immersed, as per Table I and Fig. 1

Number of Sample	Grams of Tin Taken up per Gram of Fibroin	Grams of Chlorine Taken up per Gram of Fibroin	Ratio of Tin to Chlorine Taken up (Average of 6 Determinations)
3	0.0461	0.0566	0.81
4	0.0492	0.0616	0.80
5	0.0544	0.0627	0.84
			Average 0.82

Changes in the Stannic Chloride Bath.

Analyses for tin and chloride were made on the solutions following the treatments just described. Tin was determined by hydrolyzing the solution with boiling water and igniting the tin to the oxide. The analyses for chloride were made by adding an excess of silver nitrate and titrating the excess with potassium sulfocyanide, ferric sulfate serving as the indicator.

It was found that with the largest weight of fibroin which could be handled in a given volume of solution, the two lower concentrations shown in Table I and Fig. 1 gave excessive percentage errors when but slight errors in weighing or titrating were made. Analyses were therefore recorded for three higher concentrations only. These are listed as samples 3, 4, and 5 in Table III.

In order further to increase the amounts of tin and chloride removed from the bath, successive samples of fibroin were immersed in the same bath for a period of one hour per sample. In this manner, it was found possible to use as much as 60 grams of silk as adsorbent in 125 cc. of solution. This reduced the probability of error to one-tenth of that prevailing when 6 gram samples were treated in the same volume of solution. The average ratio of tin to chloride removed from the bath, as computed from nine determinations on baths in which successive samples were thus treated, agreed with the average shown in Table III.

The ratio of tin to chlorine in stannic chloride is 0.837; it would seem, therefore, that the removal from solution of stannic chloride by fibroin is one of apolar adsorption.

The ratio of tin to chlorine removed from the solution agreed with the ratio found by Fichter and Reichart[1] who measured the tin content of silk fibroin which had been treated with stannic chloride. They found that the weight of tin in the fibroin as compared with the observed total gain in weight of the fibroin indicated that tin and chlorine had been removed from the bath in the ratio of one atom of tin to four of chlorine.

The above-mentioned investigators,[2] found further that the concentration of the bath was diminished each time the fibroin was passed through it, but that the ratio of tin to chlorine in the solution remained constant. They showed also that the stannic chloride taken up as a whole by the silk was later partially hydrolyzed upon washing in the ordinary way and that hydrolysis was the more complete, the more thorough the washing. This hydrolysis, they reported, would remove hydrochloric acid and leave stannic acid in the fibroin.

If this conclusion be correct, it affords an explanation of the fact that the gain in weight of the silk in the present studies was found to be less than the total amounts of tin and chlorine lost from the solution, as determined by analysis, since stannic acid or intermediate products of hydrolysis are uniformly lower in molecular weight than stannic chloride.

The Effect of Temperature of the Stannic Chloride Bath on the Gain in Weight of Fibroin.

Samples of bone-dry fibroin were immersed in stannic chloride solutions at temperatures of 15°C., 40°C., 80°C., and 100°C., for one hour, using four different concentrations of stannic chloride. The concentrations of the stannic chloride baths are plotted against the increases in weight of the fibroin samples at 15°C. and 40°C. in Fig. 3.

At 40°C. the same general type of curve was obtained for adsorption as at 15°C. The adsorption of stannic chloride at 40°C. was found to take place at approximately the same initial concentration of the bath as that at 15°C., but the amount adsorbed at 40°C. was slightly greater at all other concentrations whenever all conditions other than temperature remained constant. The fact that the take-up of stannic chloride at 40°C. was greater than that at 15°C. was probably due to a greater degree of swelling at the higher temperature. At 80°C. signs of deterioration of the silk were evident; at 100°C. the samples were decomposed to such an extent that they could not be weighed.

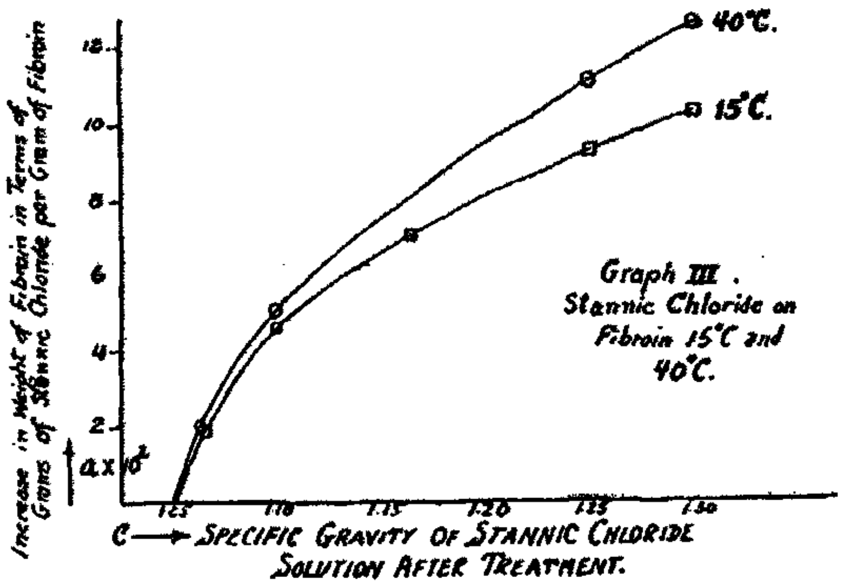
---

[1] Helv. Chim. Acta., 7, 1078 (1924).

[2] Arch. sci. phys. nat., 42, 123-141 (1916).

pH Values of Stannic Chloride Solutions before and after Treatment.

The pH values of the stannic chloride solutions used were found to be 3 in all cases, both before and after immersion of the silk, and at the various temperatures used. This acidity of the solutions explains the rapid deterioration of the silk at the higher temperatures of the temperature study. The failure of the solutions to change in pH during the immersion of the silk substantiates the conclusion that the adsorption was found to be apolar, as mentioned previously.



Effect of Change of pH on the Gain in Weight of Fibroin immersed in Stannic Chloride.

Studies were made on the effect of acidity on the gain in weight of fibroin immersed in stannic chloride solution. The pH of the stannic chloride solutions, which was uniformly 3 in the studies already described, was adjusted by additions of hydrochloric acid to values below the isoelectric point of silk. The latter, as measured by Hawley and Johnson,[1] lies between pH 1.4 and 2.8. The concentrations of the stannic chloride solutions in which the samples were immersed were 0.150 and 0.075 moles per liter. In the preparation of these stannic chloride solutions hydrochloric acid was added until normal, five-tenths normal, and one-tenth normal acid solutions were obtained. Solutions having lower pH values than zero could not be used because they tended to cause the fibroin to disintegrate.

Very small additional increases in weight of fibroin were observed in each case. The additional increases were independent of the concentration of the stannic chloride, but were the same for the same hydrogen ion concentration. The largest increase was found in the case of a stannic chloride concentration of 0.15 moles per liter. This increase was such as to give a value for a (the amount adsorbed in terms of millimoles per gram of fibroin) equal to 0.030. This is to be compared with the value of 0.080 which would have been required had the point fallen on a curve similar to that in Fig. 1, but passing through the origin.

---

[1] Ind. Eng. Chem., 22, 229 (1930).

Treatment with Disodium Phosphate

Preliminary studies were made in which pieces of fibroin previously treated with stannic chloride solutions were immersed in baths of disodium phosphate for one hour at 40°C., followed by a thorough rinsing in distilled water.

When samples containing but small amounts of tin were immersed in disodium phosphate baths of varying concentrations and rinsed as described above, decreases in weight were observed without exception. When samples containing larger amounts of tin were treated with phosphate, however, small but uniform increases in weight occurred throughout, regardless of the concentration of the phosphate bath. The concentrations used ranged from 0.0182 to 0.1139 grams of phosphate per gram of solution and the average increase observed throughout was 0.9 per cent.

The fact that this small amount of phosphate taken up was constant over wide ranges of concentrations of phosphate solutions may be the result of some chemical reaction, but it cannot be accounted for on the basis of adsorption.

The changes in concentration of the aforementioned phosphate baths were too small to be determined by the analytical methods employed.

Samples of fibroin were then treated in a uniform manner with stannic chloride solutions having a specific gravity of 1.3. This caused them to show an increase of one-tenth of their former weight. These were next immersed in solutions of disodium phosphate of varying concentrations, and were given a modified rinsing treatment which consisted of dipping the samples for two seconds into a bath of distilled water and immediately removing them and heating them to constant weight. The increases observed were more than double those given when a thorough rinsing technique was employed, and they were remarkably uniform throughout. For ten determinations, these increases ranged from 2.9 to 2.97 per cent of the weight of the tin-treated fibroin. This indicated that the gain in weight over that in which the samples were thoroughly rinsed was due to phosphate which was mechanically removed from the bath.

An attempt was made to determine the loss of phosphate from the baths by the usual method, whereby the phosphate was precipitated as magnesium ammonium phosphate from a neutral solution by means of magnesia mixture, and the precipitate ignited to the pyrophosphate and weighed. With the smallest volume of bath suitable for use with the size of fibroin samples taken, however, the change in phosphate content of the bath was too small to be determined accurately.

pH Values of Disodium Phosphate Solutions before and after Weighting.

The pH of all phosphate baths was found to be 11 at all concentrations used, both before and after immersion of the samples. When the samples of fibroin (not previously treated with stannic chloride) were immersed in disodium phosphate baths of varying concentrations at 40°C., no increase in weight of the sample was detected. In every case where thorough rinsing followed the immersion, a slight decrease in the weight of the sample was observed.

Effect of Concentration of the Second Stannic Chloride Bath on the Gain in Weight of Silk which has been phosphated after Immersion in a First Stannic Chloride Bath

Fibroin samples used in this part of the work were given the following uniform treatment. They were first immersed for one hour at 15°C., in a stannic chloride bath of specific gravity 1.3, where an average increase in weight of 10 per cent. was observed after thorough rinsing and heating to bone-dry weight. Next the samples were immersed for one hour at 40°C. in a solution of disodium phosphate, with a density of 6.91 degrees Baumé, followed by the modified rinsing procedure described in the last section, and bone-dry weights were obtained. The samples were then immersed for one hour in stannic chloride solutions of varying concentrations and the increases in weight of the samples were determined.

TABLE IV

Effect of Concentration of the Second Stannic Chloride Bath on the Gain in Weight of Silk which has been phosphated after Immersion in a First Stannic Chloride Bath

Point Number	Concentration of Stannic Chloride Solution in Moles per Liter after Immersion	Increase in Weight of Fibroin in Grams of Stannic Chloride per gram of Fibroin	Increase in Weight of Fibroin in Millimoles of Stannic Chloride per Gram of Fibroin (Average of 3 Determinations)
1	0.1305	0.0105	0.0404
2	0.2578	0.0379	0.1454
3	0.4827	0.0669	0.2567
4	0.8400	0.0793	0.3044
5	1.2536	0.0956	0.3669

The stannic chloride solutions were analyzed for tin and chlorine content before and after immersion of the sample by the methods already described. The data for this portion of the work are given in Table IV.

Fig. 4 shows how the take-up of stannic chloride by fibroin previously treated successively with stannic chloride and disodium phosphate differed from that of fibroin which had not been so treated. The treated samples showed a large increase in gain in weight at low concentrations, and an appreciable gain in weight at a concentration of stannic chloride which was too low to produce an increase in weight in the case of the untreated fibroin. At a concentration of 0.2578 moles per liter, the curves show that the gain in weight per gram of fibroin was approximately twice as great for the treated as for the untreated samples.

The maximum amount of material removed by a given weight of sample was approximately the same both for the untreated and for the phosphated fibroin samples at the higher concentrations. The approach to the maximum increase in weight, however, was reached at much lower concentrations in the case of the treated samples, and the ratio of increase in weight to the concentration of the solution increased more rapidly with the concentration in the case of the samples containing tin and phosphate than in the case of the untreated samples.

This difference in weight increase was to be expected on the basis of theoretical considerations. Since it is possible for the disodium phosphate on the fibroin, as well as for the fibroin itself, to take up stannic chloride, a non-homegeneous adsorbent is being considered. Fibroin, for example, is a non-polar adsorbent while disodium phosphate is a heteropolar adsorbent, probably operating by exchange adsorption.

Since the adsorption of stannic chloride by fibroin which had had no stannic chloride-disodium phosphate treatment did not occur until the concentration of stannic chloride was approximately 0.15 moles per liter, it seems probable that the take-up of stannic chloride by the tin-phosphated samples at the very lowest concentrations represented in Fig. 4 was due to the presence of disodium phosphate on the sample.

Analyses of the stannic chloride solutions before and after the treatments afforded an opportunity for comparing the sum of the tin and chlorine removed from the baths with the gain in weight of the fibroin samples for every concentration of stannic chloride used. These data are presented in Table V and plotted in Fig. 5.

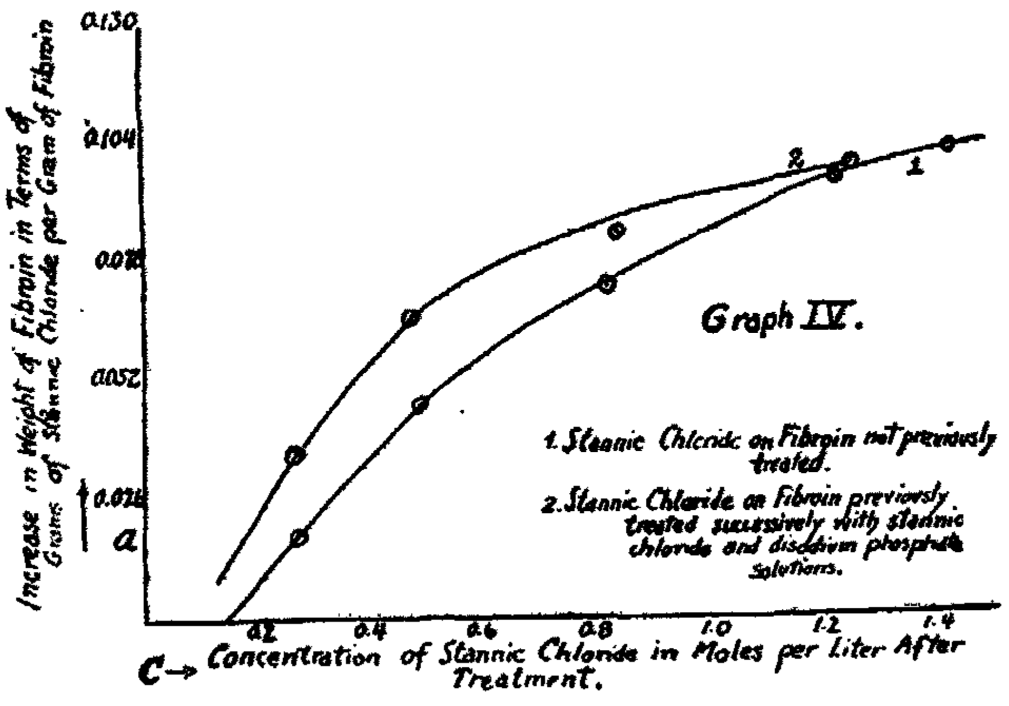
TABLE V

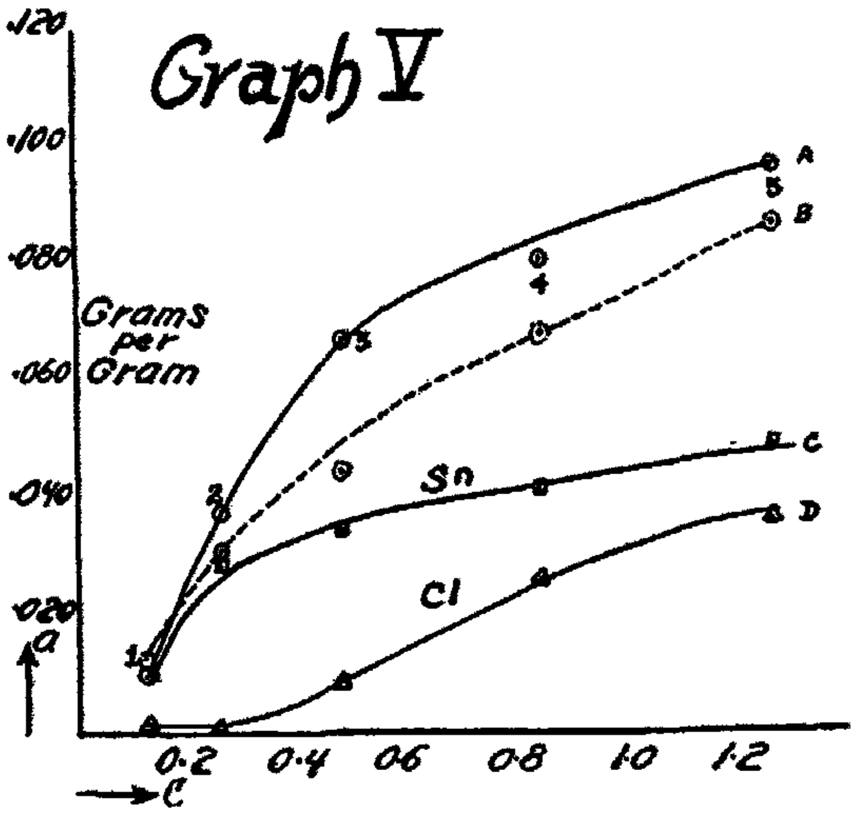
Relationship between the Total Gain in Weight of Fibroin Samples and the Loss of Chlorine and of Tin from Stannic Chloride Solutions in which Samples previously treated with Tin and Phosphate Baths have been immersed

(*Each Value is an Average of Four Determinations.*)

Point Number	Conc. of Bath in Moles/Liter	Average Increase in Weight of Sample in Grams/Gram	Loss of Chlorine Ion from Solution in Grams/Gram	Loss of Tin from Solution in Grams/Gram	Total Loss of Tin and Chloride from Solution by Analysis
1	0.1305	0.0105	0.0019	0.0098	0.0117
2	0.2578	0.0379	0.0010	0.0284	0.0294
3	0.4827	0.0669	0.0086	0.0343	0.0429
4	0.8400	0.0793	0.0255	0.0412	0.0667
5	1.2536	0.0956	0.0360	0.0485	0.0845

At the two lowest concentrations of stannic chloride it will be seen that the ratio of the loss of tin to that of chloride from the bath was much greater than the 1:4 ratio found in stannic chloride. It will be seen further that the ratio of tin to chloride removed from the solution more nearly approached the ratio of tin to chlorine in stannic chloride, as the higher concentrations were reached. This would seem to indicate that the tin and chloride were removed from the solution in approximately equivalent amounts after the influence of disodium phosphate had exerted itself.





Stannic chloride on fibroin containing tin and phosphate

a. Concentration of stannic chloride solution in moles per liter after treatment.

A. Increase in weight of fibroin in terms of grams of stannic chloride per gram of fibroin.

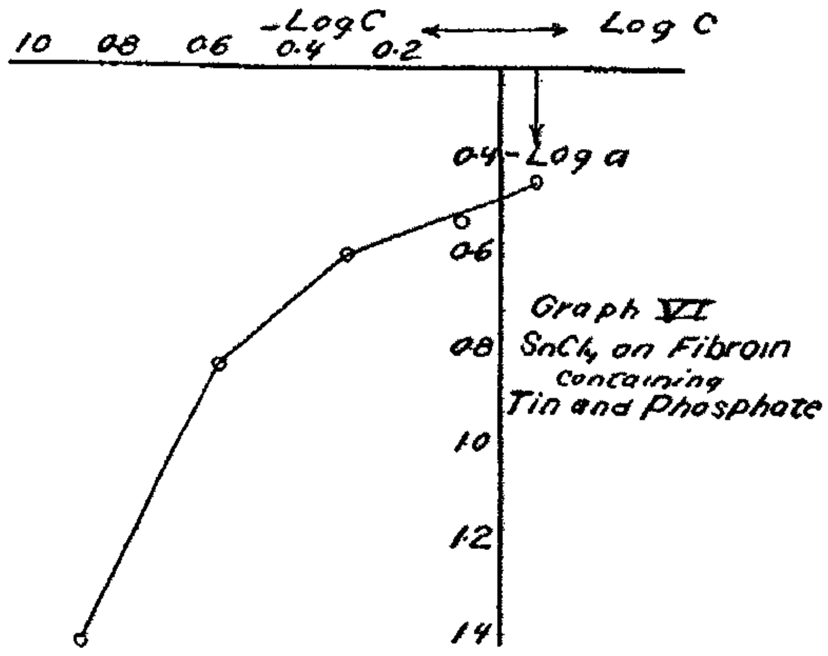
B. Loss of tin and chloride from the bath, obtained by taking the sum of C and D, in terms of grams per gram.

C. Loss of tin from the bath by analysis.

D. Loss of chloride from the bath by analysis.

Since disodium phosphate is a heteropolar adsorbent which has, as Freundlich designates them, a sluggish anion and two mobile cations, it would be expected that it would impart a negative charge to the adsorbent as a whole, and that it would therefore be expected to adsorb the stannic ion to a greater extent than the chloride ion. Exchange adsorption in which the stannic ion would replace the sodium ions, and perhaps the hydrogen ion, of the disodium phosphate would also be expected.

Studies on the area included between the lowest point of the curve and the origin in Fig. 5 indicated that the curve could not be projected beyond the lowest point as represented. When a stannic chloride solution of 0.075 moles per liter was used as a bath the samples were found to lose weight indicating that disodium phosphate began to dissolve the sample at this concentration.



The gain in weight of the treated fibroin was found to be greater than the sum of the losses of tin and chlorine from the solution as determined by analysis, for every concentration except the lowest. This may be explained on the assumption that hydration occurred in the complex formed in the fibroin during the successive treatments. In numerous trials when fibroin was alternately soaked in distilled water at room temperature and dried to constant weight in a 98-102°C. oven, successive treatments each resulted in a slight gain in weight of the fibroin, which indicated that hydration was occurring.

The influence of a non-homogeneous adsorbent upon the take-up of stannic chloride is further shown in Table VI and in Fig. 6, in which the log a, log c values for Curve A of Fig. 5 are plotted. These values are shown in Table VI.

Fig. 6 indicates that the data do not conform to the general adsorption equation since the plot of the log a, log c values is not a straight line. The graph shows that the angle of inclination of the log a, log c relationships is very large at the lower concentrations. This indicates a correspondingly large value for the adsorption exponent 1/n at these concentrations. At the higher concentrations, the slope of the log a, log c line has a small value, with a correspondingly low value for the exponent 1/n at these concentrations

TABLE VI

Logarithmic Relationships between Concentration of Stannic Chloride Solutions and Gain in Weight of Fibroin previously treated with Tin and Phosphate Baths

a	log a	c	log c
.0404	−1.39362	.1305	−0.88439
.1454	−0.83744	.2578	−0.58872
.2567	−0.59057	.4827	−0.31632
.3044	−0.51656	.8400	−0.07571
.3669	−0.43545	1.2536	0.09795

Summary

Data have been presented to show the type of phenomena involved during the increase in weight of silk fibroin by alternate immersions in stannic chloride and disodium phosphate. The effects of certain variables on these phenomena are shown.

Acknowledgment

Grateful acknowledgment should be made to Pauline Beery Mack for suggesting this problem, and for giving active assistance throughout the work; and to other members of the Department of Chemistry for helpful advice and encouragement.

Pennsylvania State College,
State College, Pennsylvania

THE THERMAL DECOMPOSITION OF STRAIGHT CHAIN PARAFFINS

BY ROBERT E. BURK

The thermal decomposition of straight chain paraffins isof outstanding interest for at least two reasons. Firstly, the reactions are basic ones in the technical "cracking" of petroleum fractions, practised on a huge scale; secondly, since the C—C bonds are probably all alike not only as the organic chemist writes them but also energetically, straight chain paraffin molecules are almost ideal ones for mechanical and statistical mechanical calculation of reaction rates, correlation with spectroscopic behavior (particularly Raman effect), etc. This paper is concerned with the correlation of existing data on the thermal decomposition of straight chain paraffins and theories of reaction velocity.

Theory

Straight chain paraffins, at least those higher than ethane in the series, decompose in accordance with the unimolecular law.[1]

The theoretical interpretation of unimolecular reactions has drawn away from the concept that the energy of activation is supplied by radiation[2] and fairly wide credence has been given to Lindeman's suggestion[3] that the activation is by collision, and that there is, for such reactions, a sufficient average time lag between activation and reaction so that the thermal equilibrium concentration of active molecules may be maintained, approximately, so that the unimolecular character of the reactions may exist in spite of the bimolecular activating process.

The high reaction rates[4] of such reactions have been accounted for by associating unimolecular decompositions with complex molecules and by drawing upon the large internal energy of complex molecules in arriving at the number of active molecules,[5] and their rate of formation.

Thus the fraction of active molecules becomes:

$$\text{I.}\quad \frac{N_1}{N} = \frac{e^{-E/RT}\,(E/RT)^{(\frac{1}{2}m-1)}}{(\frac{1}{2}m-1)!}$$

where E is the minimum internal energy a molecule must have in order to be "active" and m is the number of internal "square terms"[6] having a maximum value of $3a - 6$ where a is the number of atoms in the molecule. N_1 is the number of active molecules in thermal equilibrium where N is the total num-

---

[1] Pease and Durgan: J. Am. Chem. Soc., 52, 1264 (1930) Propane and butanes. Therefore true for higher hydrocarbons.

[2] F. Perrin: Chem. Reviews, 7, 23 (1930).

[3] Trans. Faraday Soc., 17, 598 (1922).

[4] Tolman: J. Am. Chem. Soc., 47, 1524 (1925).

[5] A discussion of these phases of the theory may be found in Hinshelwood's, "Kinetics of Chemical Change in Chemical Systems," 2nd Ed. (1929).

[6] See Hinshelwood: Loc. cit.

ber of molecules. On account of the time lag interpretation of unimolecular reactions, reaction would occur mainly between collisions and consequently for the unimolecular component of the reaction, translational energy of the molecule as a whole would not count as activational energy.

According to theory then the reaction rate would be

$$\text{II.}\quad -dN/dt = N_1/\tau$$

where τ is the average time which elapses before an active molecule decomposes if undisturbed.

Since the calculation of N_1 is on a sound basis (assuming classical partition of energy) the theoretical development centers upon the calculation of τ. This has been attempted by Polanyi and Wigner.[1]

These authors start with the acceptable assumption that a given bond must receive a certain critical energy in order for reaction to occur.[2] The probability that a given bond in a complex molecule shall have energy greater than ϵ when the energy of the whole molecule is in the range E to E + dE is[3]

$$\text{III.}\quad P = (1 - \epsilon/E)^{\frac{1}{2}m-1}$$

In getting at the average time τ_1 which elapses before the bond receives ϵ Polanyi and Wigner consider the energy to be propagated along a chain of atoms by means of a wave motion of wave length d = the distance between successive atoms in the chain, and a frequency equal to the fastest atomic vibration frequency in the chain. (There would be no ambiguity for either d or v when applied to the carbon chain of a straight chain paraffin).

The vibration period would be simply 1/v and in consideration of III the time sought τ_1 would be

$$\text{IV.}\quad \tau_1 = \frac{1}{v\,(1 - \epsilon/E)^{-(\frac{1}{2}m-1)}}$$

The differential form of equation I is

$$\text{V.}\quad N'' = \frac{Ne^{-E/RT}\,E^{(\frac{1}{2}m-1)}\,dE}{\Gamma(\frac{1}{2}m)\,(RT)^{\frac{1}{2}m}}$$

this expression giving the number of complex molecules with total internal energy in the range E to E + dE.

The reaction rate would then be according to II

$$\text{VI.}\quad \frac{dN}{dt} = \int_{E=\epsilon}^{E=\infty} \frac{Nv\,(1-\epsilon/E)^{\frac{1}{2}m-1}\,e^{-E/RT}\,E^{(\frac{1}{2}m-1)}dE}{\Gamma(\frac{1}{2}m)\,(RT)^{\frac{1}{2}m}}$$

This expression when integrated (by parts) reduces to the very simple one:

$$\text{VII.}\quad -\frac{dN}{dt} = Nve^{-\epsilon/RT}$$

(The Polanyi-Wigner unimolecular reaction velocity expression)

---

[1] Z. physik. Chem., A 139, 439 (1928).

[2] See also Rice and Ramsperger: J. Am. Chem. Soc., 49, 1617 (1927) and particularly Kassel: J. Phys. Chem., 32, 225 (1928) who have also developed this concept.

[3] Kassel (loc. cit.) gives the derivation of this probability.

Now for a straight chain paraffin whose empirical formula is C_nH_{2n+2} there are (n − 1) C-C bonds. If the probability of a particular one of them having ε is $(1-\epsilon/E)^{\frac{1}{2}m-1}$ the probability that at least one of them shall have ε is:

$$\text{VIII.}\quad (n-1)\,(1-\epsilon/E)^{\frac{1}{2}m-1} \qquad \text{(approx.)}$$

From the form of equation VII it is clear that ε is the energy of activation which would be found experimentally by applying the Arrhenius equation. This has been found to be approximately 65,000 calories[1] for the decomposition of hydrocarbons in confirmation of the conjecture that the various C-C bonds are energetically equivalent. The point then arises as to whether or not this amount of energy concentrated at a bond causes dissociation into free radicals or whether the apparent primary step (excluding dehydrogenation):

$$\text{IX.}\quad C_nH_{2n+2} \longrightarrow \underset{\text{Paraffin}}{C_{n_1}H_{2n_1+2}} + \underset{\text{Olefine}}{C_{n_2}H_{2n_2}}$$

where $n_1 + n_2 = n > 2$ takes place without involving previous dissociation into radicals.

While estimates of the strength of the C-C bonds have varied at least from about 65,000[2] to about 120,000 calories the more recent revisions[3] have been between 90,000 and 115,000 calories. If one accepts a value in the latter range it would preclude primary homogeneous dissociation into free radicals when ε is about 65,000 calories.

Even if 65,000 were an acceptable value for the strength of the C-C bond, the reaction between the two free radicals:

TABLE I

Heat of reaction for $C_nH_{2n+2} \rightarrow C_{n_1}H_{2n_1+2} + C_{n_2}H_{2n_2}$ (values from Int. Crit. Tables, Vol. V)

C_nH_{2n+2}	$C_{n_1}H_{2n_1+2}$	$C_{n_2}H_{2n_2}$	Heat of reaction (Calories/gm. mol. *of reactant*
n propane	methane	ethylene	−16,300
(butane)*	ethane	ethylene	−17,000
	methane	propylene	−17,600
n pentane	propane	ethylene	−20,000
	ethane	propylene	−20,300
	methane	*(butylene)	−19,700
n hexane	butane	ethylene	−17,335
	propane	propylene	−18,235
	ethane	*(butylene)	−17,335
	methane	amylene	−15,935

* Heat of combustion for straight chain compound was not available.

---

[1] See e.g. Pease and Durgan: J. Am. Chem. Soc., **52**, 1262 (1930); Kiss: Ind. Eng. Chem., **22**, 12 (1930).

[2] Kassel: Nature, **125**, 926 (1930); Meeke: Z. Elektrochemie, **36**, 594 (1930).

[3] Hogness: Paper presented at the Indianapolis Meeting of the Am. Chem. Soc., (1931).

$$\text{X.}\quad C_{n_1}H_{2n_1+1} + C_{n_2}H_{2n_2+1} \rightarrow C_{n_1}H_{2n_1+2} + C_{n_2}H_{2n_2}$$

would be exothermic to the extent of about 70,000-100,000 calories, since IX is endothermic to the extent of 15,000-20,000 calories (see Table I). X is a metathetical reaction, so there is no evident reason for the homogeneous formation of free radicals even if the activational energy were sufficient, which it does not appear to be.

One might object to IX as the primary step on the grounds that it is too complex, since it involves the migration of a hydrogen atom from a carbon atom one removed from those forming the bond which is in the act of rupture. However, Dr. E. Q. Adams has suggested that the primary act might be a dislocation of the electron pair forming the C-C bond giving rise to such partial ionization as is possible with 65,000 calories. The negative ion could then move in a path of constant energy as a result of the same vibration which caused the partial ionization picking up H^+ from the second carbon atom to form the olefine and paraffin. This mobility at greater distance would be possible because we are now dealing with an inverse square force law and "undirected" valence force.

The primary act after partial ionization might also involve shifts in electric charges only. Thus IX is not necessarily physically improbable as a primary act, the necessary condition being merely that the completion of the process after the partial ionization be probable compared with reversion to the original state.

If IX is assumed to be the first step it may occur symmetrically except in the case of the terminal bonds. One may, as a first approximation, give them half weight in arriving at the total probability of a C-C bond breaking. VIII would then become

$$\text{XI.}\quad (n-2)\,(1-\epsilon/E)^{\frac{1}{2}m-1}$$

and the final general expression for rates of decomposition (exclusive of dehydrogenation) would become

$$\text{XII.}\quad -\frac{dN}{dt} = N\,(n-2)\,\nu e^{-\epsilon/RT} = Nk$$

This formula (XII) would make butane decompose twice as fast as propane. This may be true within the limit of accuracy of Pease's data as seen from Table II:

TABLE II

	Temp. °C. 625 k	% Conversion	Temp. °C. 650 k	% Conversion
Propane	0.0072	16.9	0.029	14.7
	0.0057	20.0	0.019	20.8
Butane	0.020	22.0	0.058	26.5
	0.016	31.2	0.039	36.5

Equation XII would make an exception of ethane whose C-C bond could not break at all by an analogous process. This is supported by the experimental evidence[1] since the relative stability of ethane compared with propane is much greater than would be expected if the primary decomposition step were the same in each,[2] and dehydrogration occurs almost exclusively as the first thermal reaction with this paraffin.

Existing analytical data on the thermal decomposition products of normal paraffins are not very clear cut because the cracking was generally carried too far. However Hague and Wheeler found 40% of normal butane decomposed by splitting the middle C-C bond and 35% by splitting the terminal bonds whereas Hurd and Spence found 55% by splitting the terminal bonds and 40% by splitting the middle one.[3] This supports the assumption involved in Equation XI.

The percentages by weight and by volume of all primary decomposition products to be expected in the early stages of reaction on the basis of the theory outlined are shown in Table III. It is seen that they may be expressed in terms of n (from the composition formula C_nH_{2n+2} of the reactant).

Comparison with observed velocity constants.

In applying formula XII to the thermal decomposition of the straight chain paraffins the best method of evaluating ϵ is to calculate it from a known velocity constant. n is always known. There is some doubt as to the precise value to be used for v. Investigations of the Raman effect give 990 as the wave number for the vibrations of the C-C bond in ethane.[4] On the other hand there are more rapid vibrations involving C-C bonds in the higher members of the series. Dr. D. H. Andrews has suggested that 1150 would be a good value to use. This would correspond to $v = 3.45 \times 10^{13}$.

Propane. For propane $n = 3$. Pease (loc. cit) found the unimolecular velocity constant at 650°C to be 0.029 at a contact time of 5.5 sec. and a conversion of 14.7 per cent, which is chosen because it represents the smallest degree of cracking of any of the experiments reported. Substituting these values in XII one gets a value of 63,597 calories for ϵ.

In other words Pease's decomposition rate for propane under these conditions can be reproduced exactly if ϵ is taken to be 63,597 calories compared with a value estimated from the temperature coefficient to be 65,000 calories (approx.).

n butane. In the case of butane, $n = 4$ and the other values to be used in equation XII are the same as for propane. k at 650° should thus be 0.58.

---

[1] Summary, Hurd: "Pyrolysis of Carbon Compounds," p. 52 (1929); Pease: J. Am. Chem Soc., 50, 1779 (1928).

[2] e.g. free radical formation which the writer feels is probable for ethane if the C—C bond breaks unimolecularly and homogeneously.

[3] J. Am. Chem. Soc., 51, 3354 (1929).

[4] Smekal: Z. Elektrochemie, 36, 619 (1930).

TABLE III

C atoms in fragment	n − (n − 1) ..		n − 5		n − 4	
	Paraffin	Olefine	Paraffin	Olefine	Paraffin	Olefine
Prob. of formation of fragment	$\frac{1}{n-2}$	0	$\frac{1}{n-2}$	$\frac{1}{n-2}$	$\frac{1}{n-2}$	$\frac{1}{n-2}$
Wt. % formed	$\frac{100\,(16)}{(n-2)\,(14n+2)}$	0	$\frac{100[14(n-5)+2]}{(n-2)\,(14n+2)}$	$\frac{100[14(n-5)]}{(n-2)(14n+2)}$	$\frac{100[14(n-4)+2]}{(n-2)\,(14n+2)}$	$\frac{100[14(n-4)]}{(n-2)(14n+2)}$

C atoms in fragment	n − 3		n − 2		n − 1	
	Paraffin	Olefine	Paraffin	Olefine	Paraffin	Olefine
Prob. of formation of fragment	$\frac{1}{n-2}$	$\frac{1}{n-2}$	$\frac{1}{n-2}$	$\frac{1}{n-2}$	0	$\frac{1}{n-2}$
Wt. % formed	$\frac{100[14(n-3)+2]}{(n-2)\,(14n+2)}$	$\frac{100[14(n-3)]}{(n-2)(14n+2)}$	$\frac{100[14(n-2)+2]}{(n-2)\,(14n+2)}$	$\frac{100[14(n-2)]}{(n-2)(14n+2)}$	0	$\frac{100[14(n-1)]}{(n-2)(14n+2)}$

The probability of formation of a fragment gives also the average volume (vapor phase) of product corresponding to this number of carbon atoms per unit volume of reactant vapor decomposing.

Pease actually found 0.58 and 0.39. The percent conversion in these cases however, was greater than in the experiment used as a "standard" for propane, and since his constants fell with greater per cent conversion the true comparison may be somewhat poorer.

n pentane. The comparison with experiment in this instance is based upon the work of Calingaert.[1] While he did not calculate velocity constants, he states that at 600°C ± 3° with a flow of 1/6 gram mole per hour, only 30% of the original n pentane decomposes. His furnace tube[2] had an inside diameter of about 21 mms. and an effective length of about 70 cms. This corresponds to a heating time of 73.2 seconds, which corresponds to an experimental value of $k = 0.00487$.

The theorectical value for k calculated from equation XII using $n = 5$ is 0.01192.

n Hexane. While normal hexane has been thermally decomposed by various investigators[3] none of the data are very suitable for calculation of velocity constants.

Haber and Samoylowicz calculated their heating time to be about 1 second, and found 73.27% (corresponding to $k = 1.014$) of the hexane to be decomposed when a vapor bath of stannous chloride was used as the heating medium, which they considered to give them a temperature of 606°C. However, Maier[4] considers 622.5°C a better value for the boiling point of stannous chloride.

At this temperature, using $n = 6$, equation XII gives a theoretical value $k = 0.0399$. This is at first sight disappointing. However, Haber and Oechelhaeuser using a tube by no means correspondingly smaller but with an electric furnace as the heating medium found no "erhebliche" decomposition of the n hexane at 606 (thermocouple). Similarly Norton and Andrews found but incipient decomposition of hexane at 600° (air thermometer) with a heating time of the order of 10 seconds. Also Hague and Wheeler report that but little n hexane was decomposed at 600°C with a heating time of about 57 seconds. One may, therefore, conclude that Haber and Samoylowicz must have had serious superheating, and the thermal decomposition of n hexane does not contradict equation XII.

No experimental data suitable for the evaluation of thermal decomposition velocity constants could be found for straight chain paraffins between hexane and hexadecane.

Hexadecane. The thermal decomposition of hexadecane has been rather carefully investigated by Gault and Hessel[5] using a product prepared from cetyl alcohol.

---

[1] J. Am. Chem. Soc., 45, 130 (1923).

[2] Private communication.

[3] Norton and Andrews: Am. Chem. J., 8, 1 (1888); Haber and Samoylowicz: J. Gasbel., 1896, 45; Haber and Oechelhaeuser (ibid); Hague and Wheeler: J. Chem. Soc. 131, 378 (1929).

[4] Bur. Mines Tech. Paper No. 360 (1925); Int. Crit. Tables, Vol. I.

[5] Ann. Chim., 2, 319 (1924).

In a tube 2.15 cms. inside diameter and an effective heating length of about 60 cms., when the flow rate was 1 c.c. per minute (corresponding to a heating time of about 65 secs.) at 470° (thermocouple), 0.18 liters of gas were obtained per 100 gms. of substance passed through the furnace, this experiment representing incipient decomposition. If this gas is considered to be methane, ethane, ethylene, propane, propylene, butane, and butylene in amounts calculated from Table III, N molecules of hexadecane decomposing would give N/14 molecules of methane, 2N/14 molecules of ethane and ethylene, 2N/14 molecules of propane and propylene and 2N/14 molecules of butane and butylene, or 7N/14 molecules of gas. Using 0.775 as the specific gravity of hexadecane this would give 0.049 liters of gas per gram of hexadecane decomposed. The figure 0.18 liters per 100 grams of hexadecane passed through the furnace therefore corresponds to 3.675% decomposition. The initial boiling point of liquid product obtained under these conditions was 100°C. so that it could not have contained appreciable quantity of the lower hydrocarbons. This extent of decomposition corresponds to $k = 0.000576$.

If the pentane had been included in the off gas (as is probable from the initial boiling point of the liquid product) the velocity constant becomes 0.00044.

From formula XII with $n = 16$, k is 0.000091. This is a rather impressive agreement in view of the large jump from the "standard" propane to hexadecane, the uncertain method of estimating the per cent decomposition (dissolved gases and H_2 produced would bring the two values of k closer together) and in view of the fact that one experiment was performed at 650°C. and the other at 470°C, and by different experimenters with different apparatus.

The energy of activation which would be required to make an exact fit with equation XII and the experimental value of $k = 0.00044$ is 61, 265 calories. This value of ϵ would in turn give $k = 0.1038$ for the decomposition velocity constant of propane at 650°C instead of 0.029. This would give the initial rate while the value 0.029 is for 14.7% decomposition. Since Pease reported a sharp falling off in the constants with greater decomposition, $k = 0.1038$ may constitute excellent agreement for the initial rates.

Only those experiments were considered in the above calculations which were carried out in non-metallic unpacked tubes, in which case the reactions may reasonably be assumed to be predominantly homogeneous.

Frenkel[1] has objected to the Polanyi-Wigner equation VII for molecules which are not extremely large on the grounds that the "inner temperature T" (determined by vibrations) of molecules may not coincide with the external gas temperature T_0 (determined by translational and rotational energy), and derives the complex formula for the unimolecular decomposition velocity of molecules:

---

[1] Z. Physik, 62, 49 (1930).

$$\text{XIII.}\quad A = \sqrt{2\pi}\, Cve^{-\sqrt{m^2+4\alpha\beta}} \frac{W_1^{(m+1)}}{(m^2+4\alpha\beta)^{1/4}}$$

Where $\alpha = 1/kT_0$

$\beta = \epsilon(m + 1)$

v = vibration frequency

m = no. of internal "square terms" − 1.

ϵ = (as previously defined)

$w_1 = m/2\alpha + \sqrt{(m/2\alpha)^2 + \beta/\alpha}$

$C = \dfrac{N}{m!\,(k\,T_0)^{m+1}}$

In the derivation of this expression for "small" molecules, Frenkel used $ve^{-\epsilon/kT}$ as the decomposition rate of active molecules. This appears to be an analogous assumption to the one he wished to correct since the exponential term would be exact only for large molecules. At any rate equation XIII (when multipled by (n − 2) to give an equation similar to XII cannot be made to fit the data on the thermal decomposition of straight chain paraffins with anything like the accuracy of equation XII.

If one evaluates ϵ from Pease's data on propane, it turns out to be about 99,500 calories. This is the order of magnitude of recent estimates of the strength of the C-C bond and would suggest dissociation into free radicals. However, using this value for ϵ the data of Gault and Hessel are not reproduced by a factor of 10^7 (using five place log tables).

Furthermore the value of A (theor.) from

$$\text{XIV.}\qquad \frac{d \ln k}{dT} = \frac{A}{RT^2}$$

according to equation XIII using 99,500 for ϵ, comes out to be only 49,700 calories instead of the value 65,000 (approx) found by Pease and 61,000 to 63,700 from equation XII.

Possible contribution of chains. Since cracking reactions are endothermic, one would not expect thermal chains to play a part. One must give more consideration, however, to "material" chains, since they have been shown[1] to play an important part in some types of reactions, and especially since Bonhoeffer and Harteck[2] have found hydrogen atoms to have a vigorous cracking action on saturated hydrocarbons at temperatures not greater than the usual cracking temperatures (below 500°C). The H atoms could act in the following ways:

$$\text{XV.}\quad C_nH_{2n+2} + H \rightarrow \underset{\text{free radical}}{C_nH_{2n+1}} + H_2 \text{—about 15,000 calories}$$

---

[1] Polanyi and Co-workers: Z. physik. Chem., **IB**, 3, 21, 30, 62 (1928); and elsewhere; Alyea and Haber: 24, 4676 (1930), and others.

[2] Z. physik. Chem., **139**, 64 (1928).

Since the strength of the C-H bond broken is thought to be about 115,000 calories[1] and that of the H-H bond 98,000 calories[2]

XVI. $C_nH_{2n+2} + H \rightarrow C_{n_A}H_{2n_A+2} + C_{n_B}H_{2n_B+1}$ + about 0 to 25,000 calories

XVI would be expected to take place more readily than XV on energetic grounds. It is the reaction which Bonhoeffer and Harteck considered to account for their results. The following facts, however, should be stressed. Firstly, as far as the H atom is concerned, the chain ends at its first link, and therefore, if the "material chain" is to be propagated, it must be accomplished by hydrocarbon radicals. Secondly, in the conceivable formation of H atoms and hydrocarbon radicals by primary cracking according to:

XVII. $C_nH_{2n+2} \rightarrow C_{n_A}H_{2n_A+1} + C_{n_B}H_{2n_B+1}$ − 90,000 to 115,000 calories

and

XVIII. $C_n H_{2n+2} \rightarrow C_n H_{2n+1} + H$—about 115,000 calories

XVIII would be expected to occur relatively infrequently, because XVII is easier energetically and it is very much easier to split off H_2 than H in any case. Consequently, if material chains are propogated, practically the whole burden must fall upon hydrocarbon radicals. With them, the assumed reactions would be:

XIX. $C_n H_{2n+2} + C_{n_A} H_{2n_A+1} \rightarrow C_{n_C} H_{2n_C+2} + C_{n_D} H_{2n_D+1}$ + 0 calories

where $n_A + n = n_C + n_D$

Energetically this reaction might go with considerable speed, as might the corresponding dehydrogenation reaction

XX. $C_n H_{2n+2} + C_{n_A} H_{2n_A+1} \rightarrow C_{n_A} H_{2n_A+2} + C_n H_{2n+1}$ + 0 calories

The reaction

XXI. $C_n H_{2n+2} + C_{n_A} H_{2n_A+1} \rightarrow C_{(n+n_A)} H_{2(n+n_A)+2} + H$—about 0 to 25,000 calories

must be considered relatively improbable, as must the reaction

XXII. $C_n H_{2n+2} + C_{n_A} H_{2n_A+1} \rightarrow \underset{\text{olefine}}{C_{n_A} H_{2n_A}} + C_n H_{2n+1} + H_2$ —about 30,000 to 50,000 calories

on energetic grounds, and

XXIII. $C_{n_A} H_{2n_A+1} + H_2 \rightarrow H + C_{n_A} H_{2n_A+2}$ + about (—10,000 to + 15,000 calories)

and

XXIV. $C_{n_A} H_{2n_A+1} + C_{n_B} H_{2n_B+1} \rightarrow C_{n_A} H_{2n_A} + C_{n_B} H_{2n_B+2}$ + about 70,000–100,000 calories

on account of the small concentration of radicals and of hydrogen in the early stages of cracking. Olefine formation would thus be awkward.

---

[1] Mecke: Z. Elektrochemie, 36, 594 (1930). Some estimates of the strength of the C—H bond are lower than this. The precise value chosen would affect some of the following equations. However, if the C—H bond is stronger than the C—C bond, which represents the consensus of opinion, the sense of the argument is not greatly affected by the values chosen for each.

[2] Franck: Z. Elektrochemie, 36, 587 (1930).

TABLE IV

n = no. of c atoms in the straight chain paraffin being cracked
n_r = no. of c atoms in the radical assumed to be causing the cracking

c atoms in radical formed	1	2	$n - 1$
Probability of its formation	$\frac{1}{3n + 1}$	$\frac{1}{3n + 1}$	$\frac{1}{3n + 1}$
c atoms in paraffin formed	n_r	$n_r + 1$	. . . .
Probability of its formation (one link)	$\frac{2n + 2}{3n + 1}$	$\frac{1}{3n + 1}$	. . . .
		When the chain has N links	
c atom in paraffin formed	1	2	. . . . $n - 1$
Prob. of its formation	$\frac{1}{N}\left[\frac{2n+2}{3n^2-2n-1} + \frac{(N-1)(2n+2)}{(3n+1)^2}\right]$	$\frac{1}{N}\left[\frac{2n+3}{3n^2-2n-1} + \frac{(N-1)(2n+3)}{(3n+1)^2}\right]$	$\frac{1}{N}\left[\frac{3n}{3n^2-2n-1} + \frac{(N-1)(3n)}{(3n+1)^2}\right]$

Proportions of various paraffins which would be obtained by radical cracking of butane

c atoms in paraffin formed	1		2			3		
Direct cracking	N = 10	N = 10 corrected	Direct cracking	N = 10	N = 10 corrected	Direct Cracking	N = 10	N = 10 corrected
½	0.0789	0.1775	½	0.0866	0.1951	0	0.0947	0.2133

TABLE IV (Continued)

c atoms in radical formed	n	2n − 2	2n − 1
Probability of its formation	$\frac{2n+2}{3n+1}$		
c atoms in paraffin formed	. . . .		$n_r + n - 1$
Probability of its formation (one link)	. . . .		$\frac{1}{3n+1}$
When the chain has N links			
c atom in paraffin formed	n	2n − 2	2n − 1
Prob. of its formation	$\frac{1}{N}\left[\frac{n-1}{3n^2-2n-1}+\frac{(N-1)[(2n+2)^2+n-1]}{(3n+1)^2}\right]$	$\frac{1}{N}\left[\frac{1}{3n^2-2n-1}+\frac{(N-1)(2n+3)}{(3n+1)^2}\right]$	$\frac{1}{N}\left[\frac{(N-1)(2n+2)}{(3n+1)^2}\right]$

Proportions of various paraffins which would be obtained by radical cracking of butane

c atoms in paraffin formed	5			6			7		
	Direct cracking	N = 10	N = 10 corrected	Direct cracking	N = 10	N = 10 corrected	Direct cracking	N = 10	N = 10 corrected
	0	0.069	0.1555	0	0.0611	0.1377	0	0.0532	0.1200

N = 10 corrected gives the probability corrected for the formation of butane again, the probability of whose occurrence is 0.55621. See Table III for the results of direct cracking of the paraffins formed by direct cracking of butane ½ would be methane and ½ ethane.

With a radical mechanism of this type, then, one would get into the following difficulties:

a. On account of the infrequency of reaction XXIV compared with XIX and XX one would have a high ratio of paraffin (other than the starting material) to olefines if the chains are of considerable length. This does not correspond with experience,[1] and one would then have to fall back upon dehydrogenation of the paraffins formed to account for the proportion of olefines. But this is objectionable since this type of dehydrogenation is not more rapid than the original cracking step.

b. It is difficult to account for the unimolecularity of the decomposition for even if an equilibrium concentration of radicals were maintained say by a rapid surface reaction, their concentration would, nevertheless, depend upon the concentration of the hydrocarbon from which they were formed in accordance with equation XVII.[2]

c. Radical cracking would lead to synthesis of higher hydrocarbons even in the early states and at low pressures. The probability of the formation of any radical from CH_3 to $C_{(n-1)}H_{2(n-1)+1}$ by primary decomposition of the hydrocarbon C_nH_{2n+2} is $1/n-1$. The probability of this radical forming any radical from CH_3 to C_nH_{2+1} in an encounter with the hydrocarbon is given in the second horizontal row of Table IV. These probabilities will carry through other links in the chain approximately unchanged in the early stages of cracking. (Only reactions XIX and XX have been considered in Table IV. The others would not change the weight of the present argument). The probabilities for the formation of any paraffin from any radical $C_{n_r}H_{2n_r+1}$ are shown in the fourth horizontal row of the table. N_r cannot exceed $(n-1)$ in the primary decomposition and cannot exceed n in the subsequent steps. It is considered that any value involving C—C bond splitting from the upper limit down to $C_r = 1$ is equally probable when effected by radicals. The links in the chain after the first are approximately the same. On these grounds the probability for the formation of any paraffin by a chain of X links is shown in the sixth horizontal row of Table IV. In the eighth horizontal row of this table is shown a comparison of the proportion of each possible paraffin (in the early stages of cracking) as calculated in the case of butane for direct cracking (to paraffin and olefine) and for cracking by a radical chain of 10 links. It is seen that the main result by radical cracking is regeneration of the original paraffin. When this is corrected for, the final results are shown in the last horizontal row of the table. It is seen that synthesis is almost as probable as "cracking" even in the initial stages of the reaction. While heavier hydrocarbons do occur in cracking, they are generally explained as being due to the polymerization of olefines and would not be expected to be important in the early stages of cracking at low pressures. In confirmation of this Gault and Hessel[3] found the final

---

[1] See e.g. Pease: loc. cit; Calingaert: loc. cit.

[2] This was pointed out by Dr. E. Q. Adams.

[3] loc. cit.

boiling point of the liquid product obtained by cracking hexadecane, under the conditions used above for calculation, to correspond pretty closely to the boiling point of hexadecane.

d. It seems unlikely that free radicals should be formed by thermal decomposition of hydrocarbons higher than ethane when reaction XXIV can occur with the evolution of some 70,000 to 100,000 calories, and with no evident kinetic impediment, before the radicals leave the sphere of reaction.

Against this, one has the evidence of Paneth and co-workers[1] and of Taylor and Jones[2] that free radicals are formed in the thermal decomposition of metal alkyls, whereas reaction of the type

$$\text{XXV.}\quad Hg\ (C_2H_5)_2 \rightarrow Hg + C_2H_6 + C_2H_4$$

are possible in these cases also, and are energetically probable since the reactions

$$\text{XXVI.}\quad Hg\ (C_2H_5)_2 + C_2H_5 \rightarrow HgC_2H_5 + C_2H_4 + C_2H_6$$

and

$$\text{XXVII.}\quad Hg\ (C_2H_5) + C_2H_5 \rightarrow Hg + C_2H_4 + C_2\,H_6$$

are probably exothermic and of a type which should require small activational energy.[3] The argument for a reaction of this type XXIV is however less impelling for the thermal decomposition of metal alkyls than of hydrocarbons since reactions XXVI and XXVII are exothermic only to the extent that the energy of formation of $C = C$ from $C - C$ exceeds the energy of disruption of the metal $-$ C bond (ignoring possible energetic changes in Hg), instead of about 70,000 to 100,000 calories as in the case of reaction XXIV.

The ethylene or ethane in XXV might come out of the reaction sphere with energy considerably above the average for the temperature in question. The possibility of "hot" ethylene or ethane molecules giving the phenomena attributed to free ethyl radicals was not developed by Paneth and Hofeditz or by Taylor and Jones although the former authors[4] report that ethylene which had been strongly heated exhibited some of the properties which they had attributed to free radicals.

A paper on the decomposition of paraffins[5] has just appeared, in which the first step is assumed to free radical formation. Reaction XIX was not considered as a possibility. The decomposition of radicals themselves was thought to play an important part. In general Rice's point of view is widely different from that of the author.

The author is indebted to Dr. E. Q. Adams of the Lamp Development Laboratory of the Incandescent Lamp Department of the General Electric

---

[1] Paneth and Hofeditz: Ber., 62B, 1335 (1929); Paneth and Lautsch: Naturwissenschaften, 18, 307 (1930); Nature, 125, 564 (1930).

[2] J. Am. Chem. Soc., 52, 1111 (1930).

[3] Polanyi: loc. cit.

[4] Loc. cit. p. 1343 (footnote).

[5] F. O. Rice: J. Am. Chem. Soc., 53, 1959 (1931).

Company for a critical review of the manuscript and for the suggestions attributed to him in the text. A realization of the theoretical opportunities offered by the decomposition of paraffins has resulted from a research association with the Standard Oil Company of Ohio.

Summary

The Polanyi-Wigner equation for unimolecular velocity constants, $k = \nu e^{-\epsilon/RT}$ has been modified to be appropriate for the thermal decomposition of straight chain paraffins and the modified equation has been shown to fit existing data for these reactions, within their probable limits of experimental accuracy, in the early stages of decomposition.

Frenkel's modification of this equation is not in agreement with the experimental results for straight chain hydrocarbons.

The possibility of the participation of material chains in cracking has been examined and they do not seem to play a prominent part.

The thermal decomposition of straight chain paraffins offers an avenue of approach to a highly refined kinetic theory of reaction velocity.

Western Reserve University,
Cleveland, Ohio,
May, 11, 1931.

NEW BOOKS

The Dynamic Universe. *By James MacKaye. 21 × 15 cm; pp. x + 308. New York: Charles Scribner's Sons, 1931. Price: $3.50.* The chapters are entitled: separating the physics from the metaphysics of relativity; dimensional and non-dimensional explanations; the Rosetta stones of relativity; the radiation theory; questioning the radiation theory; the equations versus the assumptions of relativity; questioning the relativity assumptions; suggestions towards the extension of the radiation theory.

"Despite the standing of the theory of relativity in our day, few physicists pretend to understand it. Their position generally is one of suspended judgment. They acknowledge the competence of its sponsors and its power to predict, but its language puzzles and its paradoxes perplex them. A situation of great confusion prevails. There are reasons for believing that this state of affairs may be traced to two causes; first, a verbal confusion due to the violation of certain rules of intelligibility; and, second, a mistaken identity of magnitudes," p. 7.

"Examination of Einstein's work shows that he has constructed by definition a series of ideal magnitudes, to which he has assigned the name 'time', 'length', 'space', 'velocity', 'energy', etc. In so doing he is following the rules which guide the pure mathematician, and Eddington tells us that: 'The pure mathematician deals with ideal quantities defined as having the properties which he deliberately assigns to them.' That is, Einstein does not *discover* properties (*e.g.*, relativity) of time, space, etc., by *observation*. He *assigns* them by *stipulation*. In short, he begs the question of whether time, space, length, energy, etc., are relative or not by defining them to be so, thus removing the issue from all debate," p. 11.

"Thus in place of the statement, so commonly made by physicists, that 'time and space are relative'—which is ambiguous— we shall have two statements, namely, that 'Einsteinian time and space are relative,' and 'Newtonian time and space are not relative,' and these two statements will be both unambiguous and true," p. 23.

"In the previous chapter it was noted that Einstein, by changing the meanings of the words time (T) and length (L), obtains equations which are more successful in predicting certain phenomena than those which retain the classical definitions resting on the Newtonian definition of 'simultaneity' specified on page 16," p. 26.

"Thus the process used by Einstein is a special case of a very general one, which may be called the process of discovering 'dimensional' explanations, so called because it consists in redefining one or more of the fundamental dimensions, time, length and mass, of which most other physical magnitudes, such as velocity, acceleration, energy, etc., are functions. It may be briefly described as a process for transferring to one or more of these dimensions the variation of physical causes in such a manner that the variation of the cause, if any, is expressed in the formula by a variation (relativity) of the appropriate unit or units, and hence can be attributed to that relativity. Instead of leaving the units constant, as the Newtonians do, and correcting for the varying cause, the cause is assumed constant, and the correction made by varying the unit—both processes giving the same result. Any law of nature, in fact, empirical or otherwise, may be thus dimensionally expressed, disappearing as a law controlling phenomena, and reappearing as a law controlling the units in which phenomena are measured. All that is required is ability to make the units proper functions of the proper variables. Given the requisite mathematical ingenuity, as many kinds of relative time, length, space, mass, velocity, energy, etc., as we please may be 'discovered', and they will all have the mysterious power which the kinds devised by Einstein are found to have," p. 27.

"The conclusion reached by means of the Fizeau experiment is confirmed by the fact that Einstein gives a similar dimensional explanation of the Doppler effect and of the aberration of light (including the Airy effect), both of which are radiation displacements caused by the motion of matter. These three effects, therefore, constitute veritable Rosetta

Stones of Relativity, for in their explanations the mysterious dimensional language of relativity appears side by side with the familiar (non-dimensional) language of radiation displacement, and *all three Stones agree about the translation*," p. 44.

"Now by far the greater part of the radiation familiar to science is a function of temperature. The higher the temperature of a body, the more intensely in general it radiates, and the shorter becomes the average wave-length of the radiation. But this relation between degree of radiation and temperature is not universal, and there is at least one kind of short-wave radiation known to science which is independent of the temperature of the source—the gamma radiation from radium. On first thought it would appear that this sort of radiation is probably exceptional and plays a minor part in physical phenomena, since the radiation dependent upon temperature appears so much more universal in nature. On second thought, however, some doubts may arise. What appears to man to predominate in nature will depend, in part at least, on his capacity to observe, and we may surmise that his capacity to observe light and heat may be much greater than his capacity to observe various other radiations, which may nevertheless exist. Since radio broadcasting has become common, for instance, the rooms of our houses are filled with all kinds of strange radiations—vast potentialities of sensation—which we should never suspect did we not possess radio receiving apparatus which extends our powers of detecting radiation—and this radio radiation, by the way, is another kind that is independent of temperature. Perhaps, then, radiation depending upon temperature—thermal radiation—appears to predominate over the non-thermal kind only because of the predominance of man's capacity to detect that particular kind of radiation," p. 48.

"According to the radiation theory, these equations are dimensional disguises for Doppler-displacements caused by the motion of material particles relative to the ether, and hence are functions of the rate of motion of said particles relative to one another; because the motion of any two material particles involves motion of one or both relative to the ether, just as two bodies in a room filled with undisturbed air cannot move relative to each other unless one or both move relative to the air," p. 67.

"In order to present evidence that the above answer to the question propounded in this section is the correct one, we may follow up the interpretation of relativity effects provided by the Rosetta Stones of the third chapter, by inquiring more minutely into the resemblance between such effects and Doppler-displacements. Then, if relativity effects are dimensional disguises for such displacements, they will:

"(1) Be confined to phenomena associated with the relative motion of bodies—and they *are* thus confined.

"(2) Be a maximum in directions coinciding with the direction of motion—and they *are* a maximum.

"(3) Be zero in directions at right angles thereto—and they *are* zero.

"(4) Diminish from a maximum to zero through intermediate directions at a rate determined by the cosine law—and they *do* diminish at that rate.

"(5) Approach zero as the velocity approaches zero—and they *do* approach zero.

"(6) Approach infinity as the velocity approaches that of radiation—and they *do* approach infinity.

"(7) Reverse direction when the velocity exceeds that of radiation, so that 'time' appears to run backward, and thus effect to precede cause—and they *do* thus reverse direction.

"(8) Be relative to the motion of an observer observing by means of signals or causal impulses moving with the velocity of light—and they *are* thus relative," p. 68.

"It would seem as if the wave-mechanics theory required a radiation theory on which to rest as much as or even more than, the relativity and the classical theories. On the assumption of a static ether or an empty space, the waves of which its particles are composed are required to be perpetual motion machines, apparently moving around a centre in some manner that waves are never known to move. With a radiation theory all this would change. The atom, or other particle, considered as a wave mechanism, would react in the normal manner of waves. It would not need to be a conservative system in itself, but could radiate freely to space and yet maintain its integrity, being in dynamic equilibrium with its surroundings. Deprived of such resources, indeed, it seems impossible to imagine how an atomic wave structure could act in the slightest degree as radiation is known to act, and yet be in accord with the first law of energy," p. 85.

"That the heavenly bodies are subject to no retardation in their motion through space appears, on the old theories of matter, to be a fact difficult to reconcile with the existence of an ethereal medium which behaves like an elastic solid. But if we accept the theory that matter consists of nodes or standing waves, or some other modification of radiation, it will become at once evident that there is no reason why it should be retarded in space by the process, whatever it is, whereby one solid body obstructs the movement of another in contact with it. Thus the theory to which the whole wave-mechanics movement is trending changes our view of the nature of impenetrability and reconciles the unimpeded motion of the heavenly bodies through space with the elastic solid theory of the ethereal medium. In short, if matter is composed of radiation in such a medium, there is no more reason *a priori* why it should be impeded than light or any kind of radiation existing therein. As the radiation theory is in harmony with this trend, the old objection to the elastic solid theory does not apply to it," p. 131.

"Another comparison between the total matter theory and the radiation theory is worth noting at this point. The former is incapable of verification. Mill's canons of induction embody the rules whereby causal may be distinguished from non-causal associations in nature but none of them can be applied to Einstein's hypothesis since there seems no known way of varying the relation of material bodies to the sum total of matter in the universe. Even if we assume that moving them about on the earth's surface or observing their motions in the heavens constitutes such a variation, no confirmation of the hypothesis is forthcoming. In fact, the hypothesis is equivalent to the old theories of the will of God, or pre-established harmony. No imaginable behavior of material bodies can either confirm or refute it. There is no testing such hypotheses, and they are as well—and as ill—adapted to explain the yellowness of gold or the wetness of water as the inertial and gravitational behavior of bodies. Any one of the three here mentioned *may* be the true explanation—and one is about as plausible as another—but there is no way by which any process or reason can distinguish between them.

"How comes it then that such an hypothesis has been seriously proposed? The answer is not far to seek. It is because it is the only hypothesis, likely to commend itself to a physicist, which is left when once the theory that all motion is relative to material bodies is accepted. The relativists having definitely accepted this theory, therefore, are forced to accept its consequences. Hence the 'total matter in the universe' theory. In short, for the relativist, it is Hobson's choice. In view of the inertial behavior of bodies, including their rotational behavior, it is the only alternative which is not obviously arbitrary. But being as unverifiable, it is as useless, as the theory of pre-established harmony.

"The radiation theory, on the other hand, is subject to no such criticism. The experiments described in the last section and many others of like character show, if Mill's canons of induction are of any value, that the gravitational behavior of bodies is causally connected with the size and proximity of other bodies, whereas the inertial behavior is not, which is what the radiation theory predicts. This agreement with the facts, to be sure, does not prove the radiation theory to be true, because some other theory may be proposable which would predict them also. But as between the two theories under comparison, the decision of reason is not doubtful. The radiation theory provides an explanation of the inertial and gravitational behavior of bodies, whereas the total matter theory can neither explain nor predict anything. The radiation theory is therefore confirmed so far as the facts here under consideration can confirm it, whereas the total matter theory is not even confirmable," p. 255.

The reviewer is of course not qualified to say whether the radiation theory is right or wrong; but Mr. MacKaye has made a very interesting presentation of his point of view and one can at least hope that he may be right.

Wilder D. Bancroft

Recent Advances in Analytical Chemistry. *By C. A. Mitchell, assisted by ten contributors. Vol. I. Organic Chemistry. 20 × 13 cm; pp. x + 421. Philadelphia: P. Blakiston's Son and Co., 1930. Price: $3.50.* This is the first of two volumes which are being written to present in easily accessible form the latest information on matters connected with analytical chemistry. The present volume on organic analysis is devoted to the analysis of sugars, oils and fats, essential oils, proteins, tannins, cereals, milk and milk products, paper, petroleum and its hydrocarbons, coal and gas. Each chapter has been written by contributors with special knowledge of their subject.

"The general scheme of the work is to give a brief critical summary of the analytical methods (i.e., mainly general principles) in use up to about eight or ten years ago, with references to original literature and English abstracts. From that period onwards, recent developments are dealt with more fully, and concise working details of new methods are given. Some suggestions are also made as to the directions in which future advances in analytical chemistry in the respective subjects are to be expected.

"The work is primarily intended for those who have a general knowledge of chemistry but require information as to the best methods of dealing with the analytical problems on the various fields discussed. It is thus not intended to replace, but to supplement such works as "Allen's Organic Analysis."

The book is well written and the author is to be commended upon the manner in which his purpose in writing the book has been fulfilled.

M. L. Nichols

The Chemical Action of Light. *By N. R. Dhar. 22 × 15 cm; pp. 512. London: Blackie and Son, Ltd., 1931. Price: 25 shillings.* The first chapters of this book are devoted to a general treatment of such subjects as the absorption of light and light sources, and to an exposition of the laws and fundamental theories of photochemistry. The author then reviews the various reactions which have been made the subject of experimental investigation, whilst in the last chapters, he deals with the applications of photochemistry, more particularly with photography, with the assimilation of carbonic acid by green plants, and with certain other biological effects of light. The theory of photochemical phenomena is treated in a very summary fashion, and any value the book may have is due to its containing information on a large number of photo-reactions. The experimental results are however discussed without any critical sense. The author does not distinguish between reactions which have been carefully worked out, and those which have merely been superficially touched on, and which require further study. Similarly, when dealing with contradictory data concerning the same reaction, he seldom uses any discrimination, and groups together results which there is reason to regard as definitive with others which are clearly in error.

Finally, it must be added that Mr. Dhar has rendered his task more easy by a procedure which is certainly convenient from his point of view, but otherwise quite inadmissible. Without making any reference to the fact, he has calmly borrowed from other works a considerable fraction of his own book. In particular, the reviewer has counted nearly one hundred pages (particularly in the early and the last chapters) which are literally translated from the text of his own "Photochimie." Comment seems superfluous.

A. Berthoud

Errata

In the paper by Thayer and Stegeman entitled "The Heat Capacity and Free Energy of Formation of Ethane Gas" the following corrections should be made:—

p. 1509 on the second line from the bottom read 6.945 instead of 6.495;

p. 1510 on the tenth line from the bottom read $C_p = 5.981 + .02193$ instead of $C_p = 5.981 + 0.2193$;

p. 1511 in the second equation read $-63.2T$ instead of $-63.9T$;

p. 1511 in the third equation read $\Delta F = -18595 + 15.88 \ln T$ instead of $\Delta F = -18789 + 15.18 \ln T$.

CONTRIBUTIONS TO THE CHEMISTRY OF BERYLLIUM

Beryllium I. Electrolysis in Non-Aqueous Solvents*

11-68

BY HAROLD SIMMONS BOOTH AND GILBERTA G. TORREY

Introduction

Although the probable usefulness of metallic beryllium has long been recognized, only in very recent years have any successful methods of supplying beryllium in quantity been developed. However, these methods require very carefully purified material and the maintenance of high fusion temperatures. The present research was undertaken to investigate as wide a field as possible of non-aqueous low temperature reduction methods.

The only successful non-electrolytic reduction method uses metallic sodium or potassium.[1] The fine particles of reduced beryllium must be separated from the residues of alkali metal, beryllium salt, and alkali salt formed during reduction. As beryllium is soluble in alkali hydroxide the mix must be extracted with alcohol. The resultant metal is very finely divided, difficult to melt, and usually badly oxidized. W. R. Veazey (U. S. Pat. 1,515,082, Nov. 11, 1924) found that beryllium fluoride when plunged into molten magnesium was reduced and gave a mixture of beryllium and magnesium. When magnesium was plunged into fused beryllium fluoride the reaction was so violent that the materials were blown out of the crucible.

Lebeau and others[2] have electrolyzed fused salts or solutions of beryllium salts in fused solvents. These methods require high temperatures and make the process expensive and difficult to control. Metallic fogs are easily produced particularly when the temperature of the melt exceeds a certain suitable maximum, and thus much of the metal is lost and the efficiency of the process lowered. Lebeau[3] prepared hexagonal crystals of the metal by electrolyzing the fused double fluorides of sodium, or potassium, and beryllium. During our qualitative test of this method, the surface of the melt was continually illuminated by the flashes of light from what was apparently the burning metal. Recently, however, work by another investigator[4] in this field has shown that this method may be used successfully by carefully controlling the fusion tem-

---

* The study of beryllium was begun in this laboratory in 1921 and has been continued by various workers cooperating with the senior author. A preliminary announcement of these papers appeared as a note to the editor in J. Am. Chem. Soc., 52, 2581 (1930). This work was presented at the Symposium on Non-Aqueous Solutions at the Cincinnati meeting of the American Chemical Society, September, 1930.

[1] Wöhler: Ann. Chim. Phys., (2) 39, 77 (1828); Hunter and Jones: Trans. Am. Electrochem. Soc., 44, 35 (1923).

[2] Lebeau: Compt. rend., 126, 744 (1898); Goldschmidt and Stock: Brit. Pat. 192, 970, April 19, 1922; Chem. Abs., 17, 3459 (1923); E. A. Engle's Thesis, University of Illinois.

[3] Elektrochem. Z., 5, 31 (1898); Am. Chem. J., 27, 487 (1898).

[4] Private communication to the Authors.

perature and the current densities. Other fused mixtures have been used but many that were stated to produce metal[1] are now found to be absolutely nonconducting.

Recently the Siemens-Halske method, invented by Stock and Goldschmidt,[2] using sodium-beryllium fluoride in fused barium fluoride has been developed to a satisfactory commercial scale process, though it is said that barium-beryllium fluoride is now used. The metal is obtained in massive form but extremely high temperature operation is an undesirable factor.

Many salts possess a considerable solubility in non-aqueous media and their solutions are known to conduct electricity. Several workers[3] have investigated certain properties of these solutions but they have interested themselves mainly in the determination of conductivities at various dilutions and therefore have not obtained cathode products. Since certain other metals had been prepared by electrolysis of non-aqueous solutions of their salts this method seemed to have possibilities in the preparation of metallic beryllium. Except for the process of Siemens-Halske attempts to prepare metallic beryllium have resulted in precipitation of small non-coherent crystals. In the non-aqueous solutions it was hoped that a coherent plating of metallic beryllium could be obtained.

Choice of Solvents

Beryllium compounds have such a remarkable tendency to hydrolyze in the presence of the slightest traces of moisture that all solutions containing water or which furnish hydroxyl ion are useless. Fortunately many beryllium salts are soluble in non-aqueous solvents and the solutions are stable in the absence of moisture. Solvents from which other metals have been prepared by electrolysis of solutions of their salts were first tried. Plotnikoff[4] prepared metallic aluminum by the electrolysis of a solution of aluminum bromide in ethyl bromide. H. E. Patten[5] repeated the work and stated that aluminum could be deposited with a current density of .23 amperes per square decimeter. Kahlenberg[6] has prepared metallic lithium from a solution of the chloride in pyridine. Arguing from the usual analogy between first members of successive series of the periodic table and especially of the transitional elements, it seemed reasonable to expect that beryllium could be prepared from pyridine solutions of its salts. This phase of the study will be discussed in the second part on the electrolysis of beryllium salts dissolved in organic nitrogen compounds. The organic salts of beryllium in particular are very soluble in such liquids as alcohol, chloroform, and ethyl bromide. Apparently the conductivities of these solutions have never been investigated.

---

[1] Warren: Chem. News, **72**, 310 (1895); Z. anorg. Chem., **13**, 364 (1895); Borchers: Z. Elektrotech. u. Elektrochem., **1895**, 39; J. Chem. Soc. **70**, (2), 521 (1896).

[2] Illig: Trans. Am. Electrochem. Soc., **54**, 211 (1928).

[3] Cady: J. Phys. Chem., **1**, 707 (1897); Groening with H. P. Cady: **30**, 1597 (1926); Kraus and Bray: J. Am. Chem. Soc., **35**, 1315 (1913).

[4] J. Russ. Phys. Chem. Soc. (3), 466 (1902).

[5] J. Phys. Chem., **8**, 548 (1904).

[6] J. Phys. Chem., **3**, 602 (1899).

Purification of Beryllium Material by Crystallization as Beryllium Basic Acetate

Before preparing the individual compounds it was most convenient to purify the whole mass of beryllium material to avoid tedious and often impossible purification of the individual products. Beryllium is most easily separated from all metals except iron and aluminum by precipitation as the hydroxide with dilute ammonia; the iron and aluminum are then separated by recrystallization of the beryllium as beryllium basic acetate. Commercial beryllium nitrate, $Be(NO_3)_2.4H_2O$, was dissolved in a large quantity of water and precipitated with very dilute $NH_4OH(2-3\%)$. The gelatinous precipitate of hydroxides was separated from soluble impurities by inverse filtration with a porcelain Pukal suction funnel and washed free from ammonium salts with pure water. The cakes of partially dried hydroxide were dissolved in acetic acid and the solution evaporated in large porcelain dishes to a syrupy consistency.

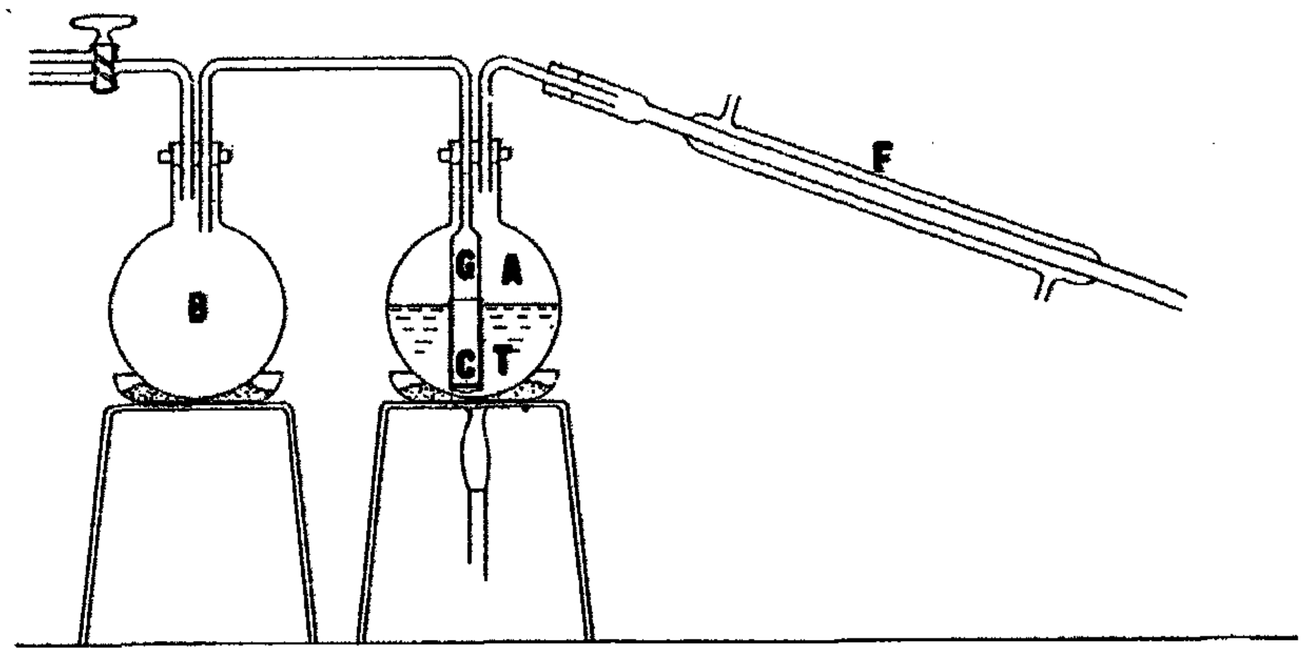


Fig. 1

Parsons and Robinson[1] recommend that this material be dissolved in boiling glacial acetic acid from which it should separate in gleaming crystals of pure beryllium basic acetate. To prevent too rapid crystallization of the salt it is necessary to filter the solution on a heated funnel. This causes considerable evaporation of acetic acid with consequent unbearable working conditions.

A special apparatus was devised for this final stage of the purification. The apparatus, shown in Fig. 1, consisted of two five-liter, round bottomed Pyrex flasks, A and B., provided with two-holed rubber stoppers. The main flask, A, carried a condenser, F, and a five millimeter delivery tube leading to the second flask. The second flask, B, carried a two-way stopcock permitting entrance of air or connection to a suction pump. The tube leading from flask

---

[1] J. Am. Chem. Soc., **28**, 555 (1905).

A to flask B was provided with a device for filtering the solution as it was transferred. This consisted of a short portion of wide tubing, G, fused to the narrow delivery tube, the wide end covered with a porcelain Witt plate, C, held in position by means of a fibre extraction thimble, T. The syrupy mass of beryllium material was placed in flask A with a quantity of glacial acetic acid and boiled to incipient crystallization. The boiling saturated solution of basic acetate, was then transferred to flask B by applying gentle suction at one exit of the stopcock and was filtered from any residue of hydroxide or other insoluble impurity on passing through the thimble and porcelain plate. On cooling the solution deposited large quantities of very pure beryllium basic acetate. One or two similar recrystallizations from glacial acetic acid produced pure beryllium basic acetate.

The material as prepared by the method just described is pure but cannot be used directly in the preparation of other beryllium salts. The basic carbonate, hydroxide, and oxide are the most convenient forms to use in the preparation of other beryllium compounds, especially salts of weak acids or compounds requiring fusion.

Preparation of Beryllium Hydroxide and Oxide

After the pure beryllium basic acetate had been obtained the next problem was to convert it to a usable form without introducing some impurity. Because of its volatility and moderate stability the basic acetate cannot be converted economically to oxide by ignition, but may be heated with nitric acid to form the nitrate. The basic acetate may be converted to basic carbonate by steam distillation of an ammonium carbonate solution of the basic acetate. Both methods permit contamination from impurities in the reagents and the bicarbonate method leaves considerable amounts of ammonium salts in even the most carefully washed beryllium basic carbonate.

It is well known that beryllium salts hydrolyze with great readiness particularly on boiling. It seemed probable that the acetic acid slowly being formed by hydrolysis when the basic acetate is boiled in water, could be continuously removed by steam distillation. A weighed sample of the basic acetate was carefully steam distilled and the distillate analyzed. A theoretical yield of acid was recovered and the residual beryllium hydroxide produced was extremely pure and quite granular.

Since the distillation method requires long periods for the preparation of small quantities of hydroxide, other methods of hydrolysis were tested. When collodion dialyzing flasks were used beryllium hydroxide was not precipitated and much beryllium ion migrated into the dialyzate before hydrolysis had progressed far. To hasten hydrolysis the collodion membrane containing the basic acetate solution was suspended in an atmosphere of steam, the acid perstilled readily and considerable hydroxide precipitated in the membrane. Unfortunately such a container could not withstand the severe operating conditions and broke before the hydrolysis was complete.

Separation of beryllium and acetic acid by electrolysis was tried. At 6.4 A/dm^2, using Pt sheet electrodes, gases were evolved very rapidly and the solutions became heated to boiling. When the cells were ice cooled, electrolysis proceeded smoothly. Large quantities of hydroxide were precipitated and migrated through the solution becoming moderately contaminated with carbon dioxide. The precipitate analyzed 73% beryllium oxide.

Each of these methods produced an easily filtered and washed granular material that was of satisfactory purity for preparation of other beryllium salts. The beryllium hydroxide was converted to oxide by heating to redness in a platinum crucible.

Preparation of Anhydrous Beryllium Chloride

The literature records several different methods of obtaining the anhydrous chloride of beryllium from the oxide. To form the anhydrous chloride, chlorine gas,[1] dry hydrogen chloride gas,[2] carbon tetrachloride vapor[3] and a mixture of chlorine and sulfur monochloride[4] have been passed over the heated oxide intimately mixed with an excess of carbon as reducing agent. The residual carbon is very difficult to separate even by sublimation of the chloride which must be performed in a dry atmosphere or, better, in a vacuum. For the present work phosgene was the most convenient chlorinating agent available and several of the older methods have been repeated using this gas instead of the chlorinating agent employed by the original investigator.

In the first experiments sugar carbon was mixed with the dry beryllium oxide and phosgene passed over the mixture. If the phosgene were passed in rapidly or the tube strongly heated, the chloride was carried out by the waste gases and could not be recovered. When the temperature was carefully controlled and the chlorinating agent passed in slowly the chloride remained in the tube but was only difficultly separated from residual carbon. Carbon dioxide passed in with the phosgene served to carry the beryllium chloride away from the carbon and the chloride condensed on the warm part of the tube at the end of the furnace.

Since reduction of beryllium oxide by carbon proved so unsatisfactory a better method was sought. If a gaseous reducing agent could be used it would serve to carry the beryllium chloride along to the exit of the tube and could easily be separated from the chloride prepared. Since phosgene contained both reducing and chlorinating elements it was thought possible to perform the operation according to the following equation with phosgene only:

$$COCl_2 + BeO = CO_2 + BeCl_2$$

For the successful preparation of anhydrous beryllium chloride the most important factor is the complete absence of water. Dry air was passed for several hours through a hard glass chlorination tube maintained at 450°, then dry phosgene to remove any possible impurity on the tube walls. Finally, the oxide, which had been heated to redness in platinum for some time, was

---

[1] Rose: Ann. Physik, **9**, 39 (1827).

[2] Debray: Ann. Chim. Phys., (3) **44**, 1-41 (1855).

[3] Meyer: Ber. **20**, 681 (1887); Camboulives: Compt. rend., **150**, 175 (1910).

[4] Bourion: Compt. rend., **145**, 62 (1907).

placed in the tube and dry air again passed through the tube until no trace of moisture was deposited on the cool end of the tube. Dry phosgene was then passed over the oxide at 450°C. and quantities of gleaming white needles of beryllium chloride formed.

This method proved very satisfactory, readily producing large quantities of pure beryllium chloride. When carbon is used the considerable volume of the reacting solids fills the whole heated zone of the tube and only one plug of chloride is formed at the warm place where the tube leaves the furnace. With the phosgene method a small mound of oxide may be placed at one end of the tube near the $COCl_2$ inlet and the tube moved along through the furnace allowing successive plugs of chloride to form where the tube emerges from the furnace. Thus large quantities of chloride may be produced without opening the tube for removal of material and there is no danger of contaminating the sublimed chloride with residual oxide. At the close of a run dry air is passed through the tube until all excess phosgene is removed.

To test the condensation of the chloride the excess phosgene and waste gases from several experiments were condensed, but on evaporation of the condensed gases no trace of beryllium material was found.

Chauvenet[1] has shown the possibility of generally applying this method of phosgene chlorination and reduction to several difficultly prepared anhydrous chlorides.

To test the possibility of the formation of a molecular compound[2] of anhydrous beryllium chloride and phosgene, liquid phosgene was condensed on some anhydrous beryllium chloride but without any sign of reaction. When air-washed beryllium chloride was allowed to stand in a sealed vessel for several months no excess pressure was ever produced and no odor of phosgene has ever been observed from the chloride prepared with phosgene. Evidently no molecular compound is formed.

Preparation of Beryllium Acetylacetonate

Since beryllium acetylacetonate is not as readily hydrolyzed as most other beryllium salts it may be prepared[3] by the action of acetylacetone directly on the moist beryllium hydroxide or basic carbonate. The beryllium material is slightly moistened with either acetic acid or water, an excess of acetylacetone is added and the mixture allowed to stand over night. The beryllium acetylacetonate is extracted with absolute alcohol and the alcoholic solution evaporated in air.

When prepared by this method the beryllium acetylacetonate is colored faintly yellow or brown, probably due to some decomposition product from the acetylacetone. Beryllium acetylacetonate is also very difficultly separated from residual beryllium hydroxide or carbonate. The following method proved satisfactory. The beryllium hydroxide or basic carbonate is heated

---

[1] Chauvenet: Compt. rend., **152**, 87 (1911).

[2] Baud: Compt. rend., **140**, 1688 (1905).

[3] Parsons: J. Am. Chem. Soc., **26**, 732 (1904).

with water until pasty. A small portion of alcohol and an excess of acetylacetone are added and the mix left for 20-30 hours to crystallize. The crystals may be extracted with hot alcohol and the solution filtered to remove the major portion of residual hydroxide. After recrystallization from alcohol the acetonate is twice crystallized from chloroform. If the alcohol recrystallization is omitted a colloidal suspension of beryllium hydroxide in chloroform is produced and the brown impurity which is very soluble in alcohol is not removed.

Considerable quantities of chloroform are occluded by the beryllium acetylacetonate. This may be removed by crushing and air-drying the crystals but is best removed by melting them on a platinum dish and heating gently until all chloroform is expelled.

Preparation of Anhydrous Beryllium Nitrate

Because of the high solubility and excellent conductivity of the resultant solutions of other nitrates the use of beryllium nitrate was considered. Beryllium nitrate crystallizes from water acidified with nitric acid as the tetrahydrate making it useless as an anhydrous solute. In order to eliminate the water, the direct union of metallic oxide and acid anhydride was attempted but without success.

Anhydrous beryllium nitrate may be obtained[1] by heating the hydrated nitrate with amyl alcohol. A saturated solution of hydrated beryllium nitrate in amyl alcohol is heated until vapors from the alcohol burn with a clear flame at the mouth of the vessel. Masses of anhydrous beryllium nitrate are deposited from the alcohol solution on cooling but are difficultly freed from a film of alcohol and very readily absorb moisture on exposure to the atmosphere.

A satisfactory method of dehydrating beryllium nitrate has been devised. Pure ammonium nitrate is carefully brought to fusion and beryllium nitrate tetrahydrate added in small quantities. The melt is heated until no further odor of nitric acid is noticed. If the melt is heated very carefully only a small amount of decomposition of the ammonium nitrate occurs and the resultant melt is moderately stable. The melt may be poured out onto dry platinum and transferred to a vacuum desiccator as soon as cool without sign of decomposition. If left to stand in air the anhydrous beryllium nitrate quickly absorbs moisture and the ammonium nitrate recrystallizes in the syrupy droplets of hydrated beryllium nitrate.

Beryllium Potassium Chloride

Parsons[2] doubts that the double chloride of beryllium and potassium has ever been prepared, although H. L. Wells[3] has listed it in his series of double halides. In the hope of obtaining an anhydrous, double chloride, a mixture of beryllium basic carbonate and potassium chloride in approximately equimole-

---

[1] Browning and Kuzirian: Orig. Com. 8th Intern. Congr. App'd Chem., 1, 87 (1912).

[2] "The Chemistry and Literature of Beryllium," p. 47.

[3] Am. Chem. J., 26, 390 (1901).

cular proportions was treated with concentrated hydrochloric acid. The solution was evaporated in an atmosphere of hydrochloric acid in a desiccator containing sulfuric acid. Our experience confirms Parsons' opinion as only large crystals of potassium chloride were obtained when the solution evaporated and the mother liquid was a characteristic viscous mass.

Beryllium Potassium Sulfate

According to Ebelman[1] beryllium oxide is very readily dissolved in fused potassium bisulfate. When first tried, the fused bisulfate produced an apparently clear glass with the theoretical portion of oxide. Careful examination showed that the fine oxide particles merely remain suspended in the melt and do not react, but are invisible due to having the same index of refraction.

Description of the Electrolyzing Apparatus

The apparatus shown in Fig. 2 was devised for the electrolysis of the non-aqueous solutions of beryllium salts and modified from time to time to suit the requirements of the individual solutions. The electrolyzing vessel, P, shaped like a test-tube, was connected to the rest of the apparatus through a conical joint, J, to facilitate removal of the tube for oven-drying and filling. Electrodes, E, were sealed in through the side arms and were insulated from

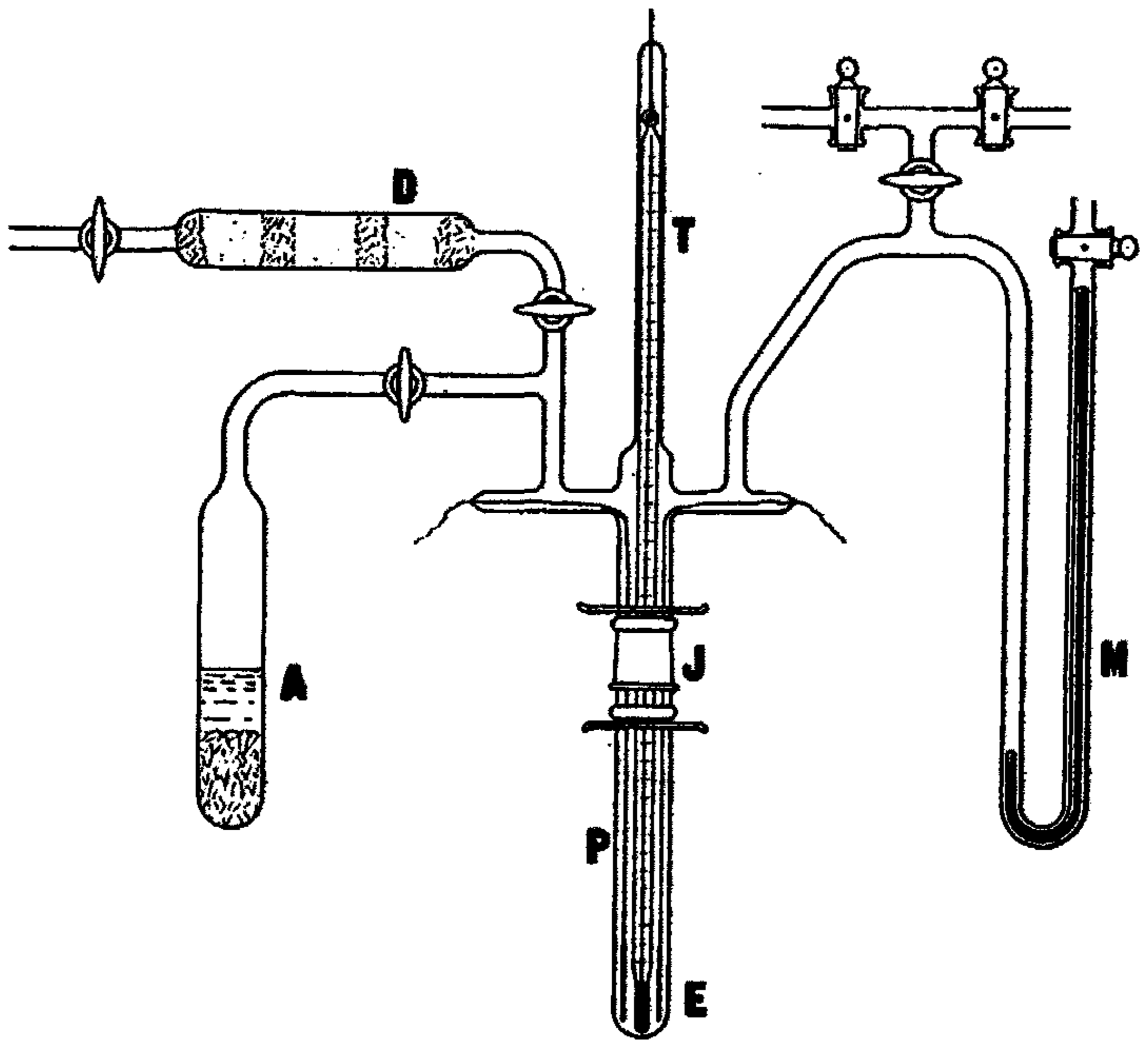


Fig. 2

---

[1] Compt. rend., 33, 526 (1851); J. prakt. Chem., 55, 342 (1852).

one another by a capillary glass sleeve not shown in the diagram. Platinum electrodes were used throughout the investigation. A short mercury manometer, M, was used to indicate the pressures approximately and when solutions were tested at temperatures above those of room conditions, a thermometer, T, was suspended from a sealed joint at the top of the central tube. In working with the non-aqueous solutions it was absolutely essential that every part of the apparatus be perfectly dry, hence the apparatus was dried by repeated rinsings with air dried by passage through the tube, D, containing phosphoric anhydride. Gases to be liquefied were condensed into an auxiliary ampoule, A, and condensed into the electrolyzing vessel as needed. In order to permit evacuation and subsequent preservation of a pure atmosphere of solvent vapor the entire apparatus was constructed of glass sealed at all joints except the conical joint, J, which was lubricated with special grease of low vapor tension. A low variable resistance and delicate milliameter to record the small currents employed, were kept in the circuit continually. A voltmeter was connected across the terminals of the cell only for short periods.

Preparation and Purification of Solvents

All solvents used were suitably purified, carefully dried and usually fractionally distilled. *Ethyl bromide* was kept over calcium chloride for several days, decanted and filtered, and fractionally distilled. The main portion of the ethyl bromide distilled over at 34.5-36°C. while another sample kept over phosphoric anhydride distilled uniformly at 37.5-39°C.

Selenium oxychloride was vacuum distilled[1] with a calcium chloride tube in the system to protect the liquid from the vapors of the suction pump. The portions used in electrolyses were obtained by distilling the oxychloride under partial vacuum directly into the electrolyzing vessel.

Phosgene was purified by bubbling it through sulfuric acid and condensing it with ether-carbon dioxide mixture. *Chloroform* was kept over calcium chloride for several weeks and then fractionally distilled. *Acetylacetone* was distilled immediately before use. Likewise *phosphorus trichloride* was fractionally distilled before use. Freshly opened, pure samples of *glacial acetic acid* and *absolute alcohol* were used without any special treatment. A sample of molecular compound formed by *methyl ether* and *boron trifluoride* was furnished by Dr. A. F. O. Germann[2] and was redistilled before use. *Sulfur dioxide* was used just as it came from a commercial tank of gas under pressure.

Experimental

1. *Solutions in Ethyl Bromide.* The work of Plotnikoff and Patten with solutions of aluminum bromide in ethyl bromide suggested the use of ethyl bromide as an electrolytic solvent for beryllium compounds.[3] Beryllium bromide was not available but beryllium chloride was found to dissolve in

---

[1] J. Am. Chem. Soc., 43, 30 (1921); 44, 1664 (1922).

[2] Science, 53, 582 (1921); Chem. Abs., 16, 3796 (1922).

[3] References cited under choice of solvents.

considerable amounts in ethyl bromide. Save for a gas at the cathode the filtered solution gave no electrode products. The highest current density obtainable with a 110 volt potential was .175 amperes/sq. dm. A few crystals of sodium trinitride were added in an attempt to form the beryllium trinitride from which the metal might be deposited but there was no apparent result except the lowered conductivity of the solution.

It is possible that a complex compound was formed between the ethyl bromide and the beryllium chloride which would account for the very marked solubility of the beryllium chloride. Gustavson[1] states that a solution of aluminum bromide in ethyl bromide on heating evolves hydrogen bromide and saturated hydrocarbons leaving a complex aluminum bromide hydrocarbon. Even on mere solution of beryllium chloride in ethyl bromide vapors of a very penetrating odor, which gave a test for halogen with silver nitrate, were evolved. On standing crystals of a form entirely different from that of beryllium chloride separated and floated on the surface of the solution while beryllium chloride itself falls directly to the bottom. The extreme hygroscopicity of the solution made a determination of the solubility of the beryllium chloride almost impossible. By careful manipulation an approximate value was obtained indicating that the solubility approached three per cent. A sample of solution was rapidly weighed in a crucible and evaporated slowly in an oven at 90°C. The crystalline residue was transparent, only slowly attacked by moisture of the air, dissolved in water with hissing and evolution of gas of a pungent odor.

2. *Solutions in Methyl ether-Boron fluoride.* The liquid, molecular compound formed by the combination of the two gases, methyl ether and boron fluoride, was found to have moderate solvent action on several beryllium compounds. From analogy with the action of calcium fluoride and boron fluoride which form a series of fluoborates,[2] it seemed possible that a fluoborate, $Be(BF_4)_2$, or a derivative might be formed by the action of boron fluoride on beryllium salts. Portions of the liquid compound were placed over beryllium-sodium fluoride, beryllium chloride and beryllium acetylacetonate and left for several days to become saturated.

A portion of the pure solvents was electrolyzed as a blank to determine the conductivity, electrode products, and behavior of the methyl ether-boron fluoride alone. On a four-volt circuit the pure solvent carried one ampere/sq. dm. with a potential across the cell of 3.45 volts. A very small amount of gas was observed at the cathode but no visible anode product. With higher voltage the temperature increased and the conductivity improved. At the higher temperatures bubbles of gas appeared at both electrodes but since no increase of pressure was observed the bubbles were doubtless boiling solvent.

a. *Sodium beryllium fluoride.* The use of sodium-beryllium fluoride as a fused electrolyte suggested the use of this salt as a solute. Unfortunately, however, this salt was found to have little, if any, solubility in this solvent

---

[1] J. prakt. Chem., (2), **34,** 167 (1886).

[2] Unpublished work of the junior author.

and electrolysis of the liquid which had stood over the solid salt gave no electrode products.

b. *Beryllium chloride.* Solutions of this salt gave fair conduction on an eight-volt circuit. At the beginning of a run the conduction was usually about 2.8 amperes/sq. dm. but slowly and steadily dropped to a uniform value of one ampere/sq. dm. where it remained for the whole period of a run. The potential difference at the latter value was 3.8 volts. A little gas was always produced at the cathode and may have been the source of the small back E.M.F. that was always observed at the end of a run. A black, amorphous, adherent material, insoluble in hydrochloric acid was produced at the cathode from which it could be removed only with difficulty.

c. *Beryllium acetylacetonate.* This salt is very soluble in methyl ether-boron fluoride but the solution does not conduct well. Only three amperes/sq. dm. were carried at a potential of 10 volts. Gas was evolved at the cathode and a black material, insoluble in hydrochloric acid, adhered to the cathode. At the anode a brown coloration was produced which eventually colored the solution a deep cherry-red.

3. *Solutions in Ethyl Alcohol.* In other experiments with fused salts of beryllium it was observed that the conductivity was improved if traces of alcohol had been left on the recrystallized salts. This suggested the use of ethyl alcohol as a non-aqueous solvent. Beryllium acetylacetonate is quite soluble in alcohol from which it may be recrystallized without decomposition. The saturated solution conducts fairly well but much gas is produced, the temperature increases rapidly and no metal is deposited on the cathode.

4. *Solutions in Amyl Alcohol.* The saturated, anhydrous solution of beryllium nitrate in amyl alcohol is very viscous[1] and does not conduct well. On warming the solution in a water-bath to lower the viscosity so much alcohol bubbles off that no observation of possible electrode gases can be made. No metal was deposited on the cathode but the electrode was covered with white crystals of anhydrous beryllium nitrate. These crystals are perfectly stable in the amyl alcohol solution but rapidly absorb moisture on exposure to air.

5. *Solutions in Glacial Acetic Acid.* Beryllium acetylacetonate is soluble in glacial acetic acid but the presence of the elements of water in this solvent did not favor its use as solvent. The solution only carried .145 amperes/sq. dm. with 110 volts potential difference. A gas was evolved at the cathode and a white, crystalline material was deposited in the region of the anode. It was possibly di-acetylacetone.

6. *Solutions in Acetylacetone.* Beryllium chloride dissolves in acetylacetone without decomposition and the solution conducts fairly well while acetylacetone alone is a non-conductor. A gas is evolved at the cathode and a white crystalline material was deposited at the anode.[2] The precipitate was soluble in water and was possibly di-acetylacetone. No deposition of metal was observed.

---

[1] Browning and Kuzirian: Orig. Com. 8th Intern. Congr. Appl. Chem., **1**, 87 (1912).

[2] R. von Schilling and D. Vorländer: Ann., **308**, 199 (1899).

7. *Solutions in Phosgene.* The possibility which has been suggested of beryllium chloride forming a molecular compound with phosgene similar to the solid phosgenate of aluminum chloride or the liquid addition compounds with magnesium chloride encouraged a trial of this mixture.[1] Dry phosgene was condensed over pure anhydrous beryllium chloride but the chloride showed no apparent solubility. The liquid over the beryllium chloride carried only .025 amperes/sq. dm. at 110 volts potential and gave no noticeable electrode products. The phosgene readily evaporated on warming with no sign of reaction.

8. *Solutions in Selenium Oxychloride.* This compound seemed to have possibilities because of its solvent power and its property of converting metallic oxides into chlorides by mere contact without heating. A sample of selenium oxychloride was distilled directly into the electrolyzing vessel on to a sample of dry beryllium oxide. The beryllium oxide displayed no definite tendency to solution but became gelatinous and fluffy. Water was added to a sample of this gelatinous material and it was found to dissolve readily, probably because of conversion to beryllium chloride. The selenium oxychloride which had stood over the beryllum oxide was electrolyzed and carried 30 amperes/sq. dm. on a 10 volt circuit. The temperature rapidly increased to 80°C. and much gas was evolved at the anode. A red coloration rapidly spread through the solution from the anode and was later proved due to platinum tetrachloride. No electrolytic products were observed at the cathode.

9. *Solutions in Phosphorus Trichloride.* In the course of another experiment it was observed that beryllium acetylacetonate was extremely soluble in phosphorus trichloride. The saturated solution, however, was non-conducting on either 10 volt or 110 volt circuits.

10. *Solutions in Liquid Sulfur Dioxide.* Other investigators have found that many salts formed solutions in liquid sulfur dioxide and the solutions were fair conductors of electricity.[2] Fused beryllium acetylacetonate was warmed in the electrolyzing vessel under vacuum to remove traces of chloroform and dry sulfur dioxide passed in. The beryllium salt was very soluble in the liquid sulfur dioxide, but the solution even in a 110 volt circuit was absolutely non-conducting.

Conclusion

1. Several compounds of beryllium have been prepared in a high degree of purity. New methods of preparation have been developed and older methods improved. Certain mis-statements in the literature have been

---

[1] Baud: Compt. rend., **140**, 1688 (1905); Germann and Timpany: J. Phys. Chem., **29**, 1423, 1469 (1925); Germann and Gagos: J. Phys. Chem., **28**, 965 (1924).

[2] Bagster and Steele: Trans. Faraday Soc., **8**, 51 (1912); Kraus and Bray: J. Am. Chem. Soc., **35**, 1315 (1913).

corrected. As this work has only been preliminary to the research on the preparation of metallic beryllium much of the work has not received the complete treatment that would be desirable but is included as a suggestion to future workers in this field.

2. A variety of beryllium salts have been dissolved in non-nitrogenous non-aqueous media and the behavior of the solutions on electrolysis observed. The majority of the solutions conduct electricity very poorly and none have been satisfactory sources of metallic beryllium.

IONIZATION PRODUCED BY RADON IN SPHERICAL VESSELS

BY GEORGE GLOCKLER AND G. B. HEISIG

In a former paper[1] a comparison was made of the two methods of calculation of the ionization produced by radon in spherical vessels now in use. The two methods compared were the average path law of Lind[2] and the method developed recently by Mund.[3] It was shown that the two modes of calculation give similar results for small spherical vessels. It will be shown that the average path law is applicable to vessels of all sizes and that the values of the ionization calculated by the average path method differ from those calculated by Mund by not more than 5%.

It will further be shown that the average intensity of ionization can be obtained by calculation without the use of graphical methods as developed by Bardwell and Doerner.[4] Average intensities calculated in this way are believed to be more accurate than those formerly obtained. It will be seen that these values of the average intensity of ionization for the three sets of alpha particles from Rn, RaA and RaC′ are different depending on the methods of averaging and weighting employed.

General Terms:

N_0 = number of Rn atoms present initially = $E_0 \times 1.772 \times 10^{16}$
t = time
r = range of αpt from Rn = 3.94 cm. (air N.T.P.)
r' = do. from RaA = 4.5 cm.; $a = r'/r = 1.142$
r'' = " " RaC = 6.57 cm.; $b = r''/r = 1.667$.
I = ionization produced
λ = decay constant Rn
R = radius of spherical reaction vessel
ρ = r/R
B = $N_0 (1-e^{-\lambda t})kr^{2/3}.(kr^{2/3} = 1.69 \times 10^5$ for α particles from Rn)
p = path of an α particle
V = volume of reaction vessel
$2R<r$ = defines a small reaction sphere
$2R>r$ = defines a large reaction sphere
F = efficiency factors used in the methods of Mund and the average path
g = Bragg's specific molecular ionization
s = stopping power

---

[1] J. Phys. Chem., **31**, 1322-31 (1927).

[2] J. Phys. Chem., **16**, 564-613 (1912) and "Chemical Effects of Alpha Particles and Electrons," 93, 95 (1928).

[3] J. Phys. Chem., **30**, 890-894 (1926).

[4] J. Am. Chem. Soc., **45**, 2593-2600 (1923).

Superscripts and subscripts to be applied to general terms:

$\bar{}$ = average

$'$ = indicates that the proper proportion of α particles originating in the gas phase and on the wall have been used, as F and F'.

1,2,3,4,5, refer to α particles from: radon, radium A and C in the gas phase, radium A and C on the wall respectively.

w = effects produced by α particles originating on the wall of the container.

g = effects produced by α particles originating in the gas phase.

a = refers to average path method of calculating ionization.

M = refers to Mund's method of calculating ionization.

s = distance α particle has traveled from point of origin.

I. The Average Path Law applied to Spherical Vessels of Any Size

Heretofore[1] the average path law has only been applied to small vessels ($2R < r$). However it will be shown that it can also be applied to the case of large vessels where $2R > r$. Two possibilities have to be considered: In the first case the alpha particle originates in the interior of the reaction vessel and in the second case it starts from the wall. The general method of procedure is to calculate the average path of those alpha particles which do not complete their range. The use of this average path in the Geiger equation allows the calculation of the loss of ionization. When this loss is subtracted from the total ionization that could have been produced had all the 3N alpha particles been able to complete their range, the actual amount of ionization is obtained.

Average path of alpha particles which originate in the gas phase and do not complete their range. ($2R > r$). In this case one observes a small group of alpha particles from Rn leaving the point C in Fig. 1a. The alpha particles leaving all the points within the spherical shell BCD have the same path between p and p + dp, if they reach the wall of the reaction vessel at A_R. The number going into unit surface (A_R) is F(p)dp having paths between zero and r. The elementary volume at the point C is shown in Fig. 1b. From the definitions given above it follows that

$$F(p)dp = \iint n\frac{\cos\Theta}{p^2}\, dV dp \qquad (1)$$

In order to find the number of alpha particles with paths between p and p + dp which leave the shell BCD the expression (1) is first integrated between the limits $\Theta = 0$ and $\Theta = \alpha$. The elementary volume dV is given by $2\pi\, p^2 \sin\Theta\, d\Theta$. The total path which these F(p)dp alpha particles describe is P_p. Each of the alpha particles in the group F(p)dp has the path p, so that

$$P_p = \int_0^r \int_0^\alpha p.\ F(p)\ dp = \pi n \int_0^r p\left\{1 - \frac{p^2}{4R^2}\right\} dp \qquad (2)$$

---

[1] J. Phys. Chem., 31, 1322-31 (1927).

The total path P_r of *all* the groups of alpha particles having paths between o and r will be obtained by summing equation (2) between the limits o and r.

$$P_r = \frac{\pi n}{2}\left\{r^2 - \frac{r^4}{8R^2}\right\} \tag{3}$$

substituting for n, multiplying by $4\pi R^2$ and simplifying gives

$$P = \frac{3}{8}\,N\,R\left\{\rho^2 - \frac{\rho^4}{8}\right\} \tag{4}$$

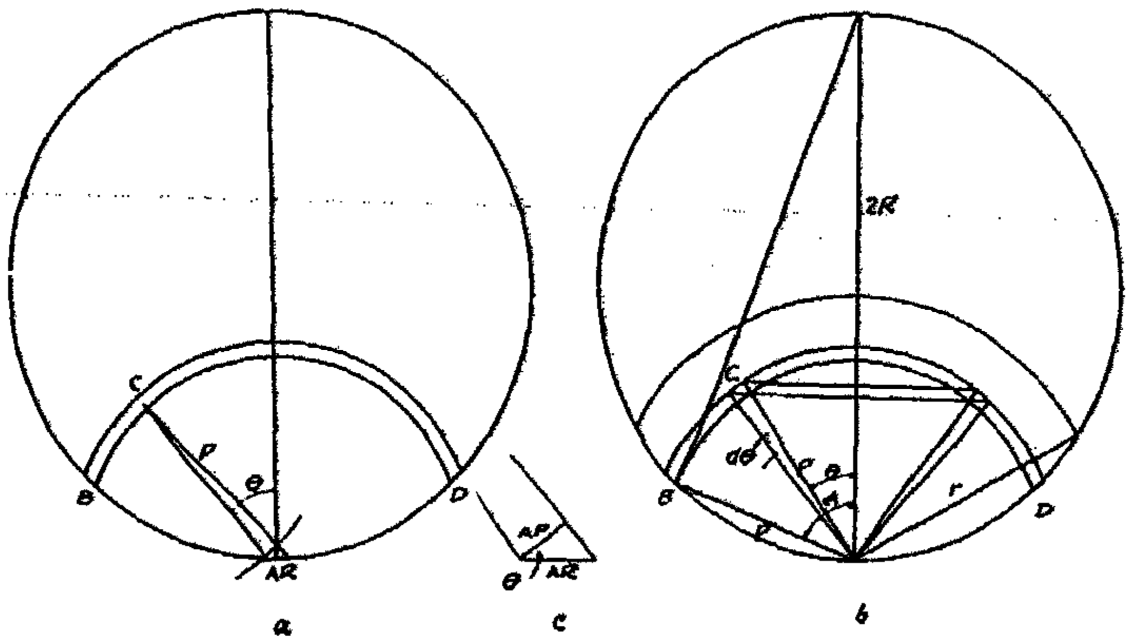


Fig. 1

The total number of alpha particles which have this total path P is obtained by integrating equation (1) between the limits:

$$\Theta = 0 \text{ to } \Theta = \cos^{-1}\left(\frac{p}{2R}\right) \text{ and } p = 0 \text{ to } p = r$$

Then

$$N_\rho = \frac{3}{4}\,N\left\{\rho - \frac{1}{12}\,\rho^3\right\} \tag{5}$$

And the average path of these N_ρ alpha particles is obtained by dividing the total path P by N_ρ.

$$p = \frac{3}{4}\,r\left\{\frac{8 - \rho^2}{12 - \rho^2}\right\} \tag{6}$$

Equation (6) may be tested by letting $r = 2R$ or $\rho = 2$ because then the limiting case of a small sphere is reached and the well known expression

$$p = \frac{3}{4}R \tag{7}$$

is secured.

Ionization produced by alpha particles originating in the gas phase. The total ionization I_t of N alpha particles is $Nkr^{2/3}$. The ionization I_L lost by N_ρ alpha particles of average $\bar{p}$ is

$$I_L = N_p\, k\, (r - \bar{p})^{2/3} \tag{8}$$

Then the ionization I_I actually produced, is

$$I_I = I_T - I_L \tag{9}$$

or

$$I_I = B\left\{1 - \left(\frac{12\rho - \rho^3)}{16}\right)\left(\frac{24 - \rho^2}{48 - 4\rho^2}\right)^{2/3}\right\} \tag{10}$$

Equation (10) is to be compared with equation (1) of Mund[3] and it should be noted that this ionization becomes

$$B\left\{1 - \left(1 - \frac{\bar{p}}{r}\right)^{2/3}\right\}$$

for the case of small vessels.[1] When relation (10), developed for Rn is applied to calculate the ionization produced by RaA it is only necessary to multiply the range r and the ratio ρ by "a" and in the case of RaC′ by "b."

Average path of alpha particles which start on the wall and do not complete their range. ($2R > r$). There are two possible ways of calculating the average path of alpha particles originating on the wall. One may include those alpha particles which enter the wall, in the consideration or one may only count those ($N/2$) which actually enter the gas phase and therefore contribute towards ionization.

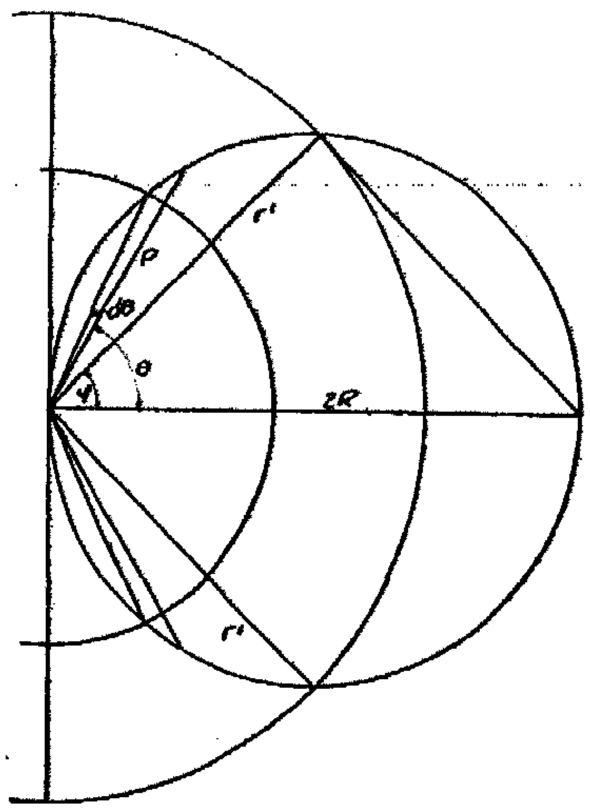


FIG. 2

The second method of averaging seems to be the more logical and simpler procedure.

The expression for the average path deduced on this basis is as follows: From the geometry of Fig. 2 it is seen that $A_\varphi = 2\pi\, r'^2\,(1 - \cos\varphi)$ = the area through which N_φ alpha particles go which complete their range, and further that

$$A'_L = 2\pi\, r'^2 - 2\pi\, r'^2\,(1 - \cos\varphi) = 2\pi r'^2 \cos\varphi$$

= the area through which N_L alpha particles go which do not complete their range, and

$$A_L = 2\pi\, p^2 - 2\pi p^2\,(1 - \cos\varphi) = 2\pi p^2 \cos\varphi$$

= an area through which the N_L alpha particles also pass.

Since $N/2$ alpha particles would pass through the hemisphere $2\pi r'^2$ if they could complete their range, it follows that

$$\frac{N/2}{2\pi r'^2} = \frac{N_\varphi}{2\pi r'^2\,(1 - \cos\varphi)} \tag{11}$$

But as

$$N_L + N_\varphi = \tfrac{1}{2} N \quad \text{(12)}$$

$$\text{and } N_L = \tfrac{1}{2} N \cos\varphi \quad \text{(13)}$$

$$\text{then } N_L = \frac{N}{2} \cdot \frac{r'}{2R} \quad \text{(14)}$$

The number of alpha particles N_L which leave the wall and do not complete their range is given by expression (14) as a fraction of the total number of alpha particles ($N/2$) which enter the gas phase. The total path the N_L alpha particles describe will next be calculated.

The number of alpha particles going through the elementary area $2\pi p^2 \sin\theta\, d\theta$ is $x_{\theta p}$:

$$\frac{N/2}{2\pi p^2} = \frac{x_{\theta p}}{2\pi p^2 \sin\theta\, d\theta} \quad \text{(15)}$$

The total path $P_{r'}$ described by $x_{\theta p}$ alpha particles is

$$P_{r'} = \int_{\varphi}^{\pi/2} x_{\theta p}\, p\, dp$$

and the average path is

$$\bar{p}_w = \frac{1}{N_L} \cdot \frac{N}{2} \int_{\cos^{-1}\left(\frac{r'}{2R}\right)}^{\pi/2} p \sin\theta\, d\theta \quad \text{(16)}$$

From the geometry of Fig. 2

$$p = 2R\cos\theta \quad \text{(17)}$$

and

$$\bar{p}_w = \frac{r'}{2} \quad \text{(18)}$$

When this expression is applied to the limiting case of small bulbs ($2R = r'$) it gives

$$\bar{p} = R$$

which is the average path of those α particles ($N/2$) that enter the gas phase. The average path of all N alpha particles originating on the wall in all directions will be $R/2$ since $N/2$ particles enter the wall and have therefore zero paths.

Ionization produced by alpha particles which originate on the wall and enter the gas phase. The ionization produced by $N/2$ alpha particles is calculated by equation (9). For the case of RaA the ionization I_3 is given by

$$I_3 = \frac{N}{2} k r'^{2/3} - \frac{N}{2} \frac{r'}{2R} k \left(r' - \frac{r'}{1}\right)^{2/3} \quad \text{(19)}$$

$$= \frac{B}{2} a^{2/3} \left((1 - \frac{a}{2^{5/3}} \rho \right) \quad \text{(20)}$$

The complete average path law. The expressions for the ionization produced by alpha particles in the case of small reaction spheres ($2R<r$) are given by

$$I = B\left(1-\left(1-\frac{\bar{p}}{r}\right)^{2/3}\right) \tag{21}$$

where $\bar{p}_a = .75R$ for the gas phase and $\bar{p}_w = .5R$ for the wall case if all of the N alpha particles are counted in the process of averaging. If however only the N/2 alpha particles originating on the wall are considered which contribute to the ionization, then their average path is $\bar{p}_w = R$. This last method seems to be the more reasonable since all of the alpha particles which have zero path (they go into the wall) are excluded in the process of counting the average path. Then the expressions for the ionizations produced by RaA and RaC alpha particles become

$$I = \frac{B}{2}\left(1-\left(1-\frac{\bar{p}_w}{r'}\right)^{2/3}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots \tag{22}$$

where $\bar{p}_w = R$. In the case of RaC r' is replaced by r''.

The general expression for the ionization produced in spherical vessels as calculated by the complete average path method is given by the proper combination of equations, 10, 20, 21, and 22, based on the consideration that for each set of alpha particles the change from a large to a small vessel is made at the correct value of ρ. These values of ρ are obtained from the limiting case where the diameter becomes equal to the range.

For Rn: $2R = r$ or $\rho = 2$

For RaA: $2R = r' = ar$ or $\rho = 1.7513$

For RaC′: $2R = r'' = br$ or $\rho = 1.2000$

With these conditions the average path equations for the total ionization produced by N alpha particles become:

If $\rho > 2$:

$$I_T = B\left[1+\frac{a^{2/3}}{2}+\frac{b^{2/3}}{2}-\left\{\left(1-\frac{.75}{\rho}\right)^{2/3}+\frac{1}{2}\left(a-\frac{1}{\rho}\right)^{2/3}+\frac{1}{2}\left(b-\frac{1}{\rho}\right)^{2/3}\right\}\right] \tag{23}$$

$2 > \rho > 1.75$:

$$I_T = B\left[1+\frac{a^{2/3}}{2}+\frac{b^{2/3}}{2}-\left\{\left(\frac{12\rho-\rho^3}{16}\right)\left(\frac{24-\rho^2}{48-4\rho^2}\right)^{2/3}+\frac{1}{2}\left(a-\frac{1}{\rho}\right)^{2/3}+\frac{1}{2}\left(b-\frac{1}{\rho}\right)^{2/3}\right\}\right] \tag{24}$$

$1.75 > \rho > 1.2$:

$$I_T = B\left[1+\frac{a^{2/3}}{2}+\frac{b^{2/3}}{2}-\left\{\left(\frac{12\rho-\rho^3}{16}\right)\left(\frac{24-\rho^2}{48-4\rho^2}\right)^{2/3}+\frac{1}{2}\left(\frac{a}{2}\right)^{5/3}\rho+\frac{1}{2}\left(b-\frac{1}{\rho}\right)^{2/3}\right\}\right] \tag{25}$$

$1.2 > \rho > 0$:

$$I_T = B\left[1+\frac{a^{2/3}}{2}+\frac{b^{2/3}}{2}-\left\{\left(\frac{12\rho-\rho^3}{16}\right)\left(\frac{24-\rho^2}{48-4\rho^2}\right)^{2/3}+\frac{1}{2}\left(\frac{a}{2}\right)^{5/3}\rho+\frac{1}{2}\left(\frac{b}{2}\right)^{5/3}\rho\right\}\right] \quad (26)$$

The quantities in brackets of equations 23-26 are called efficiency factors (F_a) and numerical values for the case of 100% RaA and RaC′ decomposing on the wall, are given in Table I, Column 3. The complete average path law can now be compared with the results of Mund and this comparison is made graphically in Fig. 3. It is seen that the maximum deviation is at $\rho = 1.5$, where $F_M = 1.033F_a$.

II. The Efficiency Factor F′

The values for the efficiency factor F_M' when 70% of RaA and 93% of RaC′ decompose on the wall given in the earlier paper[1] have been recalculated and are to be found in Table I, Column 6. Incidentally the values of Mund's F, when 100% of RaA and RaC′ decompose on the wall have been checked and are shown in Table I, column 5.

The factor F_a' can be calculated from the factor F_M' by the following relation

$$\frac{F_a'}{F_a} = \frac{F_M'}{F_M}$$

It has been found convenient to compare the various efficiency factors and the *pressure* in a bulb of 1 cm. radius rather than the customary relation between them and ρ. Values of ρ, the equivalent air pressure and the F factors are found in Table I. The details are discussed in Section VI.

III. The Average Intensity of Ionization

The values of the average intensities of ionization obtained by Bardwell and Doerner[4] involved the use of graphical methods. However it is possible to calculate these quantities in the following manner: For one alpha particle, the average intensity is given by the mean value theorem:

$$\bar{I}_s = \frac{\int_0^{\bar{p}} I_S\,dp}{\int_0^{\bar{p}} dp} \quad (27)$$

The total ionization for one alpha particle is

$$I = kr^{2/3}\left\{1-\left(1-\frac{p}{r}\right)^{2/3}\right\} \quad (28)$$

Then

$$I_S = \frac{dI}{dp} = \frac{2k}{3(r-p)^{1/3}} \quad (29)$$

Substituting in equation (27) and integrating:

$$\bar{I}_s = \frac{kr^{3/2}}{\bar{p}}\left\{1 - \left(1 - \frac{\bar{p}}{r}\right)^{3/2}\right\} \tag{30}$$

Equation (30) may be written

$$\bar{I}_S \cdot \bar{p} = I \tag{31}$$

or the average intensity of ionization may be gotten by dividing the total ionization by the average path. The question now arises how to average expressions of the type of (31) for three sets of alpha particles. Two methods suggest themselves.

The average intensity of ionization for the three sets of alpha particles is obtained by dividing their total ionization by the sum of their average paths:

$$\bar{I}_f = \frac{\bar{I}_{1S} \cdot \bar{p}_1 + \bar{I}_{3S} \cdot \bar{p}_3 + \bar{I}_{5S} \cdot \bar{p}_5}{\bar{p}_1 + \bar{p}_3 + \bar{p}_5} = \frac{I_F}{3 \times .5833\ R} \quad \ldots\ldots\ldots (32)$$

In this method the average intensity of the individual sets are each weighted by their respective average path. This seems to be the proper procedure from the physical point of view. The division of the total ionization by the sum of the average paths is quite analogous to the usual mean value method.

A second method of getting the average intensity of ionization for the three sets of alpha particles is to divide the sum of the average intensities of each set by three:

$$\bar{I} = \frac{1}{3}\ \{\bar{I}_{1S} + \bar{I}_{3S} + \bar{I}_{5S}\} \tag{33}$$

In this method of averaging each value of the average intensity of ionization of each set is given equal weight. The two methods differ by one percent. In Table I column 7 the average intensities of ionization in air at 0°C, 76 cm. for the three sets of alpha particles (100% RaA and RaC′ decompose on the wall) are given for a sphere of 1 cm. radius.

For the case where only 70% RaA and 93% RaC decompose on the wall the values of the average intensity of ionization of the three sets of alpha particles have been obtained from the relation

$$\bar{I}_{F'} = \frac{I_{F'}}{3 \times .61R} \tag{34}$$

In this case the sum of the average paths is obtained from the experimental value .61R which is the appropriate value for the above conditions. The values of $I_{F'}$ (0°C, 76 cm.) are given in Table I column 8 for a sphere of 1 cm. radius containing air. The total ionizations involved in obtaining the above quantities have been calculated by the method of Mund, using the factors F and F′. In this calculation the value of 1.69×10^5 was used for the total number of ion pairs produced by one alpha particle from Rn.

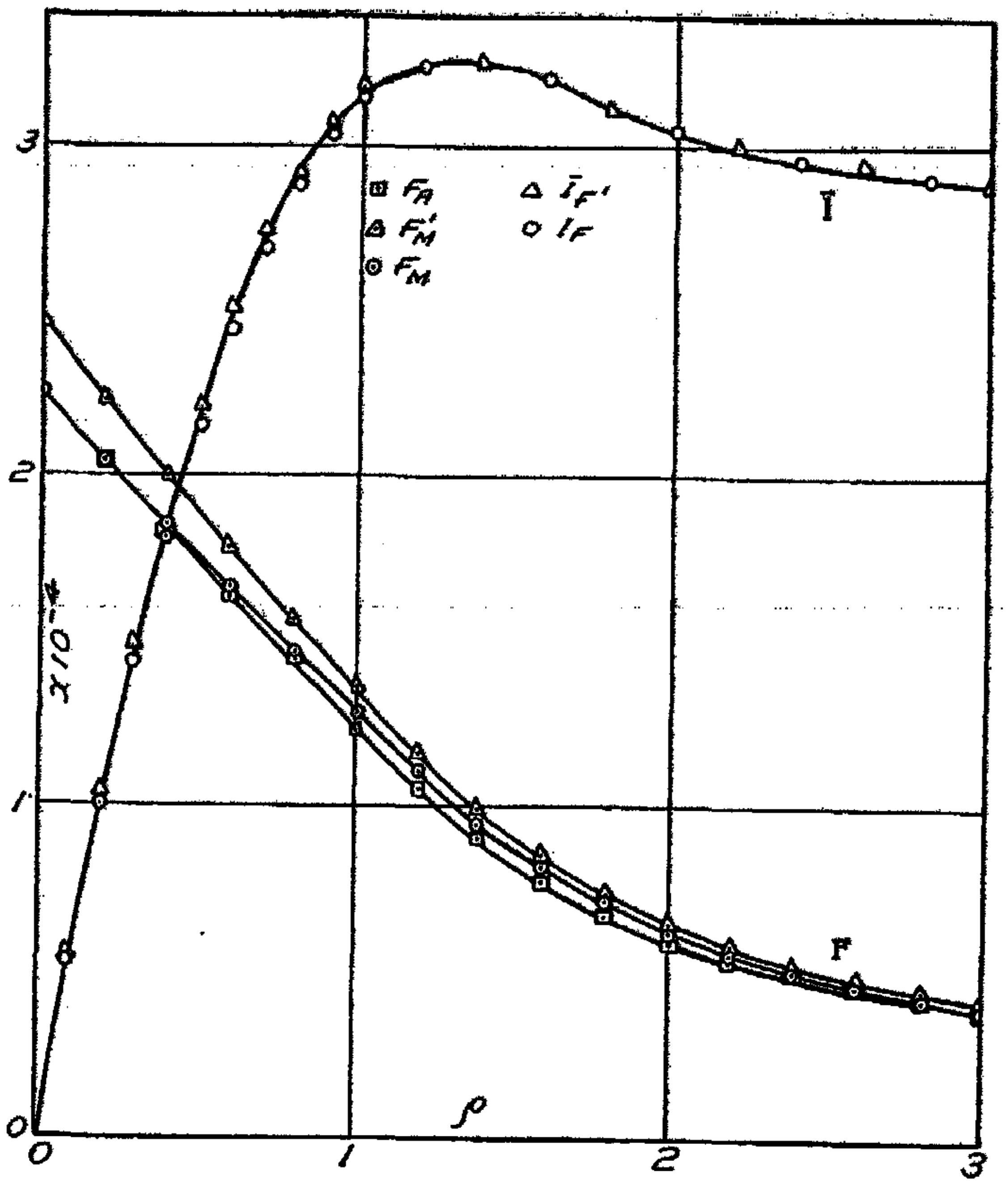


Fig. 3

IV. The Initial Intensity of Ionization

The total ionization produced by a given quantity of radon may also be expressed by the average path law, using however the *initial* intensity of ionization instead of the *average* intensity described in Section III. It is then assumed that the vessel is small enough so that the initial intensity of ionization represents the average intensity of ionization over the average path of the alpha particles.

For one set of alpha particles the initial intensity of ionization is given by[1]

$$I_{p=0} = \frac{2}{3}\,\frac{kr^{2/3}}{r} \tag{35}$$

It is necessary to average this quantity for the three sets of alpha particles and again two methods of averaging suggest themselves, which are entirely analogous to the methods expressed by equations (32) and (33). Using 2.37×10^5 as the total number of ion-pairs produced by one alpha particle

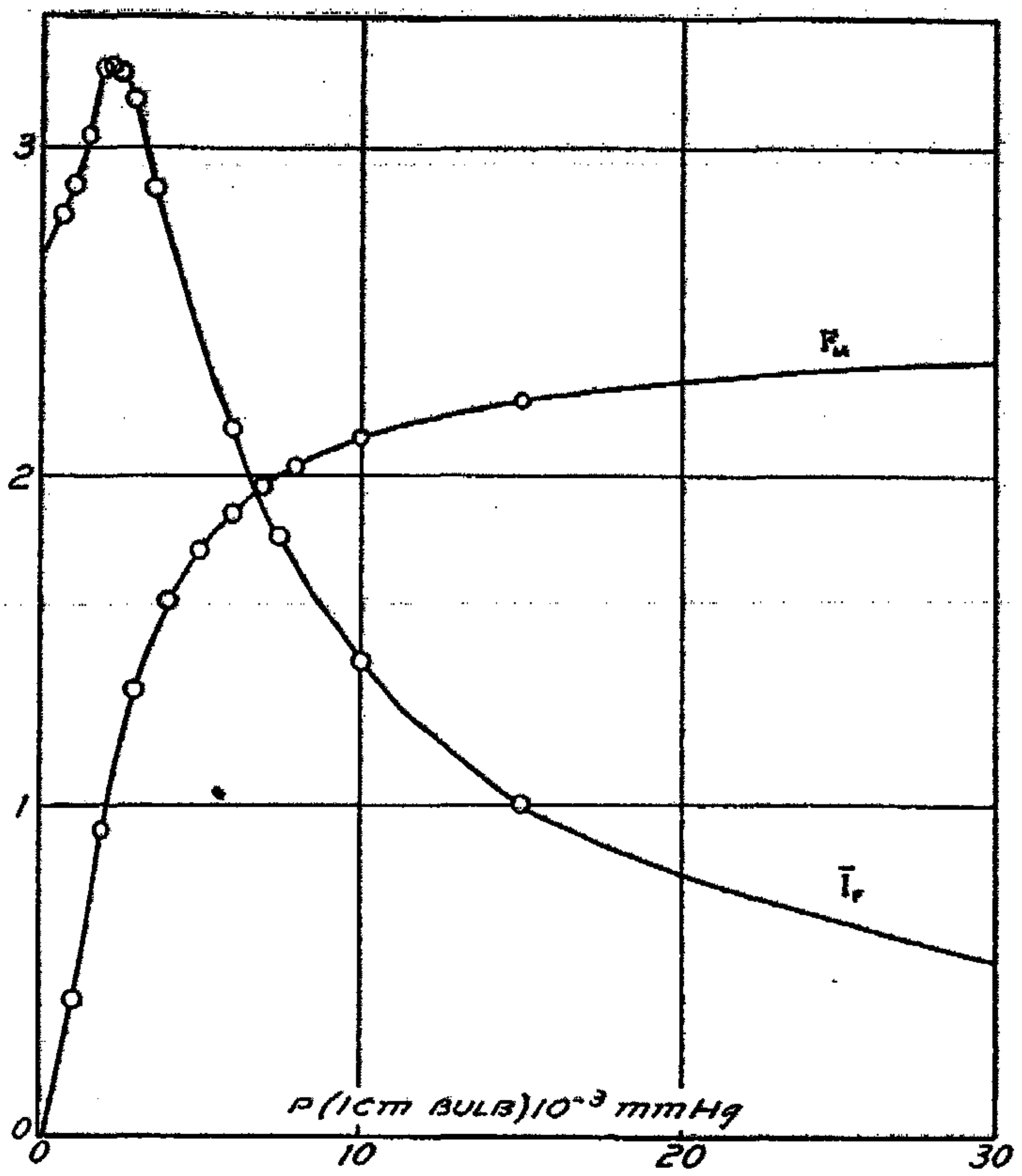


FIG. 4

from RaC′, the values obtained for the initial intensity of ionization averaged for the three sets of alpha particles, are respectively 2.692 × 10^4 and 2.664 × 10^4 ion pairs per cm. path in air at 0°C and 76 cm. Hg pressure. It is seen that these values differ by only one percent. However the method expressed in equation (32) giving the first value cited, was used, because this method of averaging was also used in the calculation of the average intensity of ionization.

It is seen from Fig. 4 that this value of the initial intensity fits into the curve as a limiting value, for at low pressure the average intensity should equal the initial intensity.

The initial intensity calculated above was for the case that 100% RaA and RaC′ decompose on the wall. In the case that only 70% RaA and 93% RaC′ decompose on the wall, it is found that the initial intensity of ionization for the 3 sets of alpha particles is equal to 2.708 × 10^4 ion pairs per cm. path.

TABLE I

Summary of Factors used in calculating Ionization produced by α Particles

p	Pressure of air in a sphere of 1 cm. Radius	Complete Average Path Fa	Mund's Efficiency Factors			Average Intensity of Ionization based on	
			F_M	F_M (Recalculated)	F_M'	$\bar{I}_F$	$\bar{I}_{F'}$
0.0	∞	2.249	2.249	2.240	2.462	.000	.000
.1	29944.0	2.143	2.150	2.151	2.347	.527	.550
.2	14972.0	2.042	2.051	2.052	2.231	1.006	1.046
.3	9981.3	1.939	1.953	1.953	2.119	1.436	1.490
.4	7486.0	1.836	1.855	1.855	2.005	1.819	1.880
.5	5988.8	1.733	1.757	1.758	1.893	2.154	2.218
.6	4990.7	1.632	1.661	1.662	1.786	2.444	2.512
.7	4277.7	1.532	1.565	1.566	1.676	2.687	2.750
.8	3743.0	1.432	1.470	1.470	1.565	2.882	2.935
.9	3327.1	1.334	—	1.377	1.462	3.035	3.084
1.0	2994.4	1.238	1.283	1.284	1.357	3.146	3.180
1.1	2722.2	1.138	1.191	1.192	1.254	3.215	3.233
1.2	2495.3	1.049	1.101	1.103	1.160	3.243	3.261
1.3	2303.4	.073	1.020	1.023	1.072	3.250	3.266
1.4	2138.9	.901	.946	.947	0.992	3.246	3.256
1.5	1996.3	.834	.880	.880	.920	3.235	3.235
1.6	1871.5	.774	.817	.817	.854	3.204	3.203
1.7	1761.4	.717	.759	.760	.794	3.163	3.164
1.8	1663.6	.667	.706	.706	.739	3.115	3.116
1.9	1576.0	.627	.659	.661	.692	3.069	3.081
2.0	1497.2	.592	.621	.620	.650	3.041	3.046
2.2	1361.1	.534	.556	.555	.582	2.998	2.999
2.4	1247.7	.486	.504	.503	.527	2.959	2.965
2.5	1197.8	.464	.480	.482	.505	2.941	2.961
2.6	1151.7	.446	—	.460	.482	2.931	2.939
2.8	1069.5	.413	—	.423	.445	2.903	2.917
3.0	998.1	.384	.391	.393	.413	2.888	2.901
3.5	855.5	.327	—	.333	.349	2.856	2.866
4.0	748.6	.285	.287	.289	.303	2.831	2.845
5.0	598.9	.227	.226	.229	.240	2.800	2.814
10.0	299.4	.112	.111	.112	.118	2.745	2.763
15.0	199.6	.074	—	.074	.078	2.724	2.749
20.0	149.7	.055	—	.055	.059	2.716	2.742
∞	0.0	—	—	—	—	2.692	2.708

V. The Ionization in Gases other than Air. The Method of Mund

In the discussion and derivation of the equations related to ionization, the gas considered heretofore was air at 0°C. It is, of course, of importance to be able to use these relations for other gases under varying conditions of temperature and pressure.

In the case of Mund's equation:

$$I_{T,air} = N\, kr^{2/3}\, F_M \tag{36}$$

The factor F_M depends on the ranges of the alpha particles and is therefore a function of both temperature and pressure as stated by Mund.[3] The factor F' depends in exactly the same way on these variables:

$$r = \frac{r_0}{S} \times \frac{760}{P} \times \frac{273 + t}{273} \tag{37}$$

If the stopping power S of the gas in question and the proper pressure P in mm Hg and the temperature t in °C are used to determine r and ρ and hence F or F′, then the Mund equation will apply to the gas under the conditions cited if the quantity $Nkr^{2/3}\, F$ is multiplied by g the specific ionization of the gas:

$$I_{T,gas} = Ngkr^{2/3}\, F_M \tag{38}$$

where $gkr^{2/3}$ is now the total number of ions produced in the gas at 0° and 760 mm.

The complete average path law. If the total ionization is calculated by the average path law (equations 23-26) the situation is entirely similar, because the factors F_a and F_a' depend on the range as do the factors F_M and F_M'. In an analogous manner to the above the factor g is used in this calculation:

$$I_{T,gas} = Ngkr^{2/3}\, F_a \tag{39}$$

The initial intensity of ionization. The total ionization in any gas can be calculated by the use of the initial intensity as stated in section IV:

$$I_{T,gas,P,t} = 3\, N\, I_{S,g,p=0,P,t}\, \bar{p} \tag{40}$$

It can be shown that,

$$I_{s,g,p=0,P,t} = I_{s,air,p=0,760,0^\circ} \cdot gs \cdot \frac{P}{760} \cdot \frac{273}{273 + t} \tag{41}$$

For

$$I_{T,g,P,t} = g\, k_g r_g^{2/3} - g\, k_g\, (r_{g,P,t} - p)^{2/3} \;\ldots\ldots\ldots \tag{42}$$

and

$$I_{s,g,p=0,p,t} = \frac{2}{3}\, g\, \frac{k_g\, r_{g,P,t}^{2/3}}{r_{g,P,t}} \;\ldots\ldots\ldots\ldots\ldots\ldots \tag{43}$$

and

$$I_{s,air,p=0,0^\circ,760} = \frac{2}{3} \cdot \frac{k_a\, r_a^{2/3}}{r_{a,760,0^\circ}} \tag{44}$$

Since $k_g r_g^{2/3} = k_a r_a^{2/3}$ and using equation (37). On dividing equation (43) by (44) there results equation (41). Combining (40) and (41) yields the equation of Lind:[2]

$$I_{T,\,gas,\,P,\,t} = 3N \cdot I_{s,\,air,\,p\,=\,0,760,\,0^\circ} \cdot \bar{p} \cdot gs \cdot \frac{P}{760} \cdot \frac{273}{273 + t} \tag{45}$$

This equation is applicable only in the case of small vessels.

Average intensity of ionization. The expression for the average intensity of ionization for air is given by (30). The same quantity can be obtained for a gas by differentiating equation (42) and averaging the result over the average path in accordance with equation (27). This gives,

$$\bar{I}_{s,\,g,\,P,\,t} = \frac{gk_g r_g^{2/3}}{\bar{p}} \left\{ 1 - \left(1 - \frac{\bar{p}}{r_g} \right)^{2/3} \right\} \tag{46}$$

dividing (46) by (30) gives a relation between the average intensity in a gas and in air at the same temperature and pressure:

$$\bar{I}_{s,\,g} = \bar{I}_{s,\,air} \cdot g \, \frac{\left(1 - \left(1 - \frac{\bar{p}}{r_g} \right)^{2/3} \right)}{\left(1 - \left(1 - \frac{\bar{p}}{r_a} \right)^{2/3} \right)} \tag{47}$$

When this relation is used in equation (31) an expression for the total ionization of any gas results, which is analogous to the equation of Lind (45); however, the initial intensity of ionization is replaced by the average intensity of ionization. Since the average path law in this form is applicable to small vessels, it is simpler to expand[1] (47) for large values of ρ and it is found that

$$\bar{I}_{s,\,g,\,P,\,t} = \bar{I}_{s,\,air,\,0^\circ,\,76cm} \cdot gs \cdot \frac{P}{760} \cdot \frac{273}{273 + t} \tag{48}$$

This relation reduces to equation (45) for $\rho = \infty$ or small pressures. Since this equation is only valid for small vessels where the ratio of range to radius is large, it is best to calculate ionization in any gas by the method of Mund. This is shown by the following test calculations where the total ionization in the case of acetylene has been obtained by the use of equations (38) and (48):

TABLE II

C_2H_2: Stopping Power = 1.12. Specific Ionization 1.26

Radius of Vessel	Pressure of C_2H_2 mm. Hg	ρ	Ionization for 3 alpha particles × 10^5		Ratio I_M/I_L
			Mund Eq. 38	(Average Intensity) (Lind) (Eq. 48)	
4.456	1200	.5	3.743	3.090	1.21
2.674	1000	1.	2.733	2.496	1.10
4.464	599	1.	2.733	2.496	1.10
1.337	1000	2.	1.322	1.391	.95
2.232	599	2.	1.322	1.391	.95
0.893	599	5.	.488	.492	.99
0.446	599	10.	.239	.245	.98

For values of ρ larger than 5 the average intensity method gives values for the total ionization which check the method of Mund.

VI. Air Equivalent Pressure

When calculations are made of the total ionization for a gas, it has been found convenient to use a relation between F_M as a function of pressure of air in a 1 cm. bulb which would give the same ionization as the gas. This corresponding air pressure is defined as the equivalent air pressure. It is calculated as follows.

The condition is that the value of ρ for the gas at P_g in a bulb of radius R_g and for a hypothetical sample of air at the pressure P_a in a one cm. bulb be the same. The gas and air samples are thought to be at the temperature t_g and t_a respectively:

$$\rho_{gas} = \rho_{air} \tag{49}$$

or

$$\frac{r_g}{R_g} = \frac{r_a}{1} \tag{50}$$

and

$$\frac{1}{R_g} \cdot \frac{r_o}{S} \cdot \frac{760}{P_g} \cdot \frac{273 + t_g}{273} = \frac{r_o}{1} \cdot \frac{760}{P_a} \cdot \frac{273 + t_e}{273} \tag{51}$$

or

$$P_a = S \cdot R_g \cdot P_g \cdot \frac{273 + t_a}{273 + t_g} \tag{52}$$

By the use of this equivalent air pressure values of F_M may be obtained from Fig. 4 or from Table I column 2.

In a similar manner an equivalent air pressure may be calculated when the average intensity method of Lind is used to obtain the total ionization for any gas. His relation is,

$$P_a = g \cdot s \cdot R_g \cdot P_g \tag{53}$$

This relation was used to obtain the average intensity of ionization needed for the calculations contained in Table II.

Summary

The methods for the calculation of the ionization produced by the three sets of alpha particles from radon in spherical vessels have been studied and a critical comparison is made. (1) The average path law has been extended to large vessels and a complete system of equations has been developed for vessels of any size. (2) The efficiency factor of Mund for the case of 100% RaA and C on the wall has been recalculated and the similar factor for the case of 70% RaA and 93% of RaC decomposing on the wall has been determined. (3) The analogous factors arising from the complete average path law have been developed. (4) The initial and average intensities have been obtained from the total ionization by an arithmetic procedure and it is shown to what extent they will give accurate values of the total ionization. (5) The concept of air equivalent pressure is defined and used to obtain efficiency factors. The validity of Geiger's two-thirds power Law connecting ionization and range has been assumed in these calculations.

Minneapolis
March, 1931.

CONTRIBUTIONS TO THE CHEMISTRY OF BERYLLIUM

Beryllium II.* Electrolysis of Beryllium Compounds in Organic Nitrogen Derivatives

18·64

BY HAROLD SIMMONS BOOTH AND GILBERTA G. TORREY

Introduction

Previous attempts to prepare metallic beryllium by electrolysis of solutions of its salts have shown that no metal can be precipitated from a solution that contains water as such or the elements of water. Apparently the salts of beryllium all undergo hydrolysis unless every trace of water is eliminated. In order to prevent hydrolysis and yet secure the ionizing properties which make water so useful an electrolytic solvent, the closely analogous compound, ammonia, was considered as a solvent for beryllium salts. However, the inconvenience of working with anhydrous liquid ammonia encouraged the trial of substituted ammonias. Since the behavior of these solutions is so similar this paper will deal only with the work done in the organic derivatives and will be followed by a paper concerning the results in inorganic nitrogen compounds.

Choice of Solvents

Kahlenberg[1] prepared lithium by electrolyzing a solution of lithium chloride in pyridine. This method was tested by us and gave a closely adhering, smooth deposit of metallic lithium. Arguing from the close analogy usually observed between transition members of successive periodic groups it was thought that beryllium could be prepared in the same way. However, in all the electrolyses with pyridine a dark brown material was formed that obscured the electrodes and made the solution so opaque that no observation could be made of the evolution of gases. This brown material also behaved like a colloid and displayed cataphoresis so that the layer of hard, brown material would prevent any beryllium being deposited if liberated at the cathode. More stable solvents that would permit observation of the products of the electrolysis were then sought.

Aniline was next tried with the expectation that it would be more stable on electrolysis. This, however, formed solutions of considerable resistance as compared with those in pyridine, and quinoline was selected as being more analogous to pyridine and yet possibly more stable toward the electric current. The solutions of quinoline were non-conducting so recourse was had to a less complex molecule containing nitrogen such as pyrrole. Although the conductivity of these solutions was satisfactory the troublesome brown material

---

*For "Beryllium. I" see this Journal, 35, 2465 (1931);

[1] J. Phys. Chem., 3, 602 (1899).

was still formed to some extent, nevertheless, metallic beryllium was deposited. A saturated compound was next tried. Piperidine is merely pyridine with all the bonds saturated with hydrogen but this solvent formed solutions of such high resistance that only very small quantities of metal could be obtained after very long continued runs. Phenylhydrazine would not dissolve beryllium salts. The alkyl-substituted ammonias dissolved quantities of beryllium salts but apparently have no ionizing power as the solutions were absolutely non-conducting. Formamide was a good solvent but no metal was deposited from it.

Preparation and Purification of Materials

Pyridine was purified by letting it stand over solid potassium hydroxide, distilling it and collecting the fraction boiling between 116°-117.5°C. Aniline was treated with sodium chloride, dissolved in ether and distilled. The fraction distilling at 182°C. was collected for use. Quinoline was redistilled while the other solvents were used just as obtained in sealed containers fresh from the Eastman Kodak Company. The container was opened, the solvent placed in the dried electrolyzing tube, beryllium salt added, and the tube quickly attached to the rest of the apparatus.

All beryllium salts were prepared as described in a previous article. (See Beryllium I.)

For the work in pyridine a series of solutions of all the available beryllium salts was prepared by allowing the solvent to stand over the solid salt until saturated. The behavior of the salts soon showed that only the chloride, acetylacetonate, and double fluoride of sodium and beryllium were useful as solutes. In the case of the other solvents as much beryllium salt was added as would dissolve quickly and no attempt was made to saturate the solvents completely.

Apparatus

The apparatus which was used for this work was similar to the one already described in an article on electrolysis in miscellaneous non-aqueous solvents. (See Beryllium I). The apparatus was never evacuated as these solutions do not readily absorb moisture and it was not essential to maintain a solvent atmosphere during the electrolysis. Although the tube which contained the solution was always oven dried the apparatus as a whole did not require special drying since the solvents do not vaporize to such an extent that they would become contaminated with moisture absorbed from the walls of the rest of the apparatus.

Experimental

1. *Solutions in Pyridine.* None of the beryllium salts showed a striking solubility in pyridine and their low solubility probably accounts for the small amount of current carried by these solutions. The pyridine was allowed to stand over the solid salts for several days and the supernatant liquid poured directly into the electrolyzing vessel without filtering to prevent contamination by moisture of the air. No quantitative determination was made of the solubility.

a. Beryllium nitrate. Beryllium nitrate tetrahydrate gave a solution of fair conductivity taking five amperes/sq. dm. with 6.15 volts potential across the cell terminals. On continued electrolysis the resistance of the solution increased and sufficient heating occurred to distill away the pyridine unless a cooling bath was used. The solution became brown, hydrogen and oxygen were evolved, but no metal was deposited; this was to be expected on account of the presence of water.

b. Anhydrous beryllium chloride dissolved in pyridine carried only 1.8 amperes/sq. dm. with 9.1 volts potential. Considerable amounts of gas were evolved at the anode but no apparent deposit of metal was produced at the cathode.

c. Anhydrous beryllium sulfate gave a solution of high resistance carrying .1 ampere/sq. dm. with 10.22 volts potential. A white, spongy precipitate was produced in the solution. This was doubtless beryllium hydroxide due to traces of water which are very difficult to remove completely from this salt. Both electrodes were coated with a soft, brown, gelatinous material. No metal was deposited.

d. The sodium-beryllium fluoride solution carried .1 ampere/sq. dm. at 4.5 volts potential. A curve of decomposition voltages was run and the break observed at 3.75 volts. Although on breaking the circuit a back E.M.F. of .2 volts was always observed no metal was ever permanently deposited whether electrolysis was conducted on the 10 volt or 110 volt circuits. The E.M.F. might be due to traces of gas on the electrode although no evolution of gas was ever observed.

e. Beryllium acetylacetonate gave an even more resistant solution than the fluoride taking only .07 ampere/sq. dm. at 9.15 volts, but an adherent, finely divided, black precipitate was produced on the cathode. The black material was soluble in concentrated hydrochloric acid giving a gas and tiny white crystals that rapidly deliquesced. A black E.M.F. of .37 and .49 volts was observed in two trials. The black deposit was metallic beryllium but in such small amounts as not to encourage further study.

Pyridine was also added to beryllium basic acetate, beryllium basic carbonate and beryllium orthophosphate but the supernatant liquid was non-conducting in all cases probably due to the insolubility of these salts.

2. *Solutions in Aniline.* A series of solutions of beryllium salts similar to that in pyridine was prepared in aniline with the oxide added and the nitrate omitted. These solutions possessed a much greater internal resistance than the solutions in pyridine. A 100 volt potential was necessary to force even traces of current through the solutions.

The solution of beryllium sulfate was absolutely non-conducting. The solutions of the phosphate and the sodium-beryllium fluoride carried .001 ampere/sq. dm. and the oxide .005 ampere at 95 volts potential. The basic carbonate and the acetylacetonate carried respectively .015 and .15 amperes/sq. dm. but with no result save a brown coloration of the solution.

Due to the large proportion of the elements of water and the probably complex character of the beryllium basic acetate it was not considered a likely source of metallic beryllium. The solution of this salt was very resistant carrying .05 amperes/sq. dm. at 98 volts potential. However, a solid material of delicate violet color was deposited on the cathode. This material was treated with concentrated hydrochloric acid giving a white solid which rapidly dissolved on exposure to air due to its hygroscopicity. The small amount of solid obtained by electrolysis made it impossible to test more than the solubility in hydrochloric acid but it was doubtless metallic beryllium.

3. *Solutions in Quinoline.* The low conductivity of the solution in aniline indicated that a compound in which the nitrogen atom was directly in the ring was more satisfactory than one in which the nitrogen was in the side chain. The brown compound that was formed in the pyridine solutions was believed due to polymerization so a more stable compound was sought in which the nitrogen would be similarly placed. Quinoline was selected. A sample of pure quinoline was placed in the electrolyzing apparatus over anhydrous beryllium chloride and connected in series with a source of current giving 120 volts potential. No conductivity was observed. A trace of pure sodium chloride was added giving a very slightly conducting solution. A deep red color spread through the solution from the anode but no gases or other electrode products were observed.

4. *Solutions in Pyrrole.* The failure of the quinoline to produce conducting solutions suggested that the less complex compounds formed solutions of better conductivity probably due to greater solubility of the salts.

a. Beryllium acetylacetonate was found to dissolve in considerable quantities in pyrrole. Five cubic centimeters of the solvent readily dissolved .29 gram and was not then saturated. The conductivity was very low, .045 ampere/sq. dm. on a 15 volt circuit, but an adherent black deposit was formed on the cathode. The electrode was washed with alcohol and examined under the microscope. The black deposit was crystalline and metallic in appearance. With hydrochloric acid a gas was evolved. There was formed in the solution a black material of the same gelatinous nature as in former experiments with the other solvents but which did not cling to the electrodes. The current was reversed and a black deposit, also soluble in acid with evolution of gas, was obtained showing that the deposit could only be formed on the cathode. Tests indicated that it was metallic beryllium.

b. A solution of similar conductivity was obtained by dissolving beryllium chloride in pyrrole and gave the same, black metallic deposit on the cathode. The conductivity was .1 ampere/sq. dm., but slowly dropped to a constant value of .06 amperes on running for some time. The solution of acetylacetonate in pyrrole also gave the same final value for the conductivity on being allowed to run for some time.

5. *Solutions in Piperidine.* Since all the unsaturated nitrogen compounds had given the troublesome brown, gelatinous material in varying amounts it was thought that a compound in which the nitrogen was similarly placed but completely saturated might prevent the formation of the colloidal material. In piperidine the arrangement is exactly the same as in pyridine but the nitrogen is saturated with hydrogen in place of the double bond to

carbon. Piperidine dissolved beryllium acetylacetonate very readily. About .4 gram was added to five cubic centimeters of piperidine without saturating it. The resulting solution carried only a few hundredths of an ampere on a 115 volt circuit but gave a closely adherent deposit similar to that obtained on the cathode in previous experiments with pyrrole. Apparently these solutions give metallic beryllium but the amount is very small due to the low conductivity and it would require extremely long runs to produce a sufficient amount for the careful study of the metal obtained. The same brown, gelatinous material was obtained in this experiment but did not coat the electrodes.

Since all the aryl derivatives of ammonia gave polymerization products it seemed advisable to try the alkyl derivatives which might be more stable. Amines in which one, two or all of the hydrogens of ammonia were replaced were tried.

6. *Solutions in n-Propylamine.* Beryllium acetylacetonate dissolved very readily in this solvent. About .3 gram was dissolved but the solution was absolutely non-conducting on either 10 volt or 110 volt circuits. On standing several months in a sealed tube this mixture went to a solid, transparent gel.

7. *Solutions in Di-ethyl amine.* This solvent was selected as having two of the hydrogens replaced by alkyl and by analogy of structure should have behaved the same as piperidine in which two hydrogens are replaced by aryl linkages.

a. Beryllium acetylacetonate dissolved very slowly in this solvent, ten cubic centimeters of solvent requiring several hours to dissolve .2 gram. No conductivity was observed on either 10 volt or 110 volt circuits.

b. A small amount of beryllium chloride was added to a portion of the solvent but showed no tendency to solution and the supernatant liquid was non-conducting.

8. *Solutions in Tri-ethylamine.*

a. Beryllium acetylacetonate dissolved in this solvent slowly. About .1 gram was taken up by ten cubic centimeters of solvent but the solution was absolutely non-conducting.

b. Beryllium chloride showed no apparent solubility in this solvent and the supernatant liquid was non-conducting.

9. *Solutions in Phenylhydrazine.* Apparently the most satisfactory compounds of nitrogen are those in which there is no double bond to nitrogen and in which one hydrogen has been left unsubstituted. In phenylhydrazine nitrogen is linked to aryl group, to hydrogen by one bond and the third bond is satisfied by linkage to nitrogen again. However, neither beryllium acetylacetonate or beryllium chloride showed any solubility in this solvent and the supernatant liquid was non-conducting. On standing some reaction seemed to have taken place as the salts had swollen and formed new types of crystals. Probably the phenylhydrazine had formed addition products with these salts as it is known to do with other metallic salts.

10. *Formamide.* The fact that the presence of an amino group seemed to favor the formation of conducting solutions of beryllium salts suggested the use of formamide and acetamide as electrolytic solvents.

a. Beryllium chloride in formamide. A small amount of anhydrous beryllium chloride was dissolved in pure formamide. The solution carried 1.0 A per sq. dm. at 2.7 volts potential across the cell. Strong gassing occurred at the anode and small amounts of gas at the cathode but no metal was deposited. In a saturated solution of beryllium chloride a drop in potential of 8.1 V. at C.D. of 15 amperes/sq. dm. likewise gave no metal. The voltage was increased to 14.5 volts without depositing beryllium.

b. Beryllium acetylacetonate in formamide. Beryllium acetylacetonate was found to be quite soluble in formamide and at a C.D. of 15 amperes/sq. dm. showed a drop in potential across the cell of 7.2 volts. Considerably more gassing was obtained at the anode than at the cathode but no metal was deposited. Increasing the voltage failed to cause deposition of beryllium.

c. Beryllium basic acetate. This salt was quite soluble in formamide but on electrolysis at a current density of 15 ampere/sq. dm. with drop in potential of 7 volts no metal was deposited. Increasing the voltage did not cause deposition of metal.

Recently Yntema and Audrieth[1] have found that zinc, cadmium, lead, tin, cobalt, and nickel were deposited electrolytically from solutions of their salts in formamide, although they were unable to deposit metals higher than zinc in the electromotive series.

Conclusion

Solutions of various beryllium salts in organic derivatives of ammonia have been electrolyzed. Some of the solutions are absolutely non-conducting while others carry a small current and produce metallic beryllium in small quantity, particularly solutions in piperidine and pyrrole. In general the solutions form gelatinous, colloidal substances which render the practical separation of metallic beryllium from these solvents problematical.

Morley Chemical Laboratory,
Western Reserve University,
Cleveland, Ohio.

---

[1] Yntema and Audrieth: J. Am. Chem. Soc., 52, 2693 (1930).

THE RATE OF DEFORMATION OF CELLULOSE NITRATE-CAMPHOR FILMS UNDER STATIC STRESSES*

BY J. G. McNALLY AND S. E. SHEPPARD

It has been recognized for some time[1] that dynamic loading tests made on imperfectly elastic materials may give results difficult of interpretation because of the uncertain effect of the rate of application of the load on the deformation produced. The effect has been studied in the case of cellulose nitrate film by Sheppard, Carver and Sweet[2] using a machine of the Schopper type by means of which continuously increasing loads are applied to the test piece. It was found that as the rate of loading was decreased, the yield point decreased, the breaking load decreased and the elongation at rupture reached a maximum at a rate of loading intermediate between the highest and lowest employed. Dynamometer tests made at a standard rate of loading are unquestionably useful in a practical sense but such values as yield point, elongation at stretch and breaking stress have lost the fundamental significance they were formerly thought to have.

The method of studying the mechanical resistance of imperfectly elastic materials by observing the deformations produced by different static loads is inherently more free from complications than the dynamometer method and it can be made to yield results that characterize the material quite well. When a strip of cellulosic plastic is subjected to a static stress such as produced by a hanging weight, it shows an immediate elongation the magnitude of which depends on the stress applied. When this extension is reached the plastic is not in equilibrium but a slow extension continues as long as the stress remains even though the stress be very small. The rate of this extension depends on the magnitude of the stress and by plotting the rates of extension for various stresses a curve is obtained which is a good representation of the resistance of the plastic to forces of this nature. A summary is given in this paper of the results of such studies on cellulose nitrate-camphor films.

Experimental

The films used in the tests were made from a cellulose nitrate containing 11.2 per cent nitrogen. Twenty per cent solutions of the cellulose nitrate were made in acetone and various amounts of camphor added to the solutions to make the desired camphor content in the solid film. The dopes were coated on glass plates to give films approximately 0.05 mm. in thickness. After being thoroughly dried to remove residual solvent, the films were cut into strips 3.60 mm. in width and tested.

---

* Communication No. 464 from the Kodak Research Laboratories. Presented at the Indianapolis meeting of the American Chemical Society, April, 1931.

A photograph of the testing apparatus is shown in Fig. 1. It consists of a comparator on the stage of which a fixed clamp, C_1 is mounted. The free end of the film, F, is held in a clamp, C_2, which is free to move longitudinally under the influence of the tension exerted by the weight, W, which acts over the pulley, P. The spring, S, was found to be useful as it provided a method for gradually applying the weight, W, to the film. The elongation of the film at any time was determined by locating the position of a reference mark on the scale, R.

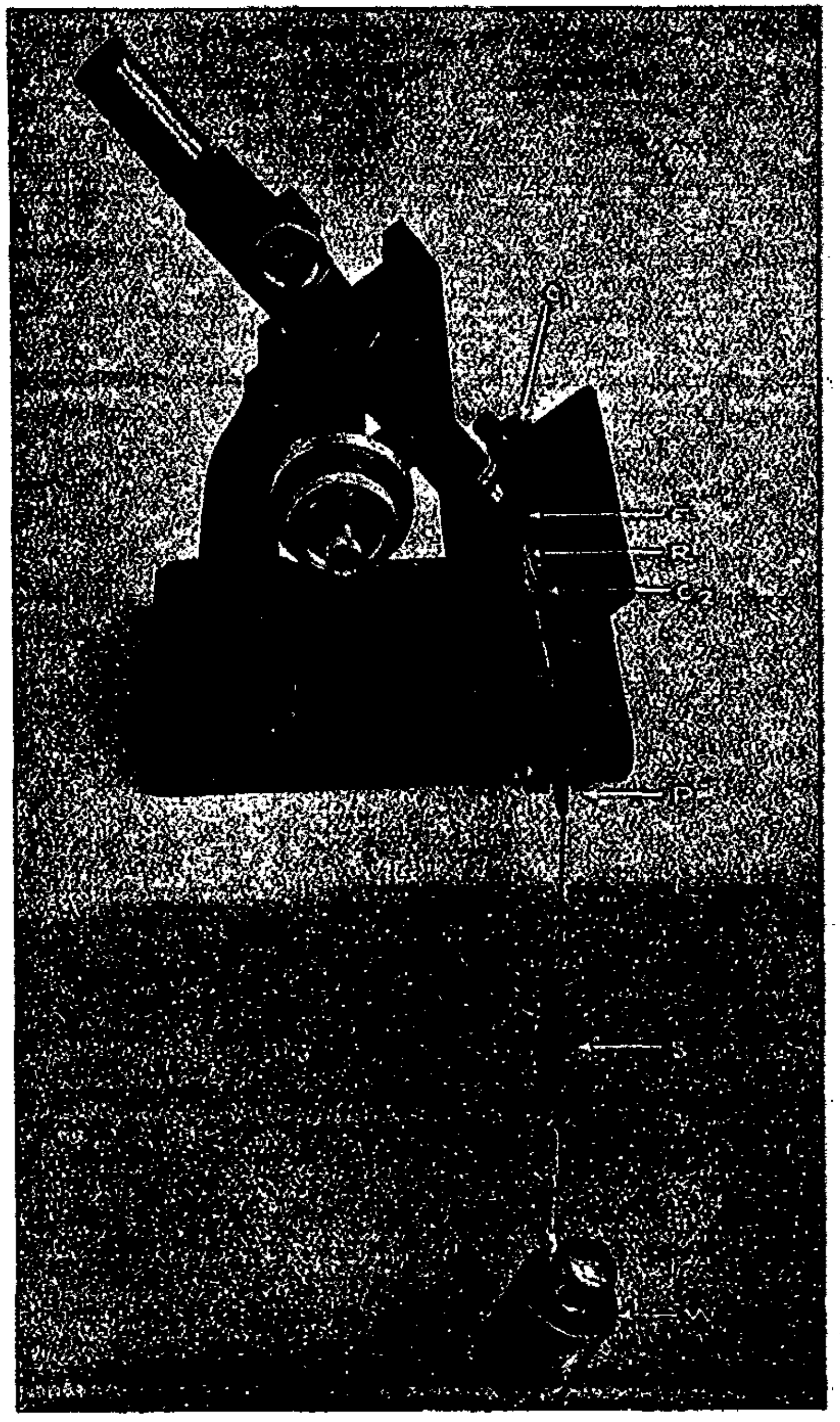


Fig. 1

The rate of extension under constant stress of cellulose nitrate films containing 0, 5, 10, 15, 20, 25, 30, 35, 40 and 50 per cent by weight of camphor are shown in the curves from Figs. 2 to 11. The numbers on the curves indicate the stress in Kg/mm.^{2} that is causing the extension. It will be seen that the shape of the time-extension curves is the same for the different camphor

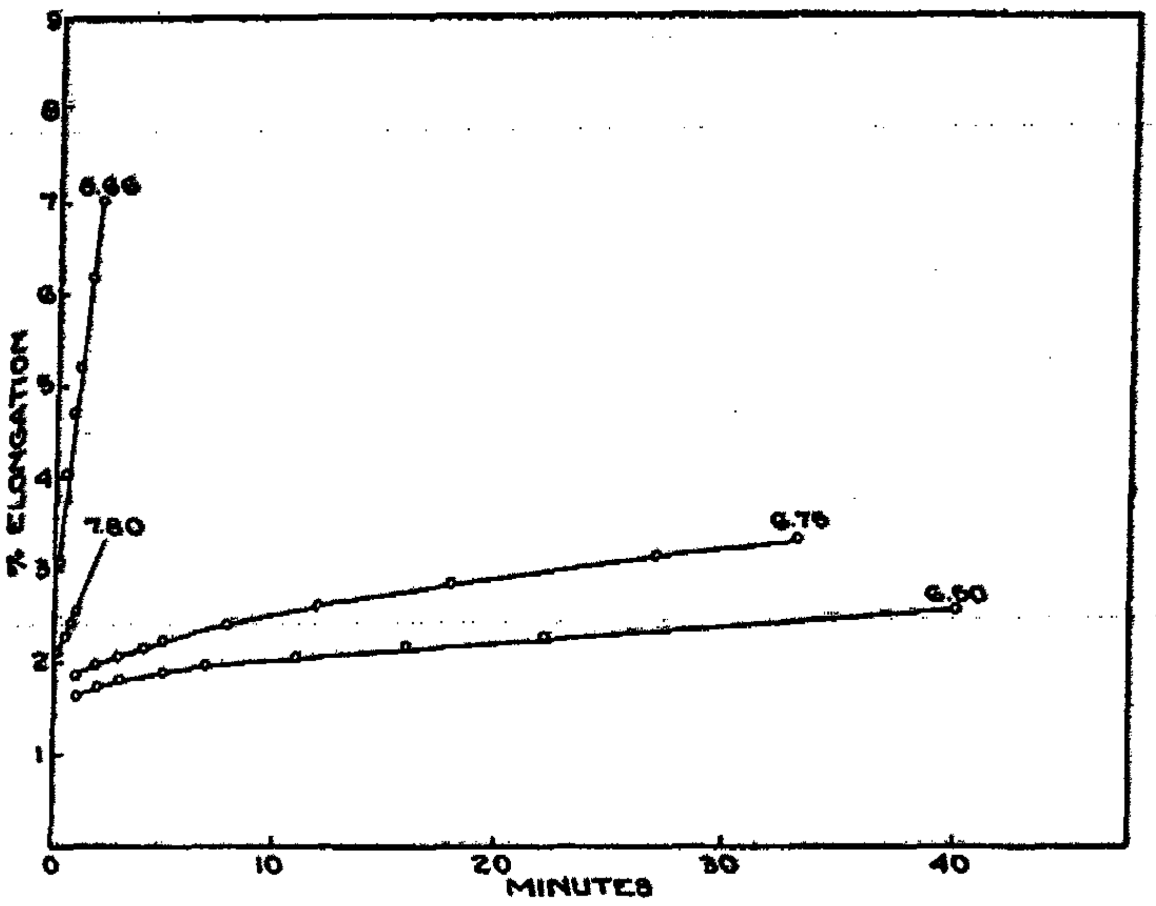


FIG. 2
Rate of Elongation of Cellulose Nitrate

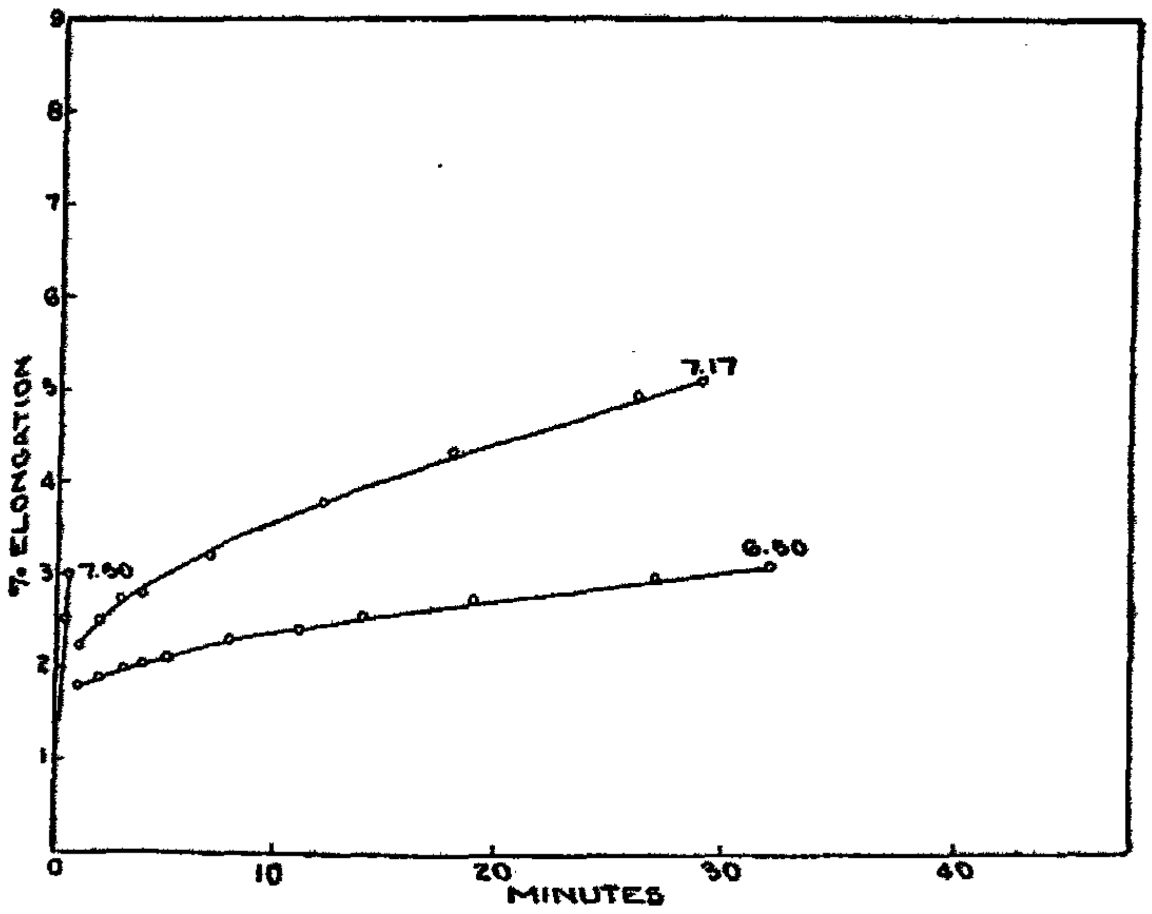


FIG. 3
Rate of Elongation of Celluloid containing 5% Camphor

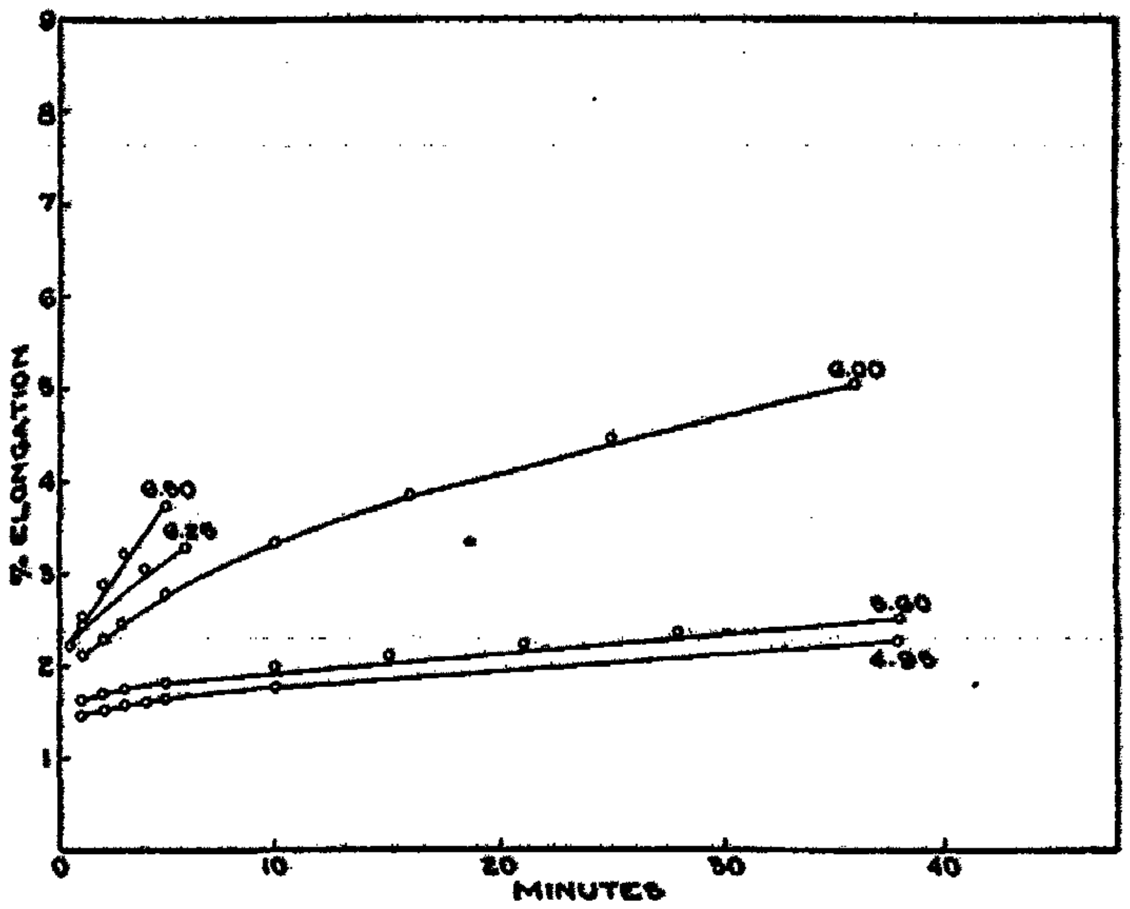


FIG. 4
Rate of Elongation of Celluloid containing 10% Camphor

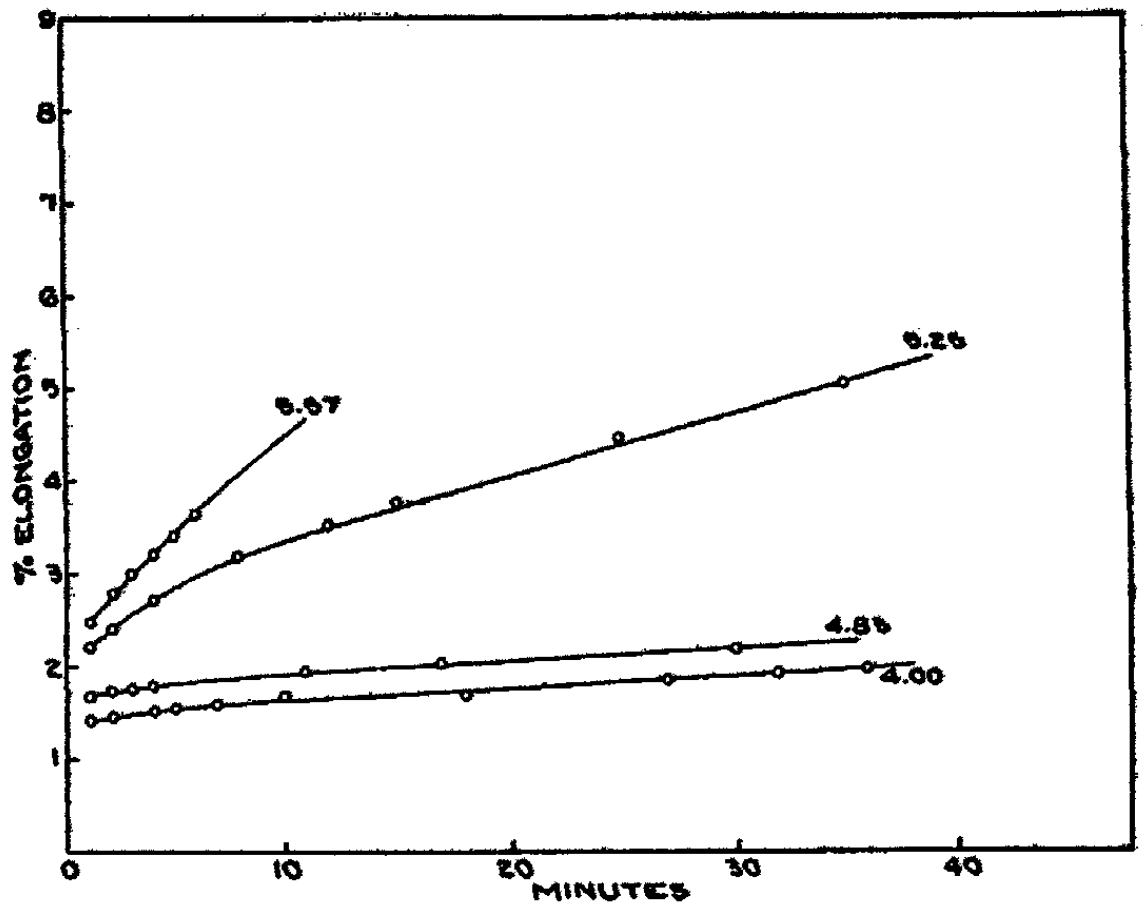


FIG. 5
Rate of Elongation of Celluloid containing 15% Camphor

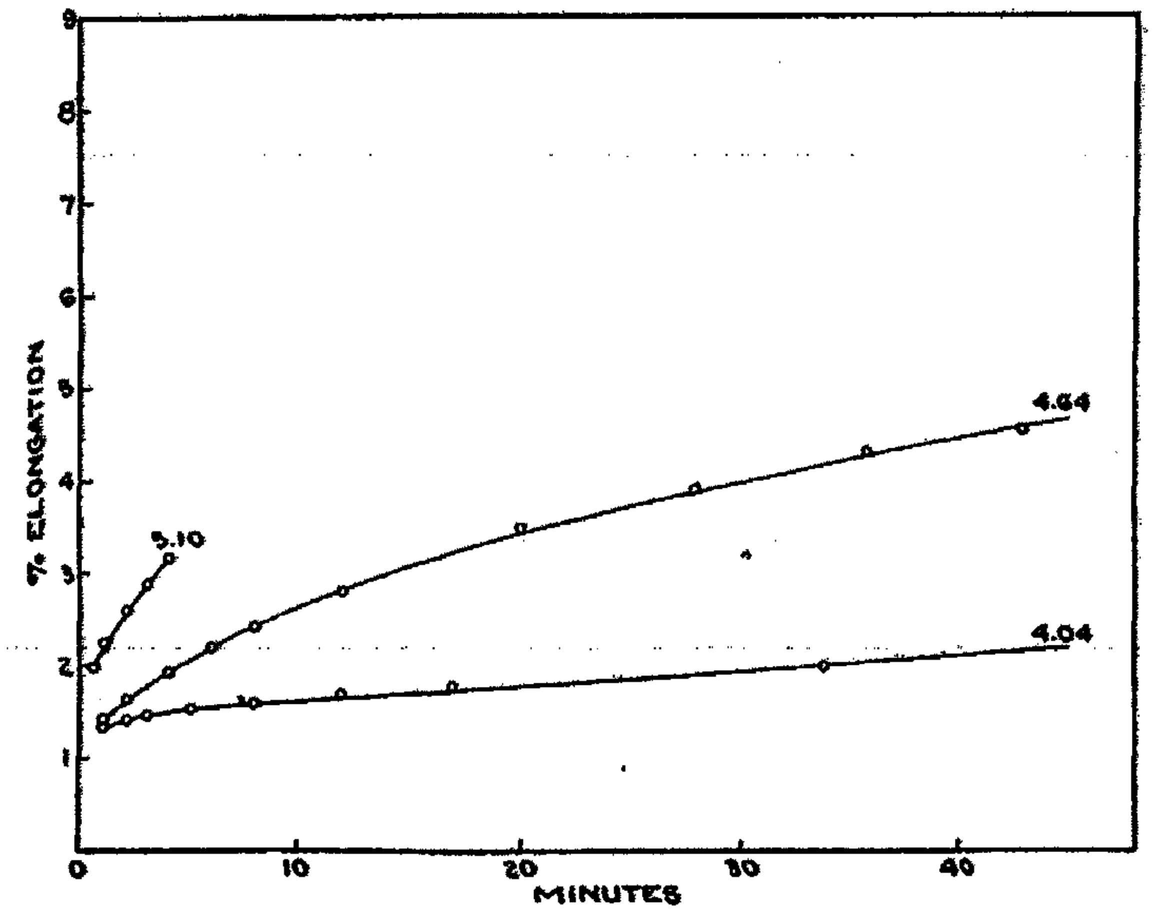


FIG. 6
Rate of Elongation of Celluloid containing 20% Camphor

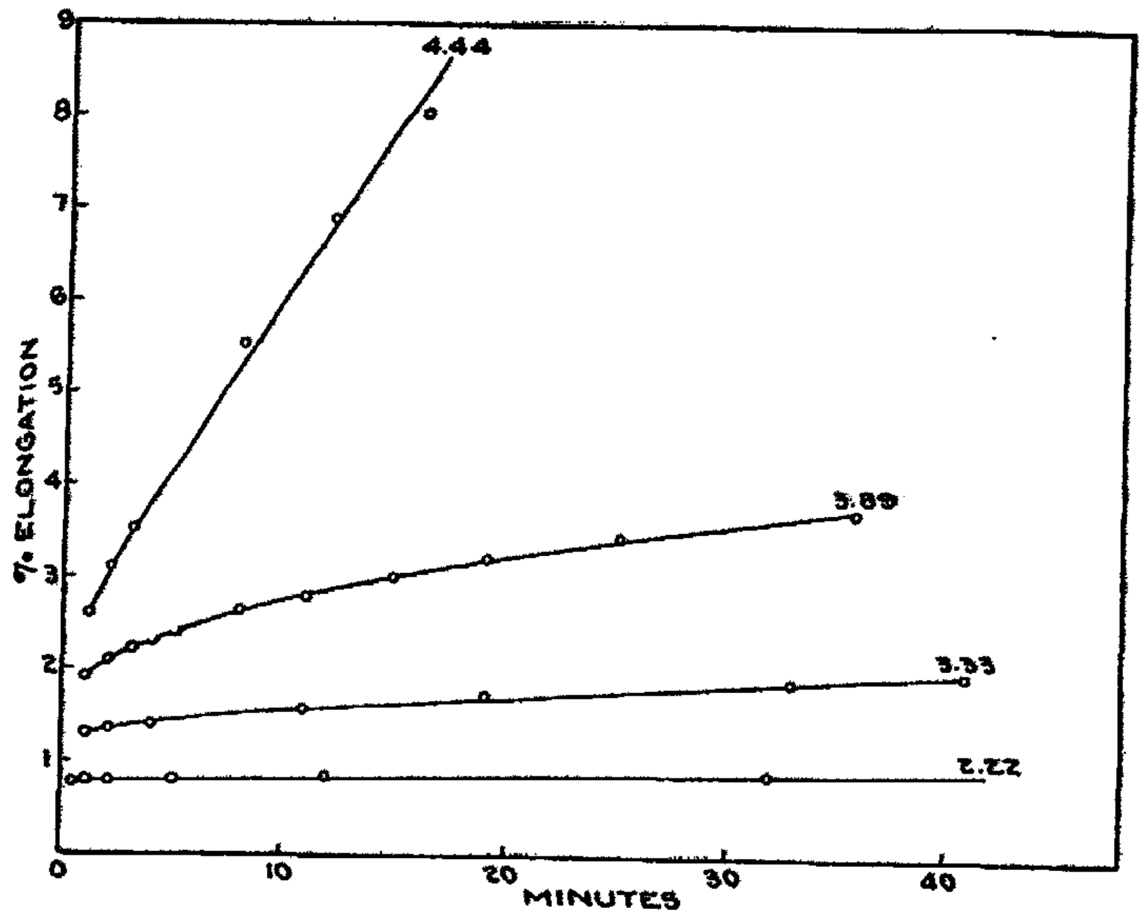


FIG. 7
Rate of Elongation of Celluloid containing 25% Camphor

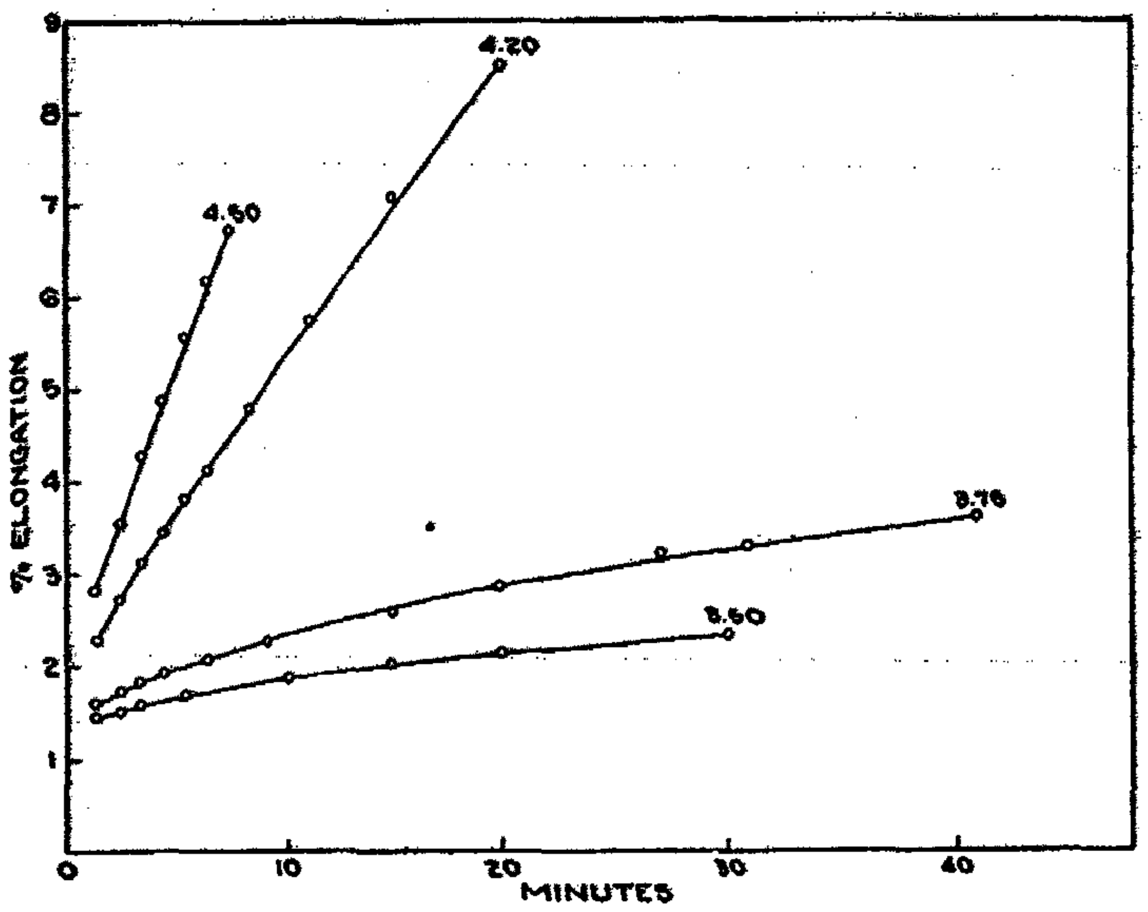


Fig. 8
Rate of Elongation of Celluloid containing 30% Camphor

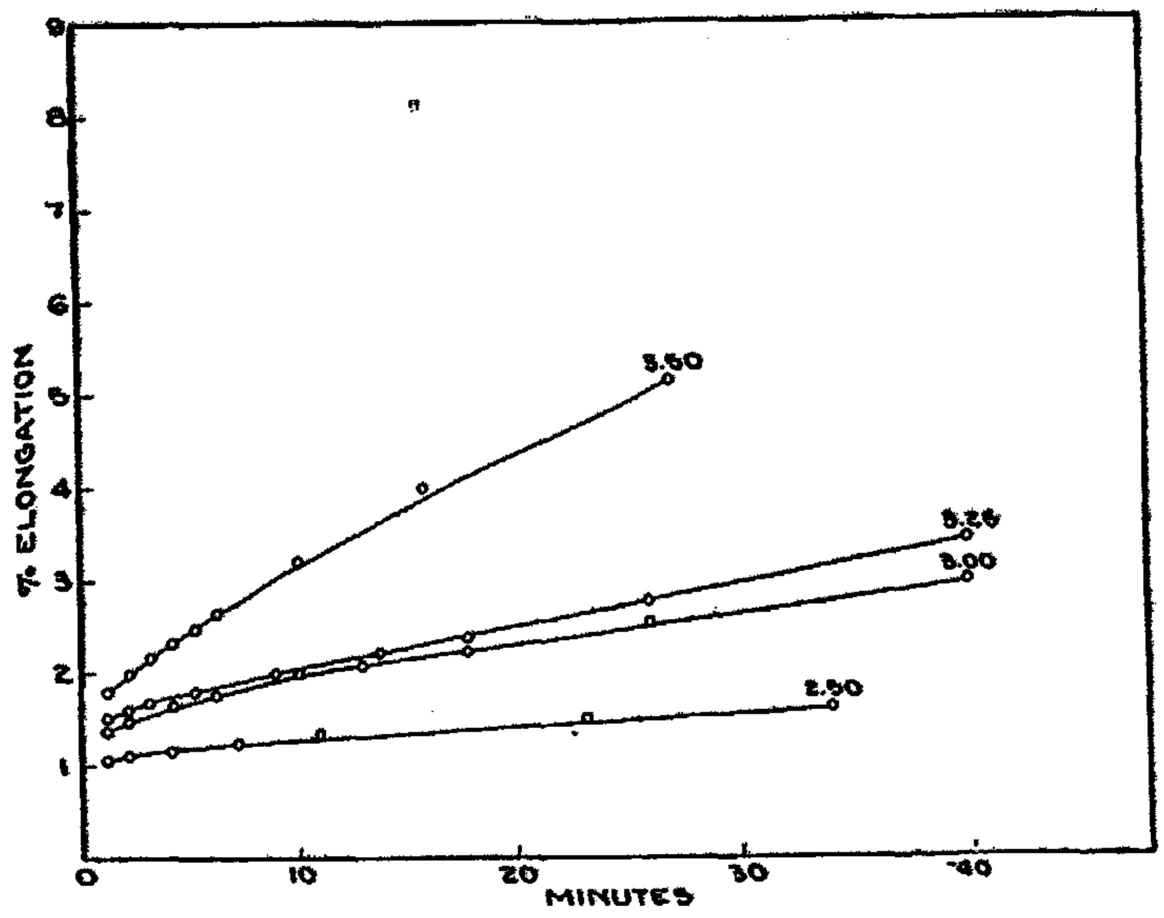


Fig. 9
Rate of Elongation of Celluloid containing 35% Camphor

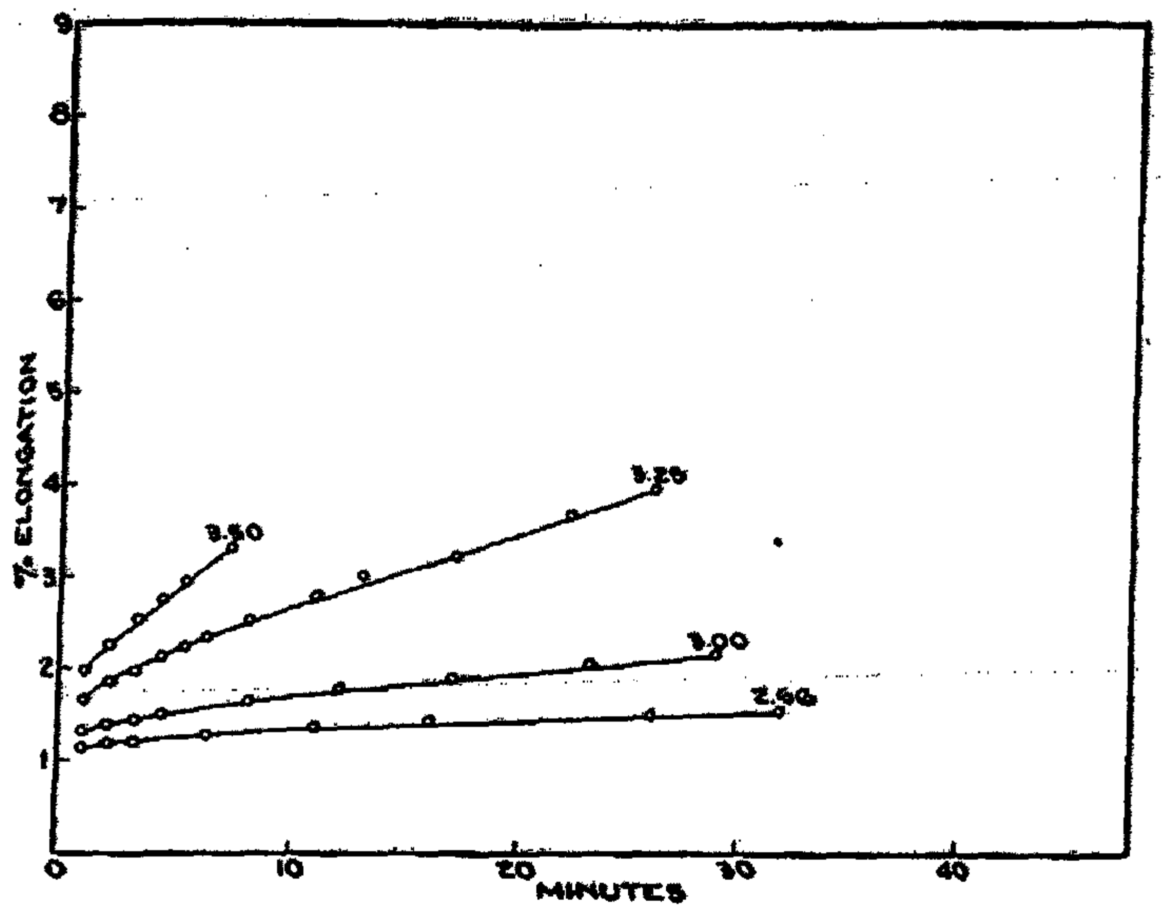


FIG. 10
Rate of Elongation of Celluloid containing 40% Camphor

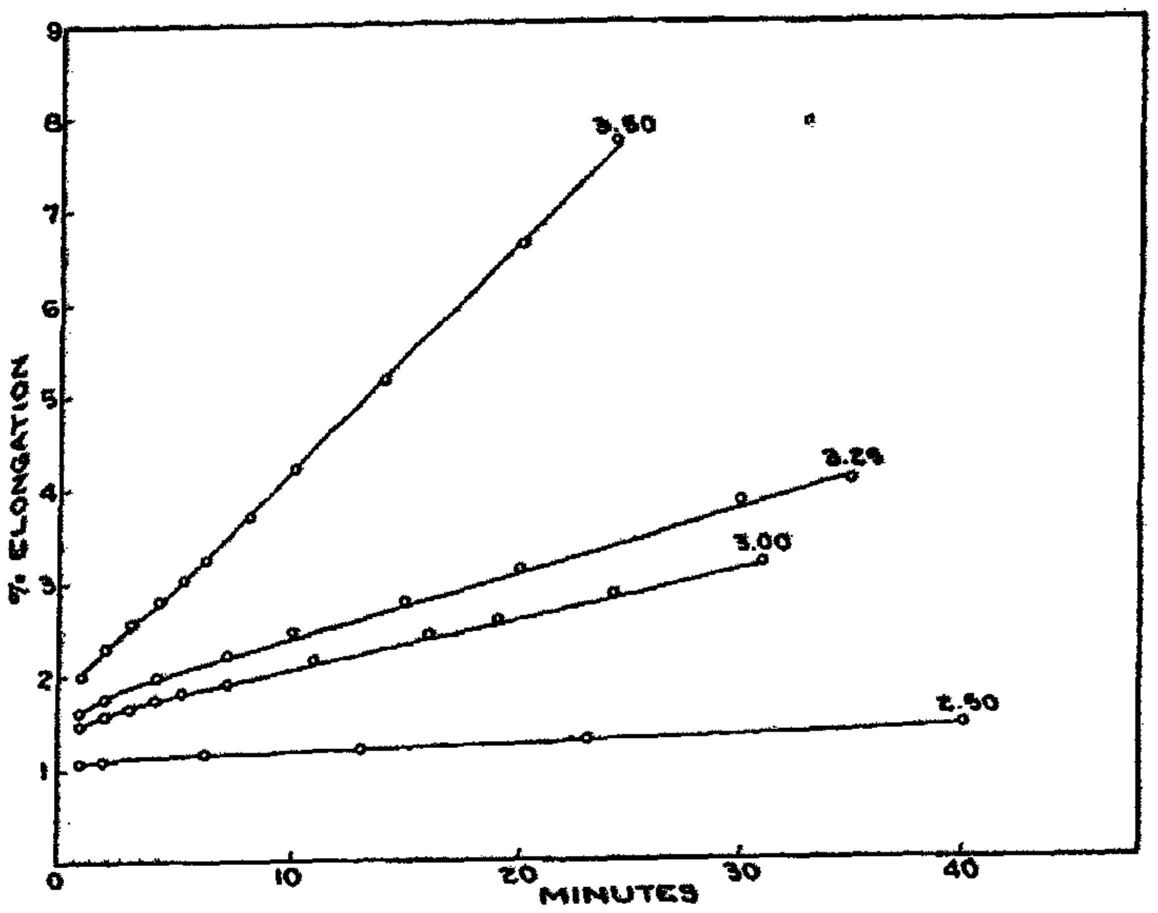


FIG. 11
Rate of Elongation of Celluloid containing 50% Camphor

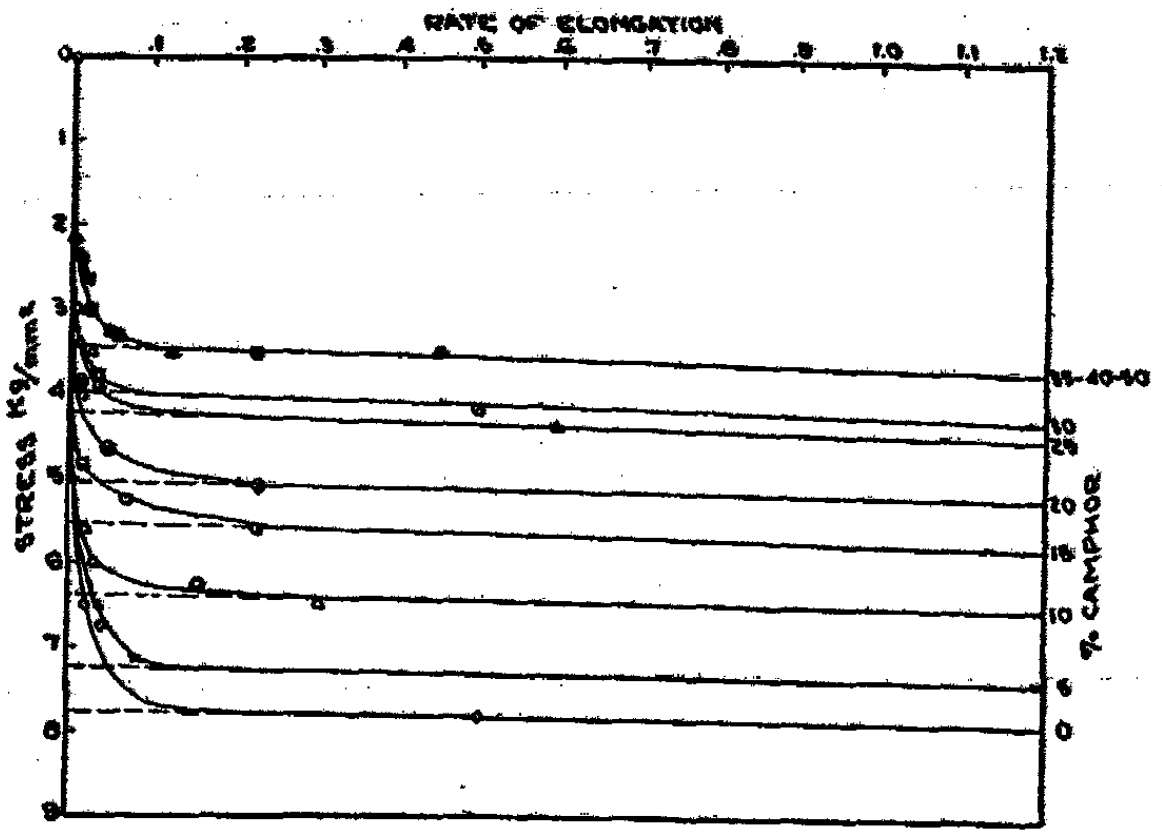


FIG. 12
The Rate of Deformation of Celluloids of Varying Camphor Content at Different Stresses

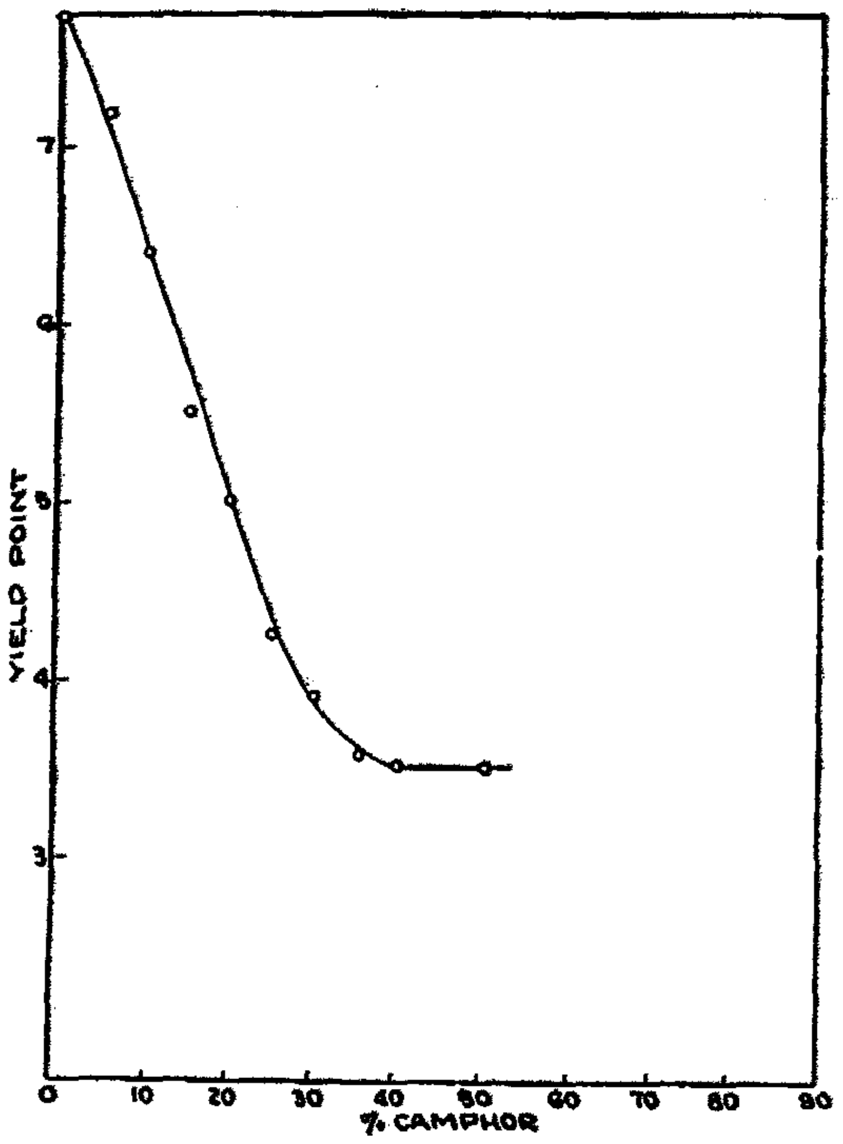


FIG. 13
The Yield Points of Camphor Cellulose Nitrate Films

contents, but the stress corresponding to similar rates of elongation varies with the composition of the films.

In Fig. 12, the velocity of elongation of each film is plotted against the corresponding stress. A curve is obtained that may be approximately represented by the equation

$$\log R = KS$$

where R is the rate of extension, S the stress and K a constant. The occurrence of the sudden change in the slope of the curve appears to be somewhat similar to the yield point observed with clays and a number of sols and gels but is distinguished from the phenomenon of plastic flow in that part of this slow extension is reversible and hence is not to be considered as a pure flow.

It is a matter of interest that increasing the camphor content of the film causes a progressive decrease in the stress at which rapid extension commences until a camphor content of 35 per cent has been reached. Further increments of camphor up to 50 per cent caused no shift in the curves. This is well illustrated by the curve in Fig. 13 where the yield point is plotted against the camphor content showing the decrease in yield point up to 35 per cent camphor and no change from that concentration up to 50 per cent. Clément and Rivière[3] have given data showing that the breaking strength of "celluloid" decreases 14.8 per cent when the camphor content is changed from 20 to 25 per cent, which is at the rate of 2.96 per cent decrease for 1 per cent increase in camphor content. A further increase to 50 per cent camphor decreased the breaking strength 22.3 per cent more, which is at the rate of 0.9 per cent for 1 per cent camphor. This indicates that dynamometer tests agree with the static loading tests in the result that some camphor concentration must be reached after which further increments cause relatively small changes in resistance to stresses.

Discussion

In order to explain the results obtained by Wächtler[4] on the double refraction of "celluloid" it seems necessary to assume at least a two-component structure for the material. These investigations have recently been extended by Derkson, Katz, Hess and Trogus[5] who have shown that cellulose nitrate plastic containing 40 per cent of camphor first becomes positively doubly refracting on stretching but further extension causes the double refraction to decrease to zero and ultimately to reverse its sign. The double refraction observed in stretched cellulose nitrate is caused by the orientation of anisotropic micelles,[6] and the circumstance that cellulose nitrate and camphor have practically the same refractive index[4] eliminates the possibility of form double refraction. The explanation of the phenomenon is that two components in the "celluloid" give rise to double refraction of opposite sign on orientation. The positive component, which is cellulose nitrate or a cellulose nitrate-camphor complex, orientates more rapidly than the negative camphor crystallites and hence the appearance of positive birefringence at low elongations. Further extensions more completely orientate the negative component so that the stretched celluloid ultimately shows negative double refraction.

The data given in this paper showing a discontinuity in the effect on the resistance to stress of camphor increments above 35 per cent can be explained by the same theory as outlined by Derkson, Katz, Hess and Trogus[5] to explain the discontinuity found at 37 per cent camphor when the double refraction at maximum strain is plotted against the camphor content. Below this concentration camphor is associated with the nitrocellulose in a different manner than additions above this concentration. At 35 per cent camphor, which is the transition point in the rate of elongation-camphor content diagram, there exists in the "celluloid" an equimolecular ratio of camphor molecules and nitrated glucosan units, which suggests stoichiometric combination of the two components. The ease by which camphor can be removed from celluloid by extraction or by steam distillation shows that such a compound must be very unstable and resemble a solvate. Below 35 per cent camphor then celluloid consists in a mixture of cellulose nitrate and the cellulose nitrate-camphor complex; above 35 per cent camphor, the components are camphor and the camphor-cellulose nitrate complex.

Acknowledgment

Our best thanks are due Mr. W. Groth, who prepared the films used in these experiments.

Rochester, N. Y.
March 10, 1931.

Bibliography

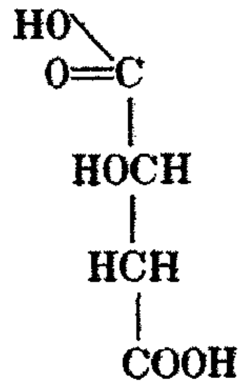
[1] S. A. Shorter: J. Textile Inst., **15**, T207 (1924).
[2] S. E. Sheppard, E. K. Carver and S. S. Sweet: Ind. Eng. Chem., **18**, 76 (1926).
[3] L. Clément and C. Rivière: "La Cellulose," p. 309 (1920).
[4] M. Wächtler: Kolloidchem. Beihefte, **20**, 157 (1924).
[5] J. C. Derkson, J. R. Katz, K. Hess and C. Trogus: Z. physik. Chem., **149**, 371 (1930).
[6] J. G. McNally and S. E. Sheppard: J. Phys. Chem., **34**, 165 (1930).

THE OPTICAL ROTATION OF LACTIC ACID*

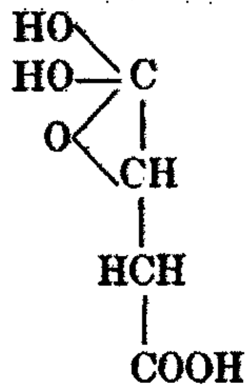
BY WILDER D. BANCROFT AND HERBERT L. DAVIS

A recent study[1] of malic acid led us to the conclusion that its optical rotatory power is due not only to the rotations of its ions and molecules as their formula is ordinarily written but also to the rotation of another tautomeric form whose rotation is in the opposite direction to that of the ions or molecules and which has an ethylene oxide formula. It was shown that solutions of l-malic acid contain mixtures of the normal form and of the ethylene oxide form.

Form I (Levo-)



Form II (Dextro-)



The levorotatory form is the one which predominates in dilute aqueous solutions and ionizes to give levorotatory ions; while the dextrorotatory form predominates in optical effect in concentrated solutions causing such solutions of the free acid or its salts to be dextrorotatory. There has been no confusion in the designation of the malic acids, the acid whose properties have just been described being always called l-malic acid.

This is by no means true of the lactic acids and even today what acid any given author means by d-lactic acid can only be determined by a careful study of the properties reported. Sarcolactic acid in aqueous solutions which are not too concentrated is dextrorotatory while its salts and esters show levorotation. This acid should most properly be designated l(+)lactic acid. The present paper will show that the properties of lactic acid are exactly analogous to those of malic acid and that the rotations are to be explained in the same manner. The study of lactic acid is further complicated by the existence of anhydride and lactide forms. Such forms have not been reported for malic acid and if they exist at all are far less stable than those of lactic acid.

The lactic acids occur in the usual three modifications: the dextrorotatory alpha-hydroxy-propionic acid called also dextrolactic, sarcolactic or paralactic acid; levolactic acid; and finally the inactive or dl-lactic acid commonly called

---

[1] Bancroft and Davis: J. Phys. Chem., 34, 897 (1930).

* This work is part of the programme now being carried out at Cornell University under a grant from the Heckscher Foundation for the Advancement of Research established by August Heckscher at Cornell University.

fermentation lactic acid. The commercial lactic acid is usually a synthetic product or a fermentation product. In the latter case we have confirmed the observations of various authors and find that the commercial lactic acid does show some activity due to a slight excess of one form of the active acid over the other. Thus a sample from Kahlbaum was found to be weakly dextrorotatory. In order to avoid confusion we shall in the present paper treat the subject entirely in terms of sarcolactic acid even though some of the data reported have been obtained from investigation of the antipodal acid or its salts. There is no authentic[1] evidence of any difference other than the direction of optical rotation between the two acids, so that anything which may be said of one optically active form may be equally said of the other form with the sign of rotation changed.

The sarcolactic acid with which we deal, then, is dextrorotatory in dilute aqueous solutions, while its salts and esters are levorotatory. As has been pointed out by us before[2] and, as will be more fully shown in this paper, this acid should be called l(+)lactic acid to indicate that its real rotation is levorotatory even though, because of abnormalities in its properties, it happens to give dextrorotatory aqueous solutions. The necessity of considering the salts and esters as giving the real rotation of such alpha-hydroxy acids as lactic acid was pointed out by van't Hoff[3] and has gradually been working into accepted practice, as is shown in the note to a paper by Frankland and Garner.[4]

"In considerations of this kind in which the sign of optical activity is concerned, much confusion often arises owing to the rotation of an acid and its salts or esters being of opposite sign. In all such cases, it is most satisfactory to denote the rotation of the acid by the sign exhibited by its salts in dilute aqueous solution, that is, the sign of the active acid ion. This convention will be adopted consistently in the present paper. Thus by l-lactic acid will be denoted the acid which gives levo-lactates."

A more recent example of the confusion which is sometimes arising in this connection is the reply of Clough[5] to a criticism from Levene. Levene and Haller (1927) showed that "the optically active form of 2-hydroxybutyric acid which is dextrorotatory in aqueous solutions at ordinary temperatures, but which yields levorotatory salts and esters, possesses the same configuration as d-lactic acid or l-tartaric acid." Clough had previously said that l-lactic acid was the acid of analogous configuration and now replies: "In order to distinguish the enantiomorphous forms of a compound from one another, the conventional symbols d and l have usually been assigned to them in a somewhat arbitrary manner. Thus d-lactic acid is the form which is dextrorotatory in aqueous solution at ordinary temperature but which gives levorotatory salts and exters, while l-aspartic acid which may be prepared from

---

[1] Herzog and Slansky: Z. physiol. Chem., 73, 240 (1911).

[2] Bancroft and Davis: J. Phys. Chem., 35, 1624 (1931).

[3] van't Hoff: "The Arrangement of Atoms in Space", 141 (1898).

[4] Frankland and Garner: J. Chem. Soc., 105, 110 (1914).

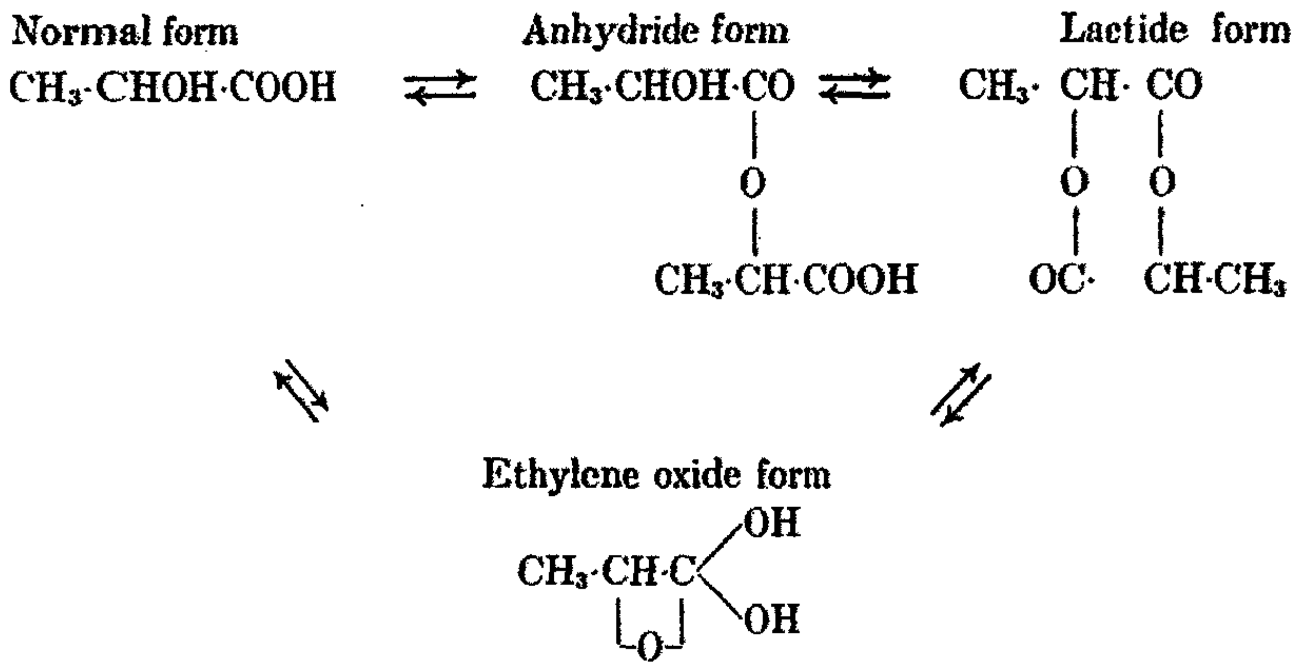
[5] Clough: J. Biol. Chem., 75, 489 (1927).

natural l-aspargine, is dextrorotatory in aqueous solution. Guye and Jordan who resolved 2-hydroxybutyric acid into its optically active forms, termed that variety of this acid, the salts and esters of which were levorotatory, 'l'acide alpha-oxy-butyrique gauche'. Beilstein refers to the same compound as 'l-alpha-oxy-buttersaure'. The present author also designated this compound l-alpha-hydroxybutyric acid and expressed the view that it was configurationally related to l-tartaric acid." Probably no better example could be cited to show the confusion resulting from a failure to understand the principle enunciated by van't Hoff and to apply it.

The numerous investigations designed to correlate the configurations of various optically active compounds have brought this question much nearer a solution and have shown clearly the necessity of thus considering the acids in terms of their salts and esters. Patterson and Lawson[1] have reported such a study for the derivatives of that form of lactic acid which is levorotatory. The derivatives are dextrototatory and their change in rotation with change in temperature classifies them with the derivatives of d-tartaric acid and the conclusion is reached that this form of lactic acid should be called d-lactic acid.

The Forms of Sarcolactic Acid

The references just cited demonstrate clearly the wisdom of an adequate system of nomenclature and designation for the lactic acids. Probably the most familar form of lactic acid is the sarcolactic acid which is dextrorotatory in dilute aqueous solutions and which gives levorotatory salts and esters. This acid should be designated as l (+) lactic acid and will be referred to hereafter as sarcolactic acid. The literature includes some discussion of at least three apparently well-authenticated forms of sarcolactic acid and to these we must now add a fourth form, an ethylene oxide form analogous to that shown to exist in the case of malic acid. These four forms take part in equilibria and will be referred to by these names.



---

[1] Patterson and Lawson: J. Chem. Soc., 1929, 2024.

The evidence indicates that the first three familiar forms of sarcolactic acid are all levorotatory while the ethylene oxide form is dextrorotatory and this evidence will now be set forth.

Wislicenus[1] made an early, extensive, and classic study of the lactic acids, their properties, and their formula. The zinc salts are the ones most commonly prepared and the active lactic acids give zinc lactates with two molecules of water (12.88%), while the inactive zinc salt crystallizes with three molecules of water (18.18%). The water content of the zinc salts together with their optical activity serve as tests of their purity. Wislicenus extracted sarcolactic acid from meat and found that when this acid was heated in a retort in a current of dry air and at 130°-150°, the lactide distilled over and crystallized, having a melting point of 124.5°. This lactide was found to be practically inactive but on removing the water from a lactic acid solution stored over sulphuric acid at room temperature, Wislicenus obtained a mixture which he believed to contain only anhydride and lactide and which in alcohol showed a specific rotation of −85.9°. Jungfleisch and Godchot repeated many of the experiments of Wislicenus and they were able to show[2] that the inactivation discovered by Wislicenus was due to the prolonged heating necessary for the distillation of large samples of lactic acid. If smaller samples were taken, dehydrated at 70°, and then distilled over in a vacuum at 150°-155°, an optically active lactide possessing a different crystalline form and melting point (95°) from the dl-lactide was obtained. In benzene solution this lactide was found to possess the following rotations:

Grams of lactide per 100 cc of solution	1.1665	0.5832	0.2916
Specific rotation	−298°	−280°	−246°

Because of the difference in solvents, these rotations are not directly comparable with those of Wislicenus but demonstrated that Jungfleisch and Godchot undoubtedly had in hand a much purer preparation of the lactide than did Wislicenus. This lactide, which they call the dilactide, was dissolved (0.117 g. of dilactide in 30 cc of aqueous solution) and the hydrolysis followed with time by means of the rotations at 13°.

Hours	0	2	6	12	48	72
Specific rotation	−192.8°	−141°	−111°	−59.8°	−42.7°	−8°

This is merely the usual reversal of the dehydration and if permitted to reach equilibrium would have shown a dextrorotation.

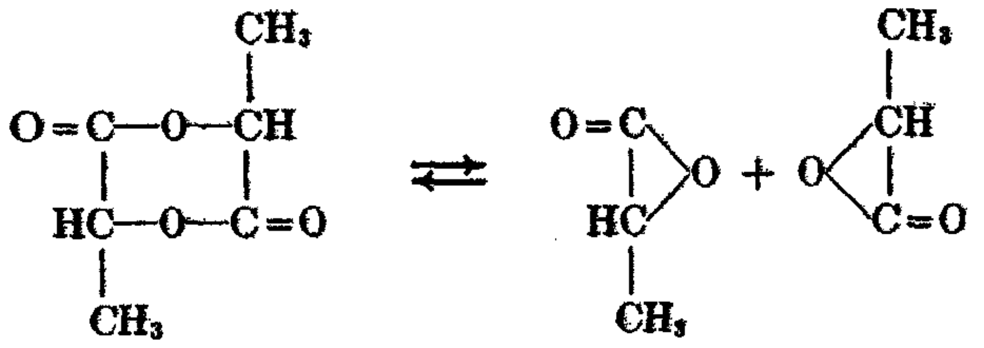
If the lactide were diluted successively in aqueous solution, the decrease in rotatory power observed would be at once attributed to the formation of the more weakly rotatory anhydride or normal form. This explanation is not valid however to explain the same phenomenon in the benzene solutions above for there is no water present. The change must therefore be due to

---

[1] Wislicenus: Ann., **167**, 302 (1873).

[2] Jungfleisch and Godchot: Compt. rend., **141**, 111 (1904).

some other cause such as the existence in equilibrium of such an ethylene oxide form as is here proposed. This change may be quite simply achieved by the mere breaking of the oxygen bonds of the lactide, producing the ethylene oxide forms minus one molecule of water.



If the ethylene oxide form is relatively more soluble in benzene, dilution of the solution with benzene will displace the equilibrium to the right and will result in a diminution of the strong levorotation of the lactide in favor of the dextrorotation of the ethylene oxide form.

The lactide has also been prepared by other methods such as by the distillation of the sodium salt of alpha-bromopropionic acid. When obtained in an optically active form the lactide from sarcolactic acid has shown itself to be very strongly levorotatory.

Now the lactide of lactic acid is the only one of the three familiar forms that has ever been isolated and examined so that the rotation values for the other two forms are much less definitely known than is that of the lactide. This is true because while there has been general agreement that any solution of lactic acid contains all three of the familiar forms there has as yet appeared no method for determining the absolute or relative quantities of these forms in a solution. It appears that the anhydride is a very logical intermediate step between lactic acid and the lactide, both of which surely exist. If the anhydride exists it is certainly levorotatory and that is of importance in the present discussion.

The proof that lactic acid does give anhydride forms is found whenever one titrates a solution of lactic acid, unless the solution be very dilute and has stood for some time. With a concentrated solution or one recently diluted from a concentrated solution the first endpoint reached with alkali and phenolphthalein fades rapidly, and more alkali must be added. The usual procedure is to titrate to the first endpoint and calculate from the alkali used the amount of free lactic acid present. Then excess alkali is added, the solution boiled for about ten to fifteen minutes and the alkali back titrated with acid. The second amount of alkali neutralized is equivalent to the amount of lactic acid originally present in the anhydride or lactide condition. The conversion of these non-acid forms into titratable lactic acid is the process for which the German word Nachsäuerung is used. There is no simple English equivalent for this term so that in this paper the term reacidification will be used to express the acidity due to the hydrolysis of the anhydride and of the lactide into titratable forms corresponding to one replaceable hydrogen for each molecule of anhydride and two hydrogens for each molecule of lactide, the first hydrogen of the anhydride being titratable as free acid without heating.

In an earlier work on the inactive lactic acid Wislicenus[1] devised a method for determining the amounts of each of the three forms in a solution. The assumption was made that, if the volume of alkali used in the original neutralization exceeded that volume used as a result of the reacidification process, then only the normal form and the anhydride form were present. If however the reacidification required more alkali to neutralize it than was required for the original titration, that indicated the presence of only the anhydride and lactide forms. Now this assumption is seen to have certain other underlying assumptions in it. One of these assumptions is that there can be only two of these three possible forms in the same solution. A second is that while the normal form of lactic acid and the one carboxyl group of the anhydride form are neutralized by the first cold alkali added, the hydrolysis of the anhydride and the lactide so as to liberate their carboxyl groups for neutralization takes place only on warming and especially in the presence of excess alkali. Neither of these assumptions is found completely justified, for Wislicenus himself reported that apparently every solution of lactic acid contains some of each of the three forms. In addition to this it is a common observation in the titration of a fairly concentrated solution of lactic acid that even in the cold and with only an excess drop of alkali this process of reacidification proceeds, slowly fading the endpoint. In spite of the evident defects in this method the weights calculated by Wislicenus do agree rather well with the weights taken. This is not surprising in the case of the more dilute solutions where the differences were expressed in terms of water but is of note in those systems which the criteria indicated to contain only the anhydride and lactide forms. This method still remains the best one for gaining some idea of the relative amounts of free acid and anhydride forms in lactic acid solutions.

The method depends essentially on a difference in reaction velocity. The equilibrium between the normal and the ethylene oxide forms of lactic acid is reached very rapidly and probably instantaneously. Therefore no evidence of this form can be obtained by titration. This is not true of the equilibria involving the three familiar forms of lactic acid, for the evidence indicates that equilibrium here is reached only very slowly. An extensive study of this has been made by Eder and Kutter[2] who followed by titration the ratio between the free lactic acid and the anhydride forms, including under the latter term also the lactide. They select as the values representing the equilbrium proportions in solutions of varying concentrations:

Total concentration of lactic acid	80%	50%	20%
Percent present as free acid	62	46.5	19.6
Percent present as anhydride forms	18	3.5	0.4

Their titrations were all reckoned on the basis of lactic acid, so again can serve only as indicators of the equilibrium existing. They diluted various concen-

---

[1] Wislicenus: Ann., 164, 181 (1872).

[2] Eder and Kutter: Helv. Chim. Acta, 9, 355 (1926).

trations of lactic acid to the same final concentrations and by titrations were able to follow the changes as the anhydride forms hydrolyzed to the free acid. Thus were obtained the equilibrium data just given; and, as a result of these runs, they concluded that the attainment of equilibrium in such solutions requires one hundred days at room temperature or about twelve hours at the boiling point. A fundamental defect in this whole method is of course the conditions under which the titrations are made. Thus in the method of Eder and Kutter they apparently diluted five cc samples to 50 cc and then titrated. At once some hydrolysis will start and this will be affected by the concentration of the alkali and by the speed with which the alkali is added. Thus, adding a very dilute alkali very slowly might reveal practically no anhydride form since it might be largely hydrolyzed as a result of the dilution and of the constantly increasing pH. In the presence of excess alkali and at the boiling point the hydrolysis is complete as Wislicenus reported in one half to three quarters of an hour or is practically complete within ten to fifteen minutes depending on the amount of the anhydride present.

Jungfleisch and Godchot (1904) claimed that by adding zinc carbonate o an aqueous solution of the lactide of sarcolactic acid they obtained a levorotatory solution of the zinc salt of the anhydride which they call lactyllactic acid. This zinc salt continued to hydrolyze giving one mol of zinc lactate and one mol of lactic acid which could be titrated as it formed. It is not clear from their report that they did not merely neutralize half the lactic acid as it formed with zinc carbonate and the other half with alkali but at least there were only levorotatory solutions starting with the lactide and ending with the salts of lactic acid.

If we accept the method of Wislicenus as giving something like the true condition of affairs in a concentrated lactic acid solution we may get an idea as to the rotatory power of the lactyllactic acid. The thick syrup obtained by storing a lactic acid solution in a vacuum over sulphuric acid for 21 months was titrated. The amounts of alkali used corresponded to a content of 84% anhydride and 16% lactide. It was this mixture which in alcohol gave a specific rotation of −86° according to Wislicenus. Assuming that the rotations are directly additive and that the value found for the rotation of the lactide in benzene by Jungfleisch and Godchot may be used for its solution in alcohol we have; $0.84\ X + 0.16\ (-300°) = -86°$ or $X = -45°$ as the specific rotation of the anhydride form. Admittedly this is a rather rough approximation, but such a value for the rotatory power is about that observed for such substituted lactic acids as the methoxy and ethoxypropionic acids and we might well expect these compounds to show similar rotatory powers. The inevitable conclusion is that the anhydride of sarcolactic acid is a levorotatory substance.

Proceeding apparently from the complex to the simple, we may now investigate the optical rotatory power of the normal straight form of sarcolactic acid. This study reveals that, contrary to the common impression, the normal form can not be dextrorotatory but must be levorotatory and of a power comparable to the dilute solutions of its alkali salts. When this is demonstrated, it will be clear that since the dextrorotation of dilute aqueous solutions of sarcolactic acid can not be due to the normal form, the anhydride form, or the lactide form, all of which are known to be levorotatory, such dextrorotation must be due to some such ethylene oxide form as is here proposed.

The need for great caution in observing the optical rotatory power of certain types of electrolytes was pointed out very clearly by van't Hoff[1] many years ago. Since extensive quotations from the chapter on The Numerical Value of the Rotatory Power were made in our previous paper,[2] only those sections of especial interest in connection with lactic acid are here presented. It was pointed out that since the magnitude of the rotation is so greatly influenced by such factors as the wave-length of light, the solvent, the temperature, and polymerization or ionization of the solute, no true idea of the real rotation of an optically active molecule can be obtained unless it be examined as a rarefied gas. Since this is obviously impossible in most cases, the next best method is to use dilute solutions. Here we find applicable the generalization known as the Landolt-Oudemann's law, according to which in sufficiently dilute solutions the rotation of any optically active ion is independent of the variation in the inactive ion. The theory of electrolytic dissociation sees in the equivalent molecular rotation of such dilute solutions evidence for the existence of free and relatively unaffected ions in solution.

The organic acids, however, form a separate class of weak or imperfect electrolytes and as such are intermediate between the salts and the non-electrolytes. They must fit into the electrolyte scheme if they can be observed in solutions sufficiently dilute. Some of these such as tartaric and malic acids give evidence for the existence in their solutions of tautomeric oppositely rotatory forms in equilibrium with the forms giving the ordinary ions. These give rise to abnormal changes in the rotatory power on dilution and to anomalous rotatory dispersion. Both these abnormalities disappear when the hydrogen atom of the hydroxyl group directly attached to the asymmetric carbon atom is replaced by less labile groups, or when the hydroxyl group itself is replaced, as by chlorine. This clearly indicates the migration of the hydroxyl hydrogen to be responsible for the abnormalities and, as the previous paper on malic acid showed, this migration is to the adjacent carboxyl group, as in the mechanism here shown.

"Evidently, however, there is something else concerned besides electrolytic dissociation, and that is the point of attack offered to the carboxyl group in another part of the molecule as appears from the following.

"5. Great change of rotation on dilution manifests itself specially with the oxy-acids. Malic acid is remarkable in this respect. The change of rotation which we have observed to characterize this acid is no longer found in methoxysuccinic acid and in the corresponding ethyl derivative, nor in chlorosuccinic and acetylmalic acids. Thus when the hydroxyl group disappears the rotation becomes more constant. The peculiar part played by

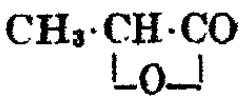
---

[1] van't Hoff: "The Arrangement of Atoms in Space" (1898).

[2] Bancroft and Davis: J. Phys. Chem., 35, 1629 (1931).

this group is, however, still more plainly manifested in the gradual change which often occurs in oxy-acids after a change of concentration or of temperature. This was first observed in the case of lactic acid, the rotation of which decreased on simple standing of the freshly prepared solution; it was recently proved in the case of glyceric acid,[1] and is due to etherification or lactone formation, as Wislicenus showed.

"In the oxy-acids, then, the alteration of the rotation on dilution may be due to a phenomenon akin to lactone formation, which also is probably influenced by electrolytic dissociation. Finally several acids, and not oxy-acids only, possess a double molecule, and accordingly on changing the concentration they may break up in a way which will affect the optical examination. *Comparable results for acids are therefore scarcely to be obtained except by an investigation of dilute solutions of the alkali salts.*

"The interaction of several of the groups attached to the asymmetric carbon atom, which may be accompanied by ring formation, appears to have a quite extraordinary influence on the magnitude and the sign of the rotation. The change of rotation was first observed in the case of lactic acid, $CH_3CHOHCOOH$ $(a)_D = +2°$ and $+3°$, while the lactone  $\underbrace{CH_3\cdot CH\cdot CO}_{O}$ (lactid) has the enormous rotation $(a)_D = -86°$." van't Hoff is in error on this point for nobody has defended the single molecule formula for the lactide and Wislicenus was very clear that $-86°$ represented the rotation of a mixture containing a large excess of the anhydride.

"The same change has been observed for glyceric acid and in the sugar group has indeed become a simple test to distinguish between the isomeric saccharic acids, e.g., of which one forms a lactone, a second a double lactone, a third no lactone." A table shows that in the sugar acids for the most part the rotation of the acid is in the opposite direction to that of the lactone but this is not always the case. "Where the figures, especially those for the acid, are uncertain, because they are strongly influenced by the time and probably also by the concentration, we cannot avoid the conclusion that lactone formation exerts an influence equally profound; for lactic acid the difference amounts to about 90°, for arabonic acid to 70° or more, the same for gluconic acid, for saccharinic acid 100°, and for the double lactone 200°. If the acids had been investigated as sodium salts, and the lactones pure, some relation would perhaps have been found.

"The phenomenon of multi-rotation corresponds completely to that observed in the case of the lactone-forming acids; if these (galactonic acid, e.g.) are set free from their salts in solution, the gradual change of rotation manifests itself here also, only it proceeds faster in the case of the acids. Moreover, the lactone-forming bodies and those possessing multi-rotation are most intimately related to one another; the aldehydes exhibiting multi-rotation, glucose, galactose arabinose, xylose, rhamnose: correspond to the lactone-forming acids, gluconic and saccharic, galactonic, arabonic, xylonic and rhamnonic acids.

---

[1] Frankland and Appleyard: J. Chem. Soc., 63, 296 (1893).

"Then the multi-rotating compounds and the oxy-acids have the hydroxyl and the carboxyl (carbonyl ?) groups in common. Finally, since the lactone formation, which is accompanied by the closing of a ring, in general brings about an increase of rotation, and in the cases now under consideration (maltose excepted) there is a decrease, there is perhaps here a ring opened up.

"And it may be observed that the marked changes of rotation with the concentration and temperature, observed with glucose, galactose, and rhamnose, and especially with levulose and the lactone-forming acids, are to be attributed to changes in equilibrium.

"There are other isolated cases of great change of rotation through ring formation which are also related to lactone formation. Propylene-glycol (−4° 55′ 22 mill.) changes the sign of rotation on being transformed into propyleneoxide (+1° 10′ 22 mill.). The same is the case with the left diacetyltartaric acid $a_D = -19.23°$ which forms a right-handed anhydride, $a_D = +62.04°$. This change of sign does not occur with acetylmalic acid," p. 150.

In view of these considerations advanced by van't Hoff it is clear that the real rotatory power of an asymmetric carbon atom such as is found in lactic acid will be exhibited only in the form of the dilute solution of the alkali salt. Further than this when the alcoholic hydrogen of the lactic acid is replaced by a less labile group the appearances will be much less confused by the formation of such a tautomeric form as the ethylene oxide form. Therefore a study of such compounds will reveal what we might expect to find in the case of the analogous lactic acid if the ethylene oxide form were not present. Sarcolactic acid produces a levorotatory methoxy-propionic and a levorotatory ethoxy-propionic acid,[1] the salts and esters of which are also levorotatory. These acids show remarkably constant rotatory power with change of concentration, and the same is true of the alkali salts, the rotation of the sodium methoxy-propionate being very little different from the rotation of the acid itself. There is a decrease in the levorotatory power of the acid itself. There is a decrease in the levorotatory power of the salt with increase in concentration and this becomes marked in the case of the bivalent cations where other factors may enter. This point will be discussed later but the approximate equivalence of the rotatory power of the acid and of the sodium salt, which in the dilutions used must be nearly or quite completely ionized, shows that in this case the rotation of the ion is not far different from that of the acid itself. This is for an acid in which the tendency to change to the ethylene oxide form is small or absent and the same result would undoubtedly be observed with lactic acid were it not for the large ethylene oxide formation there. It will be shown now that the molecular rotation of sodium l(+) lactate and the equivalent rotation of the zinc salt extrapolate to −14° as the value for infinite dilution. It therefore follows that the rotatory power of the straight normal form of sarcolactic acid, without admixture of the ethylene oxide form, would, if it could be prepared, have a value not far different from −14°.

---

[1] Purdie and Irvine: J. Chem. Soc., 75, 483 (1899).

In the work on malic acid it has been found that a solution of malic acid of about 2.7 M is inactive, more dilute solution being levorotatory while more concentrated solutions show dextrorotations. The concentrations of inactivity for the sodium malate is 3.5 M. A similar phenomenon was expected for lactic acid and its salt but was realized in neither case. The tendency to the ethylene oxide form is so strong in the free acid that in the most dilute solution that can be measured it still exceeds the rotatory power of the levorotatory normal form and the solution shows small but definite dextrorotation. In the case of the salt, although this tendency to ethylene oxide form is still present, the relatively higher rotation of the straight form makes it impossible at least in those concentrations observed, to obtain other than levorotatory solutions of the salts. It is quite possible that some other salt of sarcolactic acid may show dextrorotations in very concentrated solutions, since supersaturated solutions of the zinc salt show rapidly decreasing levorotations. It is also true that infinitely dilute solutions of sarcolactic acid must show levorotation and the value for the molecular rotation must approach that of the sodium salt, since only lactate ions can exist in such solutions, and indeed ions of the normal form.

The lactic acid and salts used in this investigation were made from samples of dextrorotatory and levorotatory zinc lactates, containing respectively 12.97% and 12.94% of water (theoretical for the active zinc lactates with two molecules of water is 12.88%). These salts were prepared and very kindly furnished us by Prof. W. H. Peterson of the University of Wisconsin, who prepares the lactic acids by the action of purified strains of bacteria on several sugars.[1]

The first sample of lactic acid was made by passing hydrogen sulphide into a hot solution made by dissolving 55 grams of the zinc lactate in 300 cc of boiling water. The zinc sulphide was filtered off and the filtrate concentrated first in a vacuum distillation apparatus in which the vapor temperature did not exceed 40°, and then the residue 53 cc stored over sulphuric acid in a vacuum desiccator over night was reduced in volume to 35 cc; titration of this solution showed about 78% yield of lactic acid.

This concentrated solution was examined in the polarimeter, diluted with an equal volume of water, its rotation taken again, and so on for four successive dilutions. The rotation of the fifth dilution was too weak to be read. At various times in this process the amount of reacidification was found to be negligible and even for the most concentrated solution after two days the reacidification amounted to less than one percent of the total alkali used. The conclusion, to be supported by later data, is that these solutions represent lactic acid practically free from anhydride or lactide. The most concentrated solution was prepared by rapid concentration and was used promptly, thus allowing little time for the slow reaction to the anhydride forms.

Expressing the results of this dilution-rotation experiment in terms of sarcolactic acid (actually the d(−)lactic acid was used), we have for a 2 dm. tube at room temperature:

---

[1] Peterson, Peterson, and Fred: J. Biol. Chem., 68, 151 (1926).

TABLE I

Rotation-Dilution of Sarcolactic Acid

Grams per 100 cc solution	75.7	38.5	19.2	9.72	4.84
Mols per liter	8.41	4.28	2.13	1.08	0.537
Observed rotation	+7.97°	2.23°	0.67°	0.23°	0.08°
Specific rotation	+5.26	2.95	1.76	1.09	0.85
Molecular rotation	+4.74	2.66	1.58	0.97	0.76

Plotting these values for the molecular rotation against the normality shows that these points lie very exactly on a straight line which if it were extended would indicate a value at infinite dilution for sarcolactic acid of about +0.5°. Such an extrapolation is not justified, for the end value for lactic acid must be the same as that for the sodium lactate and that value is −14.0°.

The day after the previous dilution run the most concentrated solution above was neutralized with sodium hydroxide and diluted in steps as was done for the lactic acid. The two most concentrated solutions were examined in 0.947 dm. tubes, the rest in 2 dm. tubes. The numbers have the same meaning as above.

TABLE II

Rotation-Dilution of Sodium Lactate

C	47.17	23.58	11.79	5.89	2.95	1.47	0.74
N	4.21	2.10	1.05	0.526	0.263	0.131	0.065
a_D	−3.50°	2.37°	2.80°	1.46°	0.74°	0.36°	0.18°
$(a)_D$	−7.83	10.62	11.87	12.4	12.53	12.23	12.20
$(M)_D$	−8.78	11.9	13.3	13.9	14.05	13.7	13.68

Again these first four points lie practically on a straight line which then bends over to what amounts to a constant value for the optical rotatory power for the solution of 0.5N and less. It is this value of −14° which represents the real rotatory power of the lactate ion from whatever source it may be derived. Further evidence for this and for the abnormal character of the zinc salt is shown by similar data for zinc lactate. A sample was weighed out and dissolved in hot water, the solution being then cooled and diluted. The first three solutions were supersaturated. All were examined in 2 dm tubes.

TABLE III

Rotation-Dilution of Zinc Lactate

C	14.07	7.03	3.51	1.75	0.88
N	1.0	0.5	0.25	0.125	0.0625
a_D	−1.51°	0.97°	0.56°	0.29°	0.16°
$(a)_D$	−5.37	6.89	7.96	8.27	9.13
$(E)_D$	−6.52	8.35	9.65	10.05	11.1

In Table III is introduced a new term, $(E)_D$ the equivalent rotation and this is equal to half the molecular rotation in the case of zinc lactate. The specific rotation is the rotation that would be observed in a tube one decimeter in length and filled with a solution containing one gram of solute per cubic centimeter of solution and is calculated on the assumption that the rotation is independent of the concentration. The molecular rotation is the specific rotation multiplied by the molecular weight divided by 100. The equivalent rotation is the specific rotation multiplied by the equivalent weight divided by 100. This enables one to compare directly solutions containing the same number of the active lactate radicals.

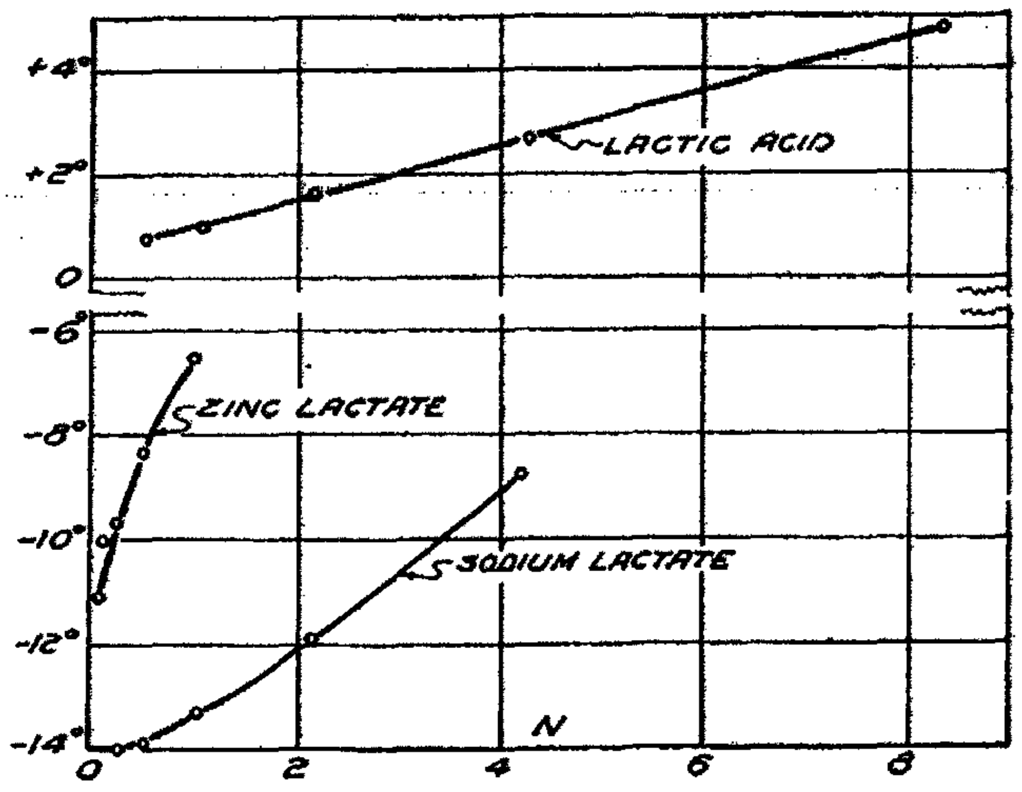
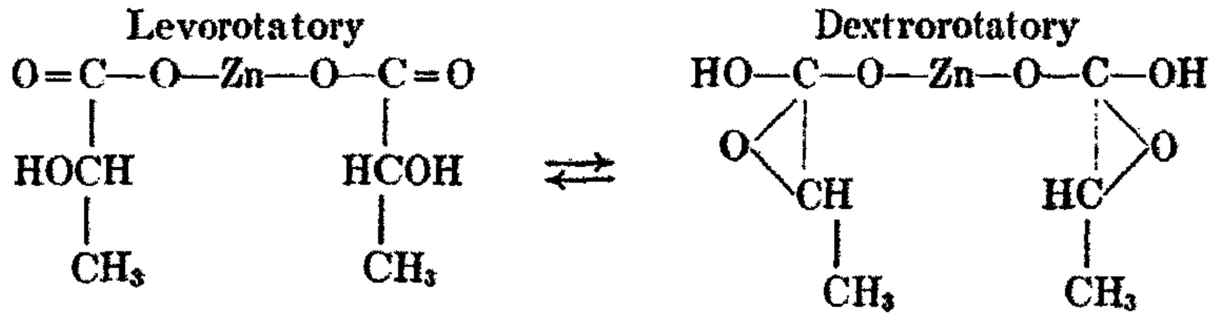


Fig. 1
Rotation-Dilution of Sarcolactic Acid and Lactates

The graph of these rotation-dilution data shown in Fig. 1 demonstrates that both sodium lactate and zinc lactate approach the value of −14° in the dilute solution and that for each concentration the rotation of the zinc salt is below that of the sodium salt, the former changing much more rapidly with concentration. This may be attributed to the lower dissociation of the zinc salt or to the hydrolysis resulting in the formation of some of the free acid and hence the dextrorotatory ethylene oxide form, or what seems most likely, to a markedly increased tendency in concentrated solutions of the zinc salt to form the ethylene oxide form of the ion or of the salt molecule. This might go according to the scheme;



These data agree with those of Purdie[1] who found the rotation of the Na, K, and NH_4 salts 14° in 0.1 M solutions, while lactates of six bivalent metals were below this value but extrapolated to it.

The abnormality in the case of the rotation of zinc lactate may be associated with the observation of Irvine.[2] "Reference may be made here to experiments which are in progress in this laboratory on the solubilities of the zinc lactates. It has been found that although active zinc lactate when crystallized in the usual manner readily loses its water of crystallization at 110°, the residue left on evaporating an aqueous solution of the salt on a water bath does not become completely anhydrous even at 150°. It is evident, therefore, that in estimating the specific rotation of active zinc lactate the concentration of the solution cannot be determined by the evaporation of a measured volume of the solution." There appear to be two possible explanations for this observation. It may very well be that heating brings about the hydrolysis of the zinc lactate, the consequent loss of some of the lactic acid and a residue of a basic zinc lactate or even the hydrous oxide losing water with much greater difficulty. The other possibility is that the hot saturated solution of zinc lactate formed quantities of the ethylene oxide form of the salt and that this form for some reason loses water much more slowly than does the normal zinc lactate in crystal.

The present section established the fact that the normal form of lactic acid is levorotatory and probably of about the same rotatory power as the sodium salt derived from it. In the field of the indicators it has been established that dilute colored acids give ions and dilute salt solutions of the same color *unless some internal rearrangement takes place.* The same thing is probably true of the rotatory power of the acid, its ions and salts. Failure of these three to show the same direction of rotation will in general be an indication of some internal rearrangement. Since, therefore, the normal form of sarcolactic acid, the anhydride form, and the lactide forms are all levorotatory, the explanation of the dextrorotation of its aqueous solutions must be referred to a rearrangement into a dextrorotatory ethylene oxide form. The next section will demonstrate how these forms enter into the various equilibria and how they affect the rotatory power of the aqueous solutions.

Equilibria in Lactic Acid Solutions

It has now been shown that solutions of sarcolactic acid may contain mixtures of three levorotatory forms and one dextrorotatory form. The equilibria involving these forms are reached with different velocities and may be followed by means of the optical rotatory power of the solution. The data indicate that if one starts with a dilute solution containing only the normal and the ethylene oxide form the rotation will be to the right as a consequence of the greater rotatory effect of the ethylene oxide form. As one withdraws water from such a solution, the equilibrium between these two tautomeric forms

---

[1] Purdie: J. Chem. Soc., 67, 616 (1895).

[2] Irvine: J. Chem. Soc., 89, 935 (1906).

is displaced in favor of the ethylene oxide form and the dextrorotation increases. As concentration of the solution increases there begins another very slow reaction, the conversion of the normal form or of the ethylene oxide form to the relatively strongly levorotatory anhydride and to the very strongly levorotatory lactide. A rapid concentration of the lactic acid solution leads to increasing dextrorotation, while, if the concentration is carried far enough, this dextrorotation is found to diminish with time and to change to fairly large levorotations. We shall thus have for freshly prepared solutions a regular increase in dextrorotations while, if these solutions are permitted to come to equilibrium, there will be with increasing concentration, first an increasing dextrorotation to a maximum, and then for solutions sufficiently concentrated to develop the anhydride or lactide forms, decreasing dextrorotations leading finally to levorotatory solutions of a power several times that of the original lactic acid.

This change in the rotatory power of lactic acid solutions was demonstrated by the first preparation of lactic acid already reported. The tube containing some of this original most concentrated (8.4 N) solution was examined from time to time.

TABLE IV

Time-Rotation of Sarcolactic Acid

Time in days	0	1	5	7	10	12	15	17
Specific rotation	+5.26°	5.0	4.03	3.54	2.75	2.27	1.93	1.37

The final value did not represent equilibrium but the change in this tube was not followed beyond this point. It is of interest to note that the most concentrated sodium lactate solution did not change appreciably in seven days while the acid dropped to 70% of its initial value in that period. Now in the acid solution the decrease in rotation is to be attributed to the formation of the anhydride with its levorotation. The constancy of the rotation of the sodium salt shows the absence of such an effect there, for of course neither anhydride nor lactide can form in the sodium lactate solution. In other words, in the salt solution, only the normal-ethylene oxide equilibrium is added to the ionization effect while in the free acid these and the anhydride and lactide must be considered.

Another evidence of this change is shown in the dilution-time-rotation runs on this same original acid. On the day of the original dilutions this acid diluted with fifteen volumes of water in steps gave a solution for which $(M)_D = +0.763°$, while when the original acid had stood in the concentrated form for five days and was then diluted from 8.4 N to 0.52 N the resultant solution showed $(M)_D = -0.286°$. The explanation of this is that during the five day period there had formed in the concentrated solution sufficient of the levorotatory anhydride form so that when on dilution the equilibrium was at once adjusted to a relatively low ethylene oxide concentration, this was not sufficient to overcome the levorotation of the anhydride form. Certainly the latter situation did not represent equilibrium while the dilution of the freshly prepared solution did represent very nearly an equilibrium condition. If the levorotatory solution had been permitted to stand it would have changed toward or to the dextrorotation shown by the same concentration of lactic acid freshly prepared. This demonstrates at the same time the possibility of preparing levorotatory dilute solutions of sarcolactic acid even though they are surely not in equilibrium and also the necessity of having careful regard to the history of any lactic acid solution if one is to draw any conclusions from its rotation.

A very striking confirmation of these explanations was obtained from the study of another sample of sarcolactic acid. This second preparation was as the first, the final filtrate being evaporated in the vacuum still to 47 cc and then stored over sulphuric acid for a week in a desiccator until its volume was 20 cc (as compared to 35 cc for the first preparation). At the end of that time the reacidification observed on letting the neutralized solution stand at room temperature for five hours was about 0.5 of one per cent of the total alkali required so that no large amount of anhydride had developed.

This concentrated sarcolactic acid was placed in a 0.947 dm tube, another portion was diluted to twice its volume with water and a third sample was made by diluting the first dilution to twice its volume. The ratio of concentrations then was 1 : 0.5 : 0.25. The first two solutions were placed in 0.947 dm tubes while the third was examined in a 2 dm tube, all being left at room temperature and being observed from time to time.

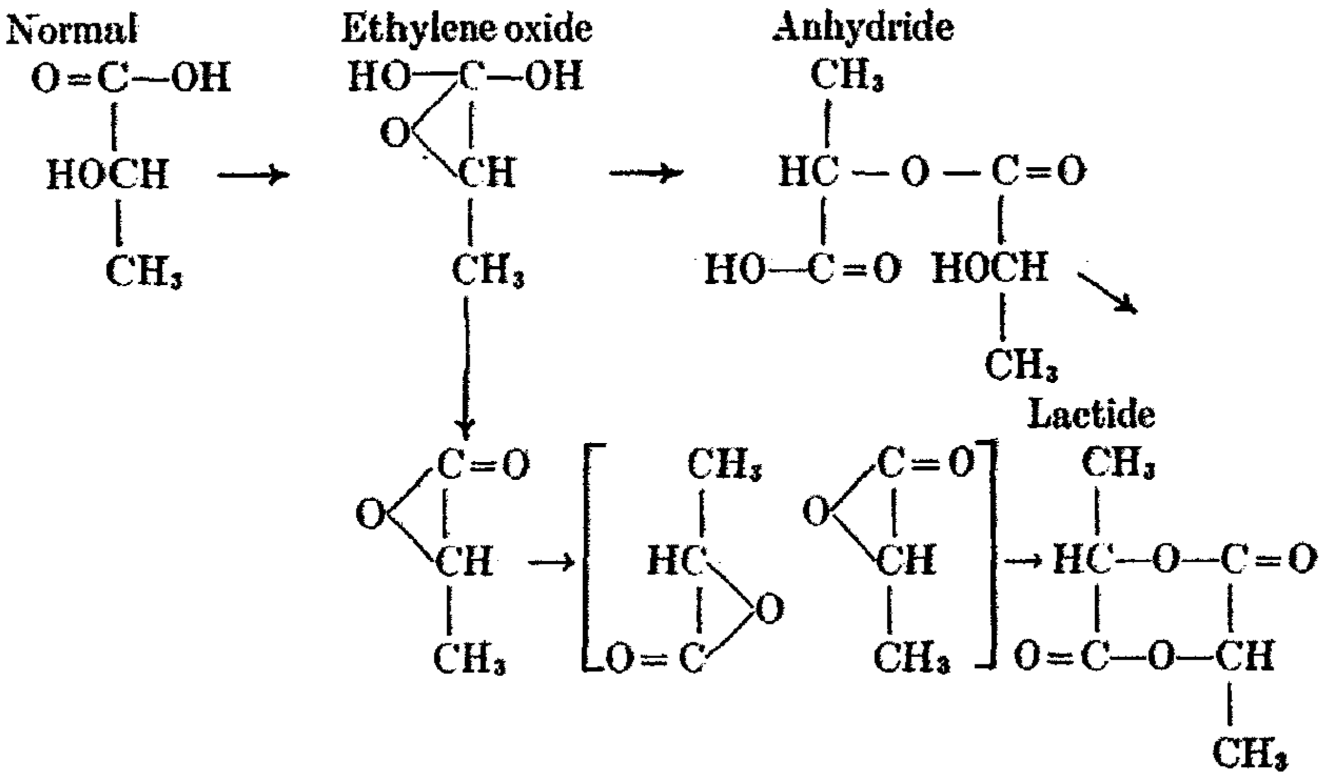
TABLE V

Time-Rotation-Dilution of Sarcolactic Acid

	0	4 days	41 days
Original (0.947 dm tube)	+3.16°	−5.01°	−19.36°
First dilution (0.947 dm tube)	+0.77°	+0.84°	+ 1.17°
Second Dilution (2 dm tube)	−0.21°	+0.15°	———

These data are at first glance quite incomprehensible but on further examination are found to agree with the explanations previously made. The first dilution solution reached a constant value within the 41 days and did not change further in eighteen months. A similar behavior would have been shown by the second dilution but this tube developed a leak and was lost. The behavior of the original concentration solution is most interesting, for even 41 days was not sufficient to enable this solution to reach equilibrium, and after eighteen months it showed a reading of −21.8°, having changed but 0.5° in the previous year. It appears quite probable that in agreement with the results of Eder and Kutter something like one hundred days are required for the attainment of equilibrium in such systems. It is noted that temperature control of this experiment was inadequate, only after 41 days were the tubes placed in a constant temperature room at about 23° where they were free from the daily and seasonal fluctuations of temperature and in which they could also be examined polarimetrically. A repetition of this experiment is planned but the qualitative results leave no doubt as to their interpretation. These experiments were carried out without the guidance of a satisfactory theory and hence failed to show all that they might have shown. Thus it is very probable that if the evaporation of the lactic acid solution had been carried out all the way in the vacuum still and the most concentrated solution examined at once under these same conditions it might well have shown a positive rotation of something like +15° as this is the value obtained by extrapolating back the curve of rotation for this solution to six days before the beginning of these observations. We should then have the phenomenon of a lactic acid solution changing its rotation from +15° to −21° on standing. Truly such a remarkable indication of a fundamental change demands explanation.

In view of what has been shown before it is clear that the process of concentrating the solution builds up at each step very rapidly a concentration of the ethylene oxide form which is directly proportional to the total concentration of the solution. A consequence of the low rate of reaction to the anhydride or lactide form is that these are present in the quickly concentrated solution in far less than the equilibrium amounts. On standing the anhydride and lactide forms appear primarily at the expense of the ethylene oxide form.



Of these reactions the second course seems much more probable since the first requires the splitting off of water in the concentrated solution. It appears, then, that the ethylene oxide form loses water as the solution is concentrated and is then capable of condensation directly into the familiar lactide, thus replacing a moderate dextrorotation with an enormous levorotation. This is the explanation of the rotation change of the most concentrated solution and is supported by the fact that when first examined polarimetrically, titration of this solution showed about 0.5% present as reacidification while after standing for eighteen months and reaching equilibrium, titration showed 23% of the total alkali required was required to neutralize the reacidification. The titration of a two cc sample weighing 2.304 g. required 18.74 cc N NaOH and the reacidification required 5.66 cc N NaOH. If one should adopt the Wislicenus method of calculation it shows 0.916 g anhydride, 1.175 g lactic acid. This is equivalent to 51% lactic acid, 39.7% anhydride, and 9.3% water. The defects of this method of calculation have already been pointed out and it cannot be taken to prove that there is not present some of the lactide form also. It is emphasized merely that the process of coming to equilibrium is accompanied by a very large increase in the fraction of the lactic acid which is not immediately titratable by alkali in the cold. In order to show these data comparably, the specific rotations of these mixtures of anhydride and lactic acid have been shown in Fig. 2.

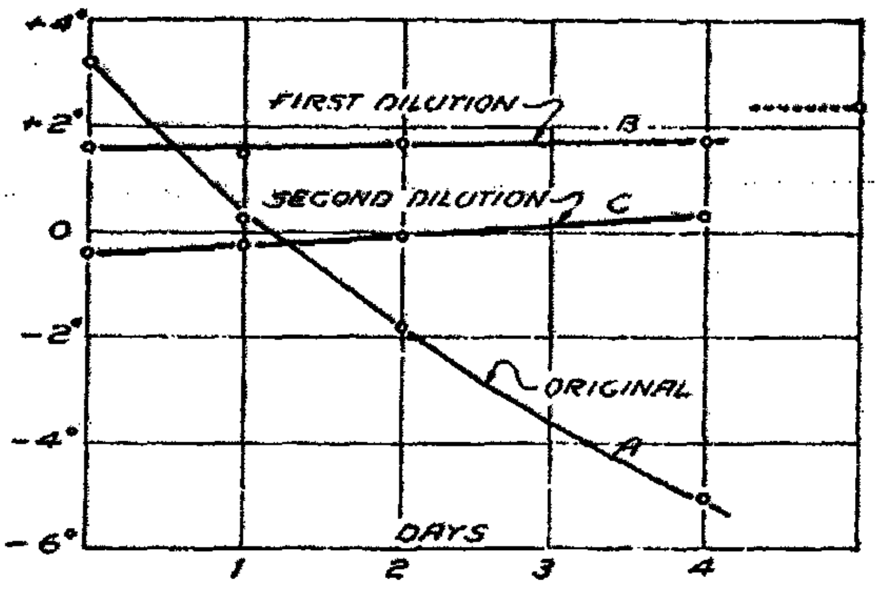


Fig. 2

Time-Rotation of l (+) Lactic Acid
Ordinates are specific rotations

Specific Rotations

	41 days	1.5 years
A	−19.55°	−22.0°
B	+ 2.88°	+ 2.88°

The explanation of the rotations of the more dilute solutions follows the same line. The original concentrated lactic acid contains an amount of the ethylene oxide form which is above the equilibrium value for any more dilute solution so that dilution will always be accompanied by a rapid decrease in the proportion of this form. The amount of the anhydride or lactide forms present in the original concentrated solution is far below the equilibrium value for such a concentration but may be above the equilibrium concentration for a more dilute solution. When the original solution is first diluted the ethylene oxide form at equilibrium with the new concentration is more than sufficient to overcome the small amount of the levorotatory anhydride forms so that the solution is dextrorotatory. The anhydride forms are contained in larger than the equilibrium amounts and hydrate slowly, the disappearance of these levorotatory forms in favor of the dextrorotatory ethylene oxide form giving rise to the increased dextrorotation of the first dilution solution.

Exactly the same explanation applies to the second dilution solution except that here the very low equilibrium value of the ethylene oxide form is unable to overcome the levorotation of the anhydride forms even though the latter be low in actual amount. The anhydride forms hydrate (at a faster rate than in the first dilution) and once more the dextrorotation of the ethylene oxide forms is the strongest rotation. It should be noted that so little time elapsed that diluting the first dilution was practically the same as diluting the original solution 1:4 all at once.

Such a phenomenon as that just reported was noted by Wislicenus and he says, p. 328: "A paralactic acid, which contains only a few percent of the esteranhydride rotates the plane of polarized light to the left. When I did not know as yet about the spontaneous esterification and had already concluded that the specific rotation of paralactic acid is about +3.5°, I made this observation first with not exactly happy astonishment. The preparation was a thin syrup made by evaporation on the water bath which first showed this phenomenon. Addition of water and long standing depressed the optical activity to zero, some time later positive rotation appeared with growing power." Wislicenus had reported that a solution of lactic acid (0.4 g per cc) gradually became more strongly dextrorotatory with time. If the solution were diluted somewhat, its specific rotation fell sharply; on standing, this diluted solution again showed increasing dextrorotation and so for as many as three dilutions. These solutions were thus more dilute than the original solution here reported and in addition to this Wislicenus avoided the discovery of this phenomenon for in general his solutions were not examined until about two weeks after their preparation. As has been shown in the case of the second dilution solution, the increase in dextrorotation is merely the continuation of the same process going on in the levorotatory solution. The continuity of the curve indicates that even in the dextrorotatory solution we have decreasing amounts of the anhydride form.

The wide variation in the rotatory power of solutions of sarcolactic acid is now apparent. A rapidly concentrated solution has strong dextrorotation which on standing may change to an even stronger levorotation. If the original solution be diluted, it may show levorotation which will then gradually change to dextrorotation. There are, of course, some intermediate stages of dilution for which the change in rotation will be small. If one considers sarcolactic acid solutions at equilibrium, increase in concentration will be accompanied by an increase in dextrorotatory power up to a maximum; beyond this the dextrorotation will decrease and finally change to levorotation as the formation of the anhydride and lactide becomes important. Infinitely dilute solutions of sarcolactic acid will also be levorotatory but are not susceptible of observation ordinarily. The ionization constant shows that the 0.5 N solution of lactic acid is 0.0164 ionized. Thus rotation observations end about where dissociation begins.

In conclusion we may add that the supporting evidence for the existence and properties of such an ethylene oxide form of lactic acid is quite analogous to that given in the case of malic acid.[1] It was shown that if the hydroxyl hydrogen were replaced by less labile groups compounds were obtained whose rotations were remarkably constant when compared to the malic acid. The same is true of the acids analogous to lactic acid. Many of these acids and their derivatives have been made by Purdie and his students.[2] They report data for methoxy and ethoxypropionic acids and their salts. The acids are found to be of nearly a constant rotatory power over rather wide concentration ranges while the behavior of the salts is to be explained by ionization differences, with greater approach to constancy in the substituted acids. Thus we find, p. 877: "The rotation of calcium lactate is not only much less than strontium and barium lactate, but on dilution shows no sign of approaching the common maximum nearly reached by these and the alkali salts. This anomaly it will be seen disappears in the calcium alkoxypropionates. The behavior of calcium ethoxypropionate is quite similar to that of the barium and sodium salts, taking into account its probably smaller degree of dissociation, and the same may be said of the propoxy salt."

A more recent indication of the influence of the labile hydrogen atom has been pointed out.[3] "It was suggested by Wood, Such and Scarf (1923) that the complex rotatory dispersion of the esters of lactic acid is due (a) to their persistent low rotatory powers, (b) to the influence of the hydroxyl group attached to the asymmetric carbon atom. The rotatory power of ethyl d-alpha-p-toluenesulphonoxy-propionate was determined over a large range of temperature and for light of several wave-lengths. Under the experimental conditions tried, it exhibited simple rotatory dispersion in marked contrast to the complex rotatory dispersive power shown by ethyl 'd' lactate. It is remarkable that this complexity of rotatory dispersion of ethyl 'd' lactate should disappear when the p-toluenesulphonyl group is substituted for the hydrogen atom of the hydroxyl group attached to the asymmetric carbon atom." Such a decrease in abnormality would be predicted on the basis of the present paper.

Summary

1. Sarcolactic acid, commonly called dextrolactic acid, should be designated as l(+)lactic acid to show that, although its dilute aqueous solutions happen to be dextrorotatory, the levorotations of its salts and esters show it to be essentially the levo form of lactic acid.

2. This problem is directly analogous to that previously encountered in the case of l-malic acid and the solution is similar. It is shown that as with malic acid, so also in the case of sarcolactic acid there is an additional tautomeric modification to be taken into account. Again the evidence supports a dextrorotatory ethylene oxide form.

---

[1] Bancroft and Davis: J. Phys. Chem., 34, 897 (1930).

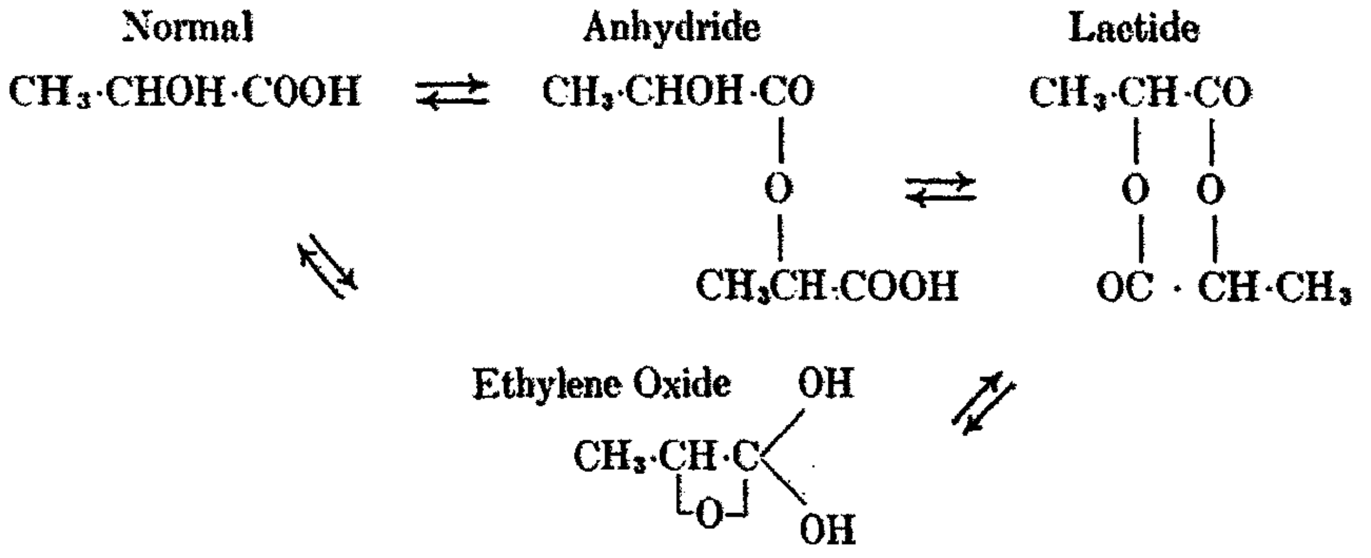
[2] Purdie and Lander: J. Chem .Soc., 73, 862 (1898); Purdie and Irvine: 75, 483 (1899).

[3] Kenyon, Phillips and Turley: J. Chem. Soc., 127, 409 (1925).

3. The literature of lactic acid includes the description of three forms. The lactide form possesses a very large specific rotation of about −300° and exists in very concentrated solutions and as a solid. The anhydride has a moderately large rotation which is of the order of −45° but has never been isolated. The normal form of lactic acid corresponding to the formula as ordinarily written is also levorotatory with a power which is not far different from −14° in molecular rotation.

4. Since the three forms of sarcolactic acid which have been studied are all levorotatory it follows that some other explanation must be offered for the dextrorotation of its aqueous solutions.

5. The full picture of a sarcolactic acid solution will include equilibria between the four forms.



6. The equilibria involving the anhydride or lactide forms are reached very slowly, while that between the normal form and the ethylene oxide form is reached very rapidly. Thus a rapidly concentrated solution will contain an equilibrium amount of the ethylene oxide form but far below the equilibrium amounts of the anhydride and lactide forms. This solution may, on standing, change from a rotation of +15° to −21° as a result of formation of the anhydride forms from the ethylene oxide form.

7. If a freshly prepared, rapidly concentrated, sarcolactic acid solution be diluted sufficiently, it will show levorotation instead of the dextrorotation of the concentrated solution. This is evidence for the existence in the solution of sufficient of the strongly levorotatory anhydride forms to overcome the dextrorotation of the small amount of the ethylene oxide form in the diluted solution. On standing, this diluted solution becomes increasingly dextrorotatory and the anhydride forms slowly hydrate.

8. Solutions of sarcolactic acid which are in equilibrium will show, with increasing concentration, increasing dextrorotations as the proportion of the

ethylene oxide form increases. Then the formation of the anhydride forms becomes important; the dextrorotation passes through a maximum and then becomes increasingly levorotatory.

9. The supporting evidence for the ethylene oxide form of sarcolactic acid is quite similar to that advanced in the case of malic acid. When the alcoholic hydrogen, whose migration to the ketonic oxygen of the adjacent carboxyl group is responsible for the formation of the oppositely rotatory substance with different rotatory dispersion and hence for the abnormalities in the lactic acid systems, is replaced by less mobile groups, the resultant compounds possess very different properties with the disappearance of the abnormalities in the dispersion and in the rotation-dilution phenomena.

Cornell University

THE INHIBITORY ACTION OF ANTHRACENE IN THE AUTOXIDATION OF BENZALDEHYDE*

214-19

BY HANS L. J. BÄCKSTRÖM AND HAROLD A. BEATTY

Introduction

On the chain-reaction theory of inhibition, the role of the inhibitor consists in the breaking of reaction chains. In previous papers[1] it has been pointed out that, in autoxidation reactions, the mechanism of this process appears to involve an induced oxidation of the inhibitor. In one case, *viz.* the inhibition of sodium sulfite oxidation by alcohols, this was definitely established, since it was shown that the alcohol is oxidized along with the sulfite, and that the rate of this induced oxidation is such as to link it directly to the breaking of the chains.

Further insight into the mechanism of such a chain-breaking reaction would be of considerable interest as it would serve to throw light on the nature of the chain mechanism itself, a problem about which at present we know little. The present paper gives the results of an attempt in this direction. As, for various reasons, the inhibition of sulfite oxidation by alcohols does not lend itself very readily to such an attempt, a different case of inhibition was selected for this study, *viz.* the action of anthracene in the autoxidation of benzaldehyde.[2]

Induced oxidations were first observed by Schönbein[3] in 1845, and have since been the subject of a great many investigations.[4] It has been found that, under favorable conditions, for each atom of oxygen taken up by the autoxidizable substance (the inductor), one atom is also taken up by another oxidizable substance (the acceptor) which is present but is not itself attacked by molecular oxygen. This was explained by Engler, Bach and others[5] on the theory that in autoxidations the primary reaction product of the inductor is a peroxide which possesses strong oxidizing properties and which can give one atom of oxygen to the acceptor. This theory receives strong support from the fact that in many reactions the intermediate formation of such peroxides can be demonstrated. From the photochemical oxidation of benzaldehyde in acetone solution, Jorissen and van der Beek[6] isolated the pure peroxide in 63% yield and showed it to be benzoperacid,

---

* Contribution from the Frick Chemical Laboratory, Princeton University.

[1] Bäckström: Medd. K. Vet.-Akad. Nobelinstitut, 6, No. 16 (1927); Trans. Faraday Soc., 24, 601 (1928); Alyea and Bäckström: J. Am. Chem. Soc., 51, 90 (1929).

[2] Bäckström: J. Am. Chem. Soc., 49, 1460 (1927).

[3] Schönbein: J. prakt. Chem., 36, 379 (1845).

[4] For new examples and a summary of the literature, see Jorissen and Belinfante: Rec. Trav. chim., 48, 711 (1929).

[5] Engler and Wild: Ber., 30, 1669 (1897); Bach: Compt. rend., 124, 951 (1897); Bodländer: "Über langsame Verbrennung," Ahrens Sammlung, vol. 3, 385 (1899).

[6] Jorissen and van der Beek: Rec. Trav. chim., 45, 245 (1926).

previously synthesized by Baeyer and Villiger.[7] In agreement with the theory, this substance is a powerful oxidizing agent.

However, if we apply the Engler-Bach theory to the problem of inhibition, we encounter a serious difficulty: it is not easy to see how an induced reaction of this kind can constitute a chain-breaking mechanism. This appears at once from the fact that, as was shown by one of us,[8] the chain reaction in the autoxidation of benzaldehyde is the formation of the peroxide, which reaction, for want of a better theory, we may write as an energy chain (A = benzaldehyde): $A + \text{Energy} = A'$ (activated); $A' + O_2 = AO_2'$; $AO_2' + A = AO_2 + A'$; $A' + O_2 = AO_2'$, etc. As was pointed out in a later paper,[9] a subsequent reaction of the deactivated AO_2, whether with another molecule of the aldehyde or with a molecule of an added substance, would obviously not cause the chain to be broken. Only a reaction of an added substance with A' or AO_2' would interfere with the mechanism of chain propagation. To account for the fact of inhibition it would thus be necessary to modify the peroxide theory of induced oxidation, by assuming that the reaction between the peroxide and the inhibitor (acceptor) is not of the ordinary type of thermal reaction but *involves an especially activated form of the peroxide.*

As a matter of fact, the literature on induced oxidations has not been lacking in indications that, at least in certain cases, the theory needed amplification in some such direction as this. Thus Engler[10] states as a well-known fact that there is generally a more energetic transfer of oxygen to the acceptor if the latter is present during the oxidation of the inductor, than if it is added after the peroxide has been formed. In the example which he gives, an indigo solution was found to be somewhat more rapidly decolorized when shaken with a benzene solution of benzaldehyde in an oxygen atmosphere, than when it was shaken, under carbon dioxide, with a corresponding solution of benzoperacid. A more striking case was reported by Jorissen and van der Beek[11] who found that the photochemical oxidation of benzaldehyde in dilute chloroform solution at 0° gave benzoperacid in good yield, but at room temperature the solvent was attacked, yielding phosgene, hydrochloric acid, carbon dioxide and unidentified products. Special experiments showed, however, that benzoperacid scarcely attacks chloroform even at the boiling point.

The results presented in this paper show that the inhibitory action of anthracene in the autoxidation of benzaldehyde is correlated with an induced oxidation of the inhibitor, and that the peroxide theory, to account for this reaction, has to be modified in the direction indicated above.

---

[7] Baeyer and Villiger: Ber., 33, 1569 (1900).

[8] Bäckström: Medd. K. Vet.-Akad. Nobelinstitut, 6, No. 15 (1927).

[9] Bäckström: Ibid., 6, No. 16 (1927).

[10] Engler: Z. Elektrochemie: 18, 945 (1912).

[11] Jorissen and van der Beek: Rec. Trav. chim., 46, 42 (1927); 47, 286 (1928).

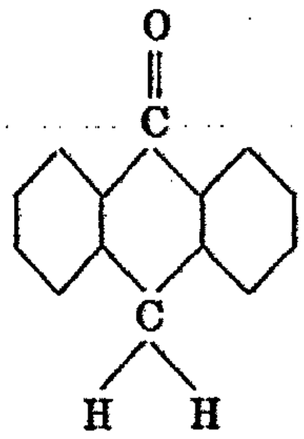
Experimental

Materials

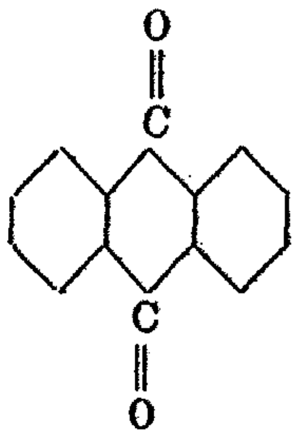
Benzaldehyde. Kahlbaum's best grade was redistilled in nitrogen and stored in brown, glass-stoppered bottles.

Anthracene. This was prepared from pure, synthetic anthraquinone by the excellent method of von Perger,[12] thus avoiding the difficult separation of other coal tar hydrocarbons. Fine crystals, snow white, with intense blue fluorescence, melting at 217°(corr.) were obtained.

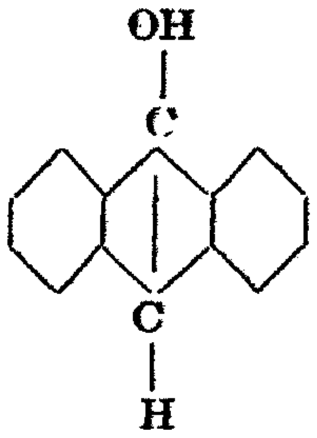
Anthrone. This was obtained by the reduction of anthraquinone according to the directions of K. H. Meyer.[13] The recrystallized product melted at 154° (uncorr.); it contained a small amount of anthraquinone.

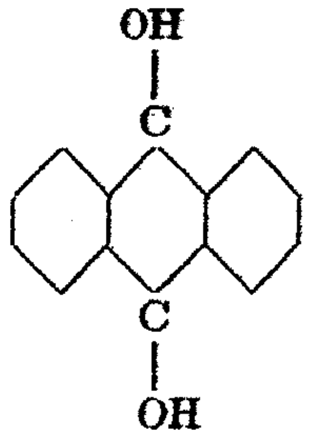


Anthraquinone. Du Pont Company's synthetic, crystalline product, "melting point 284.6°," was used without further purification.



Anthranol and Anthrahydroquinone. The preparation of these is described in connection with experiments using them.





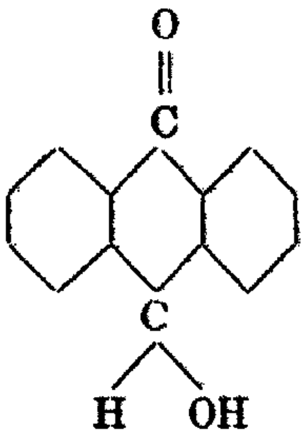
---

[12] Von Perger: J. prakt. Chem., (2) 23, 127 (1881).

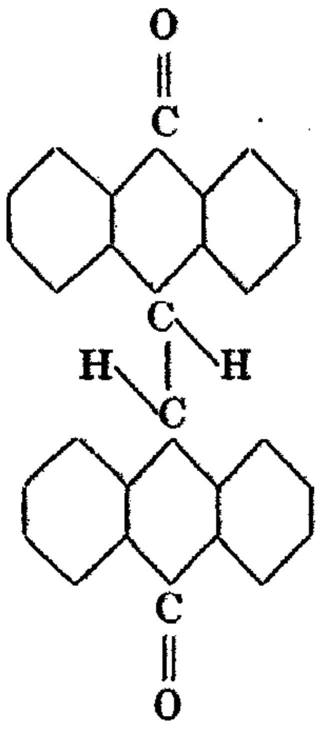
[13] K. H. Meyer: "Organic Syntheses," 8, 7 (1928).

Anthrahydroquinone dibenzoate. A pure preparation was obtained by the method of K. H. Meyer[14]; it melted at 292° (uncorr.).

Oxanthrone. An impure specimen was obtained, with considerable difficulty, by a modification of the directions given by K. H. Meyer.[14]



Dihydrodianthrone (also known as dianthrone). This was obtained by the oxidation of anthracene according to Barnett and Matthews.[15] The resulting fine white needles were quite free from anthrone and anthraquinone, and had the characteristic indefinite melting point of 255°-260°.



Alcohol. This refers throughout this paper to a good commercial grade of 95% ethyl alcohol, not further purified.

Hydrosulfite. This refers to a reducing solution of 50 g. of commercial sodium hydrosulfite and 50 g. of sodium hydroxide made up to 500 cc. with water. The solution was allowed to stand in a tightly-stoppered flask until the sediment of impurities had settled; it was then filtered, in an atmosphere of nitrogen, through a Jena glass filter, and kept in the well-stoppered filter flask. The solution suffers a slow auto-decomposition on standing.

---

[14] K. H. Meyer: Ann., 379, 37 (1911).

[15] Barnett and Matthews: J. Chem. Soc., 123, 387 (1923).

Apparatus

The shaking apparatus used in the photochemical experiments has been described elsewhere.[3] It served to keep the aldehyde solutions at constant temperature and saturated with oxygen, of which the amount and rate of absorption could be measured. The light source was a mercury arc of the Kromayer type, placed immediately in front of the quartz window of the thermostat. As a rule it was used in connection with filters: a nickel oxide glass for 366 *mμ*, and a *quartz cell*, 1 *cm. thick*, filled with 0.0004 molar potassium chromate solution, for the line at 313 mμ.

In experiments on the thermal reaction, the aldehyde was pipetted into constricted test-tubes, which were then evacuated, filled with oxygen, sealed, and wrapped in black paper,* these operations being performed in red light. The tubes were attached to a rotatory shaker, making 180 revolutions per minute, placed in a dark-room, the temperature of which remained fairly constant.

Analytical

Since preliminary experiments indicated that anthracene was oxidized in the reaction to be studied, and that gravimetric analysis of the reaction products was not feasible, an optical analytical procedure was developed which was capable of determining both anthraquinone and other simple oxidation products of anthracene. This procedure consisted of mixing a sample of the aldehyde to be analyzed with alcohol and hydrosulfite solution and adding water to make a given volume. The proportions of each liquid were such that a clear solution was obtained, except for a precipitate of anthracene which, if present, was filtered out by suction through a Jena glass filter in an atmosphere of nitrogen. Depending on the amounts of oxidation products present, two proportions were used, as follows: Combination No. 1: 40 cc. of alcohol, 2 cc. of aldehyde, 100 cc. of hydrosulfite (less than 7 days old), plus water to 200 cc.; Combination No. 2: 20 cc. of alcohol, 2 cc. of aldehyde, 10 cc. of water, 15 cc. of hydrosulfite (less than 4 days old), plus water to 50 cc.

After mixing, this solution was then subjected to spectrophotometric analysis. Under these conditions, anthraquinone is reduced to anthrahydroquinone of strong red color; anthrone and anthranol appear as the strongly yellow alkali salt of the latter; while dihydrodianthrone is converted to the yellow-orange alkali salt of its tautomer, dianthranol. As these colors indicate, anthrahydroquinone absorbs farther into the visible spectrum than the others, and it may thus be determined separately even in their presence; and a mixture of anthrahydroquinone with only one of the other substances may be analyzed for each component with accuracy by making measurements at different wave-lengths. However, anthrone and dihydrodianthrone cannot be distinguished from one another with precision, owing to the similarity of their spectra.

The spectrophotometer used was of the König-Martens type. The light source was a 150-watt tungsten filament lamp, placed in a fixed position, so

---

* Kindly supplied by the Eastman Kodak Co.

that the relative intensities of the two beams could be determined once and for all, and an analysis made by measurements with the absorption cell in one position only. The relative intensities vary slightly with the wave-length. The scale for different settings of the spectrophotometer was calibrated to read in wave-lengths by observation of the strong lines of a mercury and a cadmium arc.

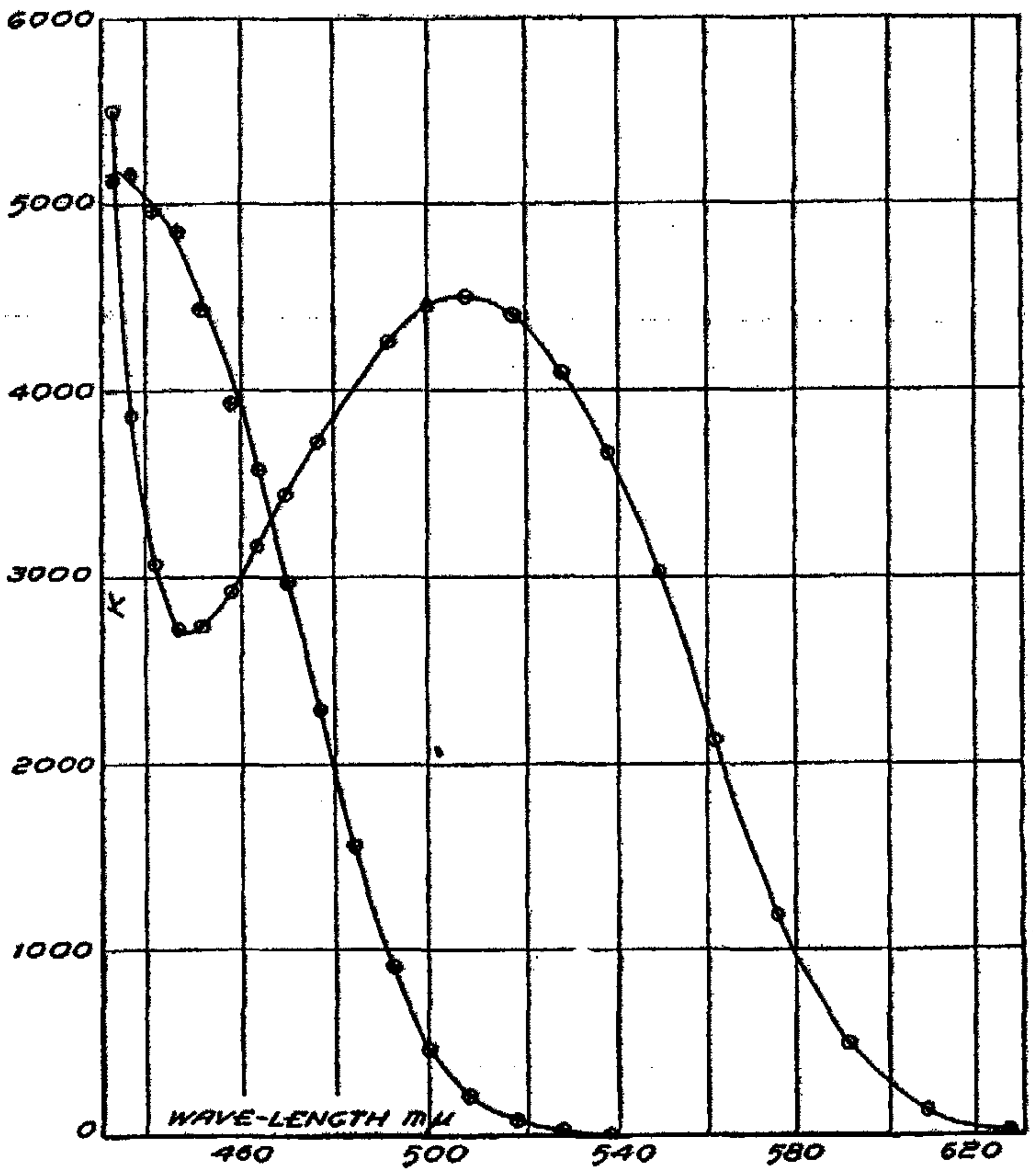


Fig. 1

Molecular Extinction Coefficients
⊙ Anthrahydroquinone
⊗ Anthranol

The solution to be analyzed was contained in a plane-parallel glass or quartz cell which was filled almost to the top and was closed by a glass plate sealed on with vaseline to exclude air. The two cells used permitted a choice of four different layer thicknesses, from 10 to 26 mm., which combined with the two dilutions employed, allowed measurements to be made under the most favorable conditions of light absorption. As the surfaces of the cells were not optically perfect, a measurement was made in each analysis at a wave-length in the red (694 mμ) where no absorption by the colored products occurred, giving a small correction for reflection. Additional slight corrections were applied for absorption by the solvent, based on a large number of blank determinations carried out in the same manner.

By this method, the absorption spectra of anthrahydroquinone and anthranol were determined, using known quantities of anthraquinone and anthrone. The results are given graphically in Fig. 1, where the molecular extinction coefficient K is defined by the formula: $\log I_0/I = Kcd$, wherein I_0 and I are the intensities of incident and transmitted light, c is the concentration in moles per liter, and d is the layer thickness of the solution in cm. The curve for anthranol has been corrected for the presence of 2.8% of anthraquinone in the anthrone used, as determined from the absorption spectrum at the longer wave-lengths. On the basis of these curves four wave-lengths were selected as being the most suitable for the identification and estimation of anthrahydroquinone and anthranol. The standard values of K at these wave lengths are given in Table I, those for anthrahydroquinone being the mean of a large number of determinations.

TABLE I

Molecular extinction coefficients, K.

Scale reading			33	30	25	21
Wave length, mμ			549.5	517.5	477	452
Anthrahydroquinone,	Combination	1	3023	4398	3732	2690
"	"	2	3041	4284	3668	2742
Anthranol,	"	1	0	81	2300	4440
Dianthranol,	"	1	0	690	7380	10500

It appears from the Table that the absorption spectrum is somewhat affected by the composition of the medium, but the effect is so small that slight accidental variations, such as might be caused by partial decomposition of the hydrosulfite, for instance, should be without influence on the results.

As regards the sensitivity of the method, the error in measuring the extinction of green light should not normally exceed 0.01 in the value of $\log I_0/I$ which, for the 50-cc. combination and a layer thickness of 25 mm., corresponds to about 0.01 mg. of anthraquinone in 2 cc. of aldehyde, or 0.000025 mole/lit., or 1 mole in 400,000. In the blue light the sensitivity of the eye is less, and the possible error is at least twice as great. Increased sensitivity could be obtained by measuring the absorption of long columns of solution, but this was not necessary in the present case.

Experimental Results

I. Induced Oxidation of Anthracene: Main and Side Reactions.

When a sample of aldehyde containing anthracene is shaken with oxygen in the light of the mercury arc, the gradual disappearance of the inhibitor manifests itself in a continuous increase in the rate of oxygen absorption. A typical curve is shown in Fig. 2, representing an experiment where 4 cc. of a

0.0306 molar solution was shaken at 30° in light of wave-length 366 mμ. The gradual increase in rate is followed by a sharp rise, indicating that all the anthracene has disappeared: the subsequent decrease is probably connected with the accumulation of peracid in the solution, as suggested in a previous paper.[16]

A number of experiments were made where the oxidation was continued until the maximum reaction velocity had been reached, and the aldehyde was then analyzed spectrophotometrically for oxidation products of anthracene. One such analysis is given in some detail in Table II. In this case 2.027 cc. of aldehyde which originally contained 0.02037 mole/lit. of anthracene was analyzed, after oxidation at 1° C., using the 200-cc. combination and a layer thickness of 16.37 mm.

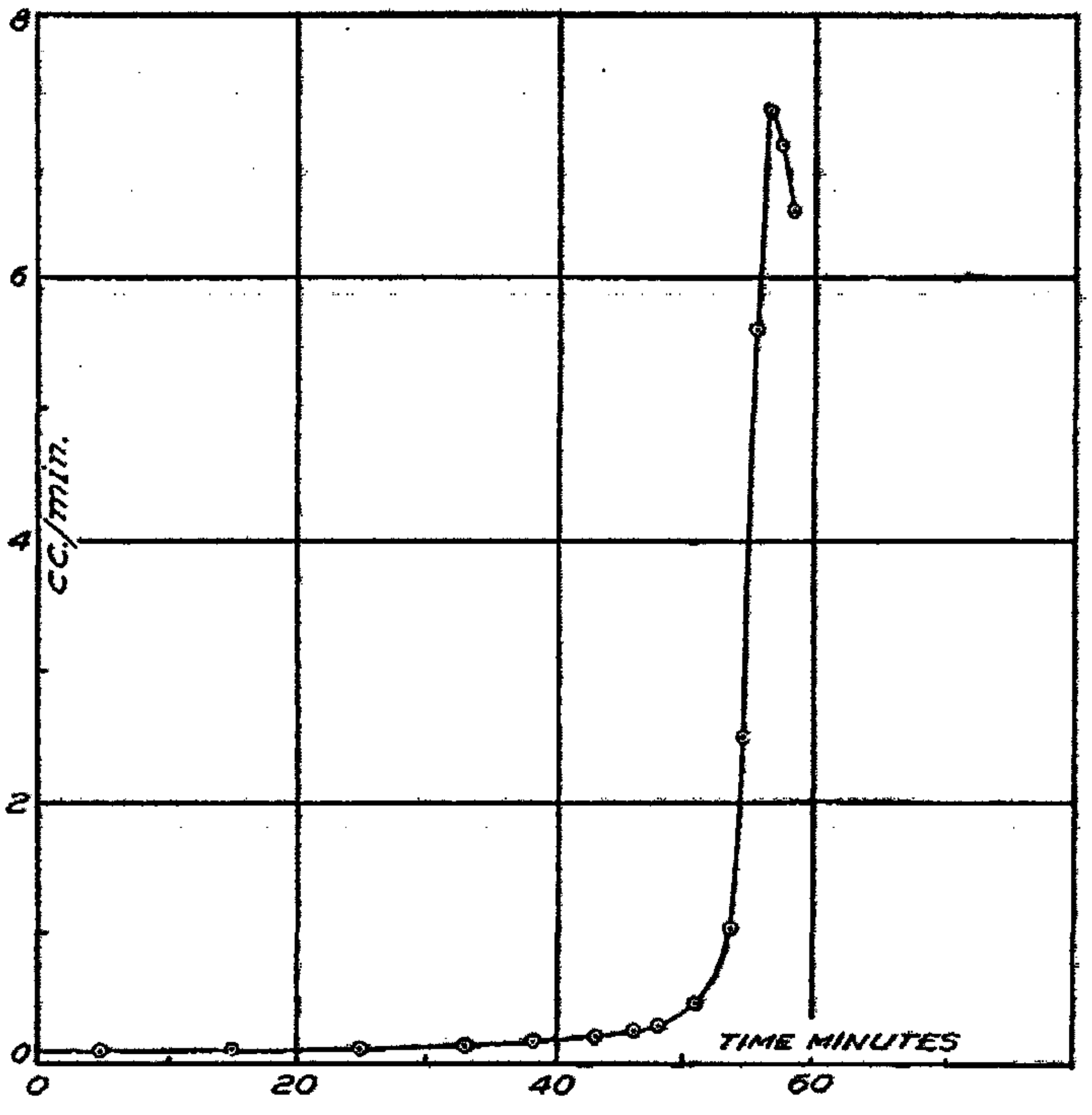


Fig. 2
Rate of Oxygen Absorption

TABLE II

Wave-length, mμ	549.5	517.5	477	452
Observed extinction	0.970	1.418	1.204	0.878
Anthraquinone, mole/lit.	0.01935	0.01942	0.01945	0.01968
Relative extinctions	100	100.4	100.5	101.7

---

[16] Bäckström: Medd. K. Vet.-Akad. Nobelinstitut, 6, No. 15 (1927); compare also Raymond: Compt rend., 191, 616 (1930).

The values in line 3 are the amounts of anthraquinone required to give the observed extinctions. The agreement at different wave-lengths shows that the spectrum is very nearly that of pure anthrahydroquinone. This is shown in a different manner in line 4 which gives the ratios (multiplied by 100) between the observed extinctions and those calculated for a pure anthrahydroquinone solution of the concentration indicated by the measurement at 549.5 mμ. This maximum value for anthraquinone, 0.01935 mole per liter of aldehyde, represents 95% of the anthracene originally present; the remaining 5% must have entered into side reactions. We may state at this point that, as shown by the following tables, these side reactions do not appear to affect the absorption at 549.5 mμ and that, accordingly, the measurements at this wave-length give a reliable value for the amount of anthraquinone present.

The results of similar experiments at three different temperatures are summarized in Table III.

TABLE III

Photochemical Reaction—Complete Oxidation

Temp.	Anthracene concentration, mole/lit.	Relative extinctions at wave-length, mμ				Yield of anthraquinone, %	Type of illumination
		549.5	517.5	477	452		
1·2°	0.0204	100	100.5	100.5	101.7	95	366 mμ
"	0.0220	100	99.8	99.8	101.5	93	Infiltered light
"	0.0155	100	100.1	101.3	103.0	94	313 mμ
"	0.0130.032	—	—	—	—	93-95*	
Averages at 1-2°		100	100.1	100.5	102.1	94	
20°	0.0177	100	101.6	105.7	110.4	83	366 mμ
"	0.0177	100	100.8	—	111.2	83	"
"	0.0298	100	101.0	106.3	112.1	84	"
"	0.0306	100	100.2	102.9	106.0	88.5	"
"	0.0308	100	100.5	—	106.0	83.5	"
Averages at 20°		100	100.8	105.0	109.1	84	
30°	0.0298	100	100.7	107.2	116.8	80	"
"	0.0306	100	100.1	106.8	117.2	82	"
Averages at 30°		100	100.4	107.0	117.0	81	

* 5 runs analyzed in green light only; 1 in unfiltered light, 4 using 366 mμ.

As appears from Table III, the yield of anthraquinone is independent of the anthracene concentration and of the conditions of illumination, but decreases with increasing temperature; at the same time, the anthrahydroquinone solutions become less and less pure, as shown by the excess absorption in the blue. In other words, besides the main reaction there is a side reaction leading to the formation of a substance which, in alkaline solution, possesses a yellow color. This is not due to any action of the light on the reaction product as the same facts are observed in the thermal reaction (Table IV). Moreover, experiments with only partial oxidation of the anthracene (Tables V and VI) show that the spectrum of the reaction product does not change during the progress of the reaction, so that the "yellow substance" must be formed as the result of a side reaction occurring *simultaneously* with

TABLE IV

Thermal Reaction—Complete Oxidation

Anthracene concentration, mole/lit.	Relative extinctions at wave-length, mμ				Yield of anthraquinone, %	Temperature (approx.)
	549.5	517.5	477	452		
0.0025	100	102.6	108.2	113.9	82	29°
0.0025	—	—	—	—	82	"
0.0113	100	99.7	104.6	114.7	84	"
0.0200	100	100.9	108.7	120.9	80	"
0.0013	100	100.8	103.1	108.7	85	25°
0.0053	100	100.2	—	—	84	"
0.0053	100	100.9	—	—	86	"
0.0054	100	99.0	106.1	114.2	86	"
Averages	100	100.6	106.1	114.5	84	27°

TABLE V

Photochemical Reaction—Incomplete Oxidation—Average Values

Anthracene concentration, mole/lit.	Number of runs	Temp.	Relative extinctions at wave-length, mμ				Anthracene oxidized, %
			549.5	517.5	477	452	
0.0250.070	9	1-2°	100	100.2	100.2	101.5	27-55
0.070	1	20°	100	101.4	103.0	107.2	27
0.0050.080	6	30°	100	100.5	105.5	113.9	20-33

TABLE VI

Thermal Reaction—Incomplete Oxidation—Average Values
Temperature 25-29°

Anthracene concentration, mole/lit.	Number of runs	Relative extinctions at wave-length, mμ				Anthracene oxidized, %
		549.5	517.5	477	452	
0.00130.0033	5	100	101.5	106.9	112.8	24-71
0.0050	3	100	101.2	105.6	112.7	27-38
0.0100	5	100	101.4	107.6	113.3	15-25
0.0100	5	100	101.3	107.7	113.7	28-46
0.0200.080	6	100	100.8	106.0	113.6	12-30
Averages		100	101.2	106.8	113.3	

the main reaction; and the experiments indicate that the temperature is the main factor, if not the only one, in determining the relative rates of these two reactions.

It will be seen from Tables III and IV that there is no direct proportionality between the deficit in the yield of anthraquinone and the excess absorption in the blue, indicating that the side reaction is of a complex nature and that some colorless product is formed besides the yellow substance. The latter absorbs in the same spectral region as the alkali salts of anthranol and dianthranol. However, if an oxidized anthracene solution is diluted with alcohol and alkali is added, the resulting solution does not fluoresce in ultraviolet light. Since a solution of anthrone in aldehyde shows strong fluorescence under these conditions, it may be stated definitely that this substance is not present among the reaction products. Dihydrodianthrone is not excluded by this test and, as a matter of fact, the absorption spectrum of the yellow substance agrees quite well with that of dianthranol, but we could obtain no other evidence of its presence. In any case, the presence of this substance could only account for a relatively small part of the deficit, as shown by the figures for its light absorption in Table I: in the thermal reaction, e.g., only 6%, which would still leave 10% of the anthracene to be accounted for.

In this connection, the possibility of dianthracene formation should be considered. The light absorption of anthracene in the ultraviolet is so strong that in most of our photochemical experiments a considerable part of the light (up to 70% in the most concentrated solutions) must have been absorbed by the anthracene instead of by the aldehyde.[17] On the basis of what has been found for solutions of anthracene in other solvents[18] one might thus expect dianthracene formation to occur as a side reaction in the above experiments. However, the close agreement between thermal and photochemical reactions, and the fact that the yield of anthraquinone is independent of the anthracene concentration, are definite evidence against this assumption. Moreover, special experiments conducted in the absence of oxygen showed that, although there is a slow formation of dianthracene in benzaldehyde solution, the rate is of a much lower order of magnitude than in a solvent like benzene. Probably this is connected with the fact that solutions of anthracene in benzaldehyde do not fluoresce; fluorescence only appears if the solution is diluted with alcohol or some other solvent. In view of what was said above about the light absorption, we must conclude that the aldehyde has a specific power of quenching the fluorescence by deactivating the excited anthracene molecules, which would also account for its effect on the formation of dianthracene. We shall return to this point later.

Besides the small-scale experiments described, a number of photochemical experiments were made on a larger scale, at 50-75° where the percentage yield of anthraquinone is small. After removal of aldehyde, benzoic acid and

---

[17] See absorption curves for the two substances in Henri: "Études de photochimie" (1919).

[18] Luther and Weigert: Z. physik. Chem., **51**, 297 (1905); **53**, 385 (1905).

anthraquinone by the usual methods, the products of the side reaction remained as a brown tar, partly soluble in alkali, and all attempts at further purification proved fruitless. We have thus had to leave the question of the nature of this reaction unsolved. There is also a slow reaction of the anthraquinone itself at these higher temperatures yielding, in part, condensation products with aldehyde. Fortunately, the amount of side reaction at 0-30° is slight, so that a study of the main reaction was sufficient for our purposes.

As regards the main reaction product, the analytical method employed does not distinguish between anthraquinone and other substances which would give the anthrahydroquinone spectrum in alkaline hydrosulfite solution. Of these, anthrahydroquinone itself may be excluded from consideration because of its instability in the presence of oxygen, and its tautomer, oxanthrone, on the ground that no red color developed when the aldehyde was mixed with alcohol and alkali alone, without adding hydrosulfite. This experiment was made in pure nitrogen under conditions where synthetic oxanthrone gave a positive result. A solution of dibenzoylanthrahydroquinone in aldehyde, when mixed with alcohol and hydrosulfite, has at first a pure yellow color which slowly changes into red; after about an hour the spectrum is that of pure anthrahydroquinone. It appears as if the substance were at once hydrolyzed to the monobenzoyl compound, which is then slowly hydrolyzed further. We may thus exclude both of these benzoyl derivatives (the latter of which has never been prepared), and anthraquinone seems to remain as the only possibility.

In agreement with this, it was observed in a number of cases that anthraquinone crystallized from the aldehyde, but it was noted that this never happened until a day or two after the oxidation. The reason for this will appear from the following section.

II. Induced Oxidation of Anthracene—Peroxides formed.

The experiments presented in this section show that the products of the main reaction include not only benzoic acid, benzoperacid and anthraquinone, but also hydrogen peroxide and an unknown peroxidic compound of anthracene, insoluble in water, and which gives the anthrahydroquinone spectrum when dissolved in hydrosulfite solution and hence appears as "anthraquinone" in the analysis.

Analytical Methods. The following analytical procedure was developed for the estimation of these acids and peroxides (benzoperacid is *not* included under the term "peroxide" for the sake of clarity). The titrating solutions were about 0.05 *N* and were delivered from 10-cc. microburettes that could be read accurately to 0.01 cc.

The determination of the peroxides in the presence of the peracid was based on the fact that the reaction of the former with hydriodic acid is relatively slow, whereas that of the latter is very rapid even when the concentration of potassium iodide is very low. To determine the total of peroxides, a 4-cc. sample of aldehyde was diluted with 20 cc. of alcohol, 1 cc. of dilute potassium iodide solution (10 mg./cc.) was added, and the iodine liberated by the peracid was at once titrated with thiosulfate, using the iodine color as indicator. Then 2 cc. of strong potassium iodide solution (1 g./cc.) was added, and the iodine liberated by the peroxides was titrated after 15-20 minutes. Finally, the remaining benzoic acid was titrated with carbon dioxide-free sodium hydroxide, using thymol blue as an indicator: to this acid must be added the amount consumed in the two previous titrations by reaction with potassium iodide. The benzoic acid can be titrated directly without removing the peroxides, as shown by special experiments, but the accuracy is not as high due to a slow drift of the end-point.

For the separate determination of hydrogen peroxide and water-insoluble peroxide, the following method was used. A 2-cc. sample of aldehyde was diluted with 5 cc. of benzene in a small separatory funnel, and shaken out 2-3 times with 20-cc. portions of water which removes all the hydrogen peroxide and a small fraction of the peracid. Mixing the aldehyde with benzene serves the purpose of reducing the specific gravity to below that of water; furthermore, the unusually high value of the distribution coefficient of hydrogen peroxide between water and benzene[19] is favorable to the method. In the water layers, any peracid was first removed by adding a drop of dilute sulfuric acid and 1 cc. of weak potassium iodide solution, and decolorizing at once with thiosulfate; the hydrogen peroxide was then determined by adding 5 cc. of 5 *N* sulfuric acid and 2 cc. of the strong potassium iodide solution, and starch, and titrating after 3 minutes. The identity and amount of the hydrogen peroxide could be confirmed by its characteristic test with titanium sulfate solution. To the benzene layer was added 20 cc. of alcohol; the peracid and water-insoluble peroxide therein were then determined as described in the previous paragraph.*

Suitable blank experiments indicated that the above method gives the true concentration of hydrogen peroxide in the aldehyde. For example, a synthetic solution gave the following titers by the two methods:

(1) total peroxide, in alcohol = 1.94 cc. of thiosulfate
(2) peroxide, in water layers: 1.73 + 0.19 + 0.02 = 1.95 " " "
peroxide, in benzene layer = 0.02 " " "

With this may be compared a typical result, by the second method, on a partly-oxidized solution of anthracene in aldehyde:

water layers, peracid = 0.00 cc. of thiosulfate
" " , peroxide: 0.65 + 0.07 = 0.72 " " "
benzene layer, peracid = 0.04 " " "
" " , peroxide = 2.36 " " "

---

[19] Mellor: "A Comprehensive Treatise of Inorganic and Theoretical Chemistry," I, 932, (1922).

* By these methods it was also found that "pure" benzaldehyde, when it is not freshly distilled, may contain measurable quantities of hydrogen peroxide. This was probably the cause of some of the irregularities observed in previous work by one of us on the reaction between peracid and aldehyde (Medd. K. Vet.-Akad. Nobelinstitut, 6, No. 15 (1927)). Possibly some recent observations of Jorissen and van der Beek (Rec. Trav. chim., 49, 138 (1930)) may also be traced to the same cause.

It is thus evident that, besides hydrogen peroxide there is another peroxide present which is not soluble in water.

Special experiments showed that hydrogen peroxide reacts with benzaldehyde to form benzoic acid, but the rate is so slow at room temperature as not to affect the accuracy of the analyses. Photochemically active light was excluded as much as possible during the titrations.

As stated, the water-insoluble peroxide may be identified as an unknown compound of anthracene, temporarily called "combined anthraquinone," which gives the anthrahydroquinone spectrum in the spectrophotometric analysis, and so appears there as anthraquinone. The method employed for the estimation of "combined anthraquinone" was based on the ease and rapidity with which equilibrium is established between solid anthraquinone and its solution in benzaldehyde. Accordingly, the solution to be analyzed was stirred with an excess of solid anthraquinone until it was saturated; an analysis then gave the sum of free and "combined" anthraquinone in solution, from which the known amount of free anthraquinone in a saturated solution was subtracted, giving the concentration of the "combined" form.

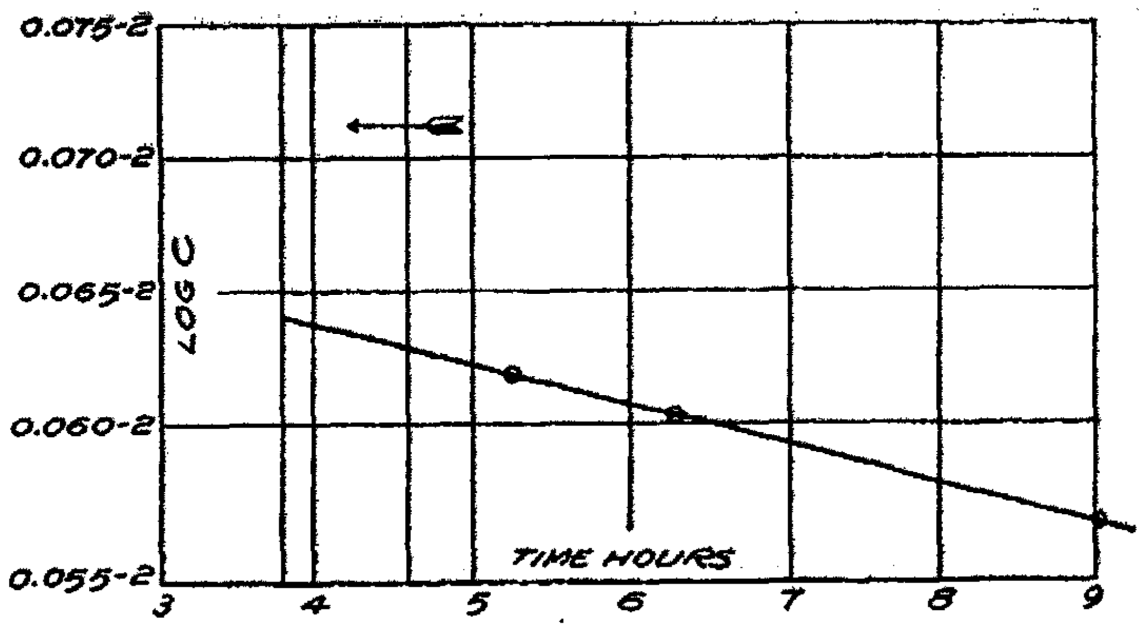


Fig. 3
The Logarithm of the Concentration of "Combined Anthraquinone" plotted against Time

The apparatus used consisted of a glass tube, 35 × 120 mm., through which a current of pure nitrogen could be passed by means of a narrow tube sealed on at the bottom. The wider tube was closed at the top by a rubber stopper containing an outlet with a stop-cock. The tube was kept in crushed ice in a Dewar vessel. 30- to 50-cc. samples of aldehyde and 1 g. of finely-crystalline anthraquinone were introduced into the apparatus and stirred with a current of nitrogen until equilibrium had been reached. 15 minutes proved to be sufficient, of which 10 minutes were required to establish thermal equilibrium. The suspension was then allowed to settle for 5 minutes, after which a sample could be taken for analysis.

By this method the solubility of anthraquinone in pure aldehyde at 0° was found to be 0.0081 mole/lit., as the average of 16 determinations ranging from 0.0078 to 0.0083 mole/lit. It was not measurably affected by the presence of benzoic acid or anthracene in concentrations up to saturation.

Experimental Results. Tables VII-IX give the results of analyses by the above-described methods on oxidized anthracene solutions obtained from the photochemical reaction in intense, unfiltered light at about 2°. They show that such solutions contain both free and combined anthraquinone, and that the concentration of the latter falls off with time, indicating that it slowly decomposes or changes over to free anthraquinone. When the logarithm of

TABLE VII

25 cc. of aldehyde + 375 mg. of anthracene (sufficient to saturate the solution until nearly the end of the reaction—average concentration close to 0.05 mole/lit.); oxidized between the times 3:48 and 4:35. 1 g. of solid anthraquinone added at 4:58.

Values with * obtained by interpolation. All concentrations in mole/lit.

(1) Time	(2) Anthraquinone	(3)	(4) Total peroxide in alcohol	(5) H_2O_2 in water	(6) Water-insoluble peroxide in benzene	(7) Ditto, calcd. from Col. 4 minus Col. 5	(8) Ratio, Col. 3 to Col. 6	(9) Ratio, Col. 3 to Col. 7
	Total	"Combined"						
4:50	0.0515	*0.0423	0.0289	0.0084	0.0271	0.0204	1.56	2.07
5:16	0.0496	0.0415						
5:29		*0.0413	0.0266			0.0181		2.28
6:16	0.0482	0.0401						
6:26		*0.0389		0.0086	0.0254		1.53	
9:02	0.0446	0.0365						
9:16		*0.0363	0.0220			0.0135		2.69

Extrapolated to the middle of the oxidation period: "combined anthraquinone" = 0.0431, free anthraquinone = 0.0515 − 0.0431 = 0.0084 mole/lit. or 16% of total.

TABLE VIII

40 cc. of 0.05 molar solution of anthracene (average concentration 0.037 mole/lit.) oxidized from 5:44 to 6:17. Anthraquinone added at 6:37.

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
6:35	0.0267	*0.0223	0.0157		0.0168	0.0122	1.33	1.83
6:57	0.0297	0.0216						
7:06		*0.0214	0.0148			0.0113		1.90
7:37	0.0286	0.0205						
7:48		*0.0203	0.0121	0.0036	0.0151	0.0086	1.34	2.36
9:27	0.0259	0.0178						
9:37		*0.0176	0.0105	0.0035	0.0137	0.0070	1.28	2.51
12:17	0.0221	0.0140						
12:27		*0.0140	0.0096	0.0035	0.0105	0.0061	1.33	2.29

Extrapolated to middle of oxidation period: "combined quinone" = 0.0233; free quinone = 0.0034 mole/lit., or 13% of total.

the concentration of "combined" anthraquinone is plotted against the time, as in Fig. 3 (data from Table VII), the points fall on a straight line. The time of oxidation has been indicated in the figure by two vertical lines. The figure shows beyond doubt that there is no agreement between the total concentration of "anthraquinone" formed in the reaction (which has been indicated in the figure by an arrow at 0.712 − 2 = log 0.0515) and the concentration of "combined anthraquinone," as determined by extrapolation. In other words, some free anthraquinone was formed also, the amount of which was estimated by subtracting from the total the amount of "combined" indicated by extrapolation to the middle of the oxidation period.

TABLE IX

40 cc. of 0.025 molar solution of anthracene (average concentration 0.017 mole/lit.) oxidized from 3:26 to 3:39. Anthraquinone added at 3:53.

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
3:48	0.0154	*0.0130	0.0098	0.0024	0.0081	0.0074	1.60	1.75
4:38	0.0198	0.0117						
4:45		*0.0115	0.0081	0.0023	0.0082	0.0058	1.40	2.0
5:25	0.0184	0.0103						
5:32		*0.0103	0.0067	0.0023	0.0075	0.0044	1.38	2.3
6:46	0.0168	0.0087						
6:55		*0.0086	0.0058	0.0023	0.0064	0.0035	1.34	2.5

In this case the extrapolation to the time of oxidation is rather uncertain: "combined anthraquinone" = 0.0134; free quinone = 0.0020 mole/lit. = 13% of total.

The following facts may be deduced from the foregoing tables:

(1) A nearly constant amount (about 15% of the total) of free anthraquinone is formed in the oxidation itself, and not by decomposition of the "combined" form. An equimolecular amount of hydrogen peroxide is likewise formed, and its subsequent reaction with aldehyde is negligible in the time interval studied. As will be shown later, these substances—free anthraquinone and hydrogen peroxide—undoubtedly result from the autoxidation of anthrahydroquinone, which therefore appears as an intermediate product in the reaction.

(2) The concentration of "combined anthraquinone" falls off with time at a regular rate in each experiment, but the rate varies between different experiments, the values for − d log c/dt being 0.015, 0.035 and 0.058 respectively (t = time in hours).

(3) This is parallelled by a decrease in the concentration of water-insoluble peroxide, indicating that these two substances are very likely identical. As the same peroxide appears to be formed in the autoxidation of anthranol, it will be further discussed in a later section.

(4) The sum of the concentrations of hydrogen peroxide (Column 5) and water-insoluble peroxide (Column 6), obtained by the benzene-water method,

is always higher than the total peroxide concentration determined in alcohol (Column 4); and no constant or simple relation seems to exist between any of these quantities and the concentration of "combined anthraquinone." We are unable to offer any explanation for these facts, that were corroborated by a large number of similar titrations. These titrations cannot therefore be used to determine the composition of the peroxide, and the only thing which may be concluded in this respect from the above experiments is that, since the peroxide is converted to free anthraquinone in the absence of oxygen or oxidizing agents, it must contain at least as much oxygen as the latter compound. This problem will be further considered in the next section.

III. Induced Oxidation of Anthracene—Oxygen consumed.

A number of experiments were made in which concentrated solutions of anthracene in aldehyde were partially oxidized under illumination, and the amount of oxygen absorbed was compared with the amount which could be accounted for in the form of the various oxidation products. One such experiment will be given in detail.

14.92 cc. of a 0.05 molar solution of anthracene was shaken at 1.5° for 137 minutes in light of wave-length 366 $m\mu$; 20.82 cc. of oxygen was absorbed. The temperature of the gas burette was 22.7°, the barometer 752 mm. Titrations, in alcohol, on 3.937 cc. samples: Before oxidation:—peracid, none; peroxide, none; benzoic acid = 8.31 cc. of 0.04885 *N* sodium hydroxide. After oxidation:—peracid = 0.03 cc.; total peroxide = 1.74 cc. of 0.04836 *N* thiosulfate; benzoic acid = 9.35 cc. of alkali. Benzene-water treatment on 2.02-cc. sample: hydrogen peroxide = 0.35 cc. of thiosulfate, water-insoluble peroxide = 0.54 cc.

Recalculated to 14.92 cc., the results are as follows:

			Oxygen, mg. Atoms
Peracid	0.003	millimole	0.006
Peroxide (total, in alcohol)	0.159	"	0.159
Increase in benzoic acid titer	0.193	"	
Acid consumed in titrating peracid	0.003		
" " " " peroxide	0.318	"	
Total benzoic acid formed	0.514	"	0.514
"Anthraquinone" 10.26 mg./2.027 cc	0.363	"	1.089
Total oxygen accounted for			1.768
Oxygen absorbed			1.698

Thus 4.1% more oxygen is accounted for than was actually taken up, which should be decidedly outside the limits of error. Two other similar runs gave yields of oxidation products, calculated as above, of 106.7% and 106.1%, and a run with 0.025 molar solution, 104.1%. This is the more striking as nothing has been allowed for oxygen consumed in the side reaction (about 6% of the total at 1.5°) leading to the formation of the "yellow substance." The only doubtful point in the above calculation seems to be

that the "active" oxygen found iodimetrically has been counted in excess of what is required to form anthraquinone. If only the hydrogen peroxide formed is taken into account (0.063 millimole = 0.063 milligram atom of oxygen), the total accounted for becomes 1.672 milligram atoms, or 98.5% of the oxygen actually absorbed, which is a more reasonable figure. Similar experiments at 30° gave yields of oxidation products (counting only the hydrogen peroxide) of 94% and 96% at an anthracene concentration of 0.08 mole/lit., and 97% at 0.04 mole/lit. The lower yield is in agreement with the fact that the side reaction is more prominent at this temperature, but apparently the amount of oxygen going into this reaction is relatively small: only about 1 atom of oxygen for every molecule of anthracene.

These experiments indicate that the composition of the water-insoluble peroxide is not that of a peroxide of anthraquinone, but that it represents the same stage of oxidation as anthraquinone itself.

This conclusion is supported by the following experiment. A 0.05 molar solution of anthracene in aldehyde was oxidized with illumination at 1°. It was then transferred to a nitrogen bubbling tube kept in a thermostat at 25.0°, and samples were taken for titration and spectrophotometric analysis. 1 g. of solid anthraquinone was then added, and the experiment continued as described in the preceding section. The solubility of anthraquinone in aldehyde at 25° had been determined as 0.0210 mole/lit. The results are given in Table X. All concentrations are in mole/lit.

TABLE X

Time, hours	Anthraquinone		Total peroxide in alcohol	Benzoic acid formed	Hydrogen peroxide	Water-insoluble peroxide in benzene
	Total	"Combined"				
0	0.0239	—	0.0125	0.0340	0.0042	0.0120
1.0	0.0360	0.0150	0.0120	0.0331	0.0042	0.0101
5.1	0.0297	0.0087	0.0087	0.0344	0.0039	0.0058
21.6	0.0249	0.0039	0.0052	0.0361	0.0027	0.0026

As seen from the table, the benzoic acid stays constant within the limits of error during the first five hours, but after 21 hours it has decreased by about 0.002 mole/lit., to which corresponds a decrease of the same order of magnitude in the concentration of hydrogen peroxide, while the decrease in concentration of water-insoluble peroxide is 4.5 times as great. This last is parallelled, as before, by a decrease in "combined anthraquinone." It is thus evident that the peroxide does not disappear by reacting with the aldehyde. Hence, if it contains oxygen in excess of what is required to form anthraquinone (or anthraquinone + water), that oxygen must be liberated again in the elementary form. Considering the behavior of hydrogen peroxide under the same conditions, this seems very improbable.

All attempts to isolate the water-insoluble peroxide from its solution in benzaldehyde were frustrated by its instability.

IV. Autoxidation of Anthrahydroquinone.

The anthrahydroquinone was prepared, stored and withdrawn as needed in an enclosed apparatus filled with nitrogen, since even the crystalline form is rapidly oxidized in the air. An alkaline solution of the phenol, obtained by the reduction of anthraquinone with zinc dust and 10% sodium hydroxide, was sucked through a Jena glass filter crucible into an acid bath from the bottom of which portions of the precipitated phenol were sucked down into a second crucible over which were delivery tubes for washing liquids and solvents. By means of the solvents, solutions of the phenol were obtained and sucked directly into suitable reaction tubes which could then be removed from the apparatus. The entire manipulation was carried out so as to avoid any contact with oxygen.

The autoxidation of alkaline water solutions of anthrahydroquinone has been studied by Manchot[20] who found that oxygen is rapidly absorbed with the formation of anthraquinone and hydrogen peroxide. A 100% yield of the latter is, however, only obtained if the peroxide is removed (e.g., as barium peroxide) from the solution as fast as it is formed; otherwise part of the peroxide reacts with unchanged phenol.

We have studied the autoxidation of free anthrahydroquinone in acetone, and obtained similar results. If oxygen was admitted very slowly to the well-stirred solution, no hydrogen peroxide remained at the end of the reaction, but if the oxygen was rapidly admitted, a 97% yield of the peroxide was obtained. There was no induced oxidation of the solvent.

A like result was obtained in benzaldehyde solution. An ether solution of the phenol was evaporated in a current of pure nitrogen, and the green, crystalline solid again dissolved in 45 cc. of a 0.05 molar solution of anthracene in aldehyde. The concentration of anthrahydroquinone was then determined spectrophotometrically and also iodiometrically (under nitrogen), the samples being taken in nitrogen-filled pipettes into which the solution was forced by nitrogen pressure. The solution was then cooled to 0° and, with the aid of an inverted, nitrogen-filled pipette, a sample of about 10 cc. was rapidly transferred to an oxygen-filled shaking tube. This was at once closed with a cork and shaken vigorously by hand for 2 minutes, by which time the anthrahydroquinone color had completely disappeared. After warming to room temperature, the solution was analyzed in the usual way. The results were as follows:

Before oxidation:—4.055 cc. of anthrahydroquinone solution plus 2 cc. of 0.1 *N* iodine solution in 20 cc. of alcohol required 2.10 cc. of 0.0477 *N* thiosulfate; 2 cc. of iodine alone = 4.12 cc. of thiosulfate. The concentration of anthrahydroquinone was therefore = 0.0119 mole/lit. The spectrophotometric determination gave a slightly higher value, 0.0129 mole/lit., indicating that a small quantity of anthraquinone was present from the start.

After oxidation:—Anthraquinone = 0.0129 mole/lit.; total peroxide (in alcohol) = 0.0113 mole/lit.; hydrogen peroxide = 0.0116 mole/lit.; peroxide

---

[20] Manchot: Ann., **314**, 179 (1901).

in benzene layer = 0.0005 mole/lit. Benzoic acid:—before dissolving the anthrahydroquinone, 0.1640 mole/lit.; after the oxidation, 0.1414 + 2 × 0.0113 = 0.1640 mole/lit.

A very slow current of oxygen was bubbled through the remaining portion of the solution until the color of the anthrahydroquinone had disappeared. This slow oxidation gave a yield of hydrogen peroxide of only 6% of the theoretical value.

The spectrophotometric analyses showed that the anthraquinone formed here was pure, i.e., no "yellow substance" was formed.

It is evident from the results that if anthrahydroquinone were formed as an intermediate product in the induced oxidation of anthracene, it would be rapidly oxidized by molecular oxygen to anthraquinone with the formation of an equimolecular quantity of hydrogen peroxide, and this reaction would not induce the oxidation of either benzaldehyde or anthracene. However, there would undoubtedly be a competition between this reaction and an oxidation by benzoperacid, to form anthraquinone and water, as there would always be some of this substance present and a qualitative experiment showed that it, also, rapidly reacts with anthrahydroquinone. In the experiments given in Tables VII-IX the inhibitor concentration was high, and the peracid concentration correspondingly low, and the results indicate that under these conditions, at least, the oxidation by molecular oxygen is the predominating reaction.

V. *Autoxidation of Anthranol.*

Preparation. An alkaline solution of anthranol can readily be obtained by dissolving anthrone in hot, aqueous alkali and filtering. However, to obtain the free phenol in pure crystalline form is difficult, since the alkaline solution is readily oxidized by air (to dihydrodianthrone and anthraquinone) and the free phenol, both in solution and in the solid state, is slowly oxidized and is rapidly tautomerized to anthrone. Even fine, large crystals are somewhat isomerized in 24 hours. The rate of isomerization in solution varies markedly with the solvent;[21] we found the rate in benzaldehyde solution (nearly free from benzoic acid) to be that of a unimolecular reaction with a half-life period of 5.0 hours at 25°.

For the preparation of pure, crystalline anthranol, the original procedure of K. H. Meyer[21] was modified as follows: Take 0.5 g. of powdered anthrone in 25 cc. of 10% sodium hydroxide; boil gently for 5 minutes; add 50 g. of ice and cool rapidly in an ice-bath; filter through a pleated paper, supported at the bottom by a platinum cone, directly into a 250-cc. separatory funnel containing 100 cc. of ice-water, 2.5 cc. of concentrated sulfuric acid and 20 cc. of toluene, through which is passed a constant stream of nitrogen. Stopper the funnel and shake the precipitated phenol into the toluene layer; withdraw the water layer (again passing in nitrogen) and wash once with oxygen-free water. To remove the remaining water from the somewhat emulsified

---

[21] K. H. Meyer: Ann. 379, 56 (1911).

toluene layer, add 5 g. of anhydrous sodium sulfate and shake. Filter the clear toluene solution into a 18 × 150 mm. test-tube, and wash the sulfate and filter paper with 10 cc. of 70°-80° ligroin (which serves simply as a diluent, to promote the formation of larger crystals); this entire operation should be carried out as far as possible in the absence of oxygen. Cork and support the test-tube within a 25 × 250 mm. tube, and immerse the latter in a carbon dioxide-ether cooling bath for several hours. Filter the crystals (a felt of fine, orange needles) rapidly, to avoid condensation of moisture; wash with a little low-boiling ligroin, and dry in a vacuum desiccator. It was found difficult to get a perfectly dry product; the amorphous or finely-divided material will tenaciously retain a large amount of water if exposed to it. The best preparation of anthranol obtained was 97% pure, and contained 2.5% of anthraquinone.

Meyer's original directions called for the drying of the precipitated material in the solid state before recrystallization. In our experience this is apt to cause more or less complete isomerization to anthrone.

Analysis. The sum of anthranol and anthrone can be accurately determined by spectrophotometric analysis, as previously indicated. For the determination of anthranol in the presence of anthrone, qualitative indication of the former is given by its *strong* blue fluorescence in most solvents; a benzaldehyde solution must, however, be diluted with 20 volumes of alcohol to observe this. For quantitative estimation it was found satisfactory to titrate the anthranol in dilute alcoholic solution with 0.1 *N* iodine in aqueous potassium iodide. A decided excess of iodine was run into 50 cc. of alcohol, then the anthranol (solid or in solution) added with good stirring, followed by four volumes of water, starch, and thiosulfate. The reaction with iodine is immediate, and was found to be exactly equivalent in titer to that with bromine, where it is known that two atoms of the halogen oxidize one molecule of anthranol.[22]

Experimental results. In the following experiments, the solvent was a 0.05 molar solution of anthracene in aldehyde, and the solutions were prepared in a current of pure nitrogen. Measured portions were transferred to a shaking tube and shaken in the dark at about 1.5° until the drop in the rate of oxygen absorption indicated that oxidation was complete. The reaction is not instantaneous, as seems to be the case with anthrahydroquinone; in the following two experiments it took about 8 minutes for the rate of absorption to fall to half its original value.

Experiment 1. 129.1 mg. of anthranol, 97% pure by titration, was dissolved in 24.0 cc. of aldehyde (containing anthracene): concentration, calculated, 0.0269 mole/lit. 5.03-cc. of the resulting solution consumed 2.72 cc. of 0.1 *N* iodine, corresponding to 0.0270 mole/lit.

Spectrophotometric analyses were made on 2.044-cc. samples before and after oxidation, using the 200-cc. combination and a layer thickness of 10.04 mm. The following extinctions were observed:

---

[22] K. H. Meyer and A. Sander: Ann., 396, 140 (1913).

Wave-length, mμ		549.5	517.5	477	452
Before oxidation,	observed	0.024	0.042	0.619	1.199
" "	calculated	0.019	0.048	0.629	1.188
After oxidation,	observed	0.674	0.996	0.948	0.810
" "	calculated	0.679	0.992	0.946	0.813

The calculated values are for mixtures of anthranol and anthrahydroquinone of the following composition, in mole per liter of aldehyde:

	Before oxidation	After oxidation	Change
Anthranol	0.0257	0.0046	−0.0211
Anthrahydroquinone	0.0006	0.0219	+0.0213

It is evident fron these figures that the anthranol is oxidized to anthraquinone, or to something else giving the anthrahydroquinone spectrum. 18% of the anthranol had escaped oxidation, however, presumably by isomerization to anthrone, which is not autoxidizable. We shall return to this point presently.

This result is not in agreement with earlier work on the atmospheric oxidation of anthranol solutions,[23] in which dihydrodianthrone was obtained as the main oxidation product beside relatively small quantities of anthraquinone. A possible explanation is that our experiments were made on rather dilute anthranol solutions, and the formation of dihydrodianthrone, involving two molecules of anthranol, would be expected to be favored by a high concentration.

Peroxide titrations on the oxidized solution gave the following results, in mole/lit.:

Total peroxide, in alcohol	Hydrogen peroxide	Peroxide, in benzene
0.0072	0.0004	0.0075

Thus, beside perhaps a trace of hydrogen peroxide, a considerable quantity of a water-insoluble peroxide had been formed, the yield being 35% of the "anthraquinone" formed, on the basis of one atom of active oxygen per molecule of quinone.

Experiment 2. 290 mg. of anthranol was dissolved in 46.1 cc. of an aldehyde solution of anthracene. This should have given a concentration of 0.0324 mole/lit., but an iodimetric determination gave only 0.0248 mole/lit., showing that the material was partly isomerized. 40 cc. of the solution was shaken with oxygen at 1.5° and later transferred to a nitrogen bubbling tube, kept in a thermostat at 25.0°. After taking the necessary samples, 1 g. of solid anthraquinone was added and the experiment continued as in previous experiments of this kind. The results are given in Table XI, where the figures represent concentrations in mole/lit. The spectrophotometric analyses showed that beside the concentrations of "anthraquinone" given under "Total anthraquinone," the samples contained a constant amount of anthrone equal to 0.0057 mole/lit. In this case the "anthraquinone" formed, 0.0253

---

[23] Orndorff and Bliss: Am. Chem. J., 18, 453 (1896).

mole/lit., corresponds closely to the result of the iodimetric determination for anthranol, 0.0248 mole/lit., indicating that all the anthranol was oxidized to "anthraquinone" and that the anthrone found at the end of the reaction had been present from the start. The sum of the two, 0.0310 mole/lit., is not far from the value calculated from the weight of the solid taken.

TABLE XI

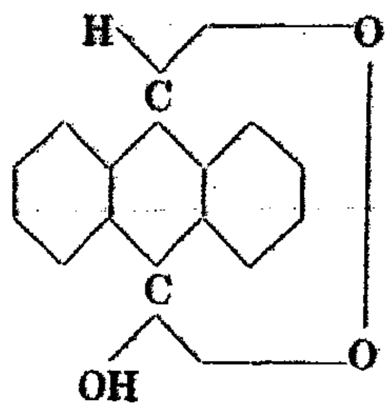
Time, hours	Anthraquinone,		Total peroxide in alcohol	Hydrogen peroxide	Peroxide in benzene	Benzoic acid*
	Total	"Combined"				
0.0	0.0253	—	0.0092	0.0002	0.0108	0.0011
0.8	0.0300	0.0090	0.0050	—	—	0.0017
2.7	0.0236	0.0026	0.0009	0.0001	0.0014	0.0017

* Excess over the amount present before dissolving the anthranol.

The experiment shows that beside water-insoluble peroxide, there is "combined anthraquinone" present among the reaction products, and that they disappear from the solution together. Furthermore, the disappearance of the peroxide is not attended by benzoic acid formation: compared to Sample 1, Sample 3 indicates an increase in benzoic acid of only 0.0006 mole/lit., whereas the decrease in active oxygen is around 15 times as large. The ratios between "combined anthraquinone" and active oxygen lie in the same region as in the case of oxidized anthracene solutions. There is thus little doubt as to the identity of the two peroxides, and we may draw the conclusion that anthranol is formed as an intermediate product in the induced oxidation of anthracene. Certain objections may be raised to this, but they do not appear to be of a serious nature. Thus the first experiment indicates the simultaneous formation of anthrone, and there seems to be no trace of this in the induced oxidation of anthracene. However, in the second experiment there was apparently no appreciable anthrone formation and furthermore, as previously stated, a direct determination of the rate of isomerization in benzaldehyde solution showed it to be a slow reaction.

A more serious objection is that, with a rate of autoxidation as low as that found in these experiments, a distinct after-effect should have been observed in the photochemical oxidation of anthracene solutions; and this was not the case. But it does not seem improbable that the anthranol molecules, at the moment of their formation, possess an increased reactivity, which would remove this objection. A further objection may be based on the fact that the rate of disappearance of "combined anthraquinone" in Experiment 2 has a much higher value than in the experiment on an oxidized anthracene solution given in Table X, which was made at the same temperature. However, as previously stated, this rate varies from one solution to another and cannot, therefore, be used to characterize the peroxide in question.

The fact that the primary reaction product in the autoxidation of anthranol is a peroxide, is in complete accord with our knowledge of autoxidation reactions in general, and the following structure immediately suggests itself for this compound:



However, such a substance, when reacting with hydriodic acid to give free iodine, would also be expected to give anthrahydroquinone or, less probably, oxanthrone, and suitable experiments indicated that neither of these is formed. As previously stated, however, the results obtained in the iodimetric peroxide titrations are so peculiar that we must assume the presence of some unknown factor in this reaction, and thus no definite conclusions may be drawn from it. Time did not permit further work on anthranol oxidation, but the results obtained are sufficient for the purposes of the present investigation.

VI. The Reaction between Benzoperacid and Anthracene.

The result of the preceding section, viz. that anthranol appears as an intermediate product in the induced oxidation of anthracene, is in perfect agreement with the Engler-Bach theory in so far as it points directly to a reaction between benzoperacid and anthracene as the primary process: $C_6H_5CO_3H + C_{14}H_{10} = C_6H_5COOH + C_{14}H_{10}O$. Experiments were accordingly made to see whether such a reaction will actually take place.

10 cc. of benzaldehyde that had just been shaken with oxygen in sunlight was mixed with 10 cc. of a 0.070 molar solution of anthracene in aldehyde, and the mixture protected against light. A sample taken immediately after mixing indicated a peracid concentration of 0.0265 mole/lit. 25 minutes later another test showed that all the peracid had disappeared. A 2-cc. sample was then analyzed spectrophotometrically: the result showed that neither anthrahydroquinone nor anthranol were present, the sensitivity of the test being about 10^{-4} mole/lit. The ratio between benzoic acid formed and anthracene oxidized was therefore *at least* $= \frac{2 \times 0.0265}{10^{-4}} = 530$. On the other hand, Table XIV shows that in the autoxidation of benzaldehyde containing 0.035 mole/lit. of anthracene, the corresponding ratio is about 1.9. This observed induced oxidation is thus *at least* $529/0.9 = 600$ times too effective to be ascribed to an ordinary thermal reaction between peracid and anthracene.

VII. Kinetics of the Reaction.

Tables XII-XIV give the results of systematic experiments on the rates of the two main reactions taking place in the autoxidation of benzaldehyde solutions of anthracene, viz. the formation of benzoic acid and of "anthraquinone," in their dependence on the concentration. The thermal reaction was studied only at one temperature, but the photochemical reaction was studied at two different temperatures and at two different wave-lengths of the exciting light. The concentration region which could be investigated was determined on the one hand by the solubility of anthracene in aldehyde at the temperature in question, and on the other hand by the sensitivity of the spectrophotometric anthraquinone determination. If any peracid was present at the time of titration, its concentration was multiplied by 2 and added to the concentration of benzoic acid. The figures for benzoic acid in the tables thus represent "total potential benzoic acid;" they give the values which would have been found if the reaction $C_6H_5CO_3H + C_6H_5CHO = 2\ C_6H_5COOH$ had had time to go to completion. All concentrations are in mole/lit.

In calculating the average anthracene concentration during a run, the assumption was made that the quantity of anthracene which had disappeared was equal to the amount of anthraquinone formed. As appears from the foregoing, this is not quite correct, but the error from this source is small since the percentage conversion was generally below 30%. The figures for

TABLE XII

Photochemical reaction at 2°

Wave-length of light 366 mμ, except in the last three runs

Initial anthracene conc.	Anthraquinone "Q"	Benzoic acid "B"	Ratio of B/Q	Average anthracene conc., "C"	k	H_2O_2 %	Time, mins.	Rate of Quinone form., moles /min. × 10^6
0.0478	0.00848	0.0115	1.36	0.0436	0.019	19	23	3.7
0.0478	0.0107	0.0147	1.37	0.0424	0.019	18	25.5	4.2
0.0500	0.0200	0.0293	1.47	0.0400	0.022	—	—	—
0.0500	0.0243	0.0349	1.44	0.0378	0.019	—	—	—
0.0438	0.0119	0.0159	1.34	0.0378	0.016	19	31	3.8
0.0350	0.0089	0.0139	1.56	0.0305	0.019	22	16	5.6
0.0282	0.0071	0.0123	1.73	0.0247	0.020	23	11.5	6.2
0.0250	0.0138	0.0261	1.89	0.0181	0.017	—	—	—
0.0210	0.0059	0.0118	2.00	0.0180	0.019	20	8	7.4
0.0111	0.00377	0.0110	2.92	0.00926	0.018	19	3.5	10.8
0.0103	0.00432	0.0125	2.89	0.00814	0.016	21	5.5	11.7
0.00629	0.00235	0.0109	4.64	0.00512	0.019	—	1.75	13.4
0.00350	0.00131	0.0104	7.94	0.00284	0.020	—	1.0	13.1
0.00350	0.00140	0.0114	8.14	0.00280	0.020	25	1.0	14.0
0.0379	0.0111	0.0174	1.57	0.0323	0.021	18	11	10.1*
0.0155	0.00550	0.0135	2.46	0.0127	0.019	17	5.5	10.0*
0.01066	0.00426	0.0136	3.19	0.00853	0.019	23	3.75	11.4*
				Average,	0.019			

* Wave-length 313 mμ.

hydrogen peroxide are in percent of total quinone formed. The values of k given in the tables were calculated from the formula $k = C(B/Q - N)$, where C is the average anthracene concentration, B the concentration of benzoic acid formed, and Q the concentration of anthraquinone. N is a constant which, in the case of the thermal reaction at 29° and the photochemical reaction at 30° is = 0.92; for the photochemical reaction at 2° it is = 0.93. Choosing these values of the constant eliminates a slight trend in the values of k with concentration which is present if N is put equal to unity.

The figures in the last columns of Tables XII and XIII give the total *amount* of anthraquinone formed in the reaction tube per minute. Since light absorbtion was complete in all cases, the rate should be independent of the volume. This volume shaken was 10 cc. in all cases except one (Table XII, run 11) where it was 15 cc.

Fig. 4 is a graphical representation of Tables XIII and XIV. In order to reduce the number of points, the determinations were arranged in groups and only the averages plotted in the figure. The full-drawn curves was obtained from the formula $C(B/Q - 0.92) = 0.035$. The dotted line represents the limiting value of B/Q at infinite anthracene concentration.

The last column in Tables XII and XIII gives the rate of formation of anthraquinone under fairly constant conditions of illumination. On the chain-reaction theory, at "high" inhibitor concentrations, where all the chains are broken by the inhibitor, its rate of oxidation should, in the ideal case, be independent of the concentration, a consequence which has previously been verified for a different case of inhibition.[24] As shown by the tables, this does

TABLE XIII

Photochemical reaction at 30°. Wave-length 313 mμ

Initial anthracene conc.	Anthraquinone "Q"	Benzoic acid "B"	Ratio of B/Q	Average anthracene conc., "C"	k	H_2O_2 %	Time, mins.	Rate of Quinone form., moles /min. × 10^6
0.0803	0.0164	0.0243	1.48	0.0721	0.040	21	26	6.3
0.0803	0.0168	0.0222	1.32	0.0719	0.029	18	24	7.0
0.0803	0.0187	0.0261	1.40	0.0709	0.034	20	26	7.2
0.0670	0.0183	0.0274	1.50	0.0578	0.034	—	—	—
0.0401	0.00792	0.0144	1.82	0.0361	0.032	21	9.5	8.3
0.0248	0.00507	0.0127	2.51	0.0223	0.035	16	—	—
0.0248	0.00609	0.0152	2.50	0.0218	0.035	25	7	8.7
0.01025	0.00258	0.0118	4.57	0.00896	0.033	13	—	—
0.00496	0.00162	0.0165	10.2	0.00415	0.039	—	1.5	10.8
0.00250	0.00070	0.0127	18.2	0.00215	0.037	—	—	—
0.00250	0.00085	0.0160	18.8	0.00207	0.037	—	—	—
0.00157	0.000382	0.0126	33.0	0.00138	0.044	—	0.5	7.6

Average, excluding the last run, 0.035

---

[24] Alyea and Bäckström: J. Chem. Soc., 51, 90 (1929).

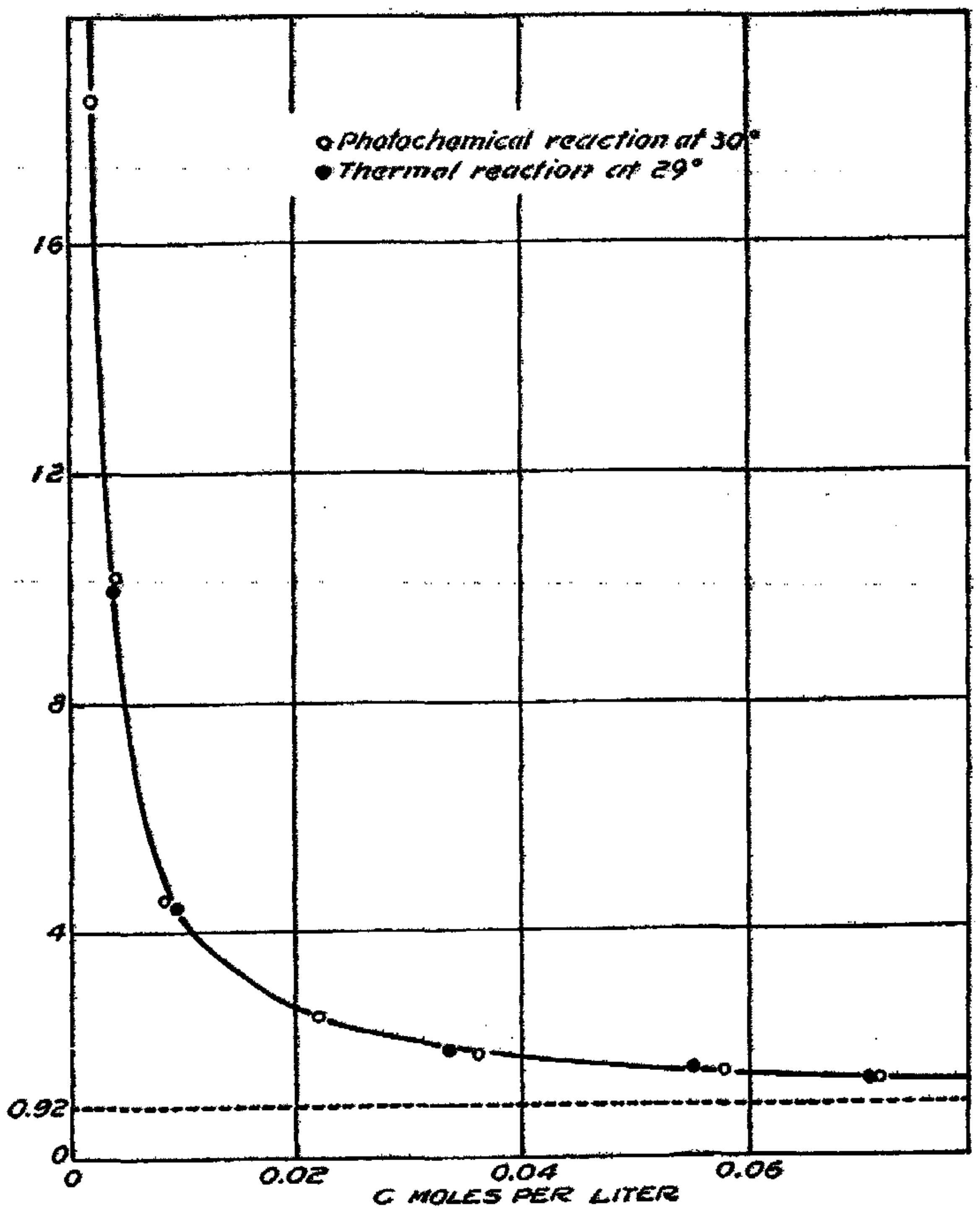


Fig. 4

Ratio of Benzoic Acid to Anthraquinone plotted against Anthracene Concentration

not hold for the present case, but the rate of oxidation of the anthracene is actually higher, the lower its concentration. The reason is undoubtedly that anthracene absorbs ultra-violet light very strongly, so that even in the rather dilute solutions that we are dealing with a considerable proportion of the exciting light is absorbed by the anthracene and not by the aldehyde. Interpolation from published absorption curves for the two substances[17] shows that when illuminating with light of wave-length 366 mμ, the anthracene absorbs about 30% of the light even when its concentration is as low as 0.01 mole/lit. At 313 mμ the anthracene absorbs relatively much less, which is reflected in the results.

We may thus draw the conclusion that the light which is absorbed by the anthracene is lost to the reaction. That there is no *direct* photochemical

TABLE XIV

Thermal reaction—Average temperature 29°

Initial anthracene conc.	Anthraquinone "Q"	Benzoic acid "B"	Ratio of B/Q	Average anthracene conc., "C"	k	Time, hours	Rate of quinone form., moles/lit./hr. × 10⁴	Vol. shaken cc.	No. of tube
0.0803	0.0128	0.0172	1.34	0.0739	0.031	144.5	89	8.5	5
"	0.0138	0.0194	1.40	0.0734	0.035	146.9	93	8.5	7
"	0.0227	0.0313	1.38	0.0689	0.032	148.5	148	4.5	6
"	0.0238	0.0339	1.42	0.0684	0.034	147.8	161	4.5	8
0.0600	0.0076	0.0113	1.49	0.0562	0.032	42.3	180	4.5	29
"	0.00655	0.0103	1.57	0.0567	0.037	58.2	113	8.5	27
"	0.0111	0.0186	1.68	0.0544	0.041	59.2	188	4.5	25
"	0.0118	0.0193	1.63	0.0541	0.038	57.5	205	4.5	28
"	0.00782	0.0120	1.54	0.0561	0.035	73.9	106	8.5	26
"	0.0144	0.0240	1.67	0.0528	0.040	76.0	190	4.5	24
0.0401	0.0151	0.0294	1.95	0.0325	0.033	112.4	134	4.5	11
"	0.0151	0.0297	1.97	0.0325	0.034	112.9	134	4.5	12
"	0.0113	0.0217	1.92	0.0344	0.034	115.5	98	8.5	9
"	0.0101	0.0195	1.93	0.0350	0.035	117.8	86	8.5	10
0.0200	0.00266	0.0068	2.56	0.0187	0.031	24.8	107	4.5	23
"	0.00435	0.0118	2.71	0.0179	0.032	39.2	111	4.5	22
"	0.00606	0.0174	2.87	0.0170	0.033	48.6	125	4.5	21
"	0.00422	0.0125	2.96	0.0179	0.037	49.6	85	8.5	20
"	0.00438	0.0125	2.85	0.0178	0.034	51.6	85	8.5	19
"	0.00791	0.0252	3.18	0.0161	0.036	64.4	123	4.5	18
0.0113	0.00172	0.0075	4.36	0.0105	0.036	21.0	82	4.5	37
"	0.00283	0.0123	4.35	0.0099	0.034	35.0	81	4.5	36
"	0.00310	0.0139	4.48	0.0098	0.035	37.5	83	4.5	35
"	0.00329	0.0149	4.53	0.0097	0.035	48.3	68	8.5	34
"	0.00293	0.0130	4.44	0.0099	0.035	49.3	59	8.5	33
0.00496	0.00231	0.0260	11.25	0.00380	0.039	35.2	65	4.5	3
"	0.00191	0.0181	9.48	0.00400	0.034	35.5	54	8.5	4
"	0.00160	0.0146	9.13	0.00416	0.034	36.4	44	8.5	1
"	0.00218	0.0219	10.05	0.00387	0.035	37.0	59	4.5	2
0.00157	0.00027	0.0066	24.5	0.00143	0.034	8.0	34	4.5	16
"	0.00027	0.0074	27.4	0.00143	0.038	10.0	27	8.5	13
"	0.00032	0.0081	25.3	0.00141	0.034	11.0	30	8.5	15
				Average	0.035				

reaction between anthracene and oxygen, at least of any importance, was confirmed by special experiments on solutions in benzene and 1,4-dioxane. A quantitative experiment with a 0.02 molar solution in the latter solvent, using light of wave-length 366 mμ, gave a rate of anthraquinone formation of only 10^{-7} mole/min. which, as seen from Table XII, is less than 1% of the corresponding value for a dilute solution in aldehyde. In both solvents illumination caused dianthracene formation and intense fluorescence. As previously mentioned, this is not the case with solutions in benzaldehyde which shows that the aldehyde molecules have a specific power of deactivating an excited anthracene molecule. It is interesting to note that, in this process, the energy is apparently lost as kinetic energy;[25] if it were taken up by the aldehyde molecule as electronic energy of excitation, for which purpose it is sufficient, it would start a reaction chain and thus *indirectly* cause the oxidation of an anthracene molecule; but the above results show that this is not the case.

The most dilute solution in Table XIII gave a very low rate of anthraquinone formation as well as an abnormally high B/Q ratio. Both facts indicate that the anthracene concentration was no longer sufficient to break all the chains, some of which were accordingly being broken in other ways, as in the uninhibited reaction.

Table XIV shows that the rate of anthraquinone formation in the thermal reaction varies between very wide limits. The same fact had been observed in preliminary experiments, and every attempt was therefore made to keep the experimental conditions as constant as possible. The aldehyde used was all from the same distillation. It was distributed among a number of 50-cc., glass-stoppered, brown-glass bottles that had previously been used a long time for the same purpose. The reaction tubes were unused test-tubes from the same carton. When cleaning them, with hot alkali, hot dilute hydrochloric acid and distilled water, they were all treated uniformly and at the same time. After being constricted, they were stored away from dust. They were later numbered in the order in which they were used; these numbers are given in the last column of the table. As appears from the table, the rate is invariably higher when the volume shaken was 4.5 cc. than when it was 8.5 cc.; in some cases the ratio between the rates reaches 1.8, which is almost the ratio between the volumes (1.9). This might indicate surface catalysis, but the fact that the rate seems to increase with the time of shaking and the age of the tube points rather to a slow diffusion of a catalyst into the surface layer of the glass and into the solution. The resulting concentration would be inversely proportional to the volume of the aldehyde.

As a further illustration we give, in Table XV, the results of some preliminary experiments made at 25°. In this case all the runs were started simultaneously, and the test-tubes were not new but had been in use for some time; before being constricted, they were merely cleaned with alcohol and ether.

---

[25] Compare J. Perrin: Compt. rend., 184, 1097 (1927).

TABLE XV

Thermal reaction—Average temperature 25°

Anthracene concentration, mole/lit.	Volume shaken, cc.	Time, hours	Rate of quinone form. mole/lit./hr. $\times 10^6$
0.0025	10	14	44
0.0025	4.5	17.5	66
0.005	4.5	21	65
0.01	4.5	42.5	36
0.01	10	44	43
0.02	10	72	32
0.02	4.5	88	49
0.04	10	160	38
0.04	4.5	164	50
0.08	10	309	43
0.08	4.5	313	77

Table XV shows that, although there are considerable variations in the rate of quinone formation, the results are much more satisfactory than in the final experiments. The table represents a 32-fold variation in concentration, and the 10-cc. runs, in particular, show very clearly that we are not dealing with a direct oxidation of the anthracene, but with an induced reaction, the rate of which is independent of the concentration. In the final experiments, this fact is almost completely masked by catalytic influences.

Kuhn and Meyer[26] claim that perfectly pure benzaldehyde does not autoxidize in the dark, and that the "thermal" reaction, as ordinarily observed, is caused by the catalytic action of traces of heavy metals. Our results tend to support this view, but they show that the action of the inhibitor does not consist in combining with or in some other way removing the positive catalyst, but in breaking the reaction chains that are started by the catalyst.

Theoretical Part

The reaction mechanism. It has been shown in the foregoing that the first step in the induced oxidation of anthracene is probably a reaction with a peroxide of benzaldehyde, giving anthranol and benzoic acid; but it has also been shown that this reaction cannot be ascribed to the stable form of this peroxide, benzoperacid. We are thus forced to the conclusion that in the formation of benzoperacid from benzaldehyde and oxygen, a short-lived, unstable peroxide appears as an intermediate product, and that it is this peroxide which is responsible for the observed reaction.

On the other hand, the fact that the formation of benzoperacid is a chain reaction shows that the energy of activation is in some way passed on from the newly-formed peracid molecule to another molecule of aldehyde. If

---

[26] Kuhn and Meyer: Naturwissenschaften, 16, 1028 (1928); see also Raymond: Compt. rend., 191, 616 (1930).

the assumption is made that the the above-mentioned unstable peroxide represents a stage in this process in which the transfer of the activation energy has not yet occurred and that, consequently, this peroxide forms a link in the reaction chain, it is possible to account for the chain-breaking character of the induced oxidation of the anthracene. We thus arrive at the following reaction scheme:

The primary process is the activation of an aldehyde molecule, photochemically or otherwise, and its subsequent reaction with oxygen:

$$C_6H_5CHO \longrightarrow C_6H_5CHO' \xrightarrow{+O_2} C_6H_5CO_3H'.$$

The active peroxide molecule thus formed can do one of two things.

(1) It can transfer the energy of activation to an aldehyde molecule:

$$C_6H_5CO_3H' + C_6H_5CHO = C_6H_5CO_3H + C_6H_5CHO'.$$

The probability of this process will be proportional to the concentration of the aldehyde, C_1. The deactivated benzoperacid molecule will eventually react with an aldehyde molecule, giving 2 molecules of benzoic acid.

(2) The active peroxide molecule may react with anthracene, giving one molecule of anthranol and one of benzoic acid:

$$C_6H_5CO_3H' + C_{14}H_{10} = C_6H_5COOH + C_{14}H_{10}O;$$

the anthranol thus formed reacts further with oxygen, eventually giving anthraquinone and water. The probability of this process will be proportional to the concentration of the anthracene, C_2.

This scheme gives directly the ratio between benzoic acid and anthraquinone formed as $\frac{B}{Q} = \frac{k_2C_2 + 2\,k_1C_1}{k_2C_2} = 1 + 2\frac{k_1C_1}{k_2C_2}$. Since C_1 may be regarded as a constant, this formula is essentially identical with the one found experimentally: $\frac{B}{Q} = 0.92 + \frac{k}{C_2}$.

The secondary activated aldehyde molecules formed in reaction (1) will again react according to the same scheme. This reaction represents the chain mechanism, and its probability, P, determines the efficiency of chain propagation and thus the chain length. Reaction (2), on the other hand, represents the chain-breaking mechanism: it may be assumed that it does not cause further activations. The chain length, L, may be defined as the total number of activated aldehyde molecules formed for every primary activation. It will obviously be given by[27]: $L = 1 + P + P^2 + \ldots$ which sum is $\frac{1}{1 - P}$ or, since $P = \frac{k_1C_1}{k_1C_1 + k_2C_2}$, $L = 1 + \frac{k_1C_1}{k_2C_2}$.

These formulae will only apply under conditions where the influence of the anthracene predominates over other possible deactivating processes, i.e. at sufficiently high inhibitor concentrations. Under these conditions, every

---

[27] Compare, Christiansen: Trans. Faraday Soc., 24, 600 (1928).

primary activation will eventually lead to the formation of an anthraquinone molecule, and the rate of quinone formation therefore measures the rate of the primary reaction.

The above reaction scheme does not take into account the formation of the "yellow substance" by a side reaction, nor the fact that part of the anthraquinone apparently is not formed in the way assumed above, but by autoxidation of anthrahydroquinone. In view of this, the agreement with the theoretical formula must be said to be remarkably good, and, indeed, it seems as if neither of these side-reactions had any effect on the B/Q ratio. The experimental results indicate a value of N which is less than unity by an amount which appears to be slightly outside the experimental error. However, this value is the same for the photochemical reaction at 2° and at 30° although there is a great difference in the amount of "yellow substance" formed at these two temperatures; and it is also the same for the thermal reaction at 29° in spite of the fact that, as will be shown presently, no anthrahydroquinone is formed in this case. Accordingly it seems probable that the deviation from unity was caused simply by a slight systematic error.

As shown in a preceding section, the amount of hydrogen peroxide formed measures the extent of a side-reaction in which anthrahydroquinone appears as an intermediate product. Tables XII and XIII show that, in the photochemical experiments, this side reaction forms a constant fraction of nearly 20% of the total reaction. Changes in anthracene concentration, temperature, wave-length of the exciting light, and effective light intensity, all appear to be without influence on the relative rates of the two reactions. In the thermal experiments, on the other hand, no hydrogen peroxide was found among the reaction products. It is true that, in these experiments, the time of shaking was so long that any hydrogen peroxide formed would undoubtedly have, in part, disappeared again by reacting with the aldehyde. However, a determination of the rate of this reaction showed that it is by no means great enough to account for the absence of the peroxide, had that been formed in an amount corresponding to the yield in the photochemical experiments. Thus samples of a 0.08 molar anthracene solution containing a small quantity of dissolved 30% hydrogen peroxide, were shaken in the dark for about 80 hours: the results showed that, in addition to the benzoic acid formed by autoxidation, which could be calculated from the amount of anthraquinone formed, a further quantity had been formed which was equivalent to the hydrogen peroxide which had disappeared. The rate of this reaction amounted to only about 1% per hour $\left(-\frac{d \log c}{dt} = 0.0047\right)$. Then if hydrogen peroxide had been formed in the experiments of Table XIV at a constant rate, at least 50% of the amount formed would still have been present at the time of analysis; but the quantities found by the benzene-water method were never more than 0.01 or 0.02 cc. of 0.05 N. thiosulfate per 2 cc. of aldehyde. Water-insoluble peroxide, on the other hand, was always present in measurable quantities.

The reason for this difference between the results of the photochemical and the termal experiments might conceivably be that, in the latter case, the reaction rate was so low that the concentrations of the various intermediate products must have been extremely small; this would prevent the occurrence of such possible side-reactions as: $C_6H_5CO_3H + C_{14}H_9OH = C_{14}H_8(OH)_2 + C_6H_5COOH$. However, the constancy of the figures for hydrogen peroxide in the photochemical experiments can hardly be explained on any such basis, as the concentrations of the intermediate products must have varied considerably from one experiment to another.

Thus it appears that we have here a real difference between thermal and photochemical reaction, caused by the difference in the activation process. This might indicate that an excited aldehyde molecule, formed by absorption of a light quantum, can undergo two different transitions, only one of which leads to the formation of an "active" molecule of the kind appearing in the above equations: the relative transition probabilities would have to be independent of the temperature and also of the wave-length of the absorbed light. But if this is true, it should manifest itself in other ways as well and, so far, confirmatory evidence is lacking; and even on these assumptions we have not been able to formulate a plausible reaction mechanism which would combine the formation of 20% of hydrogen peroxide with a limiting B/Q ratio equal to 1, which is the value indicated by the experiments. A reaction such as $C_6H_5CO_3H' + C_{14}H_{10} = C_6H_5CHO + C_{14}H_8(OH)_2$ (by 20% of the total $C_6H_5CO_3H'$) would give a ratio of only 0.8.

As regards the formation of the "yellow substance," it may be fitted into the reaction scheme by assuming that sometimes Reaction (2) does not lead to the formation of anthranol and benzoic acid, but to a condensation product of some kind, and that the latter process is favored by an increase in temperature.

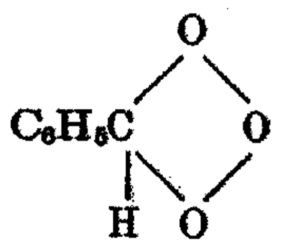
General Conclusions

As appears from the foregoing discussion, the proposed reaction mechanism is able to account for all the observed facts, except for a relatively unimportant side-reaction which, moreover, does not appear in the thermal reaction. A closer discussion of the consequences of this mechanism therefore seems to be worth while.

First of all, it may be concluded from the experimental results that this mechanism is possible only if a very considerable stability may be ascribed to the "active peroxide." From a comparison of the formula which represents the experiments at 2°, viz. $B/Q = 0.93 + \frac{0.019}{C}$, with the theoretical formula: $B/Q = 1 + 2\,\frac{k_1C_1}{k_2C_2}$, in which C_1, the concentration of the aldehyde, may be put = 10 moles/lit., it appears that the ratio between the specific velocities of the afore-mentioned reactions (2) and (1) is $\frac{k_2}{k_1} = \frac{20}{0.019} = 1050$. Neglecting differences in molecular diameters, we thus arrive at the conclusion that an active peroxide molecule suffers *at least* 1000 collisions with aldehyde molecules before giving up its energy. This figure becomes even higher if not every collision between an athracene molecule and an active peroxide molecule is effective in producing reaction, and it probably is not, as there are more effective inhibitors than anthracene. Reaction (1), in which the energy of activation is transferred from the active peroxide to the aldehyde, would accordingly have the character of a chemical reaction rather than an activation by collision. In agreement with this it is found to have a temperature coefficient: at 30° (29° for the thermal reaction), $\frac{k_2}{k_1} = \frac{20}{0.035} = 570$, which indicates that reaction (1) has an energy of activation which is higher than that of reaction (2) by 3600 calories.

The fact that we have to ascribe such a considerable stability to the active peroxide molecule indicates that there is no difference in kind between the reaction chains in the autoxidation of a pure substance like benzaldehyde and that of a solution, such as sodium sulfite in water.

Furthermore, this stability seems to exclude the possibility that the active peroxide might be identified with newly-formed peracid molecules to which the reaction energy is attached in the form of energy of vibration, or with an electronically excited state of benzoperacid; rather it must be regarded as a chemical individual. It should then be noted that, as emphasized by Engler and Weissberg,[28] the known structure of other addition compounds of the aldehydes indicates that the primary peroxide should not be identical with benzoperacid but should have the following structure, originally suggested by Bach:[29]



Engler and Weissberg accordingly assume that this represents the primary reaction product from which benzoperacid is only formed secondarily, by molecular rearrangement. This is in very good agreement with our conclusions concerning the "active peroxide," and it seems extremely probable that we may assign the above structure to this compound.

It may thus be said that, up to this point, the proposed mechanism is supported not only by our own experimental results and by the large fund of experimental evidence of a similar nature which has found expression in the Engler-Bach theory of induced oxidations, but also by structural considerations; but the further assumptions which have to be made in order to obtain a chain mechanism must be said to be of a purely hypothetical nature: it must be assumed that every such rearrangement of the primary peroxide

---

[28] Engler and Weissberg: "Kritische Studien über die Vorgänge der Autoxidation," p. 90 (1904).

[29] Bach: Monit. scientif., 1897, 479.

causes the activation of another aldehyde molecule and, since the presence of solvent molecules does not influence the process, it must either be assumed that the energy transfer can take place at a distance, by some kind of resonance effect, or, which seems more probable, that the rearrangement can only occur in a collision with an aldehyde molecule.

Under these conditions it may be asked whether the results should not be taken as proof that we are not dealing with energy chains but with material chains of the type of the hydrogen-chlorine combination, where atoms and radicals form the links in the chain. However, aside from the fact that the general character of our results seems incompatible with any such mechanism, benzaldehyde differs from chlorine in that its absorption spectrum, within the spectral region employed in the photochemical experiments, gives no evidence of dissociation.[30] In view of this, and of the large amount of evidence supporting the proposed mechanism, we seem justified in concluding that it is essentially correct.

On this mechanism, the inhibitory effect of a substance is determined by its power to *react* with the primary peroxide; it is not merely a question of the transfer of the energy of activation. This peroxide must be extraordinarily specific in its reactions with oxidizable substances; for instance, the probability of the corresponding reaction with benzaldehyde, to form two molecules of benzoic acid, must be extremely low as shown by the length of the reaction chains—that is, benzaldehyde is a very poor inhibitor for its own autoxidation.

The "active peroxide" does not, however, constitute the only vulnerable point in the reaction chain, and one should expect to find a different class of inhibitors breaking the chains by reaction with the active aldehyde molecules. As previously mentioned, the slight inhibitory action of benzoperacid is ascribed to this cause.

We have shown above that anthracene is not oxidized by stable benzoperacid. This cannot be expected to hold for all inhibitors as many of these are extremely easily oxidizable substances. For instance, if diphenylamine is added to peroxidized aldehyde a strong brown coloration develops, indicating that a reaction takes place. Consequently we should expect, in the case of many inhibitors and, especially, at higher temperatures, to find a reaction with benzoperacid going on side by side with the chain-breaking reaction with the primary peroxide.

This is presumably the explanation of some results recently reported by Wagner and Brier.[31] They studied the effect of hydroquinone on the rate of oxidation of linseed oil and found that it prolonged the induction period in proportion to the amount added, but that if further quantities of hydroquinone were added after the end of the induction period, when the normal rate of oxidation had been reached, they were without effect. From this they concluded that "the velocity of the oxidation reaction determines the ef-

---

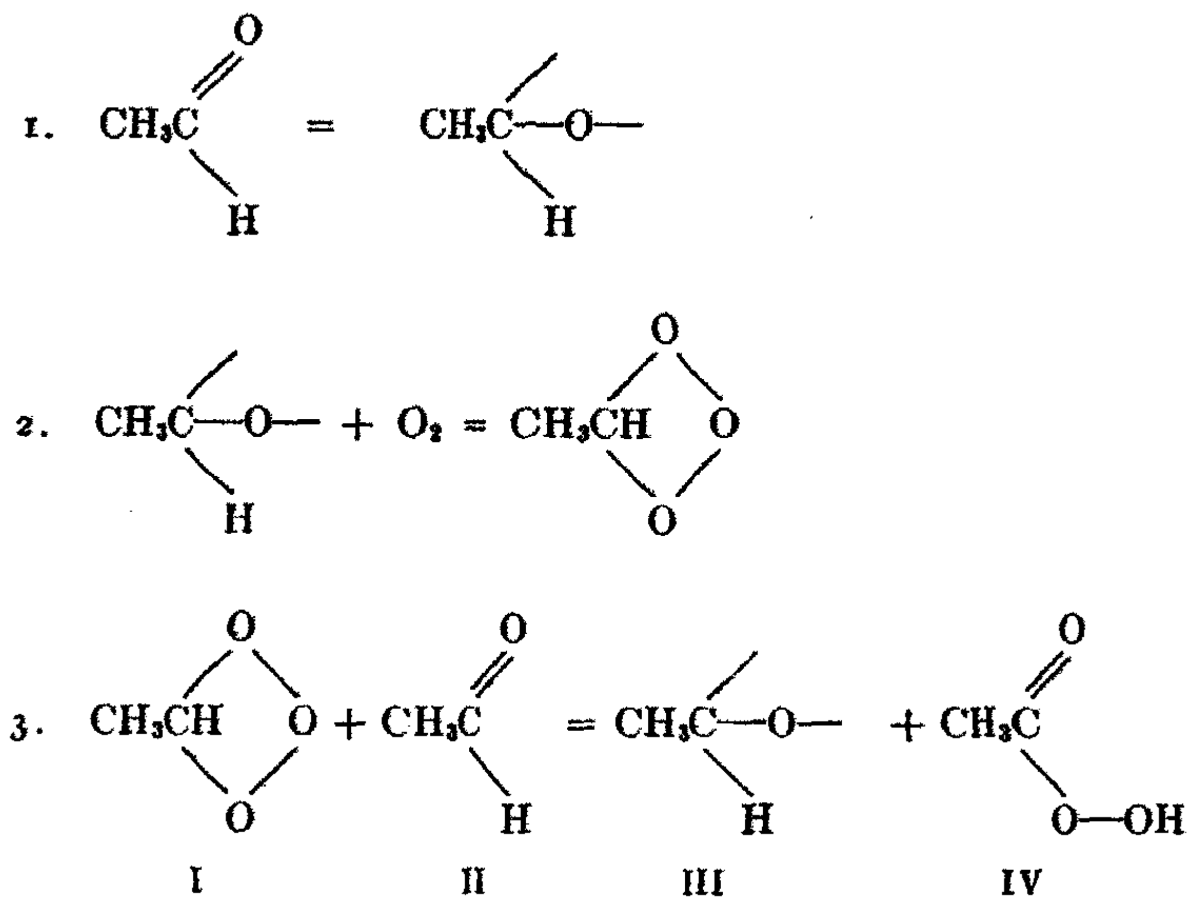
[30] de Hemptinne: J. Phys. Radium, 9, 357 (1928).

[31] Wagner and Brier: Ind. Eng. Chem., 23, 40 (1931).

fectiveness of hydroquinone as an antioxidant in hydroquinone-linseed oil systems. Apparently hydroquinone is not able to function as an antioxidant after a critical velocity of reaction is exceeded." We believe the explanation to be that, when the uninhibited reaction has been going on for a while, the liquid contains large quantities of stable peroxides that immediately oxidize any hydroquinone added at this stage.

Appendix

In a paper by Bodenstein,[32] which appeared after the completion of the above manuscript, an extremely interesting suggestion is made with regard to the mechanism if autoxidation reactions. On the basis of experiments on the oxidation of acetaldehyde in the gas phase he proposes a reaction mechanism, the essential features of which appear from the following equations:



Thus, like ourselves, he assumes the primary formation of an unstable peroxide of the Bach type, but reaction 3, which correspondes to reaction (1) of our reaction scheme, is not interpreted as a rearrangement of this peroxide but as a transfer of *two atoms* of oxygen: molecule III is assumed to be formed from molecule I, and molecule IV from molecule II. In this way he obtains a chain mechanism without having to assume a transfer of the energy of activation, which was the objectionable feature of our mechanism. On this mechanism it is understandable that, as mentioned above, the "rearrangement" appears to be possible only in a collision with an aldehyde

---

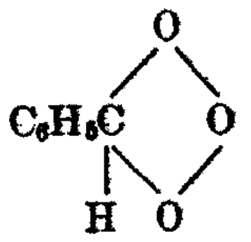
[32] Bodenstein: Z. physik. Chem., B 12, 151 (1931).

molecule. It would seem that this is the most satisfactory solution which has yet been offered for the problem of the chain mechanism in autoxidation reactions.

In one detail, however, we may add to the mechanism of Bodenstein, viz., as regards the mechanism of inhibition. Here Bodenstein, without discussing the matter further, writes an equation: $P' + K = P + K'$, (P = peroxide, K = inhibitor), thus assuming a transfer of the energy of activation; but our results show that this process, also, is a chemical reaction in which, however, only *one atom* of oxygen is transferred. This then appears to be the characteristic difference between the chain-breaking process and its opposite, the chain mechanism itself.

Summary

The inhibitory action of anthracene in the autoxidation of benzaldehyde is connected with an induced oxidation of the inhibitor. The primary oxidation product is anthranol, which substance is autoxidizable and reacts with oxygen to give a peroxide which is later slowly decomposed with the formation of the final reaction product, anthraquinone. With increasing anthracene concentration, the relative amounts of oxidation products formed approaches one mole of benzoic acid per mole of anthraquinone. The course of the reaction shows that the induced oxidation of the anthracene is the result of a reaction with a peroxide of benzaldehyde, but it may be shown that this reaction cannot be attributed to the stable form of this peroxide, benzoperacid. We are therefore forced to assume the existence of an unstable primary peroxide, presumably of the structure



which must form a link in the reaction chain. The results are best explained on a chain mechanism recently proposed by Bodenstein.

In the photochemical reaction, there is a side-reaction, amounting to nearly 20% of the total reaction, in which anthrahydroquinone appears as an intermediate product. This substance reacts with oxygen to form equimolecular quantities of anthraquinone and hydrogen peroxide. The occurrence of this side-reaction has not yet been accounted for.

A further side-reaction, common to both thermal and photochemical reaction, leads to the formation of complex, colored products which could not be identified. At 2° this reaction amounts to only 6% of the anthracene oxidized, but it is favored by an increase in temperature.

The absolute rate of the "thermal" reaction appears to be determined entirely by the quantities of positive catalysts accidentally present; but the relative rates of autoxidation reaction and induced oxidation depend only on the composition and temperature of the solution. The photochemical reaction is complicated to some extent by a screening effect of the anthracene, due to its strong absorption of ultraviolet light.

For the determination of small quantities of anthraquinone and anthranol (anthrone), a spectrophotometric method was developed, based on a determination of the light-extinction curves of alkaline solutions of anthrahydroquinone and anthranol. Methods for the separate determination of benzoperacid, hydrogen peroxide, and water-insoluble peroxides, were also developed. Methods of preparation are given for anthrahydroquinone and anthranol. The solubility of anthraquinone in benzaldehyde has been determined at 0° and 25°.

Princeton, New Jersey.

ALUMINA AS AN IONIZING ADSORBENT*

BY WILDER D. BANCROFT AND J. W. ACKERMAN

The first part of this work was undertaken to verify the results of Weiser and Porter[1] on the alizarin lakes. They claimed that the formation of hydrous aluminum oxide-alizarin lakes from sodium alizarate baths consisted in an exchange adsorption of the dye anion with the less strongly adsorbed chloride ion in the hydrous oxide and not to the direct adsorption of the neutral sodium alizarate as suggested by Bull and Adams[2] and by Williamson.[3]

The crystals of alizarin are a yellow orange color and in alcoholic solution have the same color, but the alkali and alkaline earth alizarates are dark purple. A thin film of sodium alizarate is purple in transmitted and reflected light, but the dilute solution possesses a red color.

Since we found that alumina, prepared from amalgamated aluminum, treated with a sodium alizarate solution yielded a red lake, it seemed possible that we might have adsorption of the sodium alizarate.

Experimental

Alumina from amalgamated aluminum. A pure alumina was prepared according to the outline given by Mellor[4] by amalgamating a carefully cleaned sheet of aluminum with a few drops of a mercuric chloride solution, washing thoroughly to remove the chlorides, and allowing it to react with water. The oxide first formed was discarded because it was gray in color, and on further action a white, finely divided, oxide was formed. This oxide was tested for chloride by dissolving a portion in nitric acid and adding silver nitrate. No precipitate was formed, showing the absence of the chloride. The particles of the alumina settled out on standing, but a stable sol may be obtained by adding a small amount of hydrochloric acid in order to give the alumina sufficient positive charge to keep it in suspension.

A saturated solution of alizarin was prepared from absolute alcohol. Also a solution of sodium alizarate was prepared by dissolving 2.88 g of Kahlbaum's sublimed alizarin in the required amount of sodium hydroxide and diluting to one liter.

Alumina and alizarin. While 100 cc. of alumina, prepared as above, was being stirred 5 cc of alizarin acid was added, and a pale pink coloration of the alumina was noted, indicating that little alizarin had been adsorbed. It

---

* This work is done under the programme now being carried out at Cornell University and supported in part by a grant from the Heckscher Foundation for the Advancement of Research established by August Heckscher at Cornell University.

[1] Weiser and Porter: J. Phys. Chem., 31, 1824 (1927).

[2] J. Phys. Chem., 25, 660 (1921).

[3] J. Phys. Chem., 28, 891 (1924).

[4] J. W. Mellor: "Modern Inorganic Chemistry," 774 (1925).

was thought that perhaps not enough alizarin acid had been added. With the addition of 10 cc more a yellowish brown precipitate was formed, which was not a true lake, for when examined under the microscope, silky crystals of alizarin were noted, which gave the lake the brown appearance Therefore, only a slight amount of the alizarin was adsorbed.

To this mixture 5 cc of N/20 sodium hydroxide was added and a red lake was formed. Also on another run 5 cc of concentrated ammonium hydroxide was added, and a red lake was formed.

This lake was examined with a Bausch and Lomb chemical microscope equipped with an 8 mm objective, #5 eyepiece and using transmitted axial light with daylight illumination. The sample was mounted in xylene because its index of refraction is near that of the alumina thus making the lake more transparent. A red color was homogeneous throughout the sample.

These results are due to the insolubility of the alizarin acid in water. When the alizarin acid is added to the alumina, a small amount is adsorbed, but the rest is precipitated giving the crystals of alizarin and the brown color. When the sodium or ammonium hydroxide is added, the insoluble alizarin is converted into soluble sodium or ammonium alizarates respectively. The alizarin anion can now be adsorbed by the alumina, producing the red color.

Following a suggestion of Professor Weiser of the Rice Institute the hydrous oxide was suspended in alcohol and treated with an alcoholic solution of alizarin. A red lake was formed, which was due to the adsorption of the alizarin anion. In this case the alizarin did not precipitate out, for it is soluble in the alcohol.

Alumina and sodium alizarate. Since the alumina adsorbed a small amount of alizarin producing a pink lake, an experiment was run to test the adsorption from a sodium alizarate solution.

To 100 cc of the alumina, prepared as above, containing 0.251 g of Al_2O_3 sodium alizarate was added in varying amounts. The results are given in Table I.

TABLE I

cc Na Alizarate	Observation
1	A pink lake with clear supernatant liquid.
2	A light red lake " " "
3	A red lake with " " "
4	A red lake, slightly red " "
5	" " " " " "

In this case we have a pure alumina adsorbing both ions, but the red color of the lake is due to the alizarate ion. Thus we may have direct adsorption of the sodium alizarate, although the cation does not influence the color.

Alumina gel and alizarin. An alumina gel was formed by adding 35 cc of concentrated ammonium hydroxide to 12.5 g of Kahlbaum's aluminum chloride dissolved in 750 cc of water. The alumina, which settled out, was washed five times with distilled water, and part of it was peptized due to the removal of the coagulating ions.

It was found, before, that the addition of the alizarin solution to the hydrous oxide precipitated alizarin due to its insolubility in water, and that only a small amount was adsorbed as the anion. Therefore, 75 cc of the gel was mixed thoroughly with 75 cc of alcohol and 20 cc of the solution of alizarin in alcohol was added. Immediately a bright red lake was formed, which did not lose any of its color on washing. The filtrate gave a test for chloride, which indicated that in this case, the color was due to the alizarate anion in exchange adsorption with the chloride.

Alumina gel and sodium alizarate. 75 cc of the hydrous alumina gel was treated with 30 cc of the sodium alizarate solution and a bright red lake was formed. The test for sodium in the supernatant liquid showed that practically none had been adsorbed, since nearly all was present as sodium chloride. In this case we again have the exchange adsorption of the alizarate and chloride ions.

These experiments check the work of Weiser and Porter[1] that the color of the alumina-alizarin lakes is due to the adsorption of the alizarate anion. More recently Weiser[2] published another paper showing that the adsorption of the alizarin may be exchange adsorption, direct adsorption, or both, depending on the condition of the hydrous oxide. Our results are in accord with this view.

Treatment of sodium alizarate with hydrogen peroxide. In connection with some other work on the fading of alizarin lakes, it was found that the color fade-ometer produced practically no effect. Grant and Elsenbast[3] had faded dyes by means of hydrogen peroxide, which suggested the present treatment.

The samples of sodium alizarate were treated with perhydrol as shown in Table II with the results indicated.

TABLE II

	cc Na Aliz.	cc Water	cc H_2O_2	Observations
(1)	5	10	3	A red colloidal suspension clearer than run (2)
(2)	5	10	4	A red colloidal suspension
(3)	5	10	5	An orange colloidal suspension
(4)	5	10	6	A yellow colloidal suspension
(5)	5	10	7	A yellow suspension, which settled out

Part of the suspension from run (5) was treated with sodium hydroxide and the purple color of the sodium alizarate was obtained.

---

[1] Weiser and Porter: J. Phys. Chem., **31**, 1824 (1927).

[2] Weiser: J. Phys. Chem., **33**, 1713 (1929).

[3] Grant and Elsenbast: J. Phys. Chem., **16**, 546 (1912).

These results could not be accounted for by a straight oxidation with hydrogen peroxide, for we have not only a change in color, but also a change in the physical properties of the solution to account for. However, there are acids present in the hydrogen peroxide, notably phosphoric, hydrochloric and sulphuric. On treatment of the sodium alizarate, the action is that of a strong acid on the salt of a weak acid, which results in the formation of the salt of the strong acid and liberates the weak acid, which is alizarin acid. Since it is insoluble, it precipitates. In run (1) there was not enough acid present in the hydrogen peroxide to liberate all the alizarin acid so there is a suspension of the yellow particles, of alizarin or alizarin acid in the unattacked purple sodium alizarate, giving a red colloidal appearance. In run (3) there is more acid present and more conversion over to the alizarin acid and very little sodium alizarate left. Then in the last run there is complete precipitation of the insoluble alizarin acid.

In regard to the action of acids on sodium alizarate Knecht[1] says: "Alizarin in sodium hydroxide yields a blue violet and in ammonia a purple color. It is precipitated from these solutions by hydrochloric and other acids." We can then say that the action of the hydrogen peroxide is due to the acids present and not to the oxidizing power of the hydrogen peroxide.

Treatment of alizarin-alumina lakes with hydrogen peroxide. In each case 5 cc of the standard lake was used and treated with the amounts of the perhydrol as indicated in Table III. After the addition of the hydrogen peroxide the mixture was shaken for a few minutes and then allowed to stand for an hour and the results noted.

TABLE III

Run	cc H_2O_2 (30%).	Observations
1	1	No change
2	3	" "
3	5	" "
4	6	The lake was coagulated, and the red color was lighter.
5	10	In all these runs the lake was coagulated, but the red color was left unchanged except a little lighter. In the last six runs yellow particles were noted suspended in the liquid.
6	12	
7	17	
8	28	
9	34	
10	100	

There was no change in the color or the condition of the lake up to the addition of 6 cc of hydrogen peroxide. None of the lakes lose the red color, although they are lightened a small amount. Apparently the acids have reacted with some of the sodium alizarate which was not adsorbed by the alumina and this accounts for the yellow particles in fine suspension. In no case did the lake lose its red color. Any loss of color is due to an excess of sodium alizarate present which naturally gave the lake a darker color and

---

[1] Knecht, Rawson and Loewenthal: "A Manual of Dyeing," 2, 573 (1910).

when the acids were added it was changed to alizarin. It was observed also that in the coagulated lakes the color was brighter which means that the alumina just adsorbed the correct amount of the alizarin anion and the remainder was converted to alizarin. This also bears out Weiser's statement that an excess of sodium alizarate peptizes the alumina-alizarin lake. Then the lake will coagulate when the excess of sodium alizarate is destroyed.

Hummel[1] classifies the colouring matters as monogenetic or polygenetic. Monogenetic are such as are capable of yielding one colour, whatsoever mordant may have been used on the material, either before or during the dyeing operation. Magenta, indigo, and methyl green are examples of this class. Polygenetic colours are such as are capable of producing totally different colours according to the mordant employed. Examples of this class are alizarin, cochineal and logwood.

Since we can obtain different colors with alizarin on various mordants, it must mean that the hydrous oxides adsorb the alizarin in a different manner. The alumina is colored red when treated with sodium alizarate, and also when treated with alizarin acid. In the latter case the red color is obtained if the alumina is suspended in alcohol so that the alizarin will not precipitate out when added to the suspension. This must mean that the alizarin is adsorbed in the ionized form.

If alizarin gives different colors with various hydrous oxides used as mordants, what will the color be with tin mordant?

Knecht[2] makes the following statements about tin and tin mordants used with alizarin:

"Sometimes a small amount of stannous chloride or better stannous acetate is added to the mordanting bath to produce a more fiery shade; but what part the tin has in the formation of the color lake is unknown. Nothing definite can be said as to its mode of action. Moderately fast orange shades can be obtained with alizarin on cotton mordanted with stannic oxide. The addition of a little stannous chloride to the bath renders the shade considerably brighter, but at the same time yellower. Alizarin produces with stannous chloride an orange shade on wool, fast to light, but affected by milling."

Apparently then the tin mordant must adsorb alizarin in a different manner than does the alumina.

Preparation to the tin mordant. The hydrous oxide of tin was prepared by dissolving 10 gms of stannous chloride in 240 cc of hot water and then adding 5.6 g of anhydrous sodium carbonate. The hydrous tin oxide was washed five times after its preparation.

The sodium alizarate and alizarin solutions were used as previously prepared.

Tin mordant and alizarin acid. Our previous experiments with alumina have shown that if we add an alcoholic solution of alizarin to the hydrous oxide as such, the insoluble alizarin precipitates. This was corrected by suspending the mordant in alcohol.

---

[1] Hummel: "The Dyeing of Textile Fabrics," 147 (1885).

[2] "A Manuel of Dyeing," 2, 582, 598, 599, 600 (1910).

On treatment of the mordant suspended in alcohol with a solution of alizarin in alcohol a yellow-orange lake was produced similar to the color of the alizarin. This indicated that the tin mordant took up the alizarin acid. Since the lake settles out on standing, it was filtered. The residue was washed five times with distilled water, but the color of the lake was unchanged and the filtrate was colorless. When treated with sodium hydroxide the color immediately changed to purple, and the lake was now washed again. The filtrate was a light red-blue color, but the greater part of the sodium alizarate remained adsorbed on the mordant. The residue was washed on to another filter and the lake still remained purple and the filtrate clear, which showed that the hydrous tin oxide adsorbed sodium alizarate.

We may rule out compound formation because it occurs neither with alizarin and hydrous alumina, nor with chromic oxide nor with hydrous iron oxide. Also as will be shown later we may have varying amounts of alizarin and sodium alizarate adsorbed on the mordant, which would not happen in compound formation.

We have two possibilities for the adsorption with alizarin acid, first that the alizarin acid is taken up by the mordant, and secondly that the hydrogen cation is adsorbed and drags on the anion with it. In either case the result is the same—an orange lake is produced. If the latter case were true we should have adsorption of the anion forming the red lake, but in no case do we obtain this.

Tin mordant and sodium alizarate. The mordant, which was made slightly acid with hydrochloric acid was treated with the solution of sodium alizarate and a dark brown lake was produced. On washing, the color remained the same. Another sample was run using the same amounts of mordant and sodium alizarate but increasing the acid concentration. In this case an orange lake was produced, and finally with more acid a yellow lake was formed.

The explanation of this depends on the concentration of the acid. With large amounts of acid the sodium alizarate is converted into alizarin acid, which is adsorbed by the tin mordant. With decreasing concentrations of the acid the lake becomes successively darker which is due to the adsorption of some alizarin and some sodium alizarate giving a range of colors from yellow to purple. The latter is produced only if the mordant is on the alkaline side, for any acid present converts some sodium alizarate into alizarin acid, which makes the lake lighter due to its yellow color.

The mordant was then made alkaline with sodium hydroxide and the sodium alizarate added. A deep purple lake resulted. The color was not lost on prolonged washing.

These experiments show that hydrous stannic oxide adsorbs alizarin acid, sodium alizarate or both, but does not adsorb the alizarate anion as such to give a red lake.

The same experiments were done using a mordant prepared from stannic chloride and anhydrous sodium carbonate. The results were the same as noted above.

From experiments previously conducted it appeared that hydrous zinc oxide used as a mordant adsorbed sodium alizarate. The following experiments were performed to check this.

Preparation of the zinc mordant. To 40 g of zinc chloride dissolved in 750 cc of hot water at 70° C was added 25 cc of concentrated ammonium hydroxide. The mordant was washed four times. It was white and settled out on standing. 50 cc contained 0.9113 g weighed as anhydrous ZnO.

Zinc mordant and alizarin acid. To 10 cc of the hydrous zinc oxide made slightly acid with hydrochloric acid was added 5 cc of the alcoholic alizarin solution and immediately a yellow orange precipitate was formed. Since the mordant settled out it could be washed, and most of the yellow color was washed out into the filtrate. A slight yellow color remained after repeated washings indicating a very small adsorption of the alizarin acid. This precipitate was treated with a drop of N sodium hydroxide and the lake turned purple indicating the adsorption of the sodium alizarate. This was washed repeatedly but the color of the lake remained the same, which was due to the adsorption of the sodium alizarate.

To 10 cc of the mordant made slightly alkaline with sodium hydroxide was added 5 cc of the alizarin solution and immediately a purple lake was formed. On washing, the filtrate was colored a lavender and the residue was purple, which showed that the sodium alizarate was adsorbed. Also it showed that the zinc mordant is not as strong an adsorbent as the alumina, for when the latter is used as mordant in the same amount and the alizarin acid the same the filtrate was colorless, and the mordant took up all the dye as the alizarin anion.

Hydrous zinc oxide and sodium alizarate. To 10 cc of the mordant made slightly acid with hydrochloric acid was added 5 cc of sodium alizarate and the lake was colored purple, which on washing did not change in color but remained as a purple lake. However, the filtrate was slightly colored, which indicates that some of the sodium alizarate was not adsorbed. This was generally true in the experiments performed with zinc oxide as mordant; it did not adsorb as well as the alumina or tin mordants.

To 10 cc of the zinc mordant made slightly alkaline with sodium hydroxide was added 5 cc of the sodium alizarate solution and the lake produced was purple. This was washed and although a slight amount came through into the filtrate the lake was still purple showing the adsorption of the sodium alizarate.

We can conclude then that the zinc mordant when alkaline will adsorb sodium alizarate or alizarin acid which is converted into sodium alizarate by the alkali present, to give a purple lake. Also the mordant when acid will adsorb sodium alizarate because the acid on the mordant is not enough to convert the sodium alizarate into sodium chloride and alizarin acid. As we should expect, in one case only do we fail to obtain the purple lake and this is when the mordant is acid and the alizarin acid is added. Since there is no sodium present, no sodium alizarate is formed and therefore no purple lake is produced.

From the experiments conducted we have found that alumina adsorbs the alizarate ion to produce the red lake, the hydrous tin oxide adsorbs alizarin acid, sodium alizarate or both to form a series of lakes varying from yellow to purple, and the zinc mordant adsorbs sodium alizarate and alizarin acid (slightly) to give a purple lake in the first case and a very light yellow in the second.

There are examples of other substances which are adsorbed in different ways. Thus, Witt[1] notes that rhodamine does not fluoresce in the solid state, but does so in solution. Silk dyed with rhodamine showed plainly a fluorescence. In other words, rhodamine is ionized in solution, and this produces the fluorescence. The silk adsorbs the ion giving the fluorescence, thus acting as an ionizing adsorbent. On the other hand wool dyed with rhodamine does not fluoresce, for Dreaper[2] says: "Silk dyed with rhodamine is fluorescent, wool is not."

Experiments were then undertaken using rhodamine dyed on wool, silk and cotton. Knecht[3] gives the properties of rhodamine B as follows:

"Rhodamine B is a red-brown or greenish crystalline powder; aqueous solution is magenta red with a brownish-yellow fluorescence. A light bluish-pink is obtained on unmordanted cotton. With wool and silk bright bluish-pink shades are produced with a red fluorescence.

"The aqueous solution of rhodamine 6 G gives a yellowish red with a strong greenish-yellow fluorescence. Pink or blue-pink shades are obtained with cotton. With silk, yellowish-pink shades with a very strong beautiful yellow fluorescence are obtained."

Rhodamine B dyed on wool, silk and cotton. The standard dye bath used in the experiments contained 0.05 g of rhodamine B in 50 cc, and the samples of cloth weighed one half gram. The method of dyeing was to heat the bath to 40° C, enter the cloth and raise the temperature to boiling, which was continued for one half hour. The samples were removed and dried in air.

The fluorescence was tested by means of ultraviolet light. The source of this was a carbon arc, and the light was conducted through a focusing lens and then through an ultraviolet plate (Corning Glass Works) which transmits only the ultraviolet light. If the materials are fluorescent they will emit light of a different color from that used to illuminate them.

The results were as follows:

Rhodamine B does not fluoresce in the solid state, but does so in solution with a brownish-yellow fluorescence. On silk it yields a blue-red with a strong red fluorescence. On wool it yields a blue-red with a very slight red fluorescence. On cotton it gives a blue-pink with no fluorescence.

Rhodamine 6 G dyed on wool, silk and cotton. These experiments were conducted in the same manner as the rhodamine B experiments.

---

[1] Jahrbuch der Chemie, 1, 20 (1891).

[2] Dreaper: "The Chemistry and Physics of Dyeing," 170 (1906).

[3] Knecht: "A Manuel of Dyeing," 2, 506 (1910).

The results were as follows:

Rhodamine 6 G does not fluoresce in the solid state, but does so in aqueous solution with a green-yellow fluorescence. On silk it yields a yellow-red color with a strong yellow fluorescence. On wool it gives a yellow-red color with practically no fluorescence. On cotton it produces a yellow-red color with no fluorescence.

Experiments were then tried with the hydrous oxides and the rhodamine.

(a). 2 cc of rhodamine B (1 g/liter) was added to 50 cc of alumina, and a pink lake was formed. This was filtered and dried at 60° C and then ground. On test for fluorescence a slight red-yellow fluorescence was exhibited.

(b) 2 cc of rhodamine B was added to 54 cc of tin mordant, and a purple lake was formed. This was filtered, dried and ground. There was no fluorescence.

(c). 2 cc of rhodamine B was added to 40 cc of zinc mordant, and a pink lake was formed. This was a little darker than the alumina lake. It showed a slight yellow fluorescence.

(d) 2 cc of rhodamine B was added to 50 cc of silica, and a pink lake was formed darker than the other previous ones. This gave a distinct yellow fluorescence, which was the brightest.

The same experiments were carried out except rhodamine 6 G was used. With alumina there was a yellow fluorescence (slight). With tin, no fluorescence; with zinc a slight yellow fluorescence and with silica a distinct yellow fluorescence.

Summary. (1) The tin lakes of rhodamine B and 6 G show no fluorescence.

(2). The aluminum and zinc lakes of rhodamine B and 6 G show a slight yellow fluorescence.

(3). The silica lakes of rhodamine B and 6 G exhibit a distinct yellow fluorescence.

This must mean that in the presence of the silk and silica rhodamine is highly ionized and adsorbed. This produces the strong fluorescence.

Since we believe the alumina acts as an ionizing adsorbent for the alizarin, it ought to be possible to show that it does so with some other substance. We chose violuric acid to work with after we found that alumina would not adsorb turmeric, paranitrophenol and phenolphthalein in either acid or basic color.

Violuric Acid. The violuric acid obtained was a yellow powder slightly soluble in hot water, yielding a violet solution. Wagner[1] says: "Magnanini[2] has stated that violuric acid when dissolved in pure water is colourless, and that the colour of its salts in aqueous solution cannot be attributed to a coloured negative ion. His experiments were repeated but a colourless solution was not obtained; water carefully freed from alkali always giving a violet liquid. The absorption of solutions of the acid and the sodium salt is proportional to the number of violuric ions in the solution as determined by

---

[1] Z. physik. Chem., 12, 314 (1893).

[2] Z. physik. Chem., 12, 56 (1893).

electrical conductivity. The absorption of the acid does not increase proportionally to the dilution, as it should if the presence of a salt as impurity were the cause, but to the square root of the dilution. that is, proportionally to the number of negative ions. Sixteen solid violurates were examined. They show great differences in colour, but when dissolved in water and sufficiently diluted they all give violet solutions (due to the negative ion) provided the positive ion is colourless."

Donnan and Schneider[1] performed a very carefully executed experiment which showed that a solution of violuric acid had a violet-red colour. Hantzsch's view is that in an aqueous solution of violuric acid we have to deal with the equilibria,

"Isomeric ψ acid $\rightleftharpoons$ undissociated true acid $\rightleftharpoons$ ions. The equilibrium shifts towards the colourless (or nearly colourless) ψ acid with falling temperature. The intensity of the aqueous solutions of violuric acid diminishes with decreasing temperature."

Hantzsch[2] describes as pseudo-acids those substances which do not contain a hydrogen atom directly displaceable by metals, but which are capable of changing into a salt-forming isomeride. The following tests may be used to recognize the existence of pseudo acids. (1) If an aqueous solution of a hydrogen compound neutralizes a base gradually, it is a pseudo-acid. (2) If a neutral or feebly acid hydrogen compound gives salts which are neutral or feebly basic, that is, are not dissociated hydrolytically, it is a pseudo-acid, and the salts are derived from a more strongly acid isomeride. (3) If a colourless hydrogen compound yields coloured salts and a coloured ion in solution, it is a pseudo-acid. (4) An abnormally large positive temperature coefficient in the conductivity or the dissociation constant of a solution is an indication of a pseudo-acid. (5) If a hydrogen compound does not form a salt by direct combination with dry ammonia in a non-dissociating solvent, but does so in the presence of water, it is a pseudo-acid. (6) If a substance does not combine directly with water or alcohol, but yields a stable hydrate or alcoholate by indirect methods, it is a pseudo-acid.

Violuric acid is colourless, but yields coloured salts and a coloured ion in solution, which makes it fall under classification (3).

The same author[3] notes that the sodium salt of violuric acid forms red needles, and the potassium salt crystallizes in bluish-violet needles. He claims that the alkali violurates exist in at least three differently colored forms, yellow, red and blue. As the atomic weight of the metal rises, the stability of the darkest colored modification increases. The yellow modification of the acid can only exist in the presence of lithium, the blue modification only in that of a metal of higher atomic weight.

Also Hantzsch[4] explains that the production of coloured salts from colourless acids and colourless metals must be accompanied by a constitutional

---

[1] J. Chem. Soc., **95**, 956 (1909).

[2] Ber., **32**, 575 (1899).

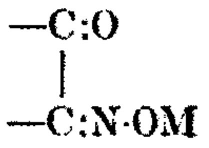
[3] *Hantzsch and Isherwood:* Ber., **42**, 986 (1909).

[4] Ber., **42**, 966 (1909).

rearrangement—an alteration of the manner in which the atoms are linked together.

"With the salts of violuric acid, about one-half are carmine, whilst the members of a smaller group comprising the potassium, rubidium, and ammonium salts are bluish-violet to blue. The existence of the colourless, yellow, red and blue isomerides may be explained by assuming that they are structural isomerides, having the following formulas—

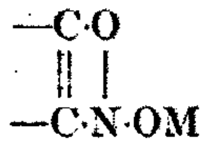
I



$$\begin{array}{l}-\mathrm{C{:}O}\\ \;|\\ -\mathrm{C{:}N{\cdot}OM}\end{array}$$

(Colourless)

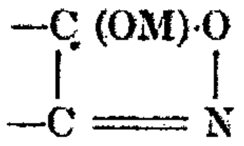
II



$$\begin{array}{l}-\mathrm{C{\cdot}O}\\ \;\,\|\;|\\ -\mathrm{C{\cdot}N{\cdot}OM}\end{array}$$

(Yellow)

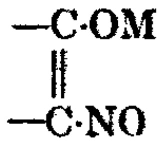
III



$$\begin{array}{l}-\mathrm{C\,(OM){\cdot}O}\\ \;|\qquad\quad\;|\\ -\mathrm{C} = \mathrm{N}\end{array}$$

(Red)

IV



$$\begin{array}{l}-\mathrm{C{\cdot}OM}\\ \;\|\\ -\mathrm{C{\cdot}NO}\end{array}$$

(Blue)

"The position of the metal depends on the nature of the solvent or catalyst which is present. When the solvent is removed the metal may retain its new position or return to its original one. This isomerism, which is due to change in linkage, and not to an alteration in the relative position of the atoms in the molecules is termed allodesmism."

The violet solution of violuric acid was treated with sodium hydroxide and a red color was produced. Another sample was treated with potassium hydroxide and a blue-red color was formed.

Alumina and violuric acid. Ten grams of violuric acid (Eastman) were dissolved in 200 cc of boiling water, and the color of the solution was violet. 10 cc of this solution was added cold to 5 cc of alumina, and a violet lake was produced. This was washed with water and most of the color went into the filtrate, but the alumina was still left a violet color after repeated washings, indicating the adsorption of the violurate ion. When treated with dilute hydrochloric acid the color was not affected. With concentrated acid, it was changed to colorless because the anion of the acid displaces the violurate ion.

10 cc of the violuric acid solution was treated until colorless with a solution of 0.1 N hydrochloric acid, and it required 0.25 cc. The violuric acid was now added to 5 cc of alumina, and a violet lake was formed comparable to the lake formed above. This was washed and the color remained violet. Also the color of the lake was not changed by the addition of dilute hydrochloric acid. Again this shows that the alumina adsorbs the violurate ion, although slightly as compared with alumina and alizarin.

Alumina and sodium violurate. Five grams of violuric acid were dissolved in 100 cc of boiling water and to this was added 20 cc of a sodium hydroxide solution (6 gms/200 cc). The color of the sodium violurate is red as indicated by the porous plate test and evaporation to dryness. In the concentrated solutions the color is red by transmitted light, but in dilute solutions it is a violet color.

10 cc of sodium violurate was added to 10 cc of alumina, and a red lake was formed. When washed the red color went into the filtrate, and the lake was violet, showing the adsorption of the violurate ion and not sodium

violurate. When 10 cc of the dilute solution was added to 10 cc of the alumina, a violet lake was formed, which lost some of its color on washing but remained violet.

Therefore, we may say that alumina adsorbs the colored violurate anion producing a violet lake.

Tin mordant and violuric acid. Since the tin mordant adsorbed the alizarin acid giving it a yellow-orange color, it may adsorb the violuric acid yielding a colorless lake.

The tin mordant prepared as previously indicated and to which a small amount of sodium hydroxide was added to bring it on the alkaline side, was treated with violuric acid. There was a violet-purple lake formed, which was washed thoroughly with water. All the color went into the filtrate, leaving the mordant. On addition of a little more sodium hydroxie a purple lake was produced. When this was washed, the color went into the filtrate. This shows that the hydrous tin mordant will adsorb a slight amount of the colorless violuric acid, but it does not adsorb the anion to form a colored lake.

Then the tin mordant was made slightly acid with hydrochloric acid and violuric acid added in varying amounts. No colored lake was produced. The mordant was washed thoroughly with water. If colorless violuric acid is adsorbed, treatment with sodium hydroxide should yield a color due to the liberation of the anion. No color was formed, which showed that under these conditions the tin mordant did not adsorb violuric acid.

Tin mordant and sodium violurate. The mordant was again made alkaline and treated with the red solution of sodium violurate. There was a red-blue lake formed, but when washed the color went into the filtrate leaving a colorless residue. This was treated with sodium hydroxide to determine if any violuric acid had been adsorbed. There was no color formed, showing there was no adsorption of violuric acid nor of sodium violurate.

The mordant was made acid and treated with sodium violurate. The color of the lake was red-blue, but when washed the color went into the filtrate, leaving the colorless mordant.

Thus we can say that the hydrous oxide of tin does adsorb sodium violurate.

The same experiments were tried with hydrous zinc oxide as mordant, and it was found that there was no adsorption of the violuric acid or sodium violurate.

Summary

1. An alcoholic solution of alizarin added to alumina gives a pink lake, indicating the slight adsorption of the red anion. Further addition precipitates out the alizarin, since it is insoluble in water.

2. If alumina is suspended in alcohol, and then treated with an alcoholic solution of alizarin, a red lake is produced.

3. Sodium alizarate added to alumina gives a red lake, but the color of the lake is unaffected by the nature of the cation.

4. The results 1-3 confirm the work of Weiser on the alumina-alizarin lakes, that the adsorbed alizarin is ionized.

5. Sodium alizarate treated with hydrogen peroxide changes its color due to the acids present and not to an oxidation.

6. Alumina-alizarin lakes coagulate and become lighter on treatment with perhydrol due to the reaction of the acids present with unadsorbed sodium alizarate.

7. The hydrous oxide of tin adsorbs undissociated alizarin to produce an orange lake, and undissociated sodium alizarate to yield a purple lake, but does not adsorb the alizarate anion to give a red lake.

8. Zinc mordant adsorbs undissociated sodium alizarate to produce a purple lake.

9. Silk dyed with rhodamine B is blue-red with a strong red fluorescence, wool is blue-red with a very slight red fluorescence, and cotton is blue-pink with no fluoresecence.

10. Silk dyed with rhodamine 6 G is yellow-red with a strong yellow fluorescence, and on wool and cotton is yellow-red with no fluorescence.

11. The tin lakes of rhodamine B and 6 G show no fluorescence, the alumina and zinc lakes show a slight yellow fluorescence, but the silica lakes exhibit a distinct yellow fluorescence.

12. In the presence of silk and silica, rhodamine is highly ionized and adsorbed, which produces the strong fluorescence. Alumina, zinc, tin, wool and cotton exhibit practically no fluorescence with rhodamine, which must mean that it is not adsorbed the same in these cases as on the silica and silk.

13. A light violet lake is formed with alumina and a solution of violuric acid, but the adsorption is slight.

14. Hydrous tin oxide adsorbs violuric acid slightly but no color is produced, and therefore it is the undissociated acid which is adsorbed. Tin oxide will not adsorb the colored ion to yield a colored lake, nor sodium violurate to give a red lake.

15. Hydrous zinc oxide adsorbs neither violuric acid nor sodium violurate.

16. Witt's theory of solid solutions in dyeing loses its only support as soon as one postulates an ionizing adsorption.

Cornell University

6.691

NEPHELOMETRIC TITRATIONS. IV. THE EFFECT OF SHAKING AND COOLING THE ANALYTICAL SYSTEMS*

BY CLYDE R. JOHNSON**

In the work described in the preceding paper[1] of this series, concerning the action of extra compounds in nephelometric atomic weight analyses, irregularities due to shaking and cooling the analytical systems were avoided. However, since the practices of "cooling to reduce the solubility of the silver chloride" and "occasional shaking" are at present employed in such analyses, it seemed advisable to continue the experiments, to determine the effect of shaking and cooling the analytical systems, in the presence of various extra compounds. The work was facilitated by the fact that the carefully prepared systems used in the earlier experiments were available.

Experimental

Equal Opalescence Tests. The analyses of the supernatant liquids were continued in the same manner described in the earlier paper. Systems No. 3, 4, 5, 7, 9, 14, 16, 17, and 18 were diluted with 0.25 M nitric acid until 0.050 M in the extra compounds. The extra compound concentration in the others remained at 0.10 M. Each system was shaken 1000 times, and samples were withdrawn and tested in the nephelometer after 8 and 24 hours. The bottles were then three-quarters immersed in shaved ice and samples were withdrawn for testing after intervals of 4, 8 and 24 hours. The samples were allowed to come to room temperature before the precipitating reagents were added. The bottles were next placed in ice-salt mixtures, until the contents had completely frozen. After melting, the supernatant liquids were subjected to another series of analyses, in which the time and temperature factors were allowed to vary rather widely. The systems were then brought to room temperature for the final tests. The results of these analyses are given in Table I. A nephelometric ratio greater than unity indicates that the samples contained excess chloride, one less than unity indicates that they contained excess silver.

Standard Solution Tests. To obtain additional information regarding the cause and magnitude of the effects observed in the equal-opalescence tests, the following experiment was tried. Three saturated solutions of pure silver chloride in different concentrations of nitric acid, over 15 gram quantities of flocculent silver chloride, were prepared and analyzed according to the method described by Johnson.[2] These analyses showed that the solutions contained silver and chloride in equivalent amounts, within 0.03 mg. of silver. The

---

* Contribution from the Frick Chemical Laboratory, Princeton University.

** National Research Fellow in Chemistry

[1] J. Phys. Chem., 35, 2237 (1931).

[2] Johnson: J. Phys. Chem., 35, 830 (1931).

TABLE I

Effect of Shaking and Cooling the Analytical Systems

No.	Extra Compound	Nephelometric Ratios; AgCl Solutions 0.25 M in HNO_3:						
		After Shaking in;		After Cooling, for:			After Freezing:	Final At Room
		8 hrs.	24 Hrs.	4 Hrs.	8 Hrs.	24 Hrs.	Max.-Min.	Temp.
1	None	1.07	1.10	1.05	1.10	1.29	2.40–0.98	0.92
2	NH_4NO_3	0.93	0.95	0.86	1.00	1.10	1.16–1.08	0.96
3	NH_4NO_3	0.94	0.93	0.89	1.18	0.99	1.01–1.00	0.98
4	$NaNO_3$	1.09	1.23	0.78	1.33	1.28	1.33–1.00	1.00
5	$NaNO_3$	0.85	1.10	0.82	1.33	1.41	1.28–1.02	0.99
6	$(NH_4)_2SO_4$	0.85	1.22	1.08	1.02	1.22	1.52–1.02	0.91
7	Na_2SO_4	0.75	1.13	0.96	1.45	1.03	1.25–1.13	0.95
8	$Ca(NO_3)_2$	0.93	1.04	1.46	1.42	1.51	1.32–1.09	0.83
9	$Cd(NO_3)_2$	1.08	1.12	0.82	1.04	1.01	2.19–0.90	0.98
10	$(NH_4)_2HPO_4$	0.93	1.17	1.25	1.19	1.70	1.46–1.15	0.94
11	H_3BO_3	0.95	1.25	1.46	1.51	1.28	1.02–0.95	0.91
12	$Al(NO_3)_3$	1.18	0.94	1.11	1.42	1.63	1.48–1.01	1.00
13	$Ce(NO_3)_3$	1.03	1.02	1.11	1.76	2.12	1.65–1.36	0.91
14	$Ce(NO_3)_3$	1.09	1.00	1.08	1.18	1.47	1.21–1.11	1.04
15	$Ce(NO_3)_3$	1.14	1.03	1.00	1.10	1.09	2.22–1.16	1.13
16	$(Na_4P_2O_7)$	1.01	1.20	1.00	0.88	1.00	1.38–1.26	0.79
17	$(Na_4P_2O_7)$	0.96	1.00	1.46	1.58	0.93	1.22–1.00	1.00
18	$Th(NO_3)_4$	1.26	1.46	1.12	1.63	1.50	2.49–1.01	0.97
19	(NH_4VO_3)	0.85	0.94	1.07	1.53	1.82	1.51–1.01	1.03

systems were then shaken occasionally over a period of several days, allowed to stand, and again analyzed by the same method, this time at room temperature. Equal-opalescence tests made upon the same solutions gave ratios from 1.08 to 1.18. The results of the other analyses are summarized below:

System No.	Temp: °C.	Molarity of HNO_3.	Time of Standing. Hours.	Grams AgCl per Liter:	
				Found as NaCl	Found as $AgNO_3$
20	29	0.25	24	0.00342	
			50	0.00304	0.00288
21	29	0.50	24	0.00375	
			49	0.00336	0.00275
			120	0.00310	0.00276
22a	29	1.00	10		0.00252
			10	0.00331	0.00253
22b	30	1.00	24	0.00340	0.00296
			26	0.00352	0.00306

Discussion of Results

In the preceding paper of this series are recorded observations which show that most of the supernatant liquids in the systems under investigation contained practically equivalent amounts of silver and chloride at the beginning of the experiments described in this paper. The present results taken as a whole, indicate that there is a marked tendency for the shaking and cooling treatments to leave in the supernatant liquids an excess of chloride, equivalent to several tenths of a milligram of silver per liter. Real or virtual, this effect represents a source of constant error which, if permitted to operate in any nephelometric atomic weight titration, would tend to yield a low value for the calculated atomic weight. An additional error in the same direction might enter into corrections applied for the removal of nephelometric test portions.

It may be assumed that cooling[1] and shaking initiated in the systems the same series of changes, whenever these were not modified or inhibited by the presence of extra compounds. That is, colloidal silver chloride, in excess of the normal solubility at the final temperature, was first formed, and next slowly coagulated in the supernatant liquids. The data in the above tables offer a somewhat fragmentary record of the accompanying changes in the silver and chloride concentrations, complicated by the action of a number of disturbing factors, operating both in the main systems and in the nephelometer tubes. The fluctuations in the observed nephelometric ratios for any given system may be ascribed to some combination of the following factors: (1) adsorption of ions by silver chloride during peptization and coagulation, (2) adsorption on the precipitate, (3) differences in the coagulating action of the two precipitating reagents, and (4) the peptizing and coagulating actions of the extra compound.

Certain trends in the tabulated data suggest that coagulating silver chloride may have a tendency to carry with it more silver than chlorine atoms. This point is worthy of some attention, as the observed effects accompanied the peptization (or condensation) and subsequent coagulation of only a few milligrams of silver chloride, in the presence of thoroughly washed and aged precipitates. Adsorption effects would be much greater in actual titrations of the type under consideration, as the analytical procedures include the precipitation of 5 to 25 grams (or more) of silver chloride in every analysis. These precipitates are not washed and are not usually aged. If silver chloride did carry down excess silver during coagulation, in any nephelometric atomic weight determination, it would produce constant errors tending to make the calculated atomic weight too low. It is evidently quite important in precise work in which silver chloride precipitated from dilute nitric acid is used, to know the relative amounts of silver and chloride atoms in the material, and the nature of the other inclusions.

A result obtained in experiments now under way in this laboratory may have some bearing on the question. A quantitative study of the solution and

---

[1] J. Phys. Chem., 35, 832 (1931).

reprecipitation of silver chloride samples has been undertaken, with the idea of obtaining information regarding their relative silver and chloride content, and the possibility of removing impurities by reprecipitation. Large samples of silver chloride can readily be dissolved by distilling ammonia into the analytical systems after replacing the supernatant liquids with pure water. The silver chloride is easily reprecipitated by boiling away the ammonia or by distilling it off under reduced pressure. The technique characteristic of atomic weight investigations may be maintained throughout. However, even the most carefully prepared and thoroughly washed samples, weighing about 12 grams each, deposit as much as two or three milligrams of silver during solution in aqua ammonia. This may be due to some reducing action occurring on the walls of the Pyrex flasks. It may indicate that part of the silver in the samples is not present as silver chloride, for this compound is quite resistant to reduction under conditions in which other silver compounds, such as the nitrate, are quickly reduced. These experiments are to be continued, in connection with experiments concerning the "loss on fusion" correction apped in precise work with silver chloride.

Thanks are due to Professor George A. Hulett, who has kindly placed his laboratory at my disposal for this work.

Summary

Data concerning the effect of shaking and cooling on a number of typical systems used in nephelometric atomic weight determinations have been recorded.

Princeton, New Jersey.

THE ELECTRO-DEPOSITION OF COPPER IN THE PRESENCE OF GELATIN[1,2]

BY ROBERT TAFT AND HAROLD E. MESSMORE

16-1920

A number of investigations upon the deposition of copper in the presence of gelatin have been made; a bibliography of many of these investigations, together with others bearing upon the topic of addition agents in general, will be found in the excellent paper of Frolich[3] published in 1924. Since that time the important papers of Fuseya and his students[4] and of Marie and Buffat[5] and Marie and Claudel[6] have been published.

While the beneficial effect of gelatin (or glue) in copper plating baths has long been known and utilized, the explanation of the process by which gelatin produces its effects has never been satisfactorily given.

Frolich has advanced the view that in plating baths of copper sulfate possessing a lower pH than 4.7 (isoelectric point of gelatin) any added gelatin will be present in the bath as particles having a positive charge. Upon the passage of an electric current these gelatin particles tend to move toward the cathode and unless removed, will tend to accumulate around this electrode. Removal of gelatin does occur, however, as it has been shown by Marie and Buffat, and others, that the cathode deposit from baths containing gelatin and copper sulfate is greater in mass than that obtained under otherwise similar conditions from baths free of gelatin. Moreover, Marie and Buffat have shown that in at least one instance, the major portion of this difference in mass between two such cathode deposits is actually gelatin.

There seems to be sufficient evidence for Frolich's explanation of the advance of gelatin toward the cathode to consider it the true explanation of this process, but, this, of course, is a phenomenon entirely distinct from the actual electrode processes. It is in connection then, with the cathode processes that the uncertainty exists, i.e. there is no accepted explanation of the mechanism whereby gelatin finds its way into the deposit.

This problem, for addition agents in general, has been reviewed by Blum[7] who suggests the following possibilities to account for those cases in which the

---

[1] Presented at the Indianapolis meeting of the American Chemical Society, April 1, 1931.

[2] Constructed, in part, from a thesis presented by Harold E. Messmore to the Faculty of the Graduate School of the University of Kansas in partial fulfillment of the requirements for the degree of Doctor of Philosophy, May, 1930.

[3] Trans. Am. Elec. Soc., 46, 67 (1924).

[4] Fuseya and Murata: Trans. Am. Elec. Soc., 50, 235 (1926) (An extensive bibliography is also given in this paper;) Fuseya and Nagano: 52, 249 (1927).
These papers do not deal specifically with the deposition of copper in the presence of gelatin but are listed here as bearing upon the general topic of the deposition of copper in the presence of addition agents.

[5] J. Chim. phys., 24, 470 (1927).

[6] Compt. rend., 187, 170 (1928).

[7] Colloid Symposium Monograph, 5, 300 (1928).

addition agent has actually been found in the cathode deposits. "(1) Co-discharge of colloid particles and metal ions, (2) discharge of complex ions containing the metal and the colloid, (3) adsorption of colloid upon the face of the metal deposit, or (4) mechanical inclusion in the deposit." Blum further states in regard to these various possibilities that "it is difficult from the meager data available to suggest the relative probabilities of these processes. . . ." However, other workers have expressed preference for one or the other of the particular views outlined above. Thus Bancroft[1] tacitly assumes that adsorption accounts for the inclusion of the addition agent in the deposit; Fuseya and Murata postulate the existence of complex cations formed from the metal ion and addition agent and produce evidence to show that such complex ions are doubtless formed. They further assume, without producing experimental evidence however, that the complex ions are discharged at the cathode and become thereby a portion of the deposit. Marie and Buffat have shown that the mass of the cathode deposit increases to a limiting maximum value with increasing content of addition agent in the case of the particular cell, Cu/$CuSO_4$, Gelatin/Cu. In fact, if the mass of the deposit is plotted against the gelatin content of the solution, the resulting curve resembles in form those typical of adsorption phenomena. We have confirmed this observation of Marie and Buffat under somewhat more varied conditions than have these investigators.[2] It would appear that this evidence would support the third view as to the mechanism of the cathode process as outlined above by Blum.

In order to obtain further evidence for one or the other of Blum's postulates we have examined the variation of the mass of the cathode deposit from cells of the type Cu/$CuSO_4$, Gelatin/Cu as functions of gelatin content, copper sulfate content, current density, time, and temperature.[3] In addition we have determined the form of the cathode deposit as a function of the gelatin content of such cells, and have likewise studied the influence of gelatin upon the magnitude of the cathode polarization. We will consider below our experimental results in the order (A) the influence of gelatin upon the form of the deposit; (B) the effect of gelatin upon the weight of the cathode deposit; (C) the influence of gelatin upon the polarization at the cathode during depositon of copper. We will then discuss these results in the light of the four possibilities suggested by Blum.

A. The Influence of Gelatin upon the Form of the Cathode Deposit

After numerous preliminary trials, some of which have already been reported in our previous paper, the following procedure was adopted to study the effect of varying the concentration of gelatin upon the form of the deposit.

---

[1] Trans. Am. Electrochem. Soc., 23, 266 (1913).

[2] Taft and Messmore: Trans. Kan. Acad. Science, 32, 42 (1929).

[3] We recognize, of course, that any evidence for one of the views which may be obtained from the study of a particular type of electrolytic cell need not, of necessity, lead to the proper explanation of the function of *all* addition agents. Considering the extremely varied character of the addition agents used in such cells it is unlikely that the same explanation will hold for all cases of addition agent action. Any conclusions which we may reach can hold only for the cells which we here consider until more general evidence is available.

A number of cells (usually fifteen) were set up in series and connected to a source of potential. These cells consisted of 100 cc. pyrex beakers containing two heavy sheet copper electrodes, 2.5 × 2.5 cm. in cross section. The electrodes were cleaned in acid and coated electrolytically with copper from an acid bath before use. The source of potential was a battery of Edison cells, adjustment of the current being made by a suitable potential divider; the circuit including the cells also contained a precision ammeter.

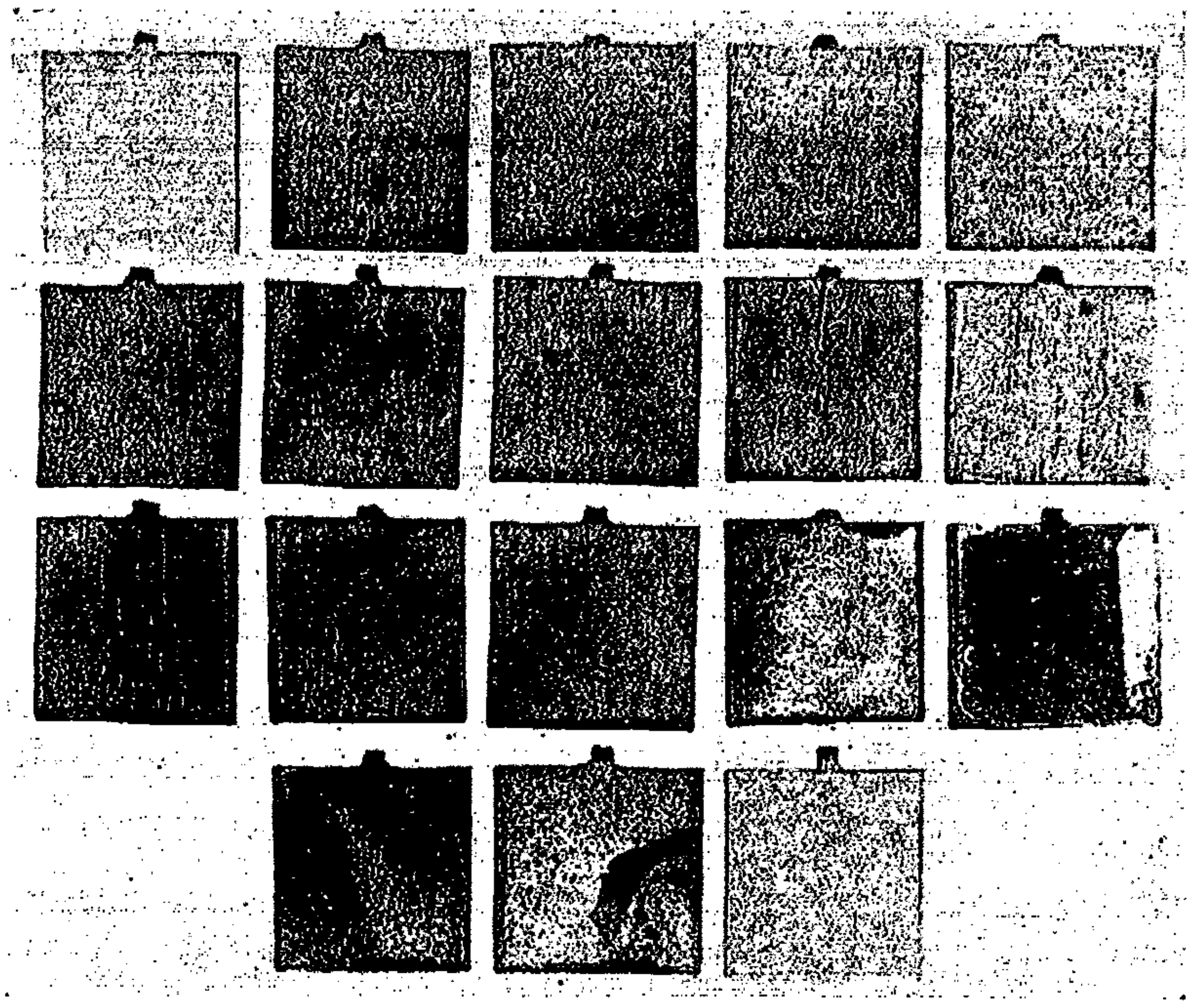


Fig. 1

The Form of Electro-Deposited Copper as a Function of Gelatin Gontent (× 1⅓). Left to right: Top row, coulometer deposit, 0.025% gelatin, 0.05%, 0.075%, 0.10%; Second row, 0.15%, 0.20%, 0.25%, 0.30%, 0.40%; Third row, 0.60%, 0.80%, 1.0%, 1⅓%, 1⅔%; Fourth row, 2.0%, 3.0%, coulometer deposit. Electrolysis at 1 amp./dm^2 for 30 minutes at 30°C; 1 molar copper sulfate.

The electrolyte was prepared from a stock solution of 1.25 *M* copper sulfate. The copper sulfate was the c p grade of a well known manufacturer and was allowed to stand for some time before use, and was then carefully decanted for use. This procedure freed the electrolyte from slight traces of basic salts without filtering the solution through paper. The stock solution was diluted to secure the desired concentration in the various trials. The gelatin used in these qualitative runs was that manufactured by Coignet, of Paris, bearing the label "Gelatin Extra." A 2 per cent solution of this gelatin in distilled water had a pH value of 5.4. A definite procedure was always employed in putting the gelatin into solution. The dried gelatin was first cut into shreds and then added to the prepared copper sulfate solution. The whole system was then warmed to 50°C, and stirred slowly until the gelatin had completely dispersed; the contents of the cell were then allowed to cool to the temperature at which electrolysis was carried out.

At the completion of electrolysis the cathodes were removed from the bath, washed first with warm water, and then with acetone. They were then dried by a stream of warm air. To secure permanent records the cathodes were photographed at natural size on a contrast plate.

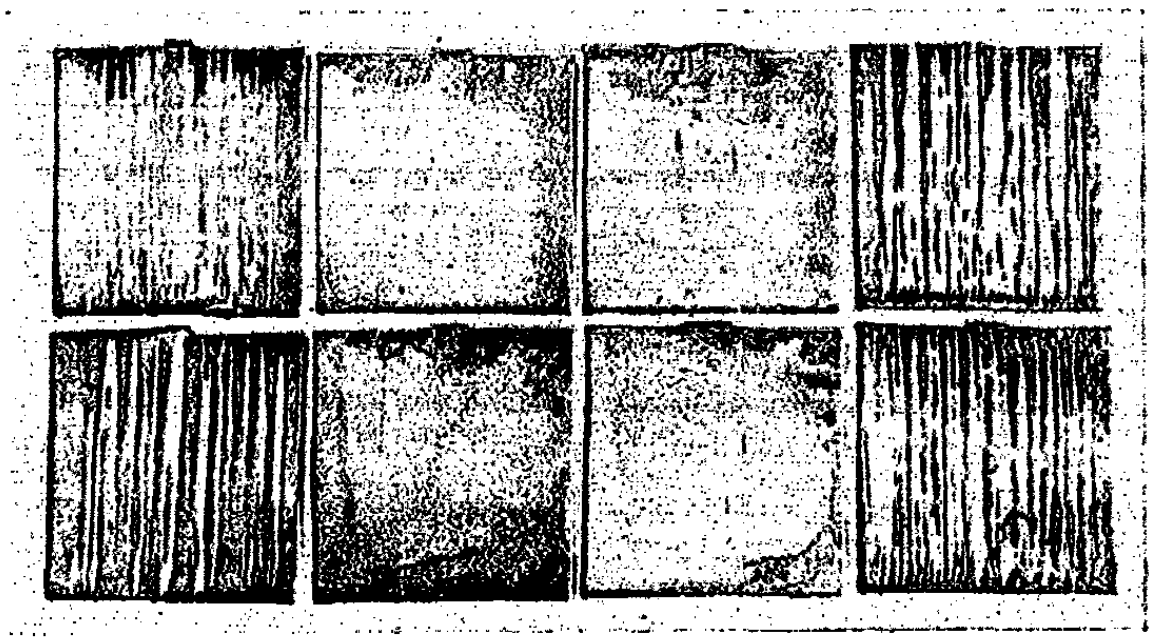


Fig. 2

Form of deposit as function of variety of gelatin (XI). Upper row thirty minutes electrolysis; lower row ninety minutes. Left to right gelatins are Difco, Knox, ash free, Coignet. Electrolysis at 30°C, 1 amp./dm^2 with gelatin content of 1/2% and 1 M $CuSO_4$.

Fig. 1 shows the typical result of such a series of electrolysis in still baths with gelatin content ranging from 0.025 per cent to 3.0 per cent. These were carried out in a constant temperature bath automatically kept at 30°C with a current density of 1 ampere per square decimeter for thirty minutes. The concentration of copper sulfate was the same in all sixteen cells containing gelatin, namely 1 molar. The coulometer deposits were obtained from the familiar bath (Oettel's) containing sulfuric acid and alcohol in addition to the copper sulfate.

The important features to be observed in connection with the deposits in those solutions containing up to 0.15 per cent gelatin are the numerous small circular deposits of copper. These stand above the level of the base metal and are darker colored than the remaining copper. A continuous deposit of copper is observable, however, between these raised areas. Further it will be noted that the number of "points" of deposit diminishes with increasing concentration of gelatin. Up to this concentration of gelatin (0.15 per cent) there is no definite alignment of these raised areas but as the concentration of gelatin increases beyond this value, definite striations appear. These striations, as the photographs show, result from the gradual growth of the "points" into each other. In those solutions containing the largest amounts of gelatin (1 1/3 per cent to 3.00 per cent) the striations have disappeared and colored films result. Somewhat similar films have already been described by Bancroft and Briggs, although our films produced are evidently not so brilliant in color[1] as those described by these investigators. The two solutions most concentrated with respect to gelatin solidified during electrolysis.

The form of the deposit can be changed by varying the concentration of copper sulphate as well as that of gelatin. These variations of form we have already described.[2] The general effect of this variation may be summarized as follows: The extent of the raised areas at a given concentration of gelatin passes through a maximum, the maximum usually occurring at 0.75 M copper sulfate, the concentrations employed being 1.25 M, 1.00 M, 0.75 M, 0.50 M, and 0.25 M. At a given concentration of copper sulfate the raised areas diminish in extent with increasing concentrations of gelatin as previously stated. The greatest production of colored films occur in the more dilute solutions of copper sulfate (0.50 and 0.25 M).

Still another factor which influences the form of the deposits from these still baths is the variety of gelatin used. Fig. 2 illustrates some results obtained using gelatin from four different sources. The conditions of electrolysis are the same as those described for the previous series, save that a different variety of gelatin was used in each cell, the concentration of the gelatin used being made one-half per cent in each case. The upper series of cathodes were obtained as a result of thirty minutes electrolysis—the lower after ninety minutes electrolysis. Duplicate cells gave deposits which, while not exact duplicates, were essentially the same.

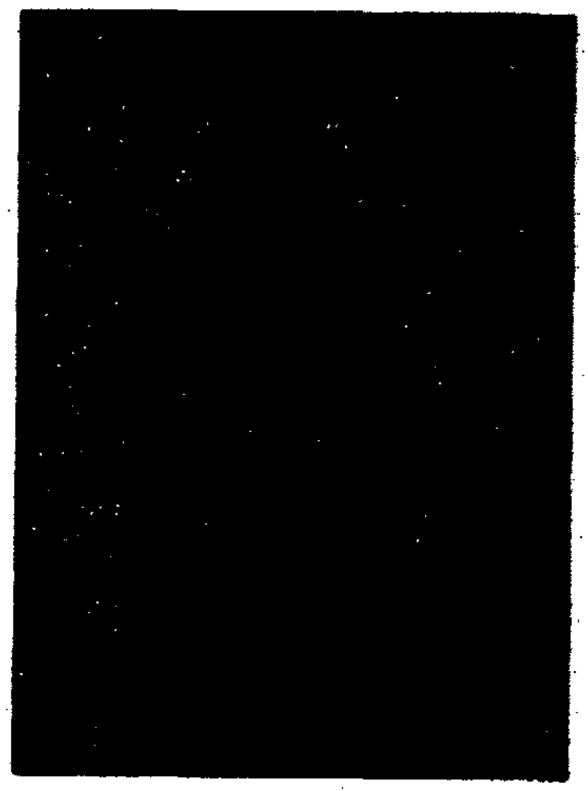


FIG. 3.
Characteristic stria (× 100).

We have also studied the effect of varying the nature of the base metal upon the form of the deposits. Cathodes of gold, platinum, silver, and brass were tried under otherwise exactly similar conditions. While some slight differences were noticeable *at first* the deposits obtained from a given concentration of gelatin and copper sulfate were of the same general type.

The physical character of the striae frequently produced is shown by the microphotograph of Fig. 3. The single stria shown is the dark half oval,

---

[1] The deposits of Bancroft and Briggs were obtained from copper acetate solution. They ascribed their formation to the adsorption of hydrous copper oxide from the solution by a copper-gelatin film; Trans. Am. Electrochem. Soc., 22, 287 (1912).

[2] Taft and Messmore: loc. cit.

whereas the copper deposited beside the stria is crystalline in character. While the top of the stria is out of focus in the figure, bringing it into sharp focus failed, at this magnification (100×), to reveal any crystalline character. The important fact in this connection is that the copper deposited in the stria is deposited in a more highly divided form than that in adjacent areas. The bearing of these experiments upon the fundamental questions involved will be considered in connection with the final discussion of our results.

B. The Effect on Gelatin upon the Weight of the Cathode Deposit

The procedure for determining the weight of the cathode deposit was somewhat similar to that described under Part A. A number of cells were set up in series; the cells consisted of 150 cc. pyrex beakers, the cathode was usually of sheet platinum 2.5 × 2.5 cm. and the anode of heavy sheet copper carefully cleaned and plated electrolytically before use. The electrolyte was the stock solution of copper sulfate described above but the gelatin used was an ash-free product, obtained from the Eastman Kodak Co.[1] The same procedure for getting the gelatin into solution was used as we have described above.

We have in the majority of cases, determined the pH of the solutions used in the experiments reported in sections B and C. Not that any great significance is to be placed upon the meaning of the pH of these solutions but chiefly because the pH measurements furnish an easily determinable "constant" or property of the systems which we have used; the work of previous investigators has frequently been criticized for failure to state specifically the properties of the solutions employed. Furthermore as the direction of migration of gelatin particle, or ion, is also determined by the pH value of the solution, it is essential if uniformity in the direction of this movement is to be secured in every case, that the pH be lower than 4.7. It will be observed by the inspection of the data to follow that the pH in every instance was considerably lower than this value.

Our pH values were determined by means of the quinhydrone electrode and a saturated calomel electrode at 25°C. and were computed from the relation, $\mathrm{pH} = \frac{0.6992\text{-}0.2548\text{-}E_c}{0.0591}$ where 0.6992 is the potential of the normal quinhydrone electrode, 0.2458 that of the saturated calomel electrode, and 0.0591 the value of the thermodynamic function ln RT/NF, all at 25°C. E_c is the measured potential of the cell comprised of the quinhydrone and the saturated calomel electrodes. As O'Sullivan[2] has shown that there is a slow drift in the potential of such cells with time, the measurements were made within a few minutes after the quinhydrone had been added to the solutions kept at 25°C.

Our results concerning the weight of the cathode deposit are given in terms of "excess weight." By excess weight we mean the difference in weight be-

---

[1] This material contained approximately 12% moisture upon drying to constant weight at 100°C. All of our concentrations of gelatin are given, however, in terms of the undried product and are accordingly 12% too high.

[2] Trans. Faraday Soc., 23, 52 (1927).

tween that of the cathode deposit in a particular cell and that produced in a copper coulometer bath kept in ice and stirred with natural gas and in series with the cell in question. The copper coulometer bath consisted of a solution of copper sulfate, sulfuric acid and alcohol in the proportions recommended by Oettel.[1]

Our reasons for choosing the copper coulometer as the reference standard rather than a cell containing copper sulfate alone, are these: (a) it more nearly indicates the actual quantity of electricity flowing through the circuit; (b) it gives one standard rather than the several which would be obtained by using a cell containing only copper sulfate. By the use of copper sulfate alone as electrolyte the mass of the deposit obtained depends upon the concentration and temperature employed as is already well known; (c) as the result of every extensive experience with deposits from baths of copper sulfate alone we have found that duplicate determinations differ to some extent among themselves. This we ascribed to oxidation of the copper cathodes in the drying process, as despite all precautions the surfaces of the electrodes obtained from such baths darkened in the course of drying.[2] Such darkening did not occur in the case of deposits obtained from acid baths or from those containing gelatin. In the case of the acid baths the deposit is evidently more compact, thus not offering such a large surface to the atmosphere as deposits from "neutral" baths; in the case of the third type of cell, the gelatin evidently protects the copper by its presence in the deposit.

In order to confirm these suppositions we have determined the magnitude of the deposits in baths containing copper sulfate alone as compared to the

TABLE I

Coulometers kept at 0°C.
Copper sulfate cells at 30°C.
Current density 2 amp/dm^2.

Coulometers		Deposit, grams
1.		1.4851
2.		1.4852
3.		1.4856
	Av.	1.4853

Copper sulfate cells	Conc. (molarity)	pH		Gain over average coulometer deposit, milligrams.
4.	1.25	3.11	1.4865	1.2
5.	1.00	3.26	1.4874	2.1
6.	0.75	3.37	1.4878	2.5
7.	0.50	3.55	1.4891	3.8
8.	0.25	3.77	1.4878	1.5

---

[1] Chem. Ztg., 17, 543 (1893).)

[2] The lack of reproducibility is also doubtless due, in part, to adsorption of cuprous and cupric hydroxides as the data, shortly to be presented, indicate.

coulometer deposits, obtained as above described, by using a series of cells of various concentration of copper sulfate, electrolysis being continued for a long period of time (9 to 10 hours) in order to minimize the relative effects of oxidation upon drying. Results were obtained as shown in Table I.

The excess weights in the case of copper sulfate cells 4, 5, 6, are apparently due to surface oxidation occurring in drying as an analysis for copper (by a method to be described) in these deposits gave results as shown in Table II.

TABLE II

Cell	Deposits, grams	Copper upon analysis, grams	Difference, milligrams
4.	1.4865	1.4848	−0.5
5.	1.4874	1.4849	−0.4
6.	1.4878	1.4854	+0.1
7.	1.4891	1.4881	+2.8
8.	1.4878	1.4844	−0.9

The "Difference" tabulated in Table II is that between the mass of the copper found upon analysis and the average value of the coulometer deposit. The magnitude of these differences for cells 4, 5, and 6, are of the same order as the experimental error and hence we have concluded that the actual mass of copper deposited in the cells is, within our experimental error, the same.

In cell 7 the increased copper content of the cathode is likely due to adsorbed cuprous oxide as Richards, Collins, and Heimrod[1] have shown that deposits from more dilute copper sulfate solutions are heavy for this reason. In the case of cell 8 the low copper content is likely due to the fact that at or near this concentration of copper sulfate, hydrogen liberation sets in. This fact combined with the greater hydrolysis of cuprous sulfate in a dilute solution and the possibility of cupric hydroxide formation and adsorption as a result of hydrogen liberation could account for a deposit greater in mass than the coulometer deposit but of smaller copper content.

The maximum weight due to oxide or hydroxide in these cases is 4 milligrams; the maximum excess weights in the presence of gelatin for a similar quantity of electricity would be in the neighborhood of ninety-five milligrams (cf Table VIII). That is, the excess weights obtained in the presence of gelatin can scarcely be due to oxides or hydroxides of copper. To further confirm this fact we have in a large number of instances analyzed the deposits for copper and have found that the major portion of this excess weight must be due to gelatin itself. Marie and Buffat have directly determined this fact for several cases by analysis for nitrogen upon large deposits (4 to 5 grams) of copper obtained in the presence of gelatin.

We have determined the variation of this excess weight as functions of (a) the gelatin content of the bath, of (b) the current density, of (c) the time and of (d) the temperature.

---

[1] Proc. Am. Acad. Arts Sci., 35, 123 (1899).

Excess Weight as a Function of Current Density and Concentration of Gelatin

Four sets of electrolyses were carried out in 0.5 M copper sulfate solutions at five concentrations of gelatin and at three current densities. The first series consisted of ten cells containing five concentrations of gelatin in duplicate and two coulometers. In this set the platinum cathodes were approximately 2.5 × 2.5 cm. in cross-section, a current density of 0.5 amperes per square decimeter (.0315 amperes) being employed for ten hours. The results obtained are given in Table III and graphically in Fig. 4 (lower curve). In this table there are tabulated the deposit obtained, the excess weight as

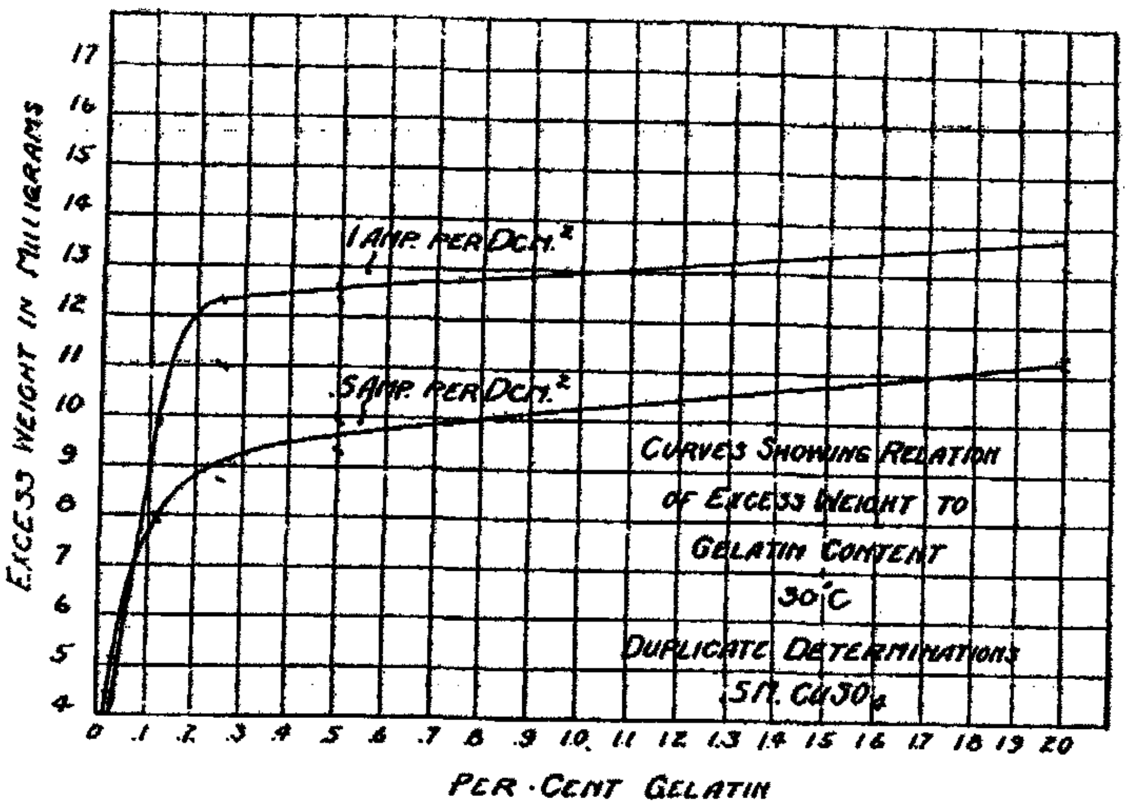


FIG. 4

TABLE III

Series 1.—0.5 amperes per square decimeter (0.0315 amperes); weights in milligrams. Temperature 30°C.

Conc. gelatin	2%		0.5%		0.25%	
	1	2	1	2	1	2
Deposit	389.9	389.7	387.8	388.4	387.2	389.6
Excess weight	11.4	11.2	9.3	9.9	8.7	11.1
Copper	380.3	380.0	379.5	379.3	379.5	380.1
Excess copper	1.8	1.5	1.0	0.8	1.0	1.6

	0.12%		0.03%		Coulometers		Av.
	1	2	1	2	1	2	
Deposit	386.5	386.4	382.9	383.6	378.3	378.7	378.5
Excess weight	8.0	7.9	4.4	5.1			
Copper	379.5	379.6	379.9	379.8	378.0	378.4	
Excess copper	1.0	1.1	1.4	1.3			

previously defined, the copper present in the cathode deposit found as a result of analysis, and the excess copper. This last quantity is the difference between the copper found upon analysis of the cathode deposit and the average coulometer deposit.

The "copper" tabulated above in this and subsequent determinations was found as follows: the platinum cathode bearing the deposit was placed in a 400 cc. beaker and 40 to 50 cc. of dilute nitric acid was added slowly enough to prevent any loss of copper by volatilization. The platinum cathode was washed and removed. Enough sulfuric acid was then added to convert the copper present to the sulfate and the solution slowly evaporated to dryness. When dry the beaker was held over the open flame of a Meeker burner to remove the excess sulfuric acid and to destroy any remaining gelatin. When cooled the copper sulfate was taken up in a little water and 1 cc. of nitric acid was added. Ammonium hydroxide was then added until neutral and a slight excess added. The ammoniacal solution was then neutralized with a small amount of nitric and sulfuric acids and diluted to 150 to 200 cc. The solution was then electrolyzed between platinum electrodes. The cathodes were light cylinders (3-4 grams) of platinum gauze and were rotated at about 300 revolutions per minute. Electrolysis was continued until a few drops of the solution gave no brown or black deposit with water saturated with hydrogen sulfide.

This method of analysis was developed after many trials when other procedures had failed to give satisfactory results. The following results obtained by analysis of coulometer deposits give some idea of the accuracy of the procedure.

Coulometer deposit, gms.	Copper upon analysis, gms.
0.3740	0.3740
0.3878	0.3879
0.3797	0.3797
0.3790	0.3788

An examination of the data of Table III and of Fig. 4, shows that the excess weight increases to a maximum with increasing concentration of gelatin. The greatest variation in the duplicate determinations occurs in the case of the 0.25% gelatin cell. Judging from the remaining data 8.7 is more nearly correct than 11.1 and it is that value that is used in plotting the results in Fig. 4 (lower curve). Large variations of this type were frequently encountered and are difficult to explain. A possible explanation will be given later. It should be noted that the excess copper is approximately the same in all cases.

In the second set of electrolyses exactly similar conditions were used as described above save that platinum cathodes 1.77 cm. on an edge were used, this giving one half the area and therefore twice the current density. The data for this set of experiments are given in Table IV.

TABLE IV

Series 2.—One ampere per square decimeter (0.0315 amperes); weights in milligrams. Temperature 30°C.

Conc. of Gelatin	2%		0.5%		0.25%	
	1	2	1	2	1	2
Deposits	392.8	394.2	391.9	392.2	391.9	392.2
Excess weight	13.2	14.6	12.3	12.6	12.3	12.6
Copper	379.9	379.6	380.0	379.8	379.8	379.6
Excess copper	0.3	0.0	0.4	0.2	0.2	0.0

	0.12%		0.03%		Coulometers		Av.
	1	2	1	2	1	2	
Deposits	389.4	389.5	383.8	383.9	379.5	379.7	379.6
Excess weight	9.8	9.9	4.2	4.3			
Copper	379.9	379.6	380.3	379.8	379.8	379.6	
Excess copper	0.3	0.0	0.7	0.8			

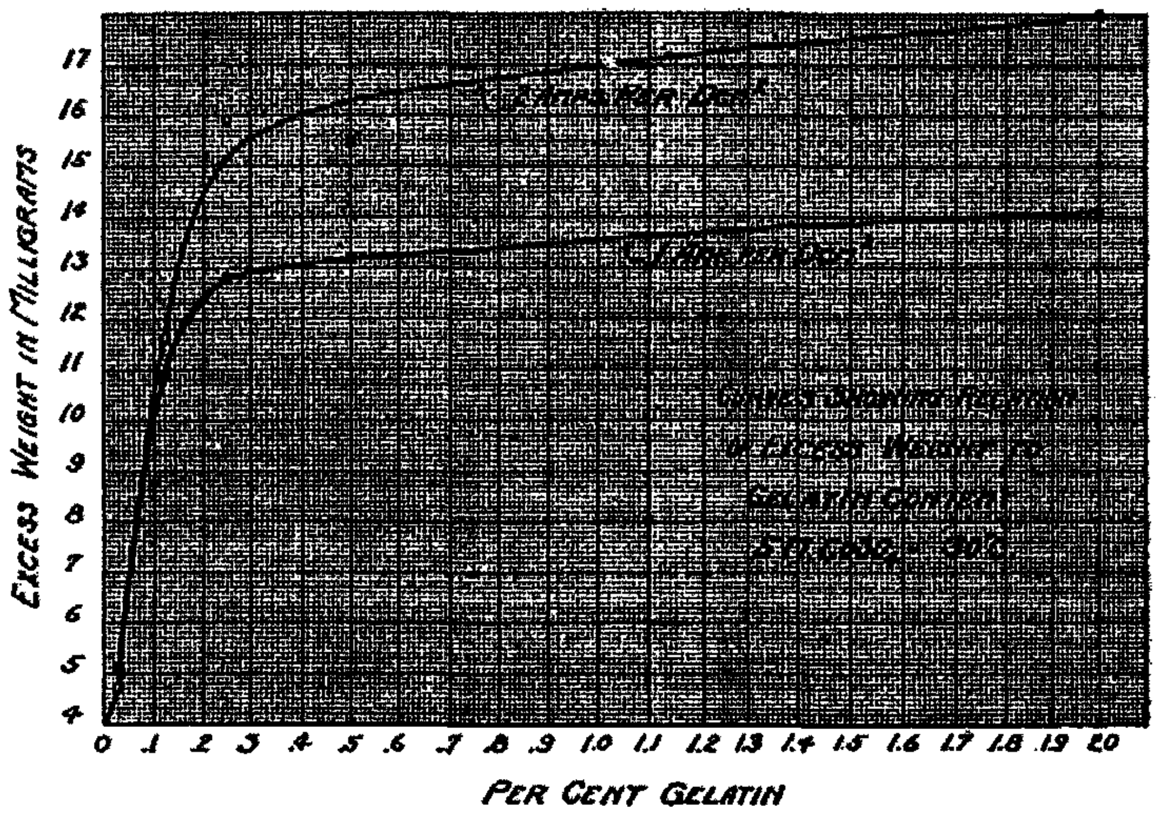


Fig. 5

The values of the excess weight at the higher current density are somewhat greater than at the lower. This is brought out more clearly in Fig. 4. It will be noticed again that the excess copper is practically the same in each case, although somewhat lower than in the first series. The third and fourth series were similar to the first and second, respectively, save that a current of 0.0625 amperes was employed for approximately five hours. This would give a current density of 1 ampere per square decimeter in the third series and of 2 amperes per square decimeter in the fourth. The data are given in Tables V and VI, and graphically in Fig. 5.

TABLE V

Series 3.—One ampere per square decimeter, (0.0625 amperes); weights in milligrams. Temperature 30°C.

Conc. of Gelatin	2%		0.5%		0.25%	
	1	2	1	2	1	2
Deposit	402.0	—	401.2	401.0	401.3	400.2
Excess weight	14.1	—	13.3	13.1	13.4	12.3
Copper	388.9	—	389.2	389.4	389.5	389.2
Excess copper	1.0	—	1.3	1.5	1.6	1.3

	0.12%		0.03%		Coulometers		Av.
	1	2	1	2	1	2	
Deposit	398.8	398.9	392.9	393.0	387.8	388.0	387.9
Excess weight	10.9	11.0	5.0	5.1			
Copper	389.7	389.5	388.9	389.0	387.9	387.4	
Excess copper	1.8	1.6	1.0	1.1			

TABLE VI

Series 4.—Two amperes per square decimeter (0.0625 amperes) weights in milligrams. Temperature 30°C.

Conc. of Gelatin	2%		0.5%		0.25%	
	1	2	1	2	1	2
Deposit	406.8	406.4	404.0	404.3	404.6	404.4
Excess weight	18.2	17.8	15.4	15.7	16.0	15.8
Copper	390.2	389.9	389.5	389.9	389.9	389.8
Excess copper	1.6	1.3	0.9	1.3	1.3	1.2

	0.12%		0.03%		Coulometers		Av.
	1	2	1	2	1	2	
Deposit	400.2	400.2	393.3	393.4	388.7	388.6	388.6
Excess weight	11.6	11.6	4.7	4.8			
Copper	389.7	389.8	388.7	389.4	388.3	388.3	
Excess copper	1.1	1.2	0.1	0.8			

Our reason for running series two and three at the same current density but at different currents, was to determine if the rate of deposition had any material effect upon the magnitude of the excess weight. The data of Tables IV and V are not exactly comparable as the coulometer deposits are not the same but if the average excess weights of Table IV are multiplied by the ratio of the coulometer deposits, $\frac{388.0}{379.6}$ as has been done in Table VII, the results can be compared.

The fact that the excess weights are slightly greater for the larger current would indicate that the process of taking up gelatin by the electrode must be an instantaneous one, for if time were involved the excess weight should be

TABLE VII

Conc. of Gelatin	Excess weights at 1 ampere per square decimeter.	
	0.0315 amperes, average values	0.0625 amperes, average values
2.%	14.2	14.1*
0.5%	12.8	13.2
0.25%	12.8	12.9
0.12%	10.0	11.0
0.03%	4.3	5.0

* Based on a single value (See Table V).

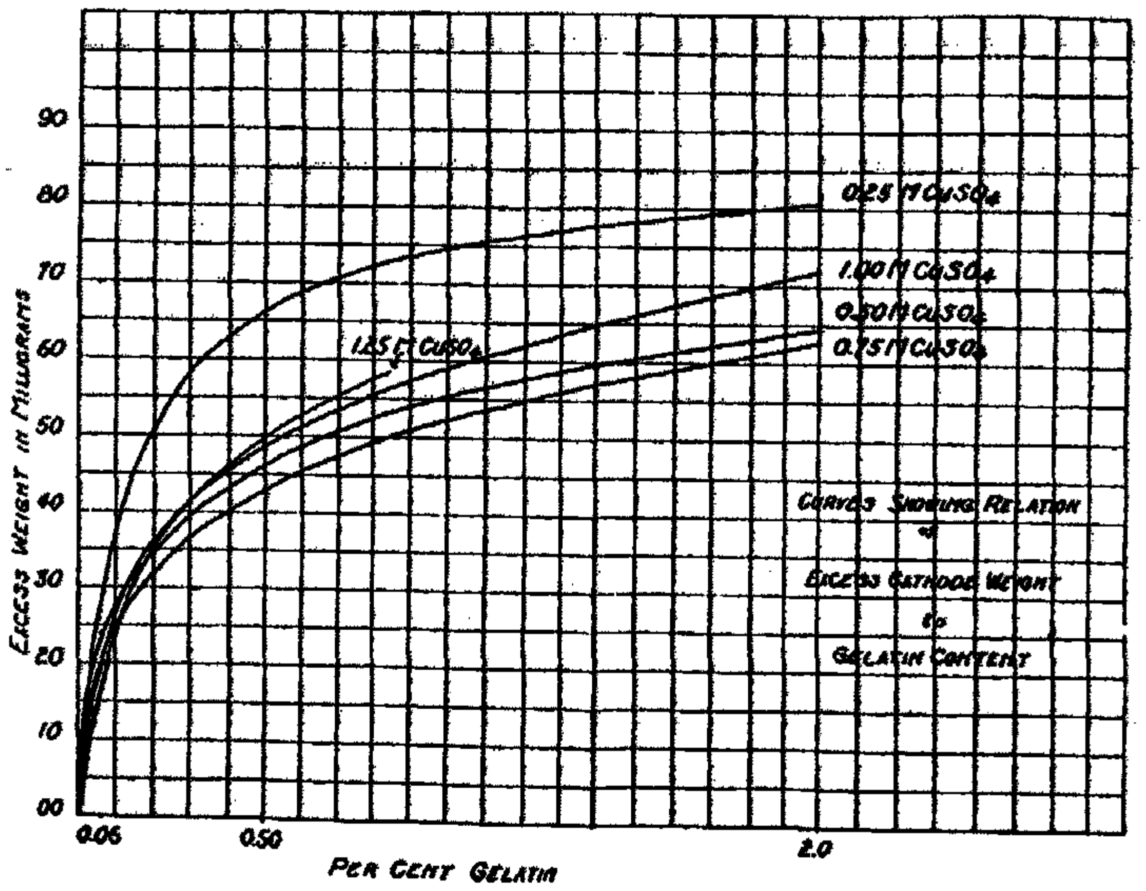


FIG. 6

greater for the slower rate of deposition. The slight increase at the greater current, if real, is evidently due to the increased amount of gelatin brought in contact with the electrode by the greater current.

To obtain further information upon the magnitude of the excess weight we have made determinations of this quantity at various concentrations of copper sulfate but at a constant current density of two amperes per square decimeter, i.e. at the current density where the effect is greatest. In the data of Tables III to VI we were not satisfied with the determinations of excess copper. The differences between duplicate determinations were, in several instances, of the same order of magnitudes as the individual quantities themselves. In order to increase the relative precision in the determination of this quantity, the deposits in the series of runs about to be described were made some three times larger. The results obtained are given in Table VII and the excess weight as a function of gelatin content is shown graphically in Fig. 6.

Table VIII

Current density, 2 amperes per square decimeter.* Temperature 30°C.
Excess weights as functions of copper sulfate and gelatin concentration.

	Current Density, 2 amp./dm²		
Per Cent Gelatin	2.0	0.5	0.06
1.25 M. $CuSO_4$, pH	3.18	3.14	3.11
Deposit (grams)	—	1.2958	1.2632
Excess weight (mgm)	—	49.5	16.9
Copper (upon analysis)	—	1.2524	1.2503
Excess copper (mgm)	—	6.1	4.0
1.00 M. $CuSO_4$, pH	3.28	3.27	3.25
Deposit (grams)	1.3181	1.2950	1.2657
Excess weight (mgm)	71.8	48.7	19.4
Copper (upon analysis)	1.2546	1.2509	1.2495
Excess copper (mgm)	8.3	4.6	3.2
0.75 M. $CuSO_4$, pH	3.44	3.41	3.38
Deposit (grams)	1.3091	1.2891	1.2671
Excess weight (mgm)	62.8	42.9	20.8
Copper (upon analysis)	1.2542	1.2506	1.2501
Excess copper (mgm)	7.9	4.3	3.8
0.50 M. $CuSO_4$, pH	3.60	3.58	3.56
Deposit (grams)	1.3106	1.2922	1.2694
Excess weight (mgm)	64.3	45.9	23.1
Copper (upon analysis)	1.2537	1.2501	1.2483
Excess copper (mgm)	7.9	3.8	2.0
0.25 M. $CuSO_4$, pH	3.84	3.82	3.80
Deposit (grams)	1.3871	1.3126	1.2749
Excess weight (mgm)	80.8	66.3	28.6
Copper (upon analysis)	1.2544	1.2534	1.2505
Excess copper (mgm)	8.1	7.1	4.5
Coulometer deposits (grams)	1.2459	1.2464	1.2464 = Av. 1.2462
Copper (upon analysis)	1.2455	1.2464	1.2456

---

* During the last half hour of electrolysis (total time approximately 10 hours) the solution containing 2% gelatin and 1.25 M. $CuSO_4$ gelatinized. This increased the resistance somewhat and as a result the current density fell. It did not fall below 1.5 amperes per square decimeter, however. *It is for this reason that no excess weight is recorded for this cell.*

The two important features of these observations show that first, for all concentrations of copper sulfate employed a limiting value of excess weight is reached, the limiting value being greatest in the most dilute solutions and second, that the excess copper increases with gelatin content, although at a decreasing rate with increasing gelatin content. The form of the curves in Fig. 6 are somewhat more rounded than in Figs. 4 and 5. This variation is likely not a real one but is due to the fact that the curves of Fig. 6 are based upon three experimental points, whereas those of the previous figures are based upon five.

A discussion of the bearing of this data upon our problem will again be postponed until all of our data have been presented.

Excess Weight and Time

From our data we have calculated the dependence of the mass of the cathode deposit upon time. If the entire mass of the deposit arises from electrolytic causes then the mass of the deposit at a constant current should be proportional to time. Comparisons of deposits to coulometer deposits at a given current and current density show that the two are roughly proportional over small differences of coulometer deposits. For greater differences of coulometer deposits, the mass of the deposit depends upon several factors including concentration of gelatin, concentration of copper sulfate, temperature, etc. The data of the following table is a specific example.

TABLE IX

1 M $CuSO_4$ at 2 amp/dm², 30°C.

Conc. of Gelatin	Series 1		Series 2			
	Deposit	Excess Cu.	Deposit	Excess Cu.	Deposit, Calculated	Calculated Excess Cu.
0.% (Coulometer deposit)	0.3684 gms.	—	1.2462 gms.	—		
2.%	0.3846	0.7 mgm	1.3181	8.3 mgm	1.3010	2.36 mgm
0.5%	0.3847	1.7	1.2950	4.6	1.3013	5.75
0.06%	0.3740	1.9	1.2657	3.2	1.2651	6.43

Under each coulometer deposit is given the mass of the deposit obtained from cells in series with it but at various concentrations of gelatin. In column six are given the masses of the deposits obtained by multiplying the data under the smaller coulometer deposit by the ratio of the coulometer deposits, $\frac{1.2462}{0.3684}$. These values should be identical with those of the fourth column, if proportionality to coulometer deposits exists. Since the current and current density are the same in both cases, the mass of the coulometer deposits are proportional to time. It is evident that the deposits are not strictly proportional to time.

On the other hand in a 0.5 M copper sulfate solution containing 0.5% gelatin at 25° when electrolyzed at a current density of two amperes per square decimeter, the mass of the deposits were found to be practically proportional to coulometer deposits for deposits whose masses lay between 0.7 grams and 1.7 grams; below the lower value considerable discrepancies from the proportionality occurred. In general, exact proportionality is not the rule.

Excess Weight and Temperature

As is well known, the extent of adsorption at a solid-liquid interface diminishes markedly with rising temperature, but is with less influence upon the magnitude of many electrode potentials. As the data obtained up to this point, resembles in some measure adsorption phenomena, we have carried out several series of experiments at temperatures ranging approximately from 20°C to 40°C to determine the effect of temperature upon the magnitude of the excess deposit. Deposits of approximately a gram were made at the temperatures 21°C, 25°C, 30°C, and 39°C. The solutions contained 0.5% gelatin and were made 0.5 M with respect to copper sulfate and electrolyzed at a current density of 2 amperes per square decimeter. In order to show the various series of trials graphically the deposits were all computed (by simple proportionality) to the mass of deposit equivalent to one gram of copper in the coulometer deposit. As the deposits were all very close to one gram in mass, no great error was introduced as the results of the previous section (on excess weight as a function of time) has already shown. The results are shown in Fig. 7.

The point plotted at 21° was the average of 8 determinations, those at 25° and 30° of three trials each, and that at 39° was the mean of six values. The individual values are given in Table X, where the excess weights are given in milligrams. Each of these deposits was analyzed for copper and the weight of copper produced in the redeposit above that of the coulometer deposit is recorded below as "excess copper."

TABLE X

21°C		25°C		39°C	
Exc. Wt.	Exc. Cu.	Exc. Wt.	Exc. Cu.	Exc. Wt.	Exc. Cu.
62.3	7.3	51.2	6.3	31.1	2.6
61.9	—	51.2	6.9	29.2	0.9
62.4	7.3	52.5	6.9	28.1	2.3
60.	8.5	30°C		28.1	1.5
61.9	8.8	Exc. Wt.	Exc. Cu.	30.6	2.7
59.5	9.4	43.8	3.0	30.7	3.3
58.7	8.1	41.7	4.7		
57.2	7.2	41.9	3.9		

Gray[1] has pointed out that the deposit obtained from a solution of pure copper sulfate is also a function of temperature, diminishing slightly in mass as the temperature rose. Gray's work was based upon solutions containing nearly double the concentration of copper sulfate used in our above trials. This diminution in mass (which is relatively small) has been ascribed to the increasing solvent action of the copper sulfate solution as the temperature rises.[2]

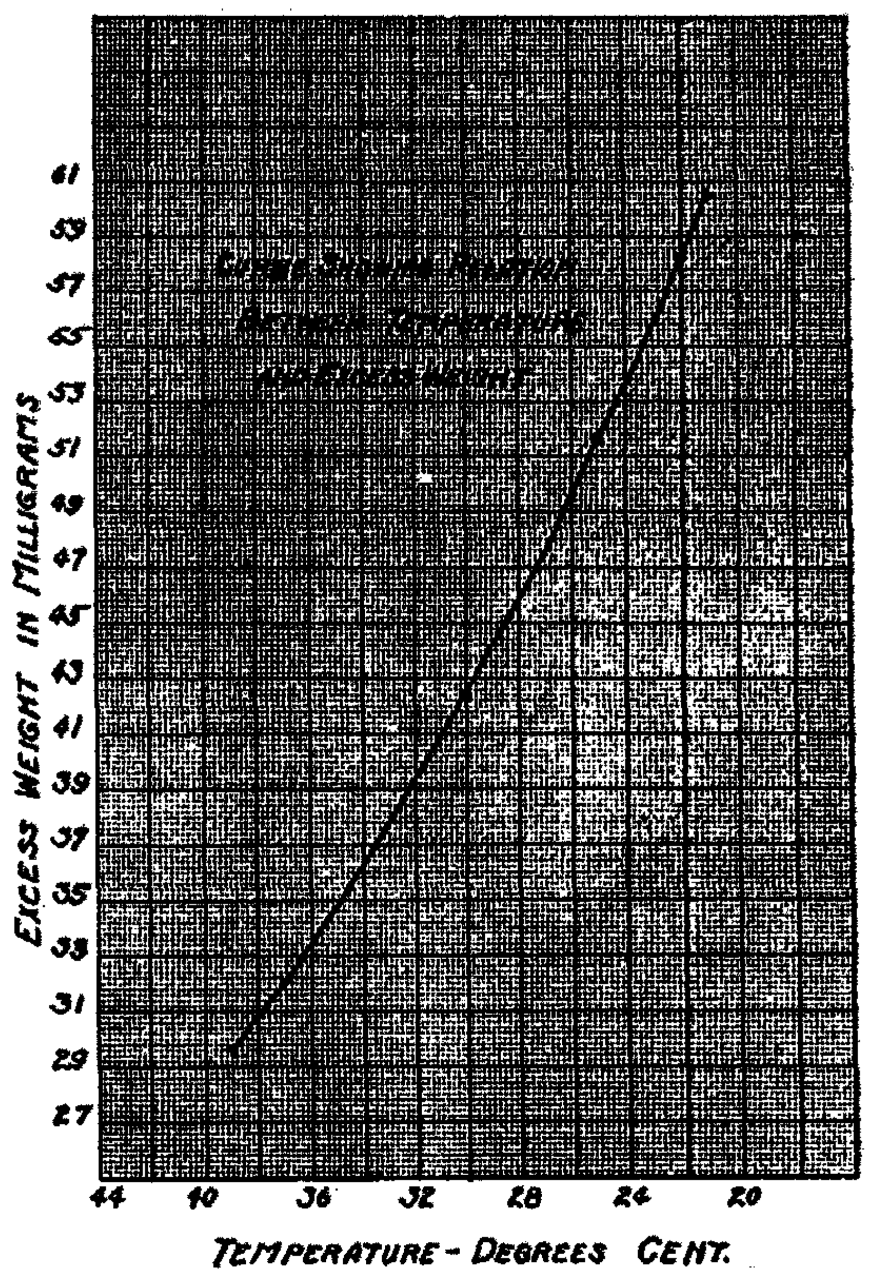


Fig. 7

In our more dilute solutions the mass of the deposit increases slightly with increasing temperature in baths containing no gelatin but obtained otherwise under conditions exactly similar to those stated in Table X. For example in a bath 0.5 M with respect to copper sulfate but containing no gelatin the excess deposit (for a coulometer deposit of 1 gram) was 2.5 milligrams at 21°C; at 30°C the excess deposit was 6.1 milligrams. The differences between our results and those of Gray's may be attributed to the decreased solvent

---

[1] Phil. Mag., (5) 25, 183 (1888).

[2] Richards, Collins, and Heimrod: Proc. Am. Acad. Arts Sci., 35, 123 (1899).

action in the more dilute solution and the increased hydrolysis of the dilute solutions; this increased hydrolysis results in the formation of a greater supply of cupric (and cuprous) hydroxide and its subsequent adsorption by the electrode. The data upon excess copper confirms this view as it will be noted there is always "excess" copper present and that the excess copper diminishes at a different rate than does the excess weight with rising temperature; evidently the increased solubility of copper in the copper sulfate solution as the temperature rises accounts for the diminution of this excess copper. It is evident from our data, then, that the gelatin content of the deposit (which forms the larger part of the excess weight) diminishes very rapidly with increasing temperature.

C. The Influence of Gelatin upon the Polarization at the Cathode during Deposition of Copper

Many workers in this field have recognized the usefulness of determining the magnitude of polarization during electrolysis as an aid in determining the mechanism of the electrode process. Blum in particular has emphasized this mode of attack.

Obviously, of the various methods of measuring polarization, one must be chosen that will give the average value of polarization over the entire cathode surface. Our results in Section A can only be interpreted by assuming that different areas of the cathode are at different potentials, as the processes taking place vary from locality to locality over the cathode surface. The method of Haring[1] while doubtless not as precise as other methods, is admirably adapted for our present needs, and was the method which we have employed in the present investigation. The method, in brief, consists in the employment of a cell, divided by means of two copper gauze partitions into three equal compartments, and containing at the two ends of the cell, the cathode and anode, respectively, of the same dimensions as the gauzes. The potential drop across each compartment is then measured while the current is flowing through the cell; that across the middle compartment is assumed to be due wholly to the IR drop. That across the other two compartments is due to the IR drop plus the cathode (or anode) polarization. As the compartments are made of equal dimensions the IR drop in each will be the same and consequently the cathode (or anode) polarization will be the differences in potential across the cathode (or anode) compartment and the middle compartment. As will be seen this method gives the average polarization over the entire surface of the electrode and not that due to any particular area.

The cell which we employed was constructed of wood and was approximately 20 centimeters in length and 2.6 cm. in cross section. The interior of the cell was thoroughly coated with a black asphalt paint which was found to be insoluble in the copper sulfate solutions used. Two copper sheet electrodes, 2.5 centimeters in cross section were then cemented into the cell with the same asphalt, the distance between these electrodes being exactly 15

---

[1] Trans. Am. Electrochem. Soc., 49, 417 (1926).

centimeters. Two 14 mesh copper gauze partitions were also cemented into the cell, dividing it into three compartments, each 5 centimeters in length. Each electrode and gauze was cut with a considerable lead, to which was soldered the leads to the potential measuring device. Before each trial the electrodes and gauzes were given a heavy coat of electrolytic copper from an acid plating bath.

Potentials were measured by the use of a Leeds and Northrup student potentiometer having a range of 0 to 2.2 volts, the current through the potentiometer being adjusted to its proper value by a certified standard cell. In some instances the drop of potential across the cathode compartment exceeded the range of the potentiometer and in these instances a potential divider, constructed of precision resistances, was employed and exactly one-half (or in some cases, exactly one-third) of the potential drop was measured. By means of suitable switches the potentials across the compartments, after considerable practice, could be very rapidly determined. The anode polarization was also measured as it required but little additional effort to obtain it. We have not considered it in our discussion, however, as we were interested only in the cathode process, but have included it for the sake of any who might be interested in such data.

Our actual measurements of polarization were made as follows: The cell, having been thoroughly cleaned was placed in a large glass cell, which was in turn immersed in a water thermostat whose temperature was automatically kept constant. The temperature within the glass cell was 25° ± 0.1° for all the measurements recorded. The control of temperature was necessary as it was soon found on attempting polarization experiments at room temperature that the value obtained fluctuated with comparatively small differences of external temperature.

The electrolyte was added to the cell until it just reached the top of the electrodes and gauzes, thereby giving a cross sectional area of electrolyte very nearly equal to 6.25 square centimeters. As soon as the temperature of the electrolyte had reached 25° the current was allowed to flow through the cell. Regulation of this "working" current was obtained by means of a sensitive rheostat included in this circuit. Preliminary trials had given us a knowledge of the proper setting of the rheostat for a desired current, the magnitude of which was measured by means of a precision ammeter placed in series with the cell. Approximately one minute after the circuit was closed the ammeter became steady at the desired current and polarization readings were taken in the order cathode, middle, and anode compartments. These readings required about one minute to complete; two or three minutes were then allowed to elapse and a second set of polarization values taken. These, in general, differed from the first set by one or more millivolts. After several minutes a third set of data was recorded; the final polarization values at this current density being obtained by the averaging of the three sets of data. As soon as the third set of readings had been obtained, the working current was adjusted to a higher value and three sets of data again obtained as outlined above. This procedure was carried out over the entire range of our experiments the current densities of which were varied between 0.16 and 3.20 amperes per square decimeter. The majority of the polarization measurements were made upon solutions containing one-half of one gram mole per liter of copper sulfate. These were compared with similar solutions containing in addition one-half of one per cent of ash-free gelatin.

Duplicate determinations were made in each instance. The data for 0.5 M copper sulfate at 25° is presented in Table XI and for a similar solution containing 0.5% gelatin in Table XII. The polarization values are expressed in millivolts, results for the first trial being recorded under I, and for a second solution under II.

TABLE XI

Current Density Amps/dm^2	Cathode polarization		Anode polarization	
	I	II	I	II
0.16	31.	39.	9.	2.
0.32	41.	50.	21.	10.
0.48	55.	61.	30.	20.
0.64	71.	72.	39.	33.
0.80	87.	84.	46.	42.
0.96	100.	98.	49.	46.
1.12	117.	113.	51.	49.
1.28	133.	129.	54.	54.
1.44	149.	145.	57.	57.
1.60	164.	162.	59.	62.
2.00	208.	201.	69.	72.
2.40	256.	245.	77.	83.
2.80	296.	295.	84.	99.
3.20	345.	339.	105.	112.

TABLE XIII

Current Density Amps/dm^2	Cathode polarization		Anode polarization	
	I	II	I	II
0.16	159.	164.	10.	1.
0.32	156.	140.	24.	5.
0.48	176.	168.	33.	8.
0.64	199.	188.	41.	13.
0.80	214.	207.	46.	19.
0.96	355.	365.	49.	25.
1.12	386.	409.	53.	33.
1.28	412.	441.	58.	38.
1.44	434.	470.	63.	44.
1.60	453.	490.	66.	49.
2.00	506.	542.	75.	61.
2.40	555.	597.	86.	76.
2.80	612.	639.	104.	95.
3.20	651.	686.	129.	128.

It will be noticed that polarization in the copper sulfate solution is very nearly a linear function of the current density whereas in the bath containing gelatin, the values are initially much higher and furthermore show a considerable rise at a current density of 0.8 amperes per square decimeter. This point will be considered again in the discussion which follows. The variation of the polarization values with current density can more clearly be seen in graphical form which we have presented in Fig. 8. The experimental points in these diagrams are the average values of both trials. As will be seen from Tables XI and XII, the polarization values are more reproducible in the copper sulfate solution alone, than when in the presence of gelatin.

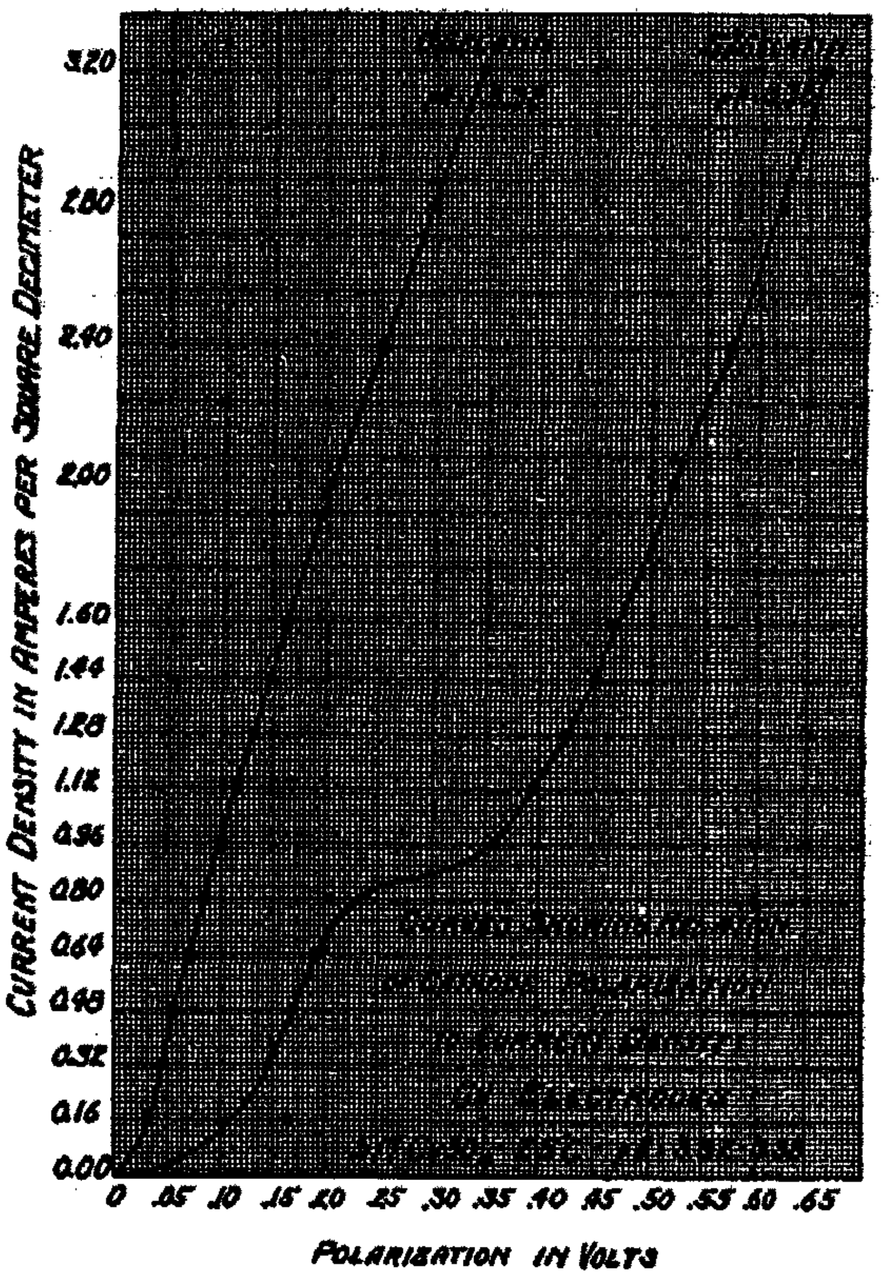


FIG. 8

In addition to determining the polarization values with copper cathodes, measurements were made substituting a platinum cathode for that of copper. Our reason for this step was to furnish polarization data more directly comparable to that obtained in the determination of our excess weights as described in Section B. It will be recalled that in those instances the cathode was always of platinum. The polarization values with the two types of cathodes would not be expected to be greatly different save for a possible initial difference, for after electrolysis had proceeded for some time we would, in either case, be dealing with a copper cathode. On the other hand, as the base metal influences to some extent the form of the deposited metal, there might possibly be considerable difference in the two cases. In order to make certain of the magnitude of these differences, measurements with a platinum cathode were carried out. The data are presented graphically in Fig. 9 each point again representing the average of six measurements (two solutions).

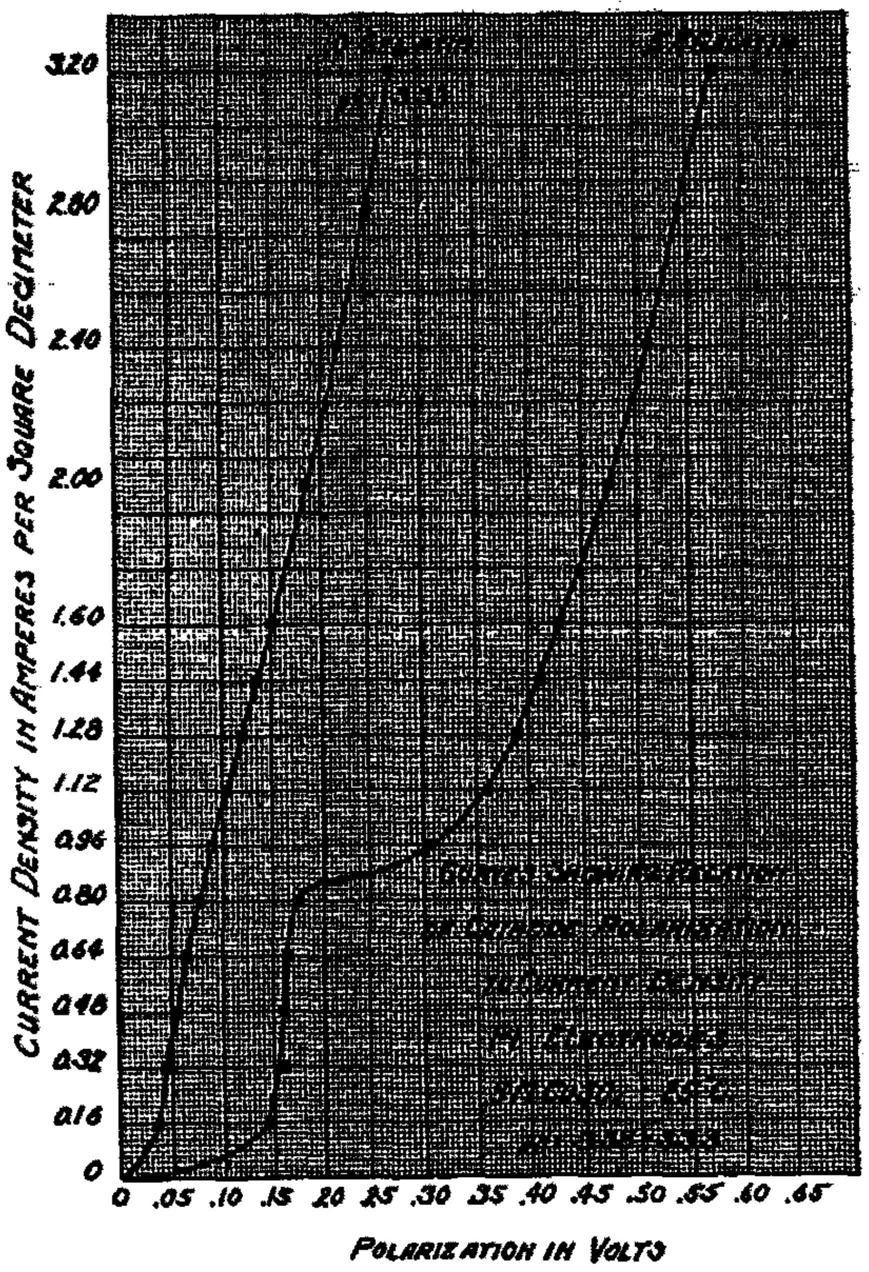


FIG. 9

When these are compared with the curves of Fig. 8 it will be noticed that the general form of the functions is the same whether a platinum cathode be used or a copper one. The values for the cathode polarization at each current density are, however, somewhat greater for the copper cathode than for the platinum cathode. We attributed this difference to the fact that the grain size of the deposits was somewhat smaller when depositing upon platinum than upon copper. The effective current density in the case of deposition upon platinum would therefore be somewhat smaller than for the same value of applied current in the case of copper and consequently a lower value of polarization would result.

Discussion of Results

Of the various views which have been advanced to explain the mechanism of the cathode processes under study we believe that our data is more satisfactorily explained by regarding the inclusion of gelatin in the copper deposit as a purely adsorption or surface phenomenon. That it is a case of simple occlusion within the interstices of the deposit is clearly not tenable, for in this case the excess weight should increase continuously with increasing gelatin content, and further should become greater (rather than smaller) as the temperature rose.[1] Such is not the case as an examination of Figs. 4-7 will show. For the same reason it is not probable that the gelatin finds its way into the cathode deposit as a result of electrolytic discharge of gelatin ions or particles, as under these conditions the amount of excess deposit should likewise increase continuously with increasing gelatin content in the bath. This case would be somewhat analogous to the deposition of alloys, say of copper and zinc from a solution containing both copper and zinc salts. In such cases it has been found that for a fixed amount of one metal in solution the proportion of the second metal in the deposit becomes greater as the amount of the second metal in solution becomes greater.[2] Not in direct proportion, to be sure, but nevertheless no limiting value is indicated in the data available in the literature for such cases.

The view that the gelatin is found in the deposits as a result of the discharge of complex ions containing gelatin and copper is only at all tenable on the assumption that other processes than the discharge of simple cupric ion and complex ion are taking place. For if only these ions were discharged the mass of the copper in the deposit, should in every instance, be considerably less than the mass of copper produced in the coulometer deposit. Our data, however, show that there is always more copper in these deposits than in those obtained from the coulometers.

That other processes than the discharge of simple cupric ion may take place at the cathode we freely admit. Any hydrolysis of cupric or cuprous sulfate to their respective hydroxides, would produce small amounts of these insoluble substances in the vicinity of the electrodes. These hydroxides may be adsorbed by the metallic copper of the electrode. We believe that this is the explanation of the excess copper found in those baths containing no gelatin, and in part, is the explanation for the excess copper found in those baths containing gelatin. Another possible process which would tend to increase the copper content of the deposit over that of the coulometer deposit

---

[1] Increasing temperature tends to increase the size of the crystals of electrodeposited copper, and hence for the same mass of copper deposited the volume of the interstices should become greater.

[2] See for example the data of Ferguson and Sturdevant: Trans. Am. Electrochem. Soc., 38, 176 (1920).

would be discharge of cuprous ion. Cuprous ions are undoubtedly present and might owe their origin to at least three processes: (1) to the solution of the cathode, according to the equation $Cu^{++} + Cu = 2Cu^{+}$; (2) to the solution of the anode, according to the equation $Cu - \epsilon = Cu^{+}$; (3) the reduction of cupric ion by the gelatin itself. Any cuprous ions formed as a result of (1) above, however, would, if discharged, mutually cancel their effects if the efficiency of the cathode process is computed upon the basis of discharge of cupric ion. The possibility of cuprous ions being formed as a result of (3) above has been tested experimentally by treating 0.5 gram of ash free gelatin dispersed in 70 cc. of water by 35 cc. of standard Fehling's solution in the cold. No red cuprous oxide was produced even after standing 48 hrs. A similar solution gave a very slight residue of the red oxide after boiling and standing hot for several hours. It should be noted that conditions are presumably far more favorable for reduction in the highly alkaline Fehling's solution than in the slightly acid solutions which actually existed in our electrolytic cells. It should also be stated that the amount of cuprous oxide formed by boiling the solution depended upon how long the solution was allowed to remain hot. If chilled immediately after boiling the mass of precipitate was a very small fraction of that obtained when the solution was allowed to remain hot for several hours. It would appear that the reducing ability is the result of chemical action of the hot alkaline solution upon the gelatin, forming other substances which possess reducing properties.

As a result of the second possibility mentioned above, cuprous ions are formed in neutral solution.[1] Such ions could only reach the cathode as a result of migration and convection. If it be assumed that initially the concentration of cuprous ions is so small as to preclude the possibility of discharge of cuprous ions, such ions would tend to accumulate about the cathode. When the concentration of cuprous ions had become such that the potential Cu/Cu^{+} had been raised to the operating electrode potential, discharge of cuprous ion would commence. In this case the proportion of excess copper, as we have defined it, would tend to show marked increases with the passage of time. In the majority of cases which we have examined, the reverse seems to be true (See Table IX) i.e. the proportion of excess copper diminishes as the electrolysis is continued.

Further, Richards, Collins, and Heimrod have shown that at a current density of 1 amp/dm² at 0°C the cathode deposits from a solution of "neutral" copper sulfate (approximately 0.4 M) when compared to deposits of silver obtained from the silver coulometer, lead to atomic weights of copper ranging from 63.53 to 63.55 depending upon the size of the cathode used, but computed upon the basis of divalent copper. The present accepted value for this atomic weight is 63.57, so that discrepancies arising from the deposition of cuprous ion could not amount to more than four parts in sixty-three hundred. Although many of our results were obtained under conditions of current density, temperature, and concentration different than that of these

---

[1] Kiliani: Berg. Hütt. Z., 44, 294, (1885).

investigators, the small difference obtained when comparing our deposits to those obtained from the copper coulometer, indicates to our minds that the discharge of cuprous ion plays an extremely small part in the electrode reaction. The maximum variation which we have observed (from some hundreds of quantitative experiments) between the mass of the coulometer deposit and the total copper in a given deposit amounted to nine parts in a thousand, and this in a case where the copper sulfate was 0.25 M. This large value may well have come as a result of hydrolysis and adsorption of copper oxides rather than discharge of cuprous ion. For these reasons, then, it does not appear likely that discharge of cuprous ion plays a more important part in baths containing gelatin than those that are free of gelatin.

One further point bearing upon the matter of excess weights is the fact that the composition of the excess weight is not constant, but depends upon several factors. While this would probably be true no matter what the cathode processes might be, in case of discharge of complex ion the proportion of the excess copper should show a tendency to become less as the gelatin content increases. That this is not so, can be seen from the following table which is computed from the data of Table VIII.

TABLE XIII

Ratio of excess Cu to excess weights (%)

Conc. of copper sulphate	Gelatin content		
	2%	0.5%	0.06%
1.25	—	12.3	23.7
1.	11.5	9.5	16.5
0.75	12.6	10.	18.2
0.50	12.2	8.3	8.7
0.25	10.	10.7*	15.7

With the exception of the starred value the magnitude of the ratio shows a minimum value at a gelatin content of 0.5%.

The polarization data which we have found tend also to confirm our belief as to the mechanism of the electrode process, altho some explanation and confirmatory evidence are required. An examination of Figs. 8 and 9 shows that at a current density of approximately 0.8 amperes per square decimeter the polarization values increase quite sharply. This rapid increase of polarization, might at first thought be indicative of a change in the nature of the cathode process. That is, if the process below this value had been discharge of cupric ions solely, this new level might indicate discharge of cuprous ion, of complex ion, of hydrogen ion, etc. If any one of these processes occurred however, a marked change in the mass of the cathode deposit as compared to that of the coulometer deposit, should occur if compared at current densities above and below 0.8 amperes. We, therefore, determined the magnitude of the excess weight as a function of current density for a

0.5 M solution of copper sulfate containing one-half of one per cent of gelatin at 25°C. The values for seven current densities are given in Table XIV and are shown graphically in Fig. 10.

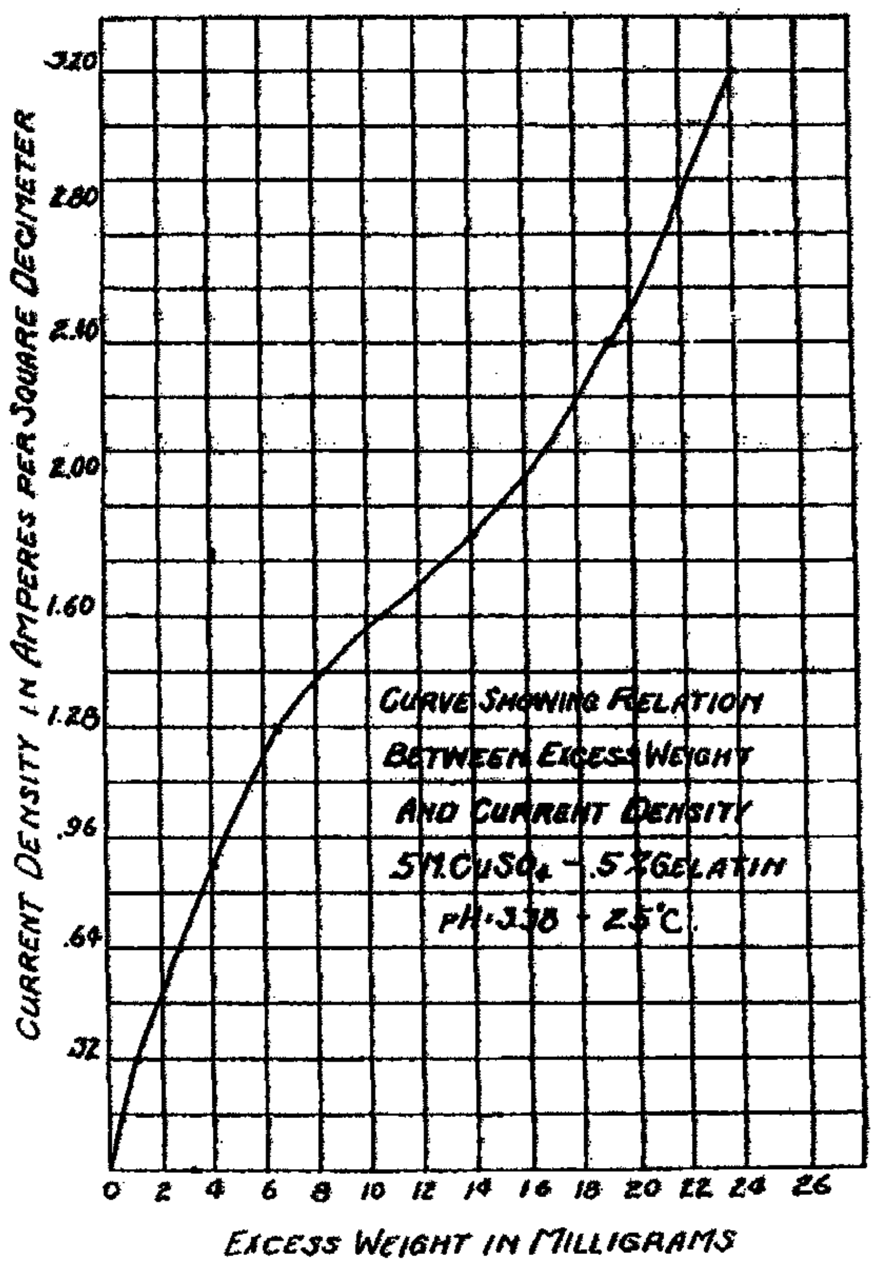


Fig. 10

Table XIV

Current density amp/dm²	Coulometer deposit grams	Deposit grams	Excess weight grams
0.32	0.0471	0.0481	0.0010
0.64	0.0942	0.0968	0.0026
0.88	0.1296	0.1336	0.0040
1.28	0.1883	0.1948	0.0065
1.84	0.2710	0.2852	0.0142
2.40	0.3536	0.3730	0.0194
3.20	0.4720	0.4921	0.0241

Inspection of Fig. 10 shows that the marked increase in polarization can scarcely be attributed to a change in the type of electrode process and that further search must be made for its origin.[1] One of the first explanations to suggest itself to us, was that the increased polarization results from mechanical causes. For example, following the suggestion of Frolich, there is the possibility that the increasing content of gelatin in the film of liquid immediately contiguous to the electrode reaches such a value that gelation sets in. A large increase in gelatin content of the film would not be necessary, as we have found that solutions containing copper sulfate tend to lower the setting point of gelatin, for example a 1 M solution of copper sulfate containing 1% gelatin, sets to a gel in a few hours at 25°. If the polarization is due to this cause, however, it should be function of time alone provided the current density were kept constant at 0.8 amperes. To check this point, several polarization measurements were made upon 0.5 M solutions of copper sulfate containing 0.5% of gelatin at 25° and at a constant current density of 0.8 amperes per square decimeter, for periods of time as long as three hours. No increase in polarization was observable as an inspection of Fig. 11 will show. We, therefore, concluded that the increased polarization was not due to mechanical causes.

It is essential, of course, that an explanation of this marked increase in polarization be made. Our data apparently indicates that it is not due to a change in the nature of the electrode process, nor to mechanical causes. It has long been known that cathode polarization in cells containing complex ions is far greater than in cells containing supposedly simple metal ions. A number of explanations of this increased polarization have been advanced and we have turned to such explanations to account for the increase in polarization in this case. Thus Cady and Groening[2] have suggested that the formation of complex ions would cause a change in the rate of increase of electrode potential with current. Their argument is briefly as follows: In a solution of a simple salt, such as silver nitrate, the cathode process is solely

$$Ag^+ + \epsilon = Ag$$

at low potentials. As the current is increased, the supply of silver ion in the immediate neighborhood of the cathode is diminished, and if not replenished

---

[1] As can be seen from the data of Table XIV different masses of copper are obtained in each trial, *i.e.* the time of electrolysis was the same in each case. It would be more logical to compare the excess weights for the same mass of copper deposited. However, if the deposits in the cells containing gelatin are reduced to similar conditions (by multiplying the mass of the deposit by the ratio of the coulometer deposits) the same effect is still noted. Thus converting the mass of the deposits to the deposit equivalent to 0.1296 grams of coulometer deposit gives in the first five cases

Current density	Mass of deposit	Excess weight
.32	0.1324 gms.	2.8 mgms.
.64	0.1332	3.6
.88	0.1336	4.0
1.28	0.1341	4.5
1.84	0.1364	6.8

[2] J. Phys. Chem., 30, 1597 (1926).

by migration, convection, or dissociation of complex ions, may result in some other electrode process occurring such as the liberation of hydrogen for example. Let it be assumed that an equilibrium such as

$$Ag^+ + nH_2O \rightleftarrows [Ag\ (H_2O)n]^+$$

has taken place, but that the reverse process is not an instantaneous one but requires an appreciable fraction of time to occur; increased potential (which is polarization) must therefore be applied to obtain the same electrode process. The additional energy involved would be assumed to compensate the energy required for the reversal of the above process.

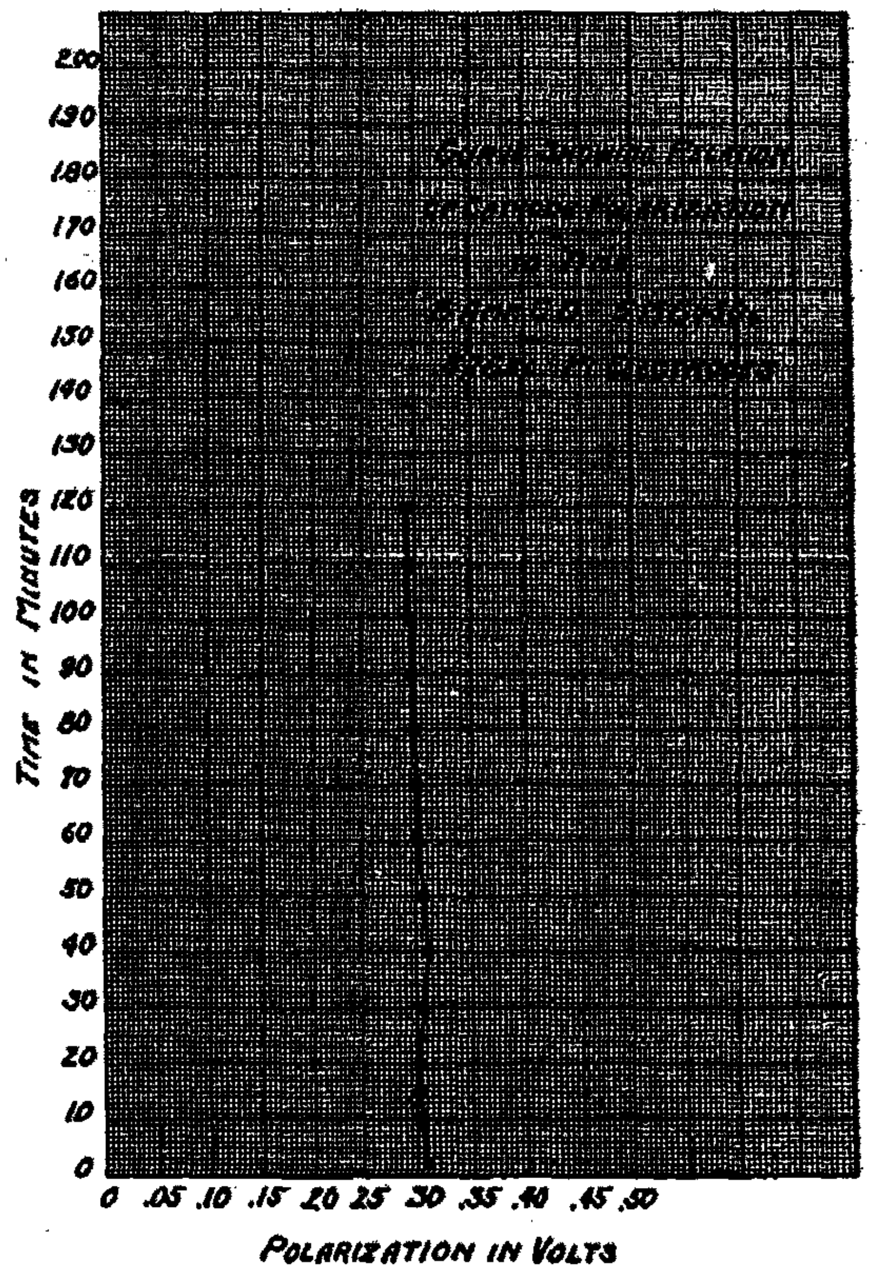


Fig. 11

In our particular case the increased polarization is explainable by modifying the assumption of Cady and Groening to fit our particular case. Let it be assumed that gelatin forms complex cations with copper; this is certainly justified when one considers the hydroxy and amino-like character of gelatin and the known ability of copper to react with hydroxy and amino (ammonia, for example) bodies.[1] In the case of electrolysis at lower current densities than 0.8 amperes per square decimeter the discharge of cupric ion will care for the current passing from solution to cathode. Above this current density, cupric ions are not supplied at a sufficiently rapid rate by convection and migration and demand must therefore be made upon the reserve supply of copper ions available in the complex cation. If this process, i.e.

$$(Cu\ (Gel)n)^{++} \rightleftarrows Cu^{++} + nGel.$$

is not instantaneous and requires energy, an increase in potential must occur if the same electrode process is to continue.[2]

Such a view is in accord with the experimental facts as we know them at present. It should be noted that there is a distinction between *formation* of complex ions and *discharge* of complex ions. We are assuming and grant that complex ions do occur in solutions of copper sulfate containing gelatin, but that the electrode process is primarily one of discharge of cupric ions.

Fuseya and Murata, and Fuseya and Nagano advocate the view that addition agents function as the result of discharge of complex cations formed from addition agent and metal ion, but present no direct evidence for this difficult problem. To our minds, it seems very unlikely that such complex ions would be discharged when it is recalled that deposits of very pure copper can be obtained from baths containing such complex ions as $(Cu(CN_2)^-$ and $(Cu(NH_3))_4^{++}$. The processes here doubtless take place by discharge of simple ion and dissociation of complex ion; it is also to be noted that the complex ion formation in the two cases cited above is probably far more complete than they would be in cases of solutions containing a large supply of copper ions and very small concentrations of gelatin.[3]

Of the various views which have been advanced to account for the presence of gelatin in the deposit, there apparently remains only that of adsorption. The positive evidence of this explanation as the correct one lies in our data involving the excess weight and the form of our deposits. The form of our excess-weight-gelatin-content curves resemble those of familiar adsorption phenomena. That these diagrams are directly comparable to adsorption curves will be evident from the following considerations. In each of a series of runs upon which these curves are based, the copper deposited electrolytically is approximately the same. We are assuming in these cases that copper is the adsorbent and therefore the difference between the weight

---

[1] There seems to be additional evidence for complex ion formation from determinations of the transport number of copper ion in the presence of gelatin, as has been done by Mutscheller (Chem. Met. Eng., 13, 353 (1915).) Mutscheller's interpretation of his data is, to our minds, entirely erroneous, no account being taken of changes in the concentration of gelatin before and after electrolysis.

[2] Isgarischew: Kolloidchem. Beihefte, 14, 25 (1921), has advanced a somewhat similar explanation of this polarization phenomenon.

[3] While the results of these investigators are based upon other addition agents than gelatin, they imply that their assumptions hold for this material as well.

of the deposit in any one case and of the copper deposited electrolytically represents the weight of the material adsorbed by the copper.[1]

If these differences are due to adsorption, plotting their values against the gelatin content of the solution should give curves similar in form to adsorption curves if the process is actually a surface phenomenon. There is this difference to be noted, however; as the gelatin content increases, the size of the copper crystals deposited tends to decrease and hence for the same mass of copper, the specific surface is greater in those solutions containing greater

---

[1] It is recognized that the excess weight is not entirely due to gelatin. A small part of it is due to "excess" copper as we have already pointed out. The form of the curves obtained, however, are the same whether excess weight is plotted as a function of gelatin content, or whether excess weight minus excess copper is used as the ordinate.

It should also be stated that in the cathode deposits from baths containing gelatin, sulfate is found, a fact which Marie and Buffat have already pointed out. Analysis for small quantities of sulfates in the presence of gelatin we found very difficult to carry out. However, a number of attempts were made, the analyses being conducted by dissolving the cathode deposit with nitric acid, evaporating to dryness, and cautiously igniting to destroy the gelatin. The residue was then redissolved in nitric acid and the usual sulfate determinations made upon this solution. The following table gives the results of such a series of analyses where duplicate cells were run; the cathode from one of a pair of duplicate cells being used to determine excess copper, and the second, sulfate.

TABLE XV

Copper and sulfate analyses from electrodes prepared from 0.5 M $CuSO_4$ at 1 amp/dm^2, and at 30°C.

	2.0% gel.		0.25% gel.		0.03% gel.	
Deposit—grams	0.3952	0.3944	0.3930	0.3938	0.3825	0.3823
Exc. wt., mgm.	17.5	16.7	15.3	16.1	4.8	4.6
Analyses for	Cu	$BaSO_4$	Cu	$BaSO_4$	Cu	$BaSO_4$
gave, grams	0.3800	0.0053	0.3789	0.0051	0.3787	0.0024
Excess copper, mgm.	2.3		1.2		1.0	
$CuSO_4$ corresponding to excess copper	5.7		3.0		2.5	
$CuSO_4$ corresponding to $BaSO_4$		3.6		3.5		1.6
Same conditions as above, but at 2 amps/dm^2						
Deposit, grams	0.4024	0.4025	0.3956	0.3956	0.3829	0.3829
Exc. weight, mgm.	24.4	24.5	17.6	17.6	4.9	4.9
Analyses for	Cu	$BaSO_4$	Cu	$BaSO_4$	Cu	$BaSO$
gave, grams	0.3804	0.0107	0.3794	0.0096	0.3787	0.0050
Excess copper, mgm.	2.4		1.4		0.7	
$CuSO_4$ corresponding to excess copper	6.0		3.5		1.7	
$CuSO_4$ corresponding to $BaSO_4$		7.3		6.6		3.4

Coulometers

1 Amp.	C.D.	2 Amps..	C.D.
.3775	.3780	.3780	.3779

As will be seen the amounts of sulfate present are of the same magnitude as the excess copper. This sulfate presumably finds its way into the deposit as a result of occlusion of copper sulfate or complex formation with the gelatin. Possibly the adsorption, which we postulate, is one of neutral particles of gelatin sulfate or of copper gelatin sulfate.

It might be of interest in passing to state that we have made analyses of sulfate upon the coulometer deposits but the sulfate found therein is negligibly small, amounting in the maximum case to less than one-fiftieth of one per cent; which small amount may have come from the reagents employed in making the analyses.

proportions of gelatin. This may account for the very rapid rise of the adsorption curves as shown in Figs. 3, 4 and 5 as compared to the more familiar rounded curves so typical of adsorption. Very likely, too, this matter of specific surface in a large measure accounts for the differences between excess weights found in solutions containing the same concentration of gelatin but different concentrations of copper sulfate. (See Fig. 6). As is well known, the grain size of the deposit is a function of the metal ion concentration and hence of the salt content. Variations in salt content would therefore tend to produce masses of different specific surfaces.

Further it is to be noted that limiting values of the excess weight as a function of gelatin content are obtained under all conditions of current density and concentration of copper sulfate which we have employed. The influence of temperature upon the mass of the excess weight also is in line with adsorption data, as the mass of material adsorbed per unit mass of adsorbent diminishes, as is well known, in all cases involving surface adsorption, with rising temperature.

Still another line of evidence tending to support the adsorption theory is the fact that the mass of the excess weight is not an easily reproducible quantity. That is, in two cells which are exact duplicates of each other as nearly as is experimentally possible, the masses of the deposits are rarely the same when electrolyzed under the same conditions. While the same is true of coulometer deposits, the magnitude of the differences is generally far greater in cells containing gelatin. An examination of those cases in our data where duplicate determinations were carried out, shows this very clearly. For example in two cells containing 0.5 M $CuSO_4$ and 0.25% gelatin, electrolyzed at a current density of 0.5 amperes per square decimeter at 30°C, the masses of the two deposits were 0.3872 and 0.3896 grams. The two coulometer deposits in the same run were 0.3783 and 0.3787 grams (an unusually large variation for duplicate coulometer deposits). The difference between the deposits in the baths containing gelatin is 2.4 milligrams and between the coulometer deposits is 0.4 milligram. This lack of exact reproducibility we ascribe to the possibility that different faces and positions of the copper crystals occur as they are deposited and hence different effective adsorbing areas are produced in the two cells.

Bearing upon the matter of addition-agent-action in general, it should be pointed out that the fact that the mass of the deposit increases to a limiting value with increasing content of addition agent is by no means restricted to the case of gelatin. The data for such evidence in the literature is meager but Datta and Dhar[1] have unwittingly provided several cases. These investigators compared copper coulometers containing varying quantities of cane sugar and of tartaric acid with silver coulometers. Each concentration of cane sugar (or of tartaric acid) was carried out as a separate experimental procedure and consequently different quantities of electricity were employed.

---

[1] J. Am. Chem. Soc., 38, 1156 (1916).

If the masses of the cathode deposit are all recomputed to the same mass of silver[1] (and therefore to the same quantity of electricity) by multiplying the mass of the cathode deposit by the ratio of the silver deposits in the two cases, it can be seen that limiting values of the deposit are reached with increasing quantities of cane sugar or of tartaric acid. We have recomputed the values of Datta and Dhar in this way and have shown the deposits as functions of the cane sugar and tartaric acid content graphically in Figs. 12 and 13, respectively. It will be noted that the last experimental point in the case of both the sugar and the tartaric acid solutions is somewhat lower than the limiting values. These two cases could be attributed either to the liberation of hydrogen or the electrolytic reduction of the addition agent, as these concentrations of cane sugar and tartaric acid are quite large (30 and 32 grams of water respectively).

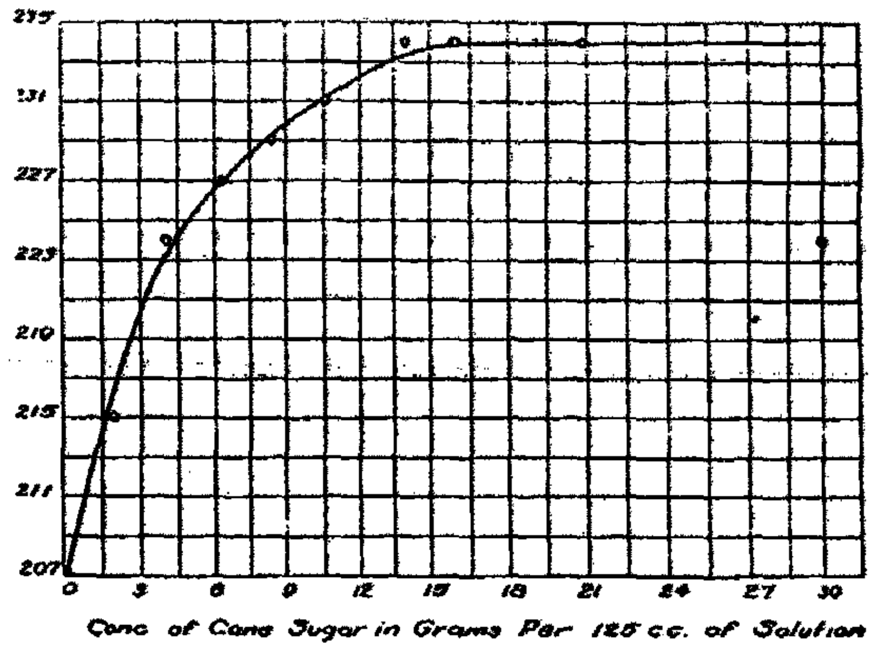


FIG. 12

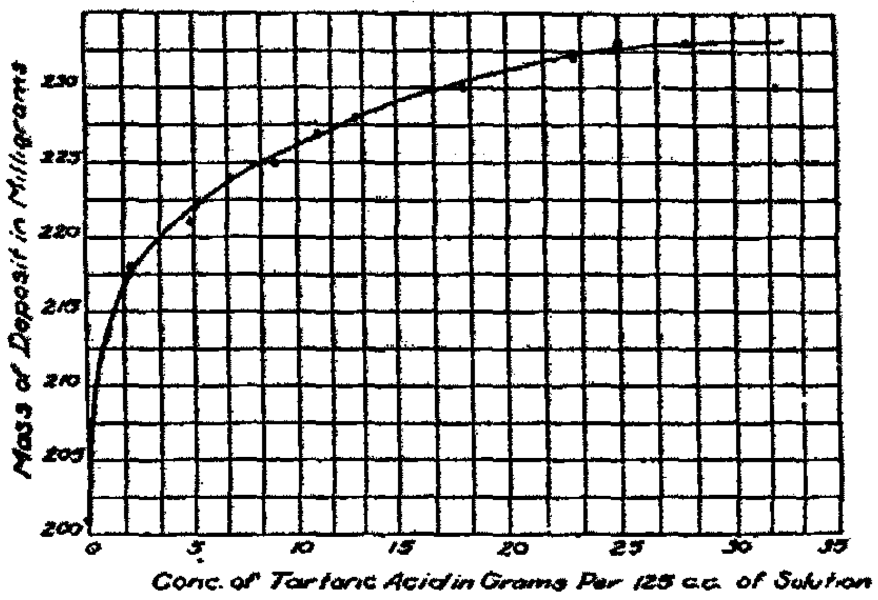


FIG. 13

---

[1] The mass of silver obtained when no cane sugar (or tartaric acid) was added to the copper sulfate solution was chosen as the basis for the computation.

Researches now in progress in this laboratory upon the deposition of copper in the presence of gum arabic, also, conform, in general, to the behavior shown by gelatin. That is, the mass of the deposit increases to a maximum value with increasing gum arabic content, provided, however, that the solubility of gum arabic in copper sulfate solutions is not exceeded. This case of gum arabic is all the more of interest as presumably the gum arabic is present in solution chiefly as the large and complex anion,[1] which should migrate toward the anode. Evidently the *direction* of migration is not an essential feature of this type of addition agent action.

The data obtained by Fuseya and Nagano upon the masses of copper deposited in the presence of glycocoll, although interpreted by these authors to mean discharge of complex cation, more logically fit into an explanation based upon surface phenomena. For example, the curves of Fig. 1 (of Fuseya and Nagano) when taken into account with their statement "as for the size of the crystals in the deposit, the greater the amount of glycocoll added or the greater the increase in the weight the finer was the crystalline structure," should more properly be regarded as evidence of surface phenomena. The steady upward slope of the curves would indicate that the limiting value of the specific surface was not reached. Fig. 3 from the paper of these authors very distinctly shows the approach to a limiting value. The very marked effect of temperature upon the mass of the deposit (the mass diminishing with rising temperature) is similar to that found by us for deposits of copper in the presence of gelatin.

In the last place the form of the deposits obtained by us can be explained by assuming that surface forces are at work. It will be recalled (Fig. 1) that the number of raised areas diminishes as the gelatin content increases, finally giving place to well developed striae. Our explanation of this phenomenon is as follows: The original electrode (copper) adsorbs gelatin upon its surface, the amount of gelatin adsorbed per unit area becoming greater as the gelatin content increases up to a limiting maximum value. When electrolysis is begun the discharge of copper ion becomes increasingly difficult as the gelatin content becomes greater. The cupric ions do find areas, however, which are bare of gelatin (or areas where the cupric ions are able to get by adjacent gelatin particles) and are discharged upon these areas. As the quantity of gelatin adsorbed increases, these bare areas diminish in extent and consequently the initial deposition of copper is restricted to fewer points. It is our belief, then, that these raised areas represent the initial points of deposit. As a result of their formation the current tends to converge upon these areas and consequently these areas tend to grow above the base metal. The new areas thus formed present new surfaces of copper which in turn are able to adsorb gelatin. As adsorption increases with increasing current density, the relative amount of gelatin adsorbed upon these new areas is greater per unit of area and of mass than upon the basal area. The gelatin thus adsorbed upon these raised areas increases the polarization upon these areas

---

[1] Taft and Malm: J. Phys. Chem., 35, 874 (1931).

and the copper ions seek new points of deposit. If the polarization (upon the raised areas) is sufficient, discharge will take place upon the basal metal adjacent to any raised area. The current density is presumable less upon the basal metal (greater IR from cathode to anode), and further, the gelatin content of the solution bathing the basal areas has been reduced as a result of adsorption upon the raised areas. Due to these two factors, the copper deposited is more crystalline (i.e. coarser) than upon the raised areas (Fig. 3). As discharge of cupric ions takes place, the solution contiguous to the cathode becomes depleted in copper sulfate and tends to rise owing to its smaller specific gravity. Where the initial points of copper deposit are few, i.e., in those solutions containing greater concentrations of gelatin, the convection currents will tend to make these deposits grow upward and lengthen out into well developed striae. As the gelatin content becomes still higher, cupric ions have apparently equal difficulty in being discharged over the entire area and consequently the deposits again present a more nearly uniform appearance. It will be noted that these deposits (from solutions containing 1 1/3% gelatin or greater) are nearly uniform in appearance and occur at similar concentration of gelatin to the maximum excess weights. Somewhat similar views have already been expressed as explanations of striated deposits. Rosa, Vinal, and McDaniel[1] have in particular, elaborated a theory of discontinuous deposits and the explanation which we have given above is chiefly an adaptation of their theory.

Summary

1. The effect of adding increasing amounts of gelatin upon the form of the cathode deposit obtained from solutions of copper sulfate has been observed and recorded.

2. The effect of the presence of gelatin upon the mass of the cathode deposit from solutions of copper sulfate has been determined for various concentrations of gelatin and of copper sulfate, for various current densities, and for various temperatures.

3. The data obtained is most directly explained by assuming that the copper deposited by the current adsorbs gelatin upon its surface.

4. Measurements of the magnitude of the cathode polarization in the cell Cu/$CuSO_4$, Gelatin/Cu have been made. We interpret our results to indicate that complex cations are formed between cupric ion and gelatin but that the electro-chemical process occurring at the cathode is primarily discharge of cupric ion.

University of Kansas,
Lawrence, Kansas.

---

[1] Bureau of Standards, Bull. 9, 277 (1913).

THE INFLUENCE OF SALTS ON THE OPTICAL ROTATION OF GELATIN. II*

BY D. C. CARPENTER AND J. J. KUCERA

In a previous communication,[1] one of the writers showed the influence of the halide salts of potassium on the optical rotation of calfskin gelatin. The first paper demonstrated, contrary to the conclusions of Loeb,[2] that the neutral halide salts clearly showed the customary Hofmeister series in their effect on the optical properties of proteins at a given constant pH. The tremendous changes in optical rotation with certain added salts seemed to indicate that the change was due to a rearrangement or change of the protein molecule that was associated with the two forms of the gelatin molecule which had been previously designated as the "gel" and "sol" forms.[3] The present paper deals with a continuation of the investigation and with the effect of other potassium salts of univalent anions, as well as those of certain bivalent anions, on the rotation.

J. Liquier-Milward[4] experimented with the effect of salts on the optical rotation of asparagine and ascribed the Hofmeister like effects which she observed to rearrangements or changes in the electrically neutral (zwitterion) part of the asparagine molecule. In her experiments which largely concerned the influence of chlorides of various metals, she found that the action on optical rotation was greatest for the metal ion having the smallest radius ($KCl < NaCl < LiCl$), this sequence being the *opposite* of that to be expected on the basis of ionic radii as deduced from measurements of the lattice distances in crystals.

In our own experiments with gelatin having a negative electrical charge, we have held the cation constant and varied the anion, and in the case of the halides, we have shown the order to be $KCl < KBr < KI$, an order for the anions as expected from lattice distances measurements. It is presumable that both ions have an effect, possibly an opposite effect, on the rotation. Levene and Rothen[5] found that their results on mandelic acid required such an assumption for the interpretation of their data.

Much of the work on the effect of neutral salts on the optical rotation of substances has been carried out with tartaric and malic acids and their derivatives. Lucas[6] concluded from dispersion data on tartaric acid that

---

*Contribution from the Chemical Laboratory of the New York State Experiment Station.

[1] D. C. Carpenter: J. Phys. Chem., 31, 1873 (1927).

[2] J. Loeb: "Proteins and the Theory of Colloidal Behavior" (1922).

[3] C. R. Smith: J. Am. Chem. Soc., 41, 135 (1919).

[4] J. Liquier-Milward: Ann. Phys., 7, 121 (1927); Trans. Faraday Soc., 26, 390 (1930).

[5] P. A. Levene and A. Rothen: J. Phys. Chem., 34, 2567 (1930).

[6] R. Lucas: Ann. Phys., 9, 381 (1928); Trans. Faraday Soc., 26, 418 (1930).

three active forms were present. From absorption spectra studies Bruhat[7] concluded that there was little or no change in the configuration of the molecule with concentration and that there was little evidence for the existence of three active forms. In reply to this, Lucas[8] has shown that, reasoning from Boltzmann's law, a system composed of substances having configurations A, B, and C will show either no maximum or one or two maxima with varying temperature, while if the configurations be limited to only A and B the system will show no maximum. Patterson[9] has shown experimentally with the tartrate esters that such a maximum exists, and hence the existence of three optically active forms in tartrates is rendered highly probable. In the cases of benzoylcamphor and ethyl acetoacetate, the two respective isomerides have actually been isolated.

The shape of the curves which we have found in the case of gelatin and their relationship to the property of gelling show that the effect with which we are dealing in gelatin is not of the same type as that encountered in the researches on the tartrates. Due to this fact it appears reasonable to try to connect the possible amino-acid structures with the phenomenon. On the basis of the inter-ionic attraction theory, the behavior of the inner-salt type $NH^+_3-R-COO^-$ should differ materially from that of the chain type $NH_2-R-COOH$. The former type, on account of its electrical charges, should suffer a diminution in activity on adding neutral salts to the solution and its solubility should be increased. It is presumable that, for instance with KI, oxonium compounds would be first formed which break down under the conditions of our experiments into the type $NH_3I-R-COOK$, corresponding in properties to the type represented by the term "sol form" which we have used in the case of gelatin.

Experimental Part

In the work described below, the same sample of calfskin gelatin was used and the same technique employed as in our former work. All of the salts were recrystallized several times before use and concentrations are expressed on a molality basis.

The salts employed were KNO_3, $KClO_3$, KCNS, HCOOK, CH_3COOK, C_2H_5COOK, K_2CrO_4, K_2SO_4, and $(COOK)_2$. The concentration series for certain of the salts (KNO_3, $KClO_3$, and K_2SO_4) are necessarily limited by the solubility of the salt and those with K_2CrO_4 and $(COOK)_2$ are limited by the precipitation of protein at high salt concentrations which renders the system optically opaque. The pH of all solutions, with the exception of the K_2CrO_4 solutions has been determined by the quinhydrone electrode. We have attempted to hold the pH constant and it has been reasonably constant, varying between pH 6 and 7 as limits. We have shown before[10] that at 40°C the

---

[7] G. Bruhat: Trans. Faraday Soc., 26, 400 (1930).

[8] loc. cit., p. 421.

[9] T. S. Patterson: J. Chem. Soc., 93, 1836 (1908).

[10] D. C. Carpenter, A. C. Dahlberg and J. C. Hening: Ind. Eng. Chem., 20, 397 (1928).

optical rotation is independent of pH between pH's 6 and 12, and at 0.5°C the decrease in rotation between pH's 6 and 7 is not greater than 2%, so we are of the opinion that the effect of the pH shifts caused by the added salt has been of small importance in the experiments here reported.

The data are given in Tables I to IX and the data at equilibrium are shown graphically in Figs. 1 and 2. In our data and graphs we have discontinued the use of "activity" of the salt, calculated on the basis of activity coefficients, and express our salt concentration in terms of molality. All solutions not marked with an asterisk gelled at 0.5°C after a period of seven days. In several solutions of the potassium salts of the weak acids, notably CH_3COOK, an optically clear gel was not obtained with the higher salt concentrations at 0.5°C, in which case the reading is omitted.

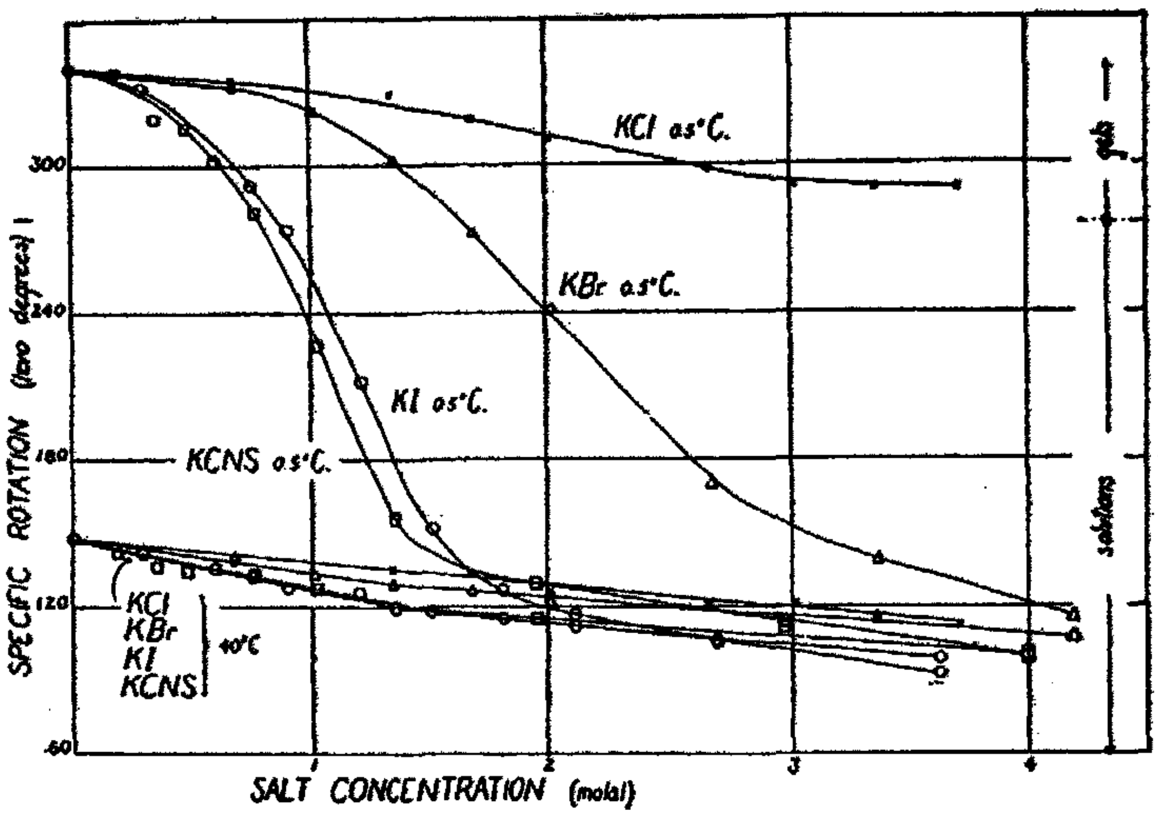


Fig. 1

Table I

Influence of KNO_3 on Optical Rotation of Gelatin at pH 6-7

Soln. No.	Molality of KNO_3 soln.	pH 25°C	Wt. gelatin per 100 gms. solvent Gms.	Density at 25°C	24 hrs. $[a]_D^{0.5°C}$ levo degrees	48 hrs. $[a]_D^{0.5°C}$ levo degrees	7 days $[a]_D^{0.5°C}$ levo degrees	$[a]_D^{40°C}$ levo degrees
1	0.000	6.19	0.700	0.9992	327	330	337	149
2	0.480	6.42	0.667	1.0281	323	334	340	140
3	0.830	6.57	0.646	1.0484	317	324	327	135
4	1.300	6.80	0.618	1.0734	301	308	317	134

TABLE II

Influence of $KClO_3$ on Optical Rotation of Gelatin at pH 6-7

Soln. No.	Molality of $KClO_3$ Soln.	pH 25°C	Wt. gelatin per 100 gms. solvent Gms.	Density at 25°C	24 hrs. $[a]_D^{0.5^\circ C}$ levo degrees	48 hrs. $[a]_D^{0.5^\circ C}$ levo degrees	7 days $[a]_D^{0.5^\circ C}$ levo degrees	$[a]_D^{40^\circ C}$ levo degrees
1	0.000	6.19	0.700	0.9986	327	330	337	149
2	0.245	6.72	0.680	1.0177	327	329	332	135

TABLE III

Influence of KCNS on Optical Rotation of Gelatin at pH 6-7

Soln. No.	Molality of KCNS Soln.	pH 25°C	Wt. gelatin per 100 gms. solvent Gms.	Density at 25°C	24 hrs. $[a]_D^{0.5^\circ C}$ levo degrees	48 hrs. $[a]_D^{0.5^\circ C}$ levo degrees	7 days $[a]_D^{0.5^\circ C}$ levo degrees	$[a]_D^{40^\circ C}$ levo degrees
1	0.000	6.13	0.700	0.9985	322	327	331	149
2	0.200	6.14	0.687	1.0087	319	328	338	142
3	0.350	6.47	0.679	1.0155	301	315	319	137
4	0.480	6.60	0.669	1.0208	289	303	316	135
5	0.760	6.83	0.651	1.0303	252	258	281	134
6*	1.020	6.94	0.638	1.0433	185	204	227	128
7*	1.350	7.05	0.619	1.0562	143	151	156	120
8*	1.950	7.05	0.589	1.0891	118	125	130	116
9*	2.960	6.97	0.548	1.1129	111	111	114	112
10*	4.000	6.98	0.504	1.1512	98	102	99.5	102

* *Solutions marked with asterisk did not gel after 7 days at 0.5°C.*

TABLE IV

Influence of HCOOK on Optical Rotation of Gelatin at pH 6-7

Soln. No.	Molality of HCOOK Soln.	pH 25°C	Wt. gelatin per 100 gms. solvent Gms.	Density at 25°C	24 hrs. $[a]_D^{0.5^\circ C}$ levo degrees	48 hrs. $[a]_D^{0.5^\circ C}$ levo degrees	7 days $[a]_D^{0.5^\circ C}$ levo degrees	$[a]_D^{40^\circ C}$ levo degrees
1	0.000	6.45	0.700	0.9994	326	328	340	141
2	0.475	6.45	0.673	1.0219	325	334	336	140
3	0.950	6.45	0.648	1.0428	325	339	330	134
4	1.425	6.91	0.625	1.0625	319	325	326	129
5	1.900	7.04	0.603	1.0794	305	312	313	119
6	2.375	6.97	0.583	1.0988	307	312	314	117
7	2.850	7.17	0.564	1.1152	269	284	296	111
8	3.490	7.30	0.541	1.1375	—	—	—	110

Table V

Influence of CH_3COOK on Optical Rotation of Gelatin at pH 6-7

Soln. No.	Molality of CH_3COOK	pH 25°C	Wt. gelatin per 100 gms. solvent Gms.	Density at 25°C	24 hrs. $[a]_D^{0.5^\circ C}$ levo degrees	48 hrs. $[a]_D^{0.5^\circ C}$ levo degrees	7 days $[a]_D^{0.5^\circ C}$ levo degrees	$[a]_D^{40^\circ C}$ levo degrees
1	0.000	6.44	0.700	0.9991	328	334	341	141
2	0.475	6.50	0.668	1.0217	326	327	328	139
3	0.950	6.54	0.640	1.0422	315	321	323	137
4	1.425	6.63	0.614	1.0616	314	314	318	130
5	1.900	6.75	0.590	1.0798	312	314	314	129
6	2.375	6.81	0.567	1.0978	299	304	—	122
7	2.850	6.90	0.544	1.1121	—	—	—	—
8	3.330	6.95	0.529	1.1284	—	—	—	116
9	3.800	7.10	0.519	1.1423	—	—	—	108

Table VI

Influence of C_2H_5COOK on Optical Rotation of Gelatin at pH 6-7

Soln. No.	Molality of C_2H_5COOK	pH 25°C	Wt. gelatin per 100 gms. solvent Gms.	Density at 25°C	14 hrs. $[a]_D^{0.5^\circ C}$ levo degrees	48 hrs. $[a]_D^{0.5^\circ C}$ levo degrees	7 days $[a]_D^{0.5^\circ C}$ levo, degrees	$[a]_D^{40^\circ C}$ levo degrees
1	0.000	6.14	0.700	0.9991	339	341	341	143
2	0.475	6.45	0.644	1.0215	333	336	337	134
3	0.950	6.57	0.632	1.0415	316	330	330	131
4	1.425	6.67	0.604	1.0606	292	298	325	124
5	1.900	6.73	0.577	1.0765	316	317	319	124
6	2.360	6.80	0.553	1.0934	306	306	308	121
7	2.850	6.95	0.530	1.1081	295	298	299	113
8	3.320	7.09	0.509	1.1235	273	273	—	104

Table VII

Influence of K_2CrO_4 on Optical Rotation of Gelatin

Soln. No.	Molality of K_2CrO_4	Wt. gelatin per 100 gms. solvent Gms.	Density at 25°C	24 hrs. $[a]_D^{0.5^\circ C}$ levo degrees	48 hrs. $[a]_D^{0.5^\circ C}$ levo degrees	7 days $[a]_D^{0.5^\circ C}$ levo degrees	$[a]_D^{40^\circ C}$ levo degrees
1	0.000	0.700	0.9991	339	341	341	143
2	0.149	0.680	1.0220	330	332	333	139
3	0.298	0.662	1.0429	331	332	333	139
4	0.448	0.644	1.0649	328	333	334	138
5	0.600	0.627	1.0858	311	320	325	134
6	0.752	0.611	1.1062	316	319	320	132
7	0.898	0.596	1.1260	306	313	313	128
8	1.090	0.568	1.1625	296	314	317	122
9	1.492	0.543	1.1967	293	294	293	112

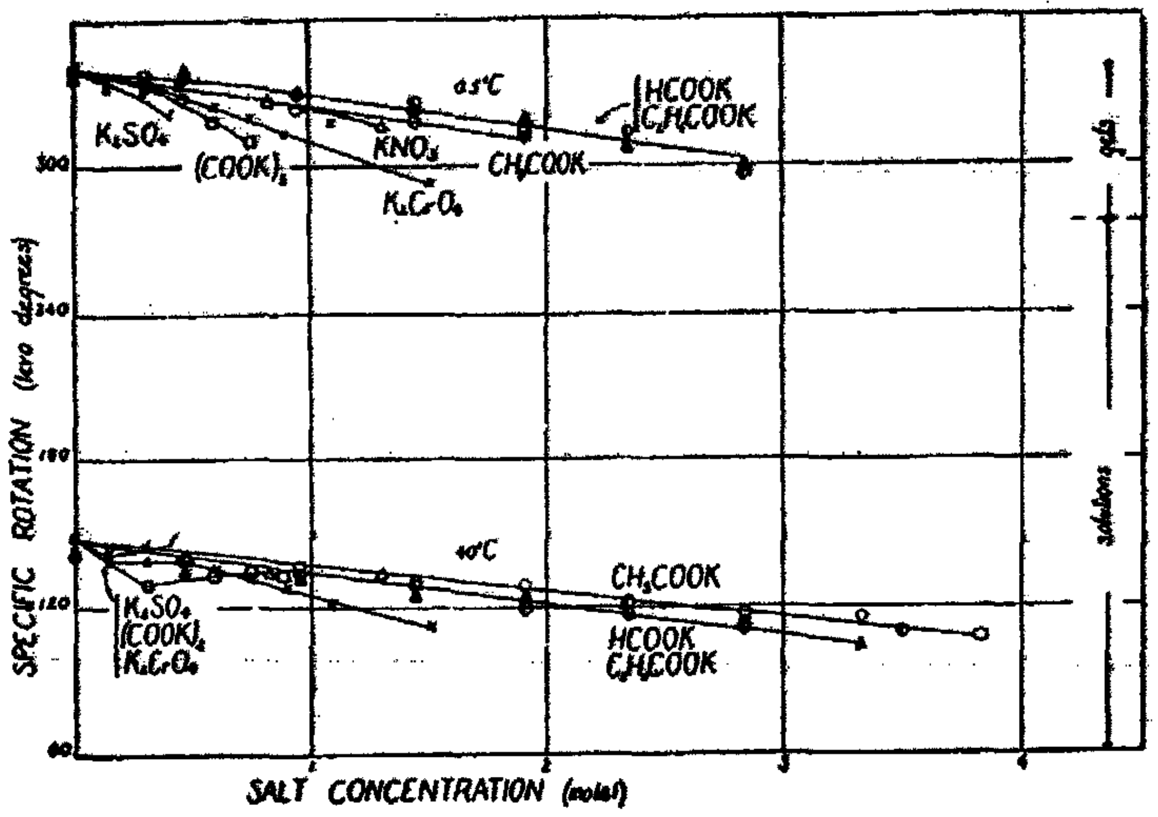


FIG. 2

TABLE VIII

Influence of K_2SO_4 on Optical Rotation of Gelatin at pH 6-7

Soln. No.	Molality of K_2SO_4	pH 25°C	Wt. gelatin per 100 gms. solvent Gms.	Density at 25°C	24 hrs. $[\alpha]_D^{0.5°C}$ levo degrees	48 hrs. $[\alpha]_D^{0.5°C}$ levo degrees	7 days $[\alpha]_D^{0.5°C}$ levo degrees	$[\alpha]_D^{40°C}$ levo degrees
1	0.000	6.19	0.700	0.9992	327	330	337	149
2	0.143	6.76	0.682	1.0191	326	328	335	141
3	0.287	6.80	0.668	1.0370	321	328	329	144
4	0.419	6.97	0.652	1.0645	314	319	321	146

TABLE IX

Influence of $K_2C_2O_4$ on Optical Rotation of Gelatin at pH 6-7

Soln. No.	Molality of $K_2C_2O_4$	pH 25°C	Wt. gelatin per 100 gms. solvent Gms.	Density at 25°C	24 hrs. $[\alpha]_D^{0.5°C}$ levo degress	48 hrs. $[\alpha]_D^{0.5°C}$ levo degrees	7 days $[\alpha]_D^{0.5°C}$ levo degrees	$[\alpha]_D^{40°C}$ levo degrees
1	0.000	6.24	0.700	0.9992	329	332	338	145
2	0.296	6.30	0.664	1.0339	338	339	339	129
3	0.591	6.45	0.630	1.0654	318	319	319	133
4	0.742	6.65	0.615	1.0808	299	305	311	135
5	0.885	—	0.600	1.0964	—	—	—	134

Discussions and Conclusions

As a class it is seen that the potassium salts of the weak acids, *viz.*, formic, acetic, and propionic acids, have very little influence on the optical rotation of gelatin at either of the temperatures investigated. Our data show minor experimental uncertainties which make it difficult to judge which salt among this class may have the greater effect. At 0.5°C the acetate seems to have a greater effect, while at 40°C it has less effect than the other weak acids. In any case the difference is of minor consequence.

The data which we have collected on the effect of various potassium salts on optical rotation show plainly that for uni-univalent salts we have a typical Hofmeister series arranged as follows—$KCNS > KI > KClO_3 > KNO_3 > KBr > KCl$, CH_3COOK, C_2H_5COOK, and $HCOOK$, and for the uni-bivalent salts we have the series $K_2SO_4 > (COOK)_2 > K_2CrO_4$. At high concentrations (above 1.5M) KI is more effective than KCNS.

The first series compares almost exactly with the series sulphocyanate, iodide > chlorate > nitrate > chloride > acetate > phosphate > sulphate > tartrate which Bancroft[11] points out is the order of adsorption of anions by albumin. This is strongly suggestive of the validity of our alternate hypothesis[12] that the salts in each case form compounds with the potassium gelatinate with a characteristic optical activity.

In working with cellulose and its swelling in thiocyanate solutions, Katz and Derksen,[13] from x-ray spectrum work, came to the conclusion that in concentrated solutions compound formation took place between cellulose and the salt.

Too little is known at present about proteins to progress very far with this line of argument. The two views are not mutually exclusive and we call attention to the close parallelism between the anion order in the adsorption series and in our own optical activity work. It is to be noted that we have found thus far only three salts which have an effect on gelatin of sufficient magnitude that the solutions will no longer gel when kept for a period of a week at 0.5°C.

We have shown that the rotation passes through practically the same numerical value at the same point that the gelling property of gelatin is lost with the three salts KCNS, KI, and KBr. This seems to point to a connection between optical activity and the "gel" and "sol" forms of gelatin, the former of which has been assumed to be responsible for gel formation, and to the conversion of one form into another. The connection between the "gel" and "sol" forms may be that one is simply a dissociated form of the other or the connection may be that of an internal salt (zwitterion) which is changing to some other form or simply the general case of one isomer changing into another. Until we have evidence bearing on what the change may be in

---

[11] W. D. Bancroft: J. Phys. Chem., 19, 349 (1915).

[12] loc. cit., p. 1877.

[13] J. R. Katz and J. C. Derksen: Rec. Trav. chim., 30, 149 (1931).

terms of molecular structure, we may as well retain the "gel" and "sol" expressions without attempting to be more specific.

The effect of uni-bivalent salts at 40°C appears to pass through a maximum between 0.1 and 0.3M and then drop off. Although this phenomenon is not of large magnitude, it repeats itself for each of the three salts examined in a very regular way. No great change is observed in the optical activity of the protein through added uni-bivalent salts even though the protein is precipitated at slightly higher salt concentrations than those examined. From this fact we infer that the uni-bivalent salts do not cause a polymerization of the protein molecule.

The results of Svedberg and Nichols,[14] in which the molecular weight of egg-albumen was examined in the centrifuge, showed that, when electro-dialyzed, the protein was homogeneous and had a molecular weight of 34,500, but that when the precipitating agent $(NH_4)_2SO_4$ was removed by ordinary dialysis, about 6% of the protein material consisted of molecules of 170,000 molecular weight. These workers were undecided from their experiments whether the material of high molecular weight was a foreign protein or was present simply as a polymerized form of the lighter species through the influence of $(NH_4)_2SO_4$.

Our experiments with gelatin and the uni-bivalent salts tend to indicate that probably a foreign protein of high molecular weight was present in their material and not a polymer produced through the action of $(NH_4)_2SO_4$ on egg-albumen.

Summary

1. The influence of several uni-univalent and uni-bivalent potassium salts on the optical rotation of 0.7% potassium gelatinate (calfskin) has been examined at pH 6-7.

2. Each salt produced a characteristic lowering of the optical activity. As to the magnitude of effect, the uni-univalent salts are arranged in the following Hofmeister series—$KCNS > KI > KClO_3 > KNO_3 > KBr > KCl$, CH_3COOK, C_2H_5COOK, and $HCOOK$. As a class, the salts of weak acids have very little effect on the rotation. Uni-bivalent salts are arranged in the series $K_2SO_4 > (COOK)_2 > K_2CrO_4$.

3. The changes in optical rotation are ascribed to an equilibrium between the "gel" and "sol" forms of the gelatin molecule. It is pointed out that reversible compound formation between potassium gelatinate and the added salt is not contrary to this view.

Geneva, N. Y.

---

[14] T. Svedberg and J. B. Nichols: J. Am. Chem. Soc., 48, 3081 (1926).

AN X-RAY STUDY OF THE ALLOYS OF SILVER WITH BISMUTH ANTIMONY AND ARSENIC. PART I

BY S. J. BRODERICK AND W. F. EHRET

The object of the present investigation is to note any regularities in the phases formed by the alloying of silver with arsenic, antimony and bismuth respectively. Silver was chosen as one of the components, not because of any commercial significance, but for the reason that it forms alloys within the ordinary laboratory range of temperature. The second elements which are alloyed with silver form a closely related series in the periodic table. The structures of arsenic, antimony and bismuth are similar, consequently one should be able to correlate the tendency towards the formation of solid solutions with the size and shape of the individual atoms in these systems. Furthermore, one would expect to find analogous phases in the different systems and perhaps be able to follow gradual changes in the structure of a particular phase due to increasing solubility.

Part I will be concerned with the systems Ag-Bi and Ag-Sb. Part II will cover the system Ag-As and the general conclusions to be drawn from this study.

Silver—Bismuth System

This alloy was studied first because of its apparent simplicity. It is one of the simpler forms of alloy systems with a eutectic occurring at a composition of 2.5% silver and a temperature of 262°C. At the silver end there is a limited solubility of bismuth in silver. One of the earlier investigators reported a compound which was not found by other workers.

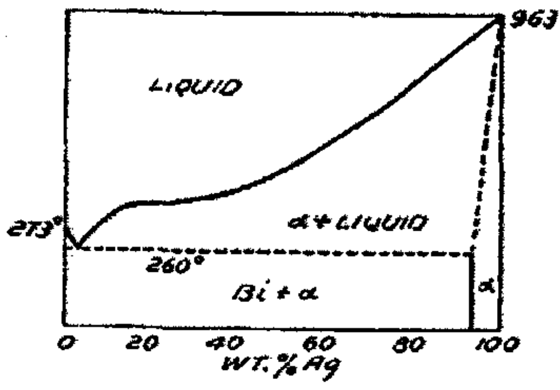


FIG. 1

Equilibrium Diagram of the Ag-Bi System according to Petrenko

Mathiessen,[1] in his article of 1860, reported that a compound of the formula Ag_4Bi existed in this system. The basis of his findings is that the pure bismuth alloy expands on cooling, while pure silver on the other hand, contracts. In the alloy of the composition in which the compound Ag_4Bi is supposed to exist he found a maximum contraction, while a transition from positive to negative volume is expected. The same experimenter investigated the conductivity of these alloys and found that the conductivity increases with the increase of silver.

---

[1] Mathiessen: Pogg. Ann., 110, 21 (1860).

Laurie[1] investigated the electromotive potential of the silver-bismuth alloys and concludes from the results that these metals form no compound.

The diagram in Fig. 1 is the work of G. I. Petrenko.[2] It is considered the correct thermal diagram for this system.

Preparation of Alloys

A series of alloys ranging from 5.8% to 97.4% silver was prepared using Eimer and Amend's 999 fine granular silver and Merck's C.P. crystalline grade of bismuth 99-100% pure. Silver and bismuth alloy very readily, so the melts were made in an unglazed porcelain crucible, covering the mixtures with powdered charcoal to keep as free as possible from air. The melting took place in an electric muffle furnace at the temperatures at which the mixtures fused together thoroughly. The alloys were allowed to cool very slowly in order to attain equilibrium conditions.

Each melt was polished and etched and examined under the microscope to be certain that the sample was homogeneous. The filings from each melt were passed through a 200 mesh sieve and then annealed in evacuated glass tubes to remove strains or distortions of the atomic planes set up during filing. These annealed powders were used to fill lead-free glass capillary tubes about 0.6 m.m. in diameter and X-ray photograms were taken. Each alloy sample was analyzed for silver by Volhard's method.

Apparatus

The X-ray powder photograms were taken on the General Electric Diffraction Apparatus using a Coolidge tube with a Molybdenum target with $K_{\alpha_1} = 0.708$Å and $K_{\alpha_2} = 0.712$Å. Diffraction patterns of sodium chloride were taken simultaneously on each film in the quadrant cassette or camera. The thin layer of zirconium oxide in the camera absorbed the K_β and K_γ X-rays thus leaving only the K_{α_1} and K_{α_2} rays to be diffracted by atomic planes within the crystal. At the smaller reflection angles the K_α doublet cannot be resolved readily, so the average length 0.710 Å is used in the calculations. The atomic interplanar distances are measured directly from the diffracted lines on the film by means of the special ruler designed for use with the camera of 8 inch radius.

By means of a correction curve, using the known interplanar spacing for sodium chloride on each photogram, the exact position of each diffraction line is located, thereby eliminating any error due to the variation in the radii of the cameras.

Experimental Results

The crystal structure of silver has been found to belong to the face centered cubic class by a number of investigators. A value as low as 4.058Å for

---

[1] Laurie: J. Chem. Soc., 65, 1031 (1894).

[2] Petrenko: Z. anorg. Chem., 50, 133 (1906).

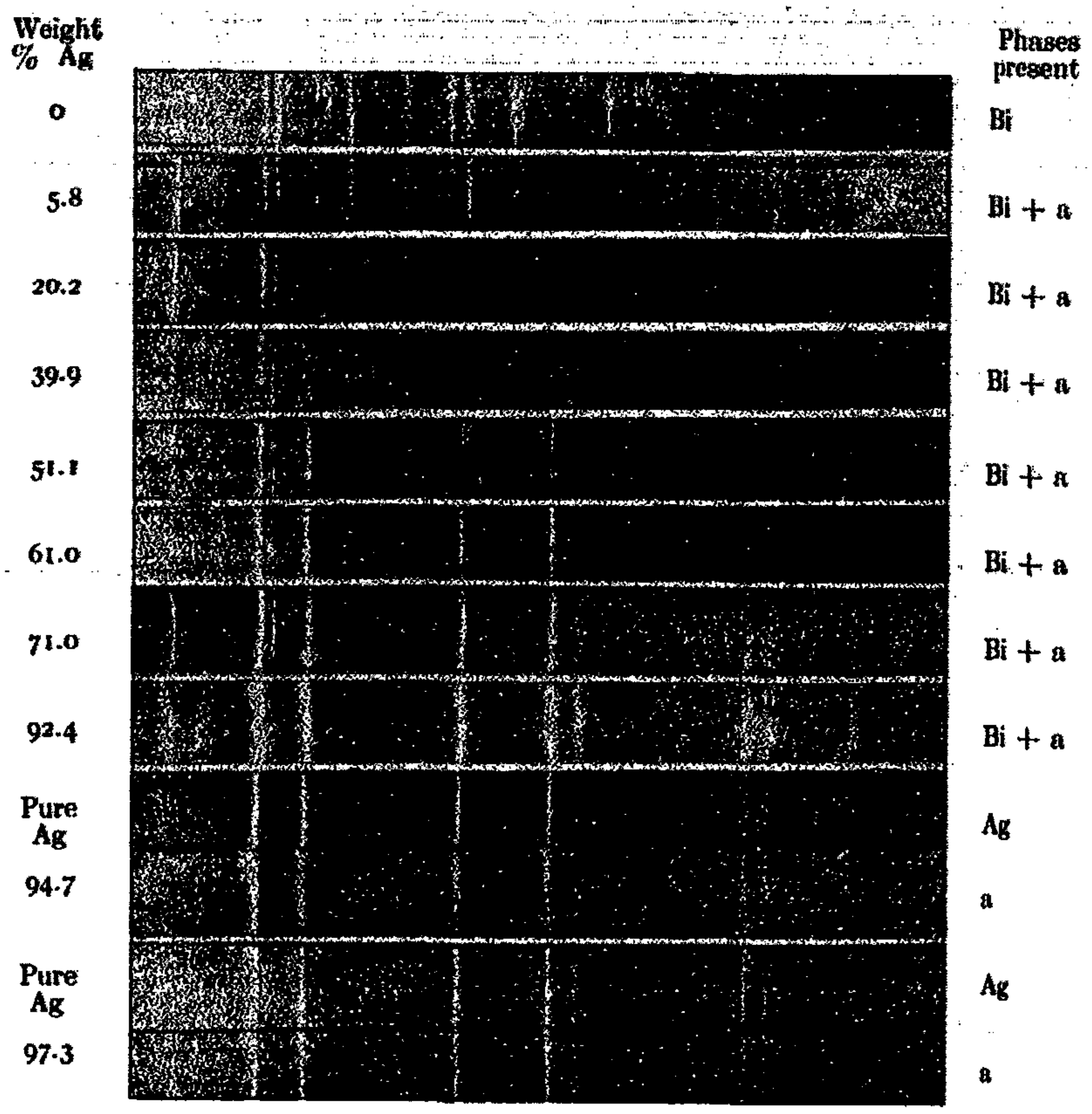


Plate I
Powder Photograms of the System Ag-Bi. Mo-K Radiation

the side of the cube (a_0) has been reported by W. P. Davey,[1] but later he reported a value of 4.079Å. Traces of copper have a marked effect in decreasing the silver lattice.

W. L. McKeehan[2] gives a value of 4.080Å, and T. Barth and G. Lund,[3] 4.078Å. Westgren[4] and co-workers have reported at different times values between 4.078Å and 4.080Å for the side of the cube.

Table I gives values of 4.075Å and 4.076Å from two different films, which agrees fairly well with the recent work done on silver. Plate 1 shows a series of powder photograms of alloys ranging from 5.8 to 97.3% silver. Up to 92.4% silver both the silver and bismuth patterns are discernible showing that there is a heterogeneous mixture of two phases present within this

---

[1] Davey: Phys. Rev., (2) 23, 292 (1924); 25, 753 (1925).

[2] McKeehan: Phys. Rev., (2) 20, 424 (1922).

[3] Barth and Lund: Z. physik. Chem., 121, 78 (1926).

[4] Westgren and Phragmén: Phil. Mag., 50, 311 (1925).

range. With increasing silver content the bismuth lines grow weaker until at 94.7% silver they disappear entirely. The solubility range of bismuth in silver extends to about 5.5% bismuth. The limit of this solubility range is more accurately determined by plotting the change in the lattice parameter in Ångström units on the ordinate axis, against composition along the abscissas. Where the curve strikes the horizontal line of maximum change of parameter is the point of maximum solubility of one component in the other.

TABLE I

Powder Photogram of Pure Silver

		Film No. 1			Film No. 2		
Indices of Form	Intensity	Spacing of planes	$\sin^2\theta$	Ag a_0	Spacing of planes	$\sin^2\theta$	Ag. a_0
111	V.S.	2.358Å	0.0226	4.084	2.358Å	0.0226	4.084
100(2)	S.	2.042	0.0302	4.084	2.040	0.0302	4.080
101(2)	S.	1.440	0.0606	4.074	1.441	0.0606	4.076
113	V.S.	1.227	0.0838	4.070	1.229	0.0835	4.077
111(2)	W.	1.177	0.0912	4.077	1.176	0.0912	4.074
100(4)	V.W.	1.019	9.1217	4.076	1.019	0.1217	4.075
133	M.	0.9345	0.1444	4.074	0.9345	0.1444	4.074
102(2)	M.	0.9110	0.1518	4.074	0.9110	0.1518	4.074
112(2)	W.	0.8315	0.1823	4.073	0.8320	0.1820	4.076
115	W.	0.7840	0.2050	4.074	0.7848	0.2048	4.078
			a_0 = 4.075Å			a_0 = 4.076Å	

S. = Strong
V.S. = Very strong
W. = Weak
M. = Medium

Thus the limit of solubility of bismuth in silver is at 97.1 atomic percent silver or 94.5 weight percent as can be seen from Fig. 2. The silver lattice increases from 4.076Å to 4.087Å within this area.

Table II gives the spacings of the planes in the alloys of 51.1% and 71.7% silver. If a compound exists where Mathiessen reported one, then we should expect to get some lines on these photograms which do not correspond to either bismuth or silver. No such lines were found and this leads us to believe that no compound is formed between bismuth and silver.

The change in the bismuth lattice lies within the experimental error on all our photograms. From this it may be concluded that the solubility of silver in bismuth is practically negligible. Silver is analogous to copper in this respect. W. Ehret and R. Fine[1] have reported that the solubility of copper in bismuth is less than 0.5 atomic percent.

---

[1] Ehret and Fine: Phil. Mag., 10, 551 (1930).

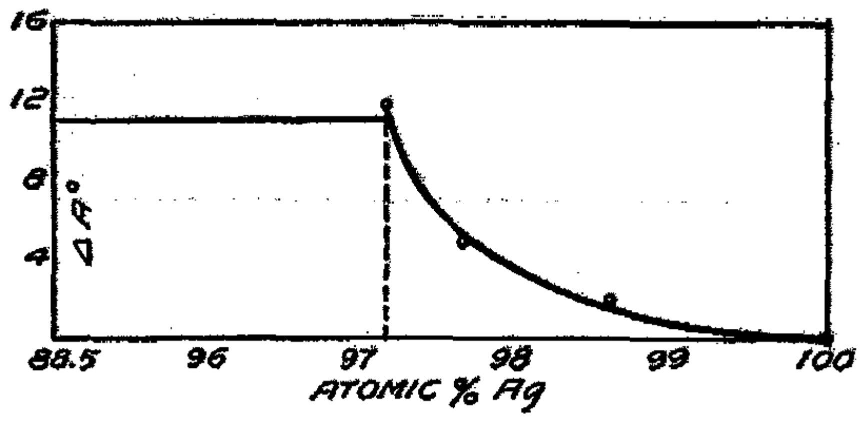


Fig. 2

TABLE II

51.1% Ag.—48.9% Bi.			71.7% Ag. —28.3% Bi.		
Intensity	Spacing of Planes Observed Å	Agrees with	Intensity	Spacings of Planes Observed Å	Agrees with
S.	3.25	Bi.	S.	3.25	Bi.
V.S.	2.355	Bi.&Ag(α)	S.	2.355	Bi.&Ag(α)
W.	2.260	Bi.	W.	2.262	Bi.
S.	2.045	Bi.&Ag (α)	S.	2.045	Bi.&Ag(α)
V.V.W.	1.970	Bi.	V.V.W.	1.970	Bi.
V.W.	1.864	Bi.	V.V.W.	1.866	Bi.
V.V.W.	1.635	Bi.	V.V.W.	1.637	Bi.
V.V.W.	1.555	Bi.	V.W.	1.555	Bi.
V.W.	1.490	Bi.	V.W.	1.489	Bi.
V.S.	1.442	Bi.&Ag(α)	V.S.	1.442	Bi.&Ag(α)
V.V.W.	1.387	Bi.	V.V.W.	1.386	Bi.
V.V.W.	1.311	Bi.	V V.W.	1.308	Bi.
S.	1.231	Ag(α)	V.S	1.232	Ag(α)
M.	1.175	Ag(α)	S.	1.178	Ag(α)
V.V.W.	1.137	Bi.	V.V.W.	1.138	Bi.
M.	1.021	Ag(α)	M.	1.021	Ag(α)
M.	0.935	Ag(α)	M.	0.937	Ag(α)
M.	0.912	Ag(α)	M.	0.913	Ag(α)
M.	0.834	Ag(α)	M.	0.834	Ag(α)

Silver—Antimony System

After our experimental work on this system was completed, Westgren, Hägg and Ericksson[1] published the results of their work on the system. There is substantial agreement between the two analyses in practically all respects.

Gautier[2] was among the first to study the melting points of this alloy system. He found that the melting point curve consisted of two branches that separated at the eutectic point. Charpy[3] studied the alloys micro-

---

[1] Westgren, Hägg and Eriksson: Z. physik. Chem., B 4, 453 (1929).

[2] Gautier: "Contribution à l'étude des alliages," p. 110 (1901).

[3] Charpy: Ibid. p. 146.

scopically and found a compound. He suggested Ag_3Sb and Ag_4Sb as possible formulas for it. Heycock and Neville[1] studied this melting curve and found that it consisted of three branches. The first break was at 25 atomic percent Sb and corresponded to the compound Ag_3Sb. The second came at 40% Sb and corresponded to the eutectic. The presence of a break at 25% was not considered sufficient evidence however, to establish the existence of the above compound. Maey[2] concluded from the results of his volumetric determinations that silver and antimony form only one compound corresponding to the formula Ag_3Sb. Puschin studied this system and came to the conclusion from his electromotive force measurements that antimony forms two compounds with silver Ag_2Sb and Ag_3Sb. G. I. Petrenko[3] found only one compound of the formula Ag_3Sb and his diagram is given in Fig. 3.

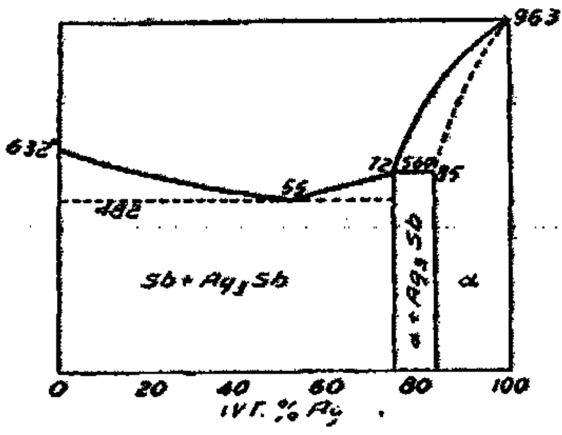


FIG. 3
Equilibrium Diagram of the Ag-Sb System according to Petrenko

The antimony used in the preparation of the alloys was Merck's crystalline C.P. grade. Since silver dissolves readily in liquid antimony and the latter diffuses easily into silver, there is very little loss of antimony due to volatilization. Accordingly the alloys were made in the same way as the bismuth series.

Experimental Results

α Phase: The series of powder photograms are shown in Plate 2. The solubility of antimony in silver is only 6%, in contrast to the 15% as reported by Petrenko. The lattice parameter of silver in this phase is increased from 4.076Å for pure silver to 4.109Å for the saturated phase. This distortion is clearly seen from the 94.0% silver photogram as the pattern of pure silver was taken on the same film. (Plate 2). In the region between 94.0% and 89.0% silver there is a heterogeneous mixture of alpha, which is the solid solution of antimony in silver, and the epsilon phase.

ϵ and ϵ' Phases: Between about 89 and 84% silver is the region of the homogeneous epsilon phase. The limits of this region are only approximate as not enough alloy photograms were taken within this area to clearly define it. Table 3 gives the spacings of this phase as taken from the film of the silver alloy. The epsilon phase belongs to the hexagonal close packed system. The $\sin^2\theta$ value of each line is calculated from the quadratic formula $\sin^2\theta = A(h^2 + k^2 + hk) + B(l^2)$, and agrees very well with the observed value (Table III), thus proving the choice of structure to be correct. The constants that fit the above equation are:

---

[1] Heycock and Neville: Phil. Trans., 189A, 25 (1897).

[2] Maey: Z. physik. Chem., 50, 200 (1905).

[3] Petrenko: Z. anorg. Chem., 50, 133 (1906).

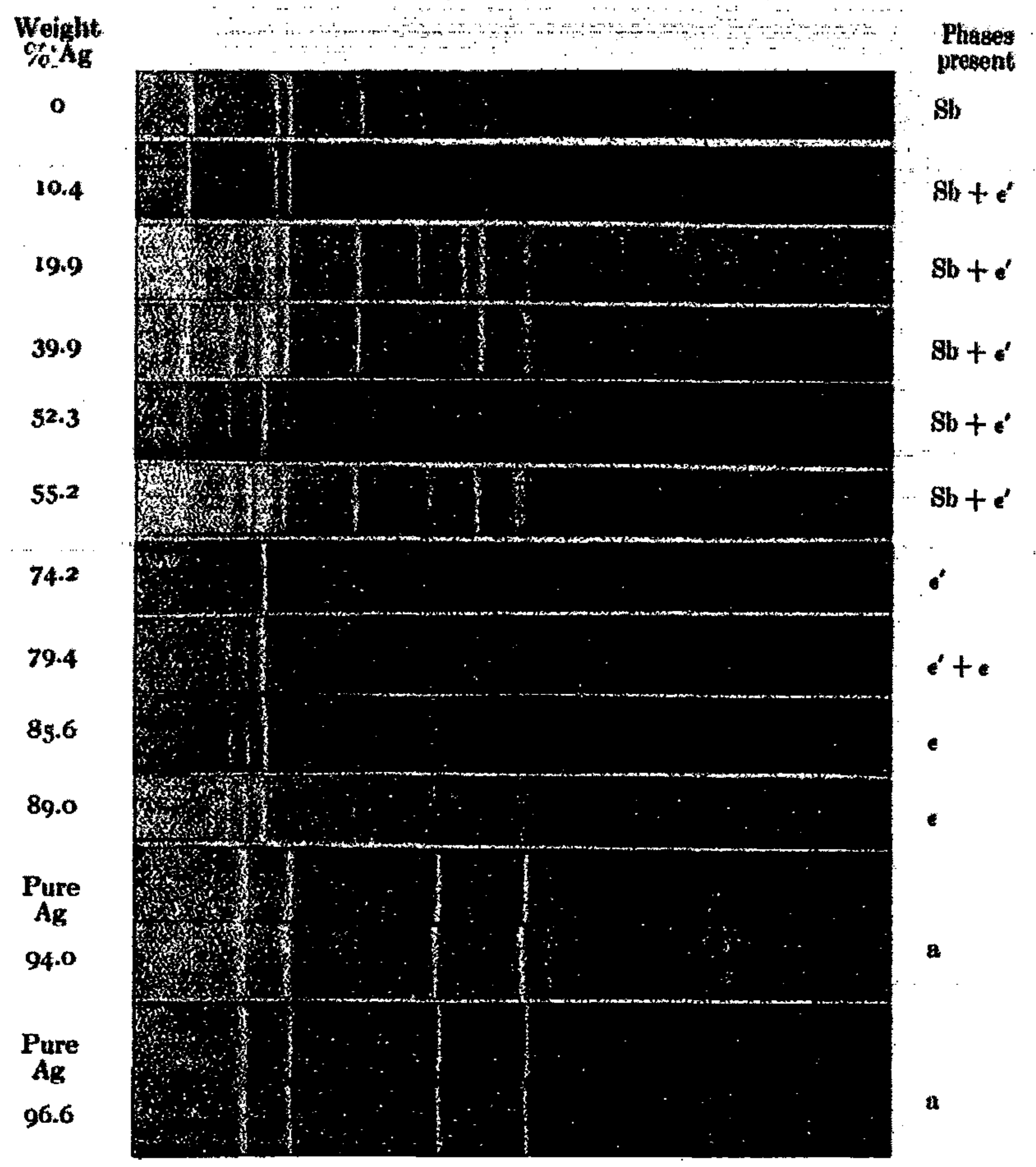


PLATE II

Powder Photograms of the System Ag-Sb. Mo-K Radiation

$$A = 0.0197 \qquad B = 0.00553$$

The size of the unit cell is found from the formula:

$$\sin^2\theta = \frac{\lambda^2}{3a_1^2}(h^2 + k^2 + hk) + \frac{\lambda^2}{4a_3^2}(l^2)$$

$$\text{hence } A = \frac{\lambda^2}{3a_1^2} \text{ and } B = \frac{\lambda^2}{4a_3^2}$$

and $a_1 = 2.920$Å (side of hexagon)

$a_3 = 4.774$Å (height of cell)

Axial ratio $\frac{a_3}{a_1} = 1.632$

TABLE III

Powder Photogram of ϵ Ag-Sb Phase with 89.0%, Ag.

Indices of Form	*Intensity*	*Spacing of Planes*	$\sin^2\theta$ Observed	$\sin^2\theta$ Calculated
100	M	2.530Å	0.0197	0.0197
001(2)	M	2.380	0.0222	0.0223
101	V.S.	2.240	0.0251	0.0253
102	W	1.738	0.0417	0.0420
110	S	1.463	0.0588	0.0591
103	S	1.348	0.0694	0.0689
112	M	1.248	0.0810	0.0814
201	M	1.225	0.0840	0.0844
001(4)	V.W.	1.195	0.0881	0.0885
101(2)	V.W.	1.120	0.1002	0.1009
104	V.W.	1.082	0.1063	0.1082
023	W	0.992	0.1282	0.1285
211	W	0.939	0.1430	0.1434
114	W	0.926	0.1470	0.1475

In the area between 72% and 79% silver these is the epsilon prime phase which has a structure very similar to the epsilon phase. The similarity of the structure can best be seen from the alloy containing 79.4% silver in which both phases are present. There is a slight broadening of the lines on the film while the fifth line is a double one, likewise the seventh and eighth ones. Table IV gives the spacings of the planes of the epsilon prime phase at a composition of 74.2% Ag. The $\sin^2\theta$ values calculated from the film fit the quadratic form,

$$\sin^2\theta = A(h^2) + B(k^2) + C(l^2)$$

Structurally this phase thus belongs to the rhombic or deformed cubic class. The constants found are:

$A = 0.0140$ $B = 0.0047$ $C = 0.0054$

The size of the unit cell may be found from the constants and the quadratic form,

$$\sin^2\theta = \frac{\lambda^2}{4a_1^2}(h^2) + \frac{\lambda^2}{4a_2^2}(k +^2)\frac{\lambda^2}{4a_3^2}(l^2).$$

Thus the size of the unit cell at a composition of 74.2% Ag is found to be $a_1 = 3.000$, $a_2 = 5.178$, $a_3 = 4.830$Å.

Westgren, in his work, used an iron target with a $K\alpha$ radiation of 1.932Å. He was able to show that there is a doubling of some of the lines at the smaller diffraction angles. With the molybdenum K_α radiation of 0.710Å we were not able to show this doubling clearly because of the shorter wave length used. However, we were able to obtain three more lines on the photogram thus giving

TABLE IV

74.2% Ag.—25.8% Sb. ϵ' Phase

Indices	Intensity	Spacing of Planes Observed $d_{(h.k.l.)}$	$\sin^2\theta$ Observed	$\sin^2\theta$ Calculated
020	M	2.585Å	0.0188	0.0188
002	M	2.400	0.0219	0.0216
110	V.V.S.	2.278	0.0243	0.0241
022	M	1.765	0.0405	0.0404
200	M	1.500	0.0560	0.0560
023	M	1.364	0.0677	0.0674
202	W	1.274	0.0766	0.0766
221	W	1.253	0.0803	0.0802
004	V.V.W.	1.205	0.0868	0.0864
042	V.V.W.	1.144	0.0963	0.0968
024 114	W	1.090	0.1060	0.1052 0.1051
223	W	1.010	0.1235	0.1234
311	W	0.963	0.1359	0.1361
133	W	0.939	0.1429	0.1427
115 025	W	0.903	0.1545	0.1537 0.1538
251 313	W	0.840	0.1787	0.1789 0.1794

A......0.0140

B......0.0047

C......0.0054

$a_1 = 3.000$Å

$a_2 = 5.178$

$a_3 = 4.830$

additional proof as to the correctness in the choice of structure. The lattice parameters of both the epsilon and epsilon prime phases vary within their respective areas thus showing that they are really solid solutions. Because both these phases exist over a range and not at a point, it is difficult to assign a formula to them. From 0 to 72.% Ag the photograms show a heterogeneous mixture of two phases, antimony and epsilon prime.

Summary

The X-ray examination of the Ag-Bi system supports the thermal diagram of Petrenko.

No compound of the two elements was found as reported by Mathiessen.

The maximum solubility of bismuth in silver is about 5.5%. The lattice parameter within this phase is increased from 4.076Å for pure silver to 4.087Å for the saturated phase.

The X-ray examination of the Ag-Sb system does not agree with the thermal diagram of Petrenko.

The maximum solubility of antimony in silver is about 6.%. The lattice parameter of silver in this phase is increased from 4.076Å, for pure silver to 4.109Å for the saturated phase.

In the region between 11 and 16% Sb, there exists a homogeneous hexagonal close packed phase. The size of the unit cell at 89.% Ag. is $a_1 =$ 2.920Å, $a_3 =$ 4.774Å and $\frac{a_3}{a_1} = 1.632$.

Another homogeneous phase which is either rhombic or deformed cubic is present in the region between 72 and 78% Ag. The size of the unit cell at 74.2% Ag is $a_1 =$ 3.000Å, $a_2 =$ 5.178Å and $a_3 =$ 4.830Å.

New York University
Washington Square College
New York, N. Y.

36-215

INTENSIFYING ACTION OF HYDROGEN PEROXIDE AND ORGANIC PEROXIDES ON THE LATENT PHOTOGRAPHIC IMAGE

BY CARL E. BARNES WITH W. R. WHITEHORNE AND W. A. LAWRANCE

The fact that both the vapor and solution of hydrogen peroxide act on the photographic emulsion in a manner very similar to that of light has been known for some time.[1] Recently Sheppard, Wightman and Quirk, of the Eastman Research Laboratories, and Dr. Lüppo-Cramer have published papers dealing with the intensification of the latent image by means of this substance. Its action, as explained by Wightman and Quirk[2] is briefly thus:

In a normal exposure of a plate to light certain of the grains are reduced sufficiently to make them developable while others may be brought nearly to that stage and still remain unaffected by the developing solution. By treating such an exposed plate with a very dilute solution of hydrogen peroxide all the grains are considered to be affected in much the same manner as when exposed to light whereby the grains not having been sufficiently reduced in the original exposure now become so. If the action of the hydrogen peroxide solution is continued or its strength increased, more and more of the grains will become developable, including those not originally acted on by light, and fog results.

Of the organic peroxides, apparently benzoyl peroxide is the only one whose action has been recorded. Furthermore the effect of hydrogen peroxide when using various developing agents has not been investigated to any extent. It is the purpose of this work to determine the effect of hydrogen peroxide on the latent image when using different developing solutions as well as to determine the action of several organic peroxides.

Methods

1. *Exposure.*

Strips of Eastman "Speedway" plates were exposed in a non-intermittent sensitometer of Hardy's design.[3]

2. *Processing.*

Three procedures were employed: (1) strips receiving peroxide treatment and wash water before development; (2) strips receiving treatment in the peroxide solvent (water in the case of hydrogen peroxide and varying proportions of acetone and water with the organic peroxides) for the same time

---

[1] S. E. Sheppard and E. P. Wightman: J. Franklin Inst., 195, 337 (1923).

[2] E. P. Wightman and R. F. Quirk: Proc. Seventh International Congress of Photography, 1928, 236.

[3] Arthur C. Hardy: J. Opt. Soc. America and Rev. Sci. Instr., 10, 149-156 (1925).

as in the peroxide treatment followed by the same time of wash water treatment in a separate beaker; and (3) strips receiving no treatment, i.e., controls.

The temperature of all solutions was maintained at 20.0°C.

Development was continued for such times as to give to the control plates gammas of approximately 0.5, 1.0 and 1.2, these times being determined for the various developing solutions by plotting time-gamma curves.

Strips were removed from all solutions five seconds before the expiration of the time of treatment to allow for draining and removing to the next solution into which they were placed promptly at the end of the five seconds.

In order to eliminate errors due to fluctuations in temperature, variations in the concentration of the developing solution, etc., three strips, one from each of the above methods of treatment, were developed together in the same solution.

The order of treatment was as follows:

1. Two-minute bath in the peroxide or peroxide solvent.
2. Two-minute rinse in distilled water.
3. Development for length of time required for desired gamma.
4. Immersion in 1% acetic acid short stop for 1 minute.
5. Fixing in acid hypo (hardened) for 15 minutes.
6. Thirty-minute wash in tap water.
7. Drying.
8. Density measurements.

Density measurements were made on the Martens Polarizing Photometer.

Formulas

Developing Solutions

D-1. Metol.

A.	Metol	8.0 g.
	Sodium Sulfite (Anhydrous)	100.0 g.
	Water to	2000.0 ml.

B.	Sodium Carbonate (Monohydrate)	112.0 g.
	Water to	2000.0 ml.

Dilute: A, 75 ml.; B, 75 ml.; water, 50 ml.

D-2. Quinol.

Hydroquinone	30.0 g.
Sodium Sulfite (Anhydrous)	100.0 g.
Sodium Carbonate (Monohydrate)	150.0 g.
Water to	2000.0 ml.

Dilute 1:3

D-2B. Quinol.

Hydroquinone	60.0 g.
Sodium Sulfite (Anhydrous)	80.0 g.
Sodium Carbonate (Monohydrate)	100.0 g.
Water to	1000.0 ml.

Do not dilute

D-3. Pyro.

A.	Sodium Sulfite (Anhydrous)	70.0 g.
	Sodium Bisulfite	17.0 g.
	Pyrogallol	20.0 g.
	Water to	1000.0 ml.

B.	Sodium Carbonate (Monohydrate)	75.0 g.
	Potassium Bromide	1.0 g.
	Water to	1000.0 ml.

Use equal parts A and B

D-6 Glycin.

Sodium Sulfite (Anhydrous)	150.0 g.
Glycin	50.0 g.
Sodium Carbonate (Monohydrate)	150.0 g.
Water to	1000.0 ml.

Dilute 1:2

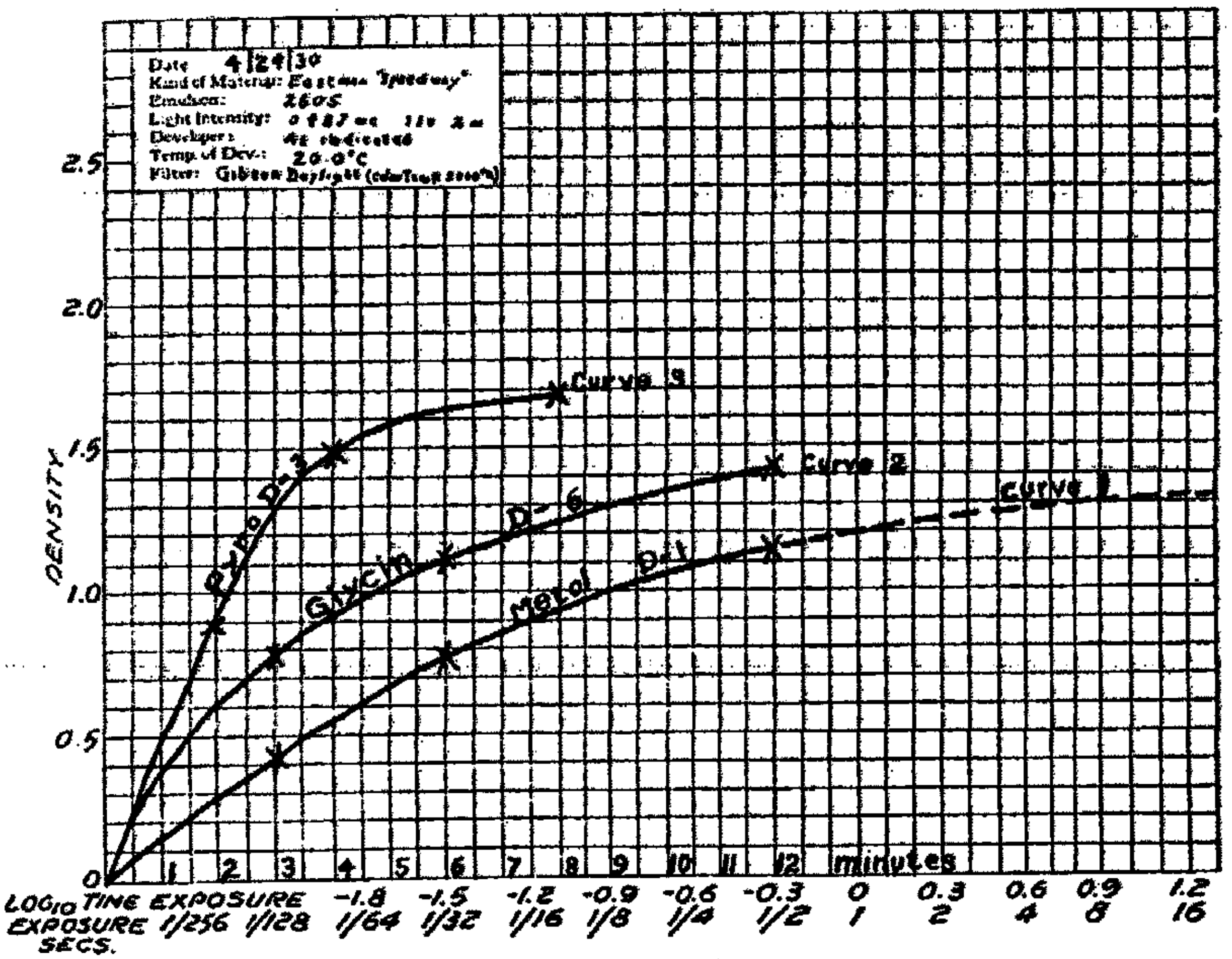
Experiments and Results

1. *Time-Gamma Curves.*

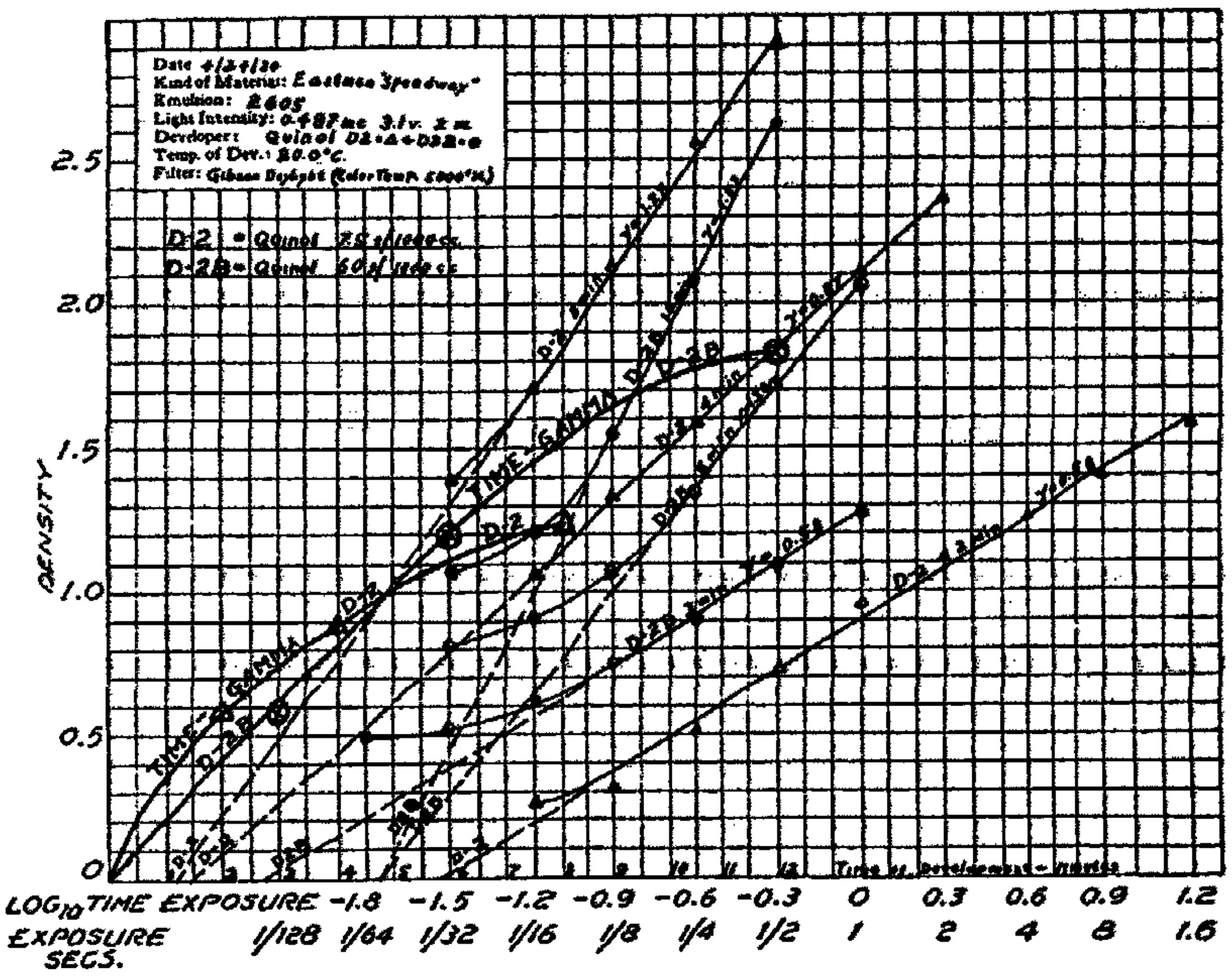
To obtain a better comparison between the different developing agents having varying rates of development, it was decided to develop to approximately the same gamma instead of the same time. In order to do this, time-gamma curves were plotted for each of the developing solutions.

Upon examination of the accompanying time-gamma curves it will be noticed that the curve for metol (curve 1) rises very gently since metol is a "soft" developer. Only with long development times can a negative of high gamma or "contrasty" negative be obtained. From the value of "gamma-infinity" (the value toward which the curve approaches asymptotically) it will be seen that no very high contrast may be attained by using metol.

As opposed to this it will be noticed that pyro (curve 3) builds up contrast rapidly in the first few minutes of development. Maximum contrast has nearly been reached at the end of five minutes with this developer. Because of this fact it is hard to develop to the same gamma with pyro, for even a slight error in stopping development (which at best is none too accurate since it must be done by removing a plate from one solution and immersing it in another) will cause an appreciable error in the gamma obtained. Mention is made of this here since it is an explanation of the slightly different



Curves 1, 2 and 3
Time-Gamma Curves



Curve 4
Time-Gamma Curves of Quinol, D-2 and D-2B

values of gamma obtained with pyro for the same developing time in the experiments with organic peroxides. Pyro was used in these experiments in order that the results might be comparable to work which has already been carried out with benzoyl peroxide in which pyro (formula D-3) was used. Metol would doubtless have been a better developing agent to use since it has no steep portion in its time-gamma curve.

The shape of the time-gamma curve for any given developing agent may be changed by varying the proportions of the constituents in the developing solution. An example of this is shown in curve 4 which gives the time-gamma curves for two concentrations of quinol. It is a peculiar fact that the more dilute solution of quinol is the more rapid developer up to a gamma of one (at five-minute development). Above this point, however, the higher concentration of quinol causes the plate to gain contrast much more rapidly than does the lower concentration. The reason for this is not quite clear but perhaps it may be explained on a basis of ionization; however, there are apparently insufficient data on the ionization of the sodium salts of quinol.[1]

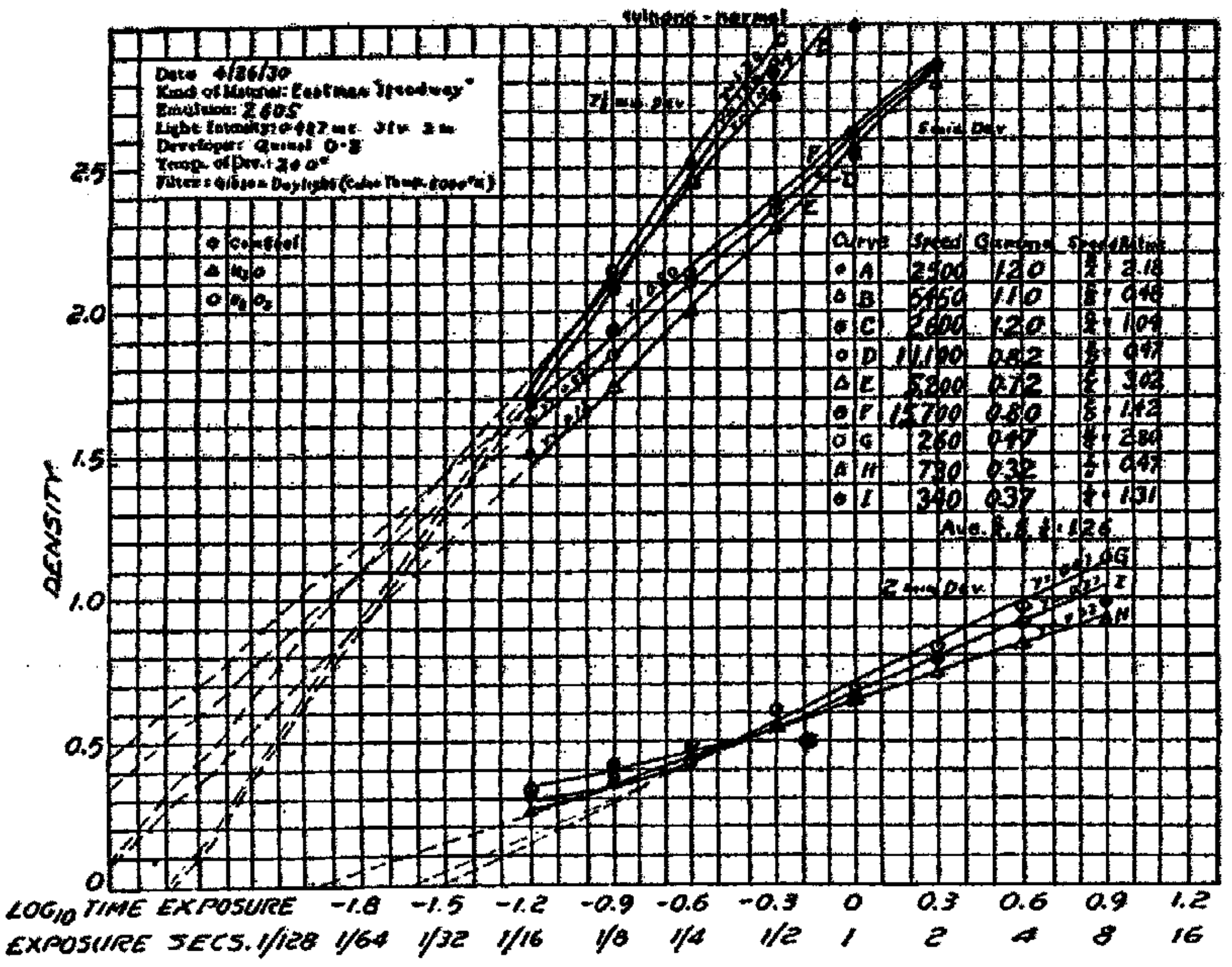
An investigation of the difference in the rate in which these two concentrations of quinol build up contrast above and below five minutes throws important light upon the effect of previous swelling of the gelatin in water on developing speed. One theory has already been proposed by Wightman[2] that previous swelling of the emulsion by water-bathing increased the speed of diffusion of the developer, thus partly accounting for the increase in speed of his water-bathed plates. On the other hand it seems logical to assume that the presence of water already in the gelatin must cause a dilution effect tending to slow up development. As may be seen by comparing curves 5 and 6, bathing in water *lowers* the gamma in the more dilute quinol developer (curve 5), but *greatly increases* the gamma with the concentrated quinol developer (curve 6). Since increase in gamma is only effected normally by an increase in developing time, any increase in gamma may be considered as an increase in developing speed.

It was pointed out in reference to curve 4, that under five-minute development the more dilute quinol solution developed more rapidly, indicating *more rapid diffusion* into the gelatin than the high concentration of quinol which developed more slowly. Above five minutes, however, the rate of penetration of the developing solution is no longer an important factor and the high concentration now goes rapidly ahead. With this in mind it is reasonable to expect that swelling the gelatin of a plate with water before immersion in the high concentration of quinol would greatly increase the gamma of that plate over one not receiving water treatment provided the development times were kept below the point where the curves cross. And this, as has been pointed out, is just what takes place (curve 6). On the other hand, it would be expected that previous swelling of the gelatin of

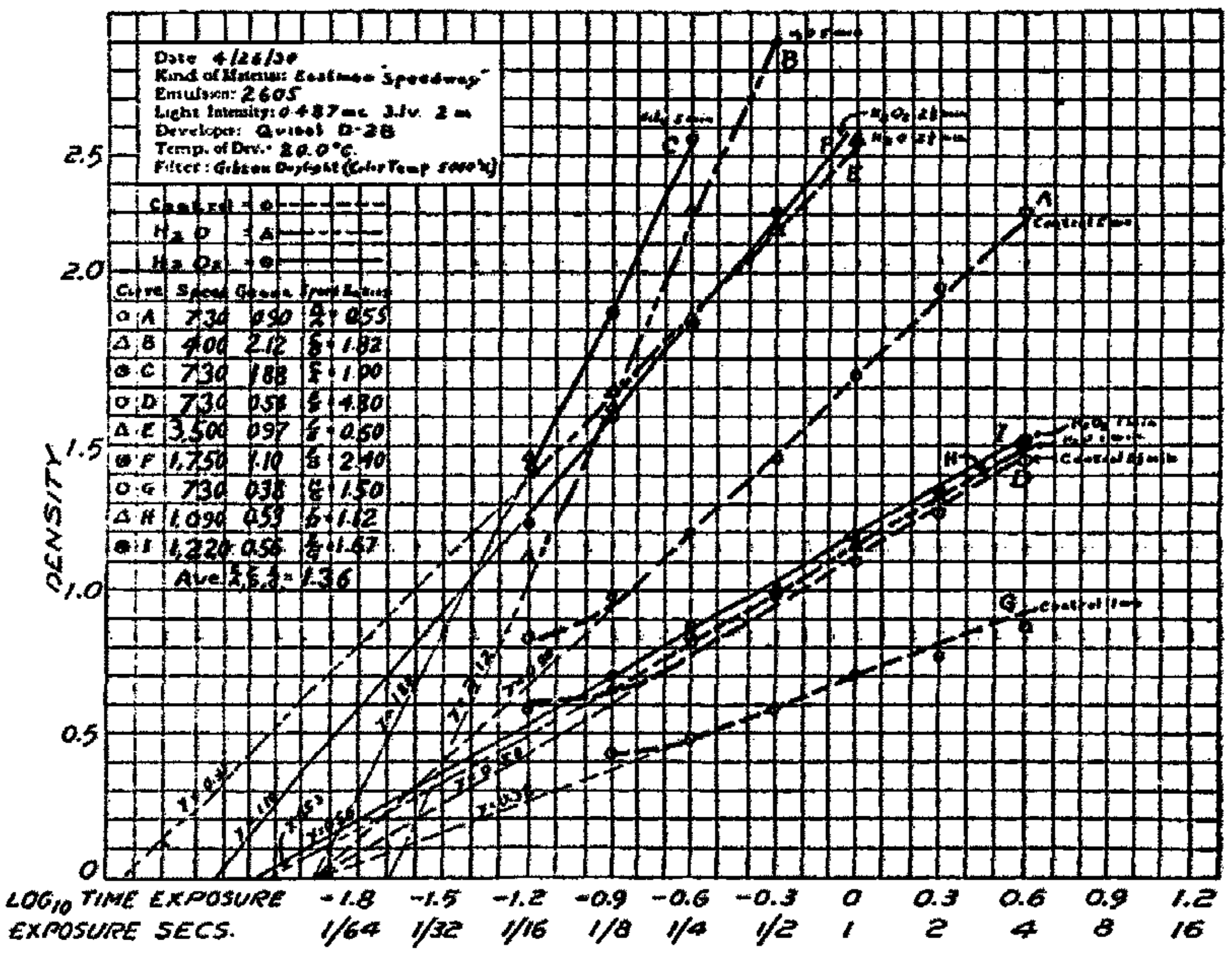
---

[1] See S. E. Sheppard: "Electrochemical Aspects of Photographic Development," Trans. Am. Electrochem. Soc., 39, 429 (1921).

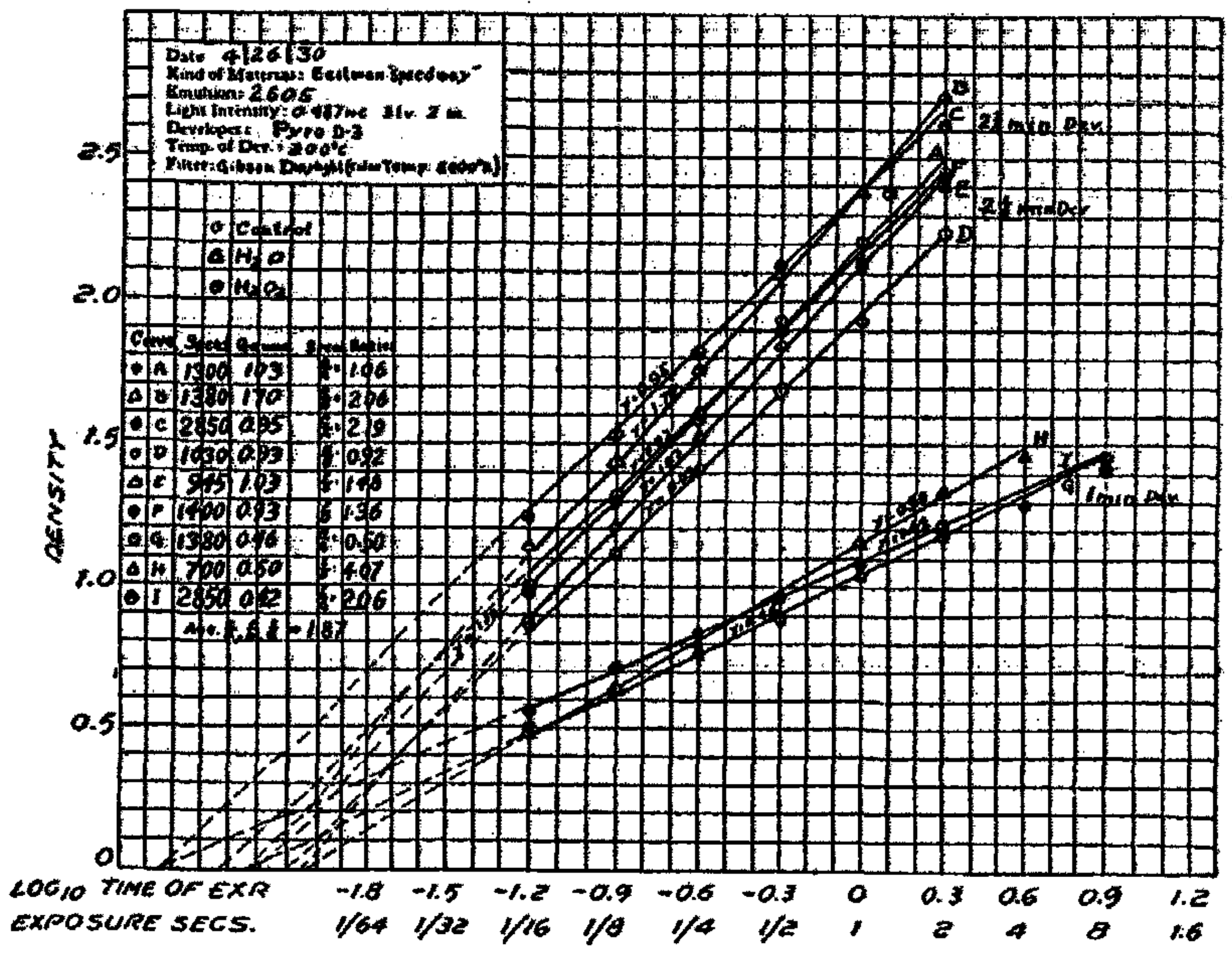
[2] E. P. Wightman and R. F. Quirk: J. Franklin Inst., 199, 286 (1927).



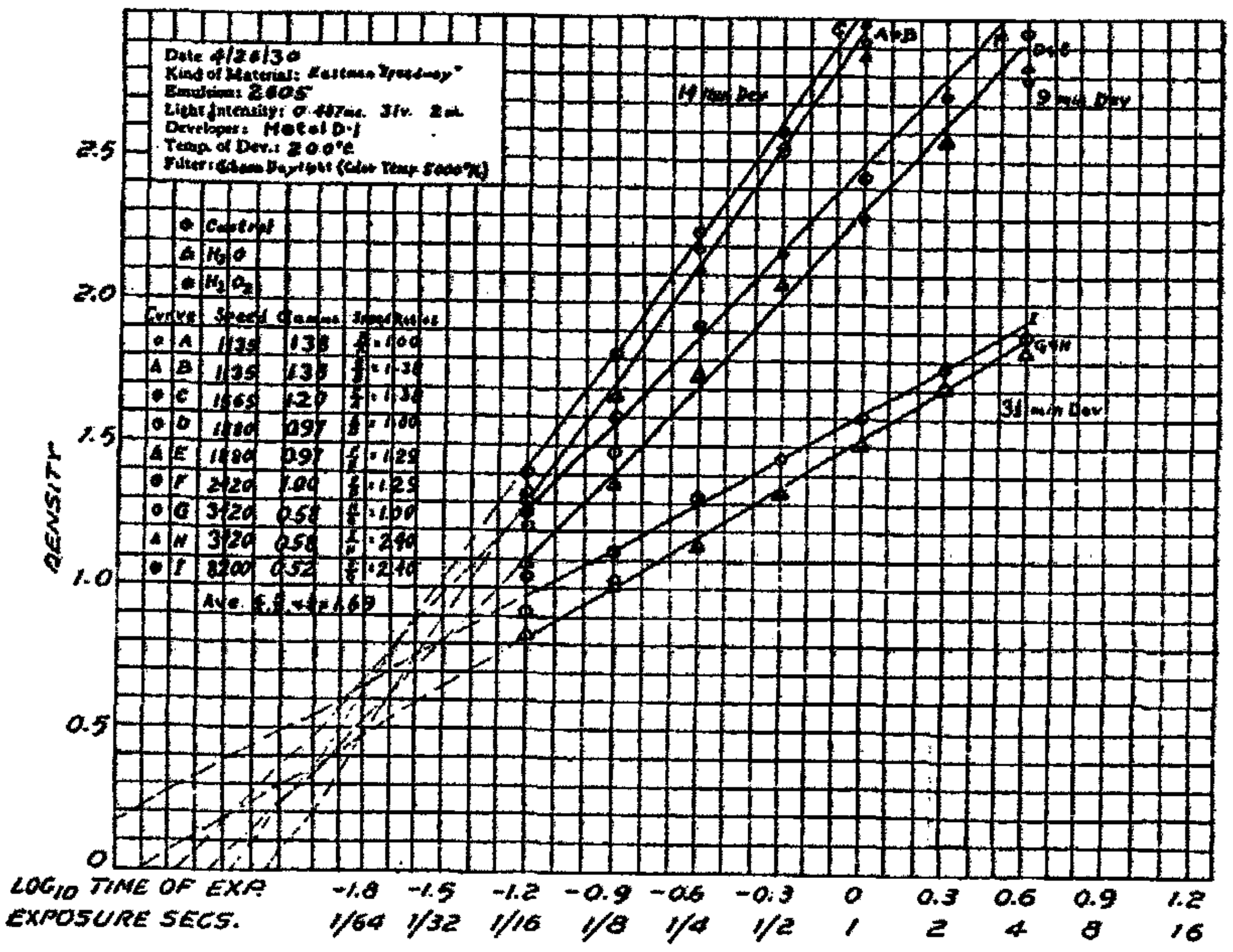
Curve 5
H_2O_2 with Hydroquinone-normal conc.



Curve 6
H_2O_2 with Hydroquinone-high conc.



Curve 7
H_2O_2 with Pyro



Curve 8
H_2O_2 with Metol

a plate to be developed in the weaker solution, which already penetrates quite rapidly, would tend to slow development since the dilution effect on the already dilute developer would outweigh any increase in the rate of diffusion. This is borne out by curve 5. Thus both effects take place and the final result is determined by the concentration of the developing agent. This being true it should be possible to make the developing solution of such strength that previous swelling of the emulsion in water would produce no effect whatever. Curve 8 shows the action of such a developing solution; the curve of the water-bathed plate coincides with that of the control plate. This concentration is more easily arrived at with metol, probably, because of its gradually rising time-gamma curve.

2. *Effect of hydrogen peroxide using different developing solutions.*

From the time-gamma curves the following development times were obtained to secure a gamma of 0.5, 1.0 and 1.2 for each of the developing solutions to be used in this set of experiments:

Development Time—Minutes

Developer	$\gamma = 0.5$	$\gamma = 1.0$	$\gamma = 1.2$
Metol, D-1	3 1/2	9	14
Quinol, D-2	2	5	7 1/2
Quinol, D-2B	2 1/2	5	1*
Pyro, D-3	1	2 1/4	2 3/4
Glycin, D-6	1 1/2	4 1/2	7 1/2

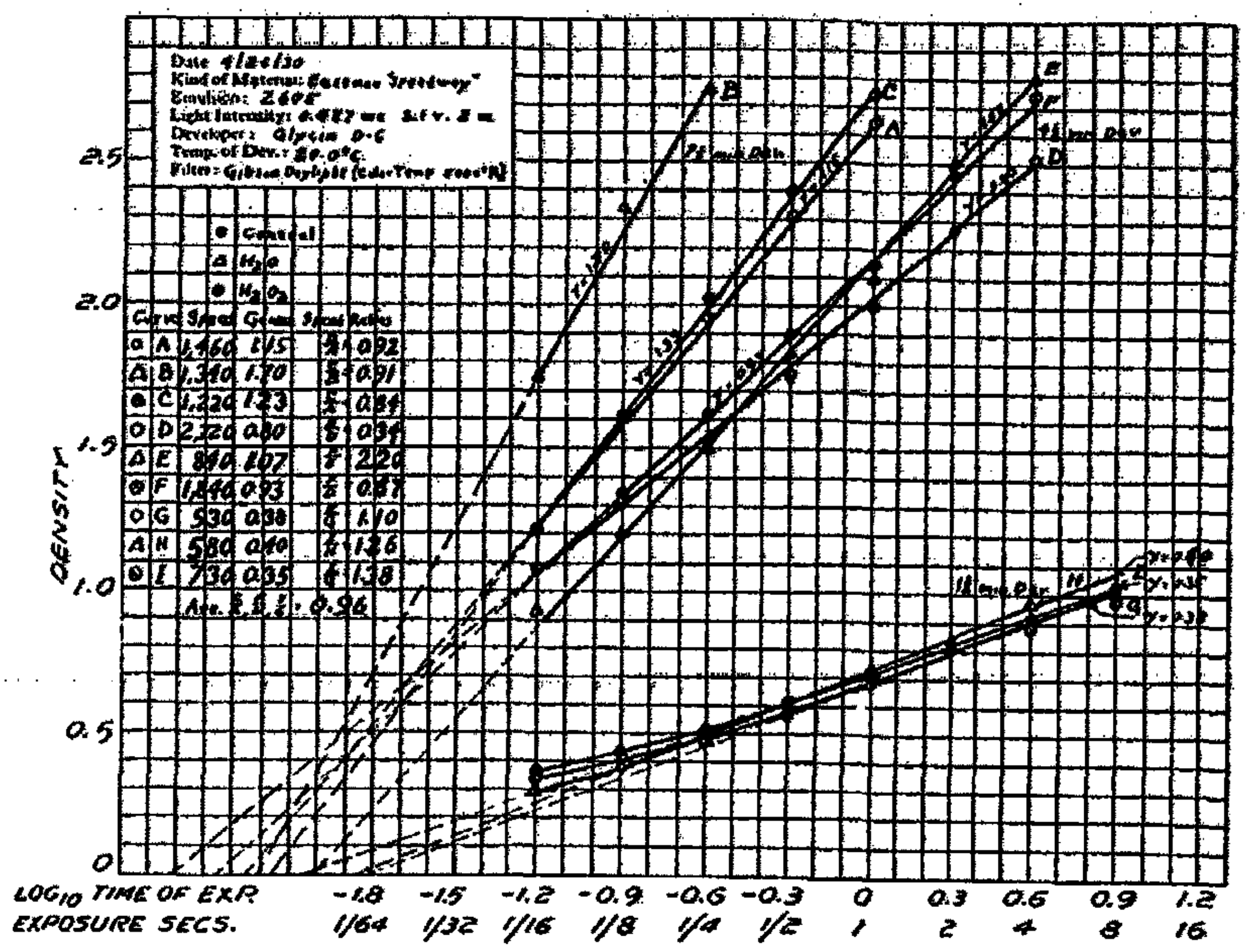
*This time is for a gamma of 0.4 for the control plate.

The concentration of the hydrogen peroxide used in these experiments was approximately 0.016%, made up from Eimer and Amend's 3.63% C. P. Hydrogen Peroxide which was acid to litmus. The order of treatment has been given above.

After exposure and treatment of the strips, density measurements were made as before and the densities plotted against log exposure time, giving families of H and D curves for the different development times. The straight-line portions were extended until they cut the base line and the H and D speeds and the gammas calculated. These appear on the curves together with calculated speed ratios.

An examination of the average speed ratios on the accompanying curves shows the following results:

Developing Solution	Intensifying Action of H_2O_2—i.e. Speed Ratio: H_2O_2/control
Metol, D-1	1.69
Quinol, D-2 (normal conc.)	1.26
Quinol, D-2B (high conc)	1.36
Pyro, D-3	1.87
Glycin, D-6	0.96



Curve 9
H_2O_2 with Glycin

From the above it will be noticed that hydrogen peroxide produces an increase in speed with all developing agents except glycin. The values, however, vary considerably and are not in accord with the conclusion of Wightman and Quirk[1] that latent image intensification is largely independent of the developer used. Wightman and Quirk suggest that one might expect some variation in the amount of intensification when one developer is used instead of another, but state that this should follow more or less the variations in the developability of ordinary latent image with various developers.

Pyro and metol show the highest degree of intensification but an examination of their time-gamma curves will show that these two developers are widely different in their action. Glycin shows a very slight falling off in speed. Accordingly, in view of these data, it would seem that latent image intensification is dependent to a considerable extent on the nature of the developing solution used.

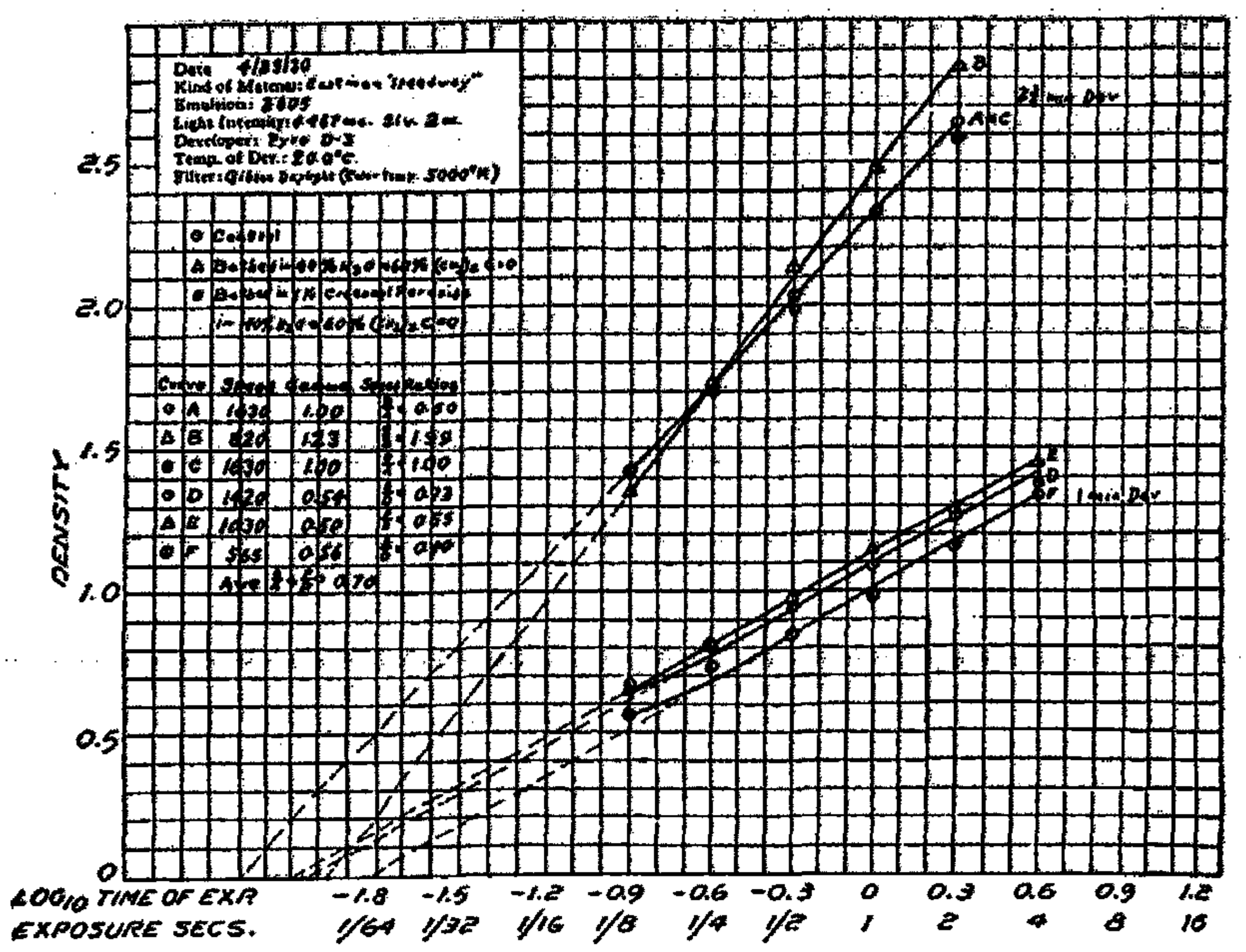
3. *Action of Organic Peroxides.*

In this group of experiments plates receiving the following treatment were developed for 1 minute and for 2 3/4 minutes in pyro:

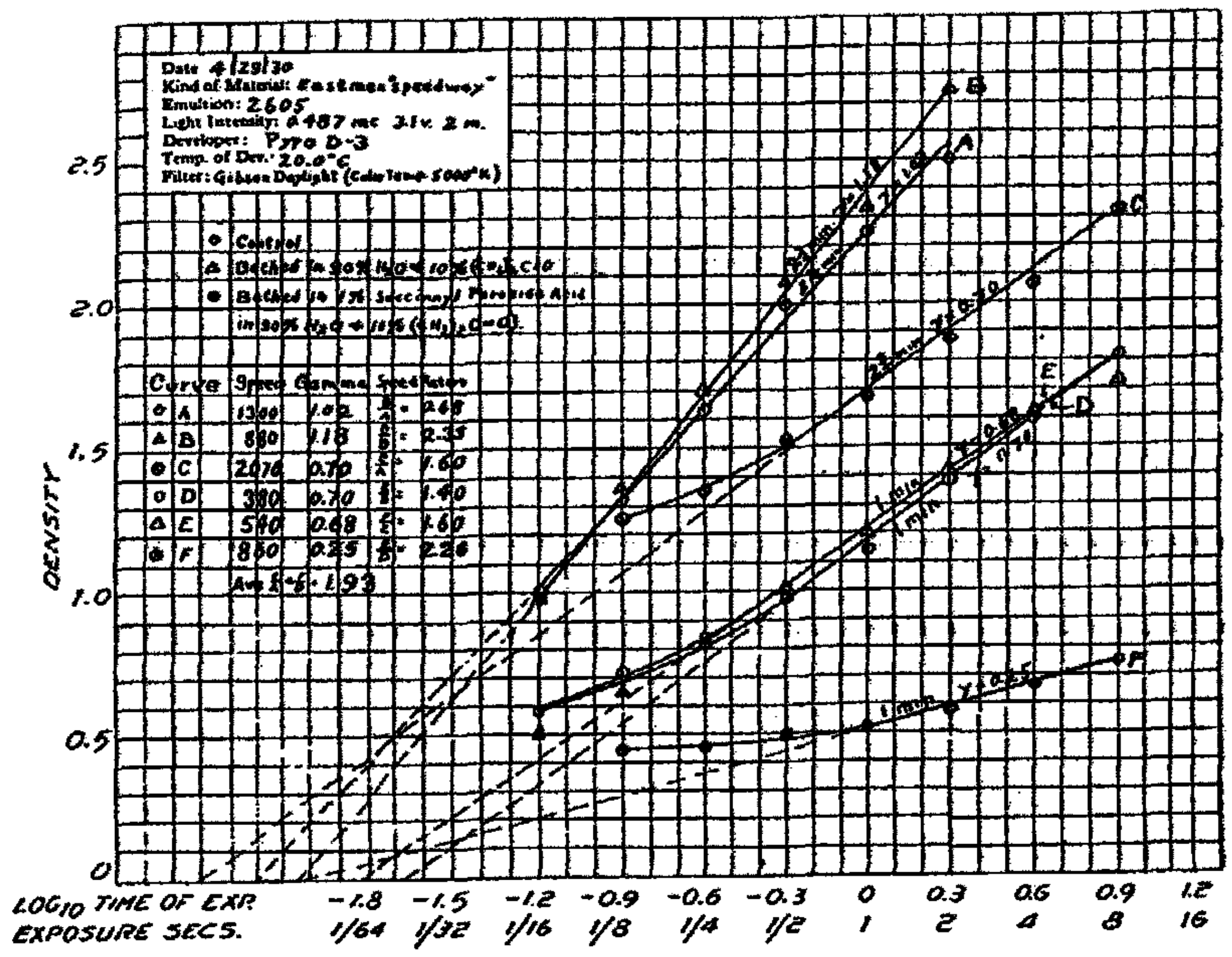
(1). Two-minute treatment in a 1% solution of the organic peroxide dissolved in varying proportions of acetone and water (depending on the amount of water which could be added to the actone solution of the peroxide without causing precipitation).

---

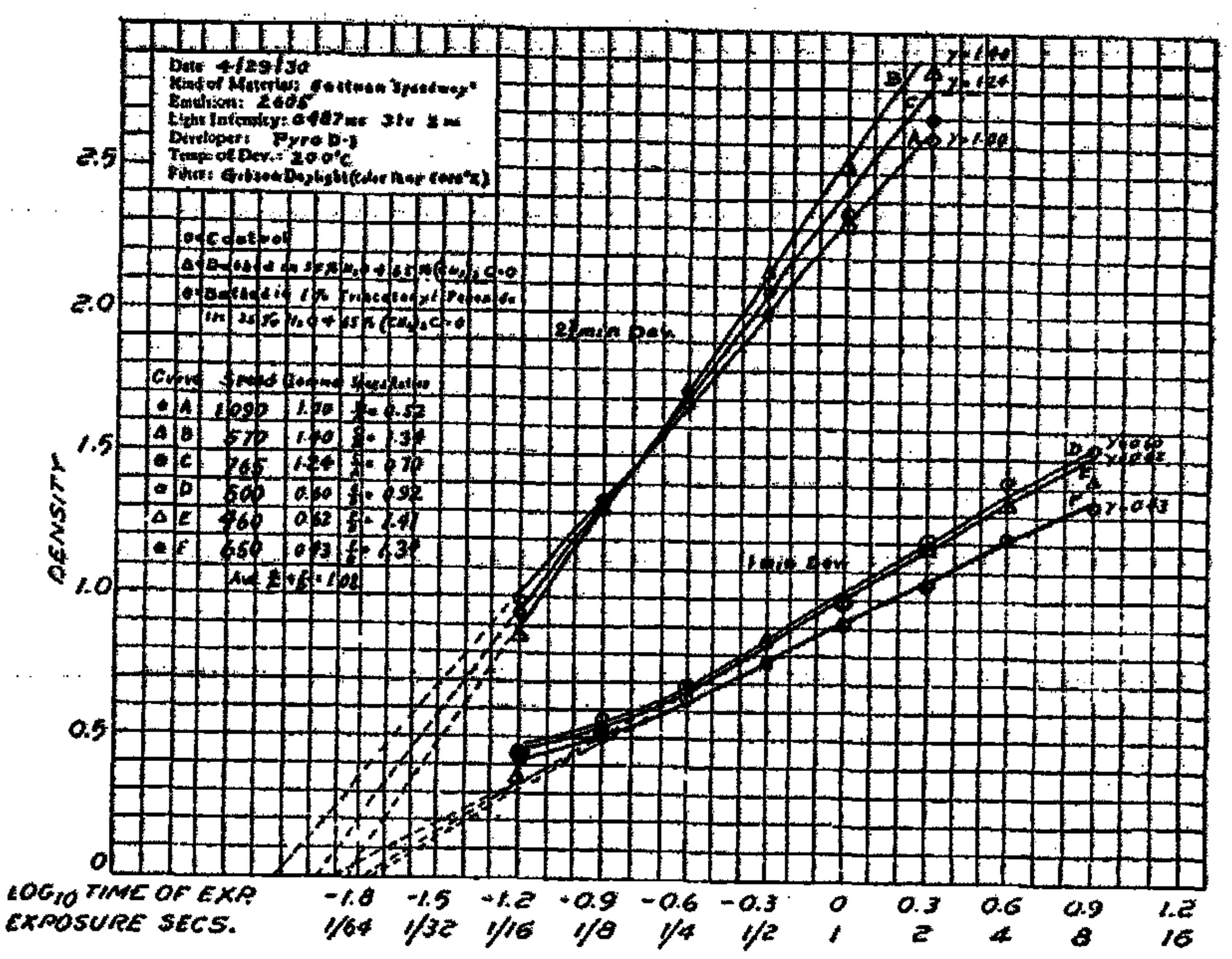
[1] E. P. Wightman and R. F. Quirk: Proc. Seventh International Congress of Photography, 1928, 242.



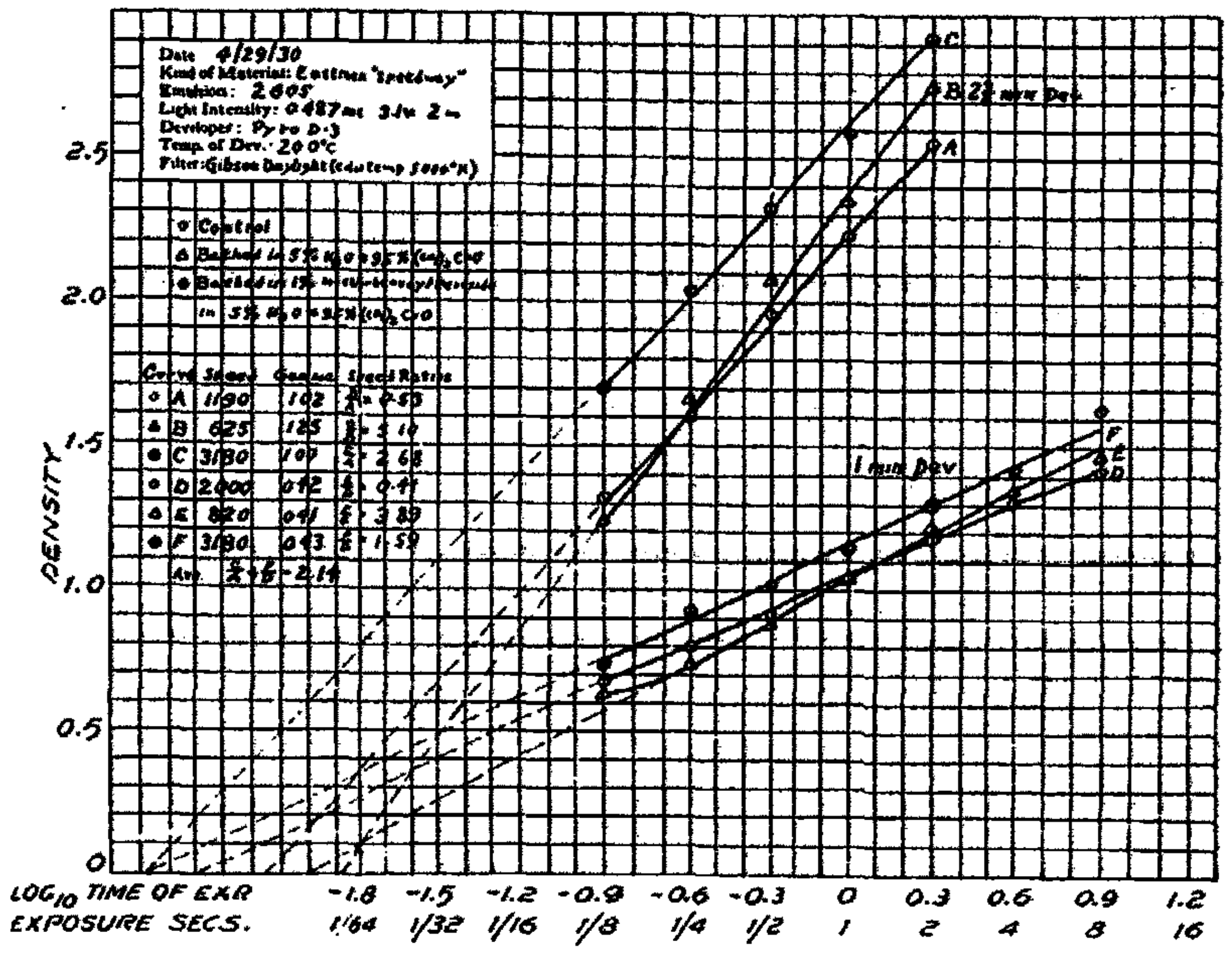
Curve 10
Crotonyl Peroxide



Curve 11
Succinnyl Peroxide Acid



Curve 12
Triacetonyl Peroxide



Curve 13
m-Chlorbenzoyl Peroxide

(2). Two-minute treatment in acetone-water of the same proportions as used in the solvent for the organic peroxide.

(3). No treatment (control).

H and D curves were plotted as in previous experiments from which gammas and speeds were determined. These have been arranged in the following table:

Peroxide	H and D Speed Ratios (average)	Gamma Ratio: 1 min.	2¾ min.
Crotonyl	0.70	0.96	1.00
Succinnyl Acid	1.93	2.8	1.5
Triacetonyl	1.02	1.4	0.80
m-Chlorbenzoyl	2.14	0.98	0.99

From an examination of curve sheets 10-13 it will be seen that the only peroxide which produces what might be termed a practical photographic intensification (i.e., each density being greater on the peroxide-bathed plate than the corresponding density for the same exposure on the control plate) is m-chlorbenzoyl peroxide. In no other case is this true. According to the speed ratios, however, succinnyl peroxide-acid and triacetonyl peroxide should also show intensification. That any intensification shown by these last two peroxides is of a different nature than that shown by m-chlorbenzoyl peroxide is obvious from the curves. For example, the densities of the succinyl peroxide acid-bathed plates are in every case markedly less than corresponding densities of the control plate. Yet because of the slope of the curve, or the gamma, the inertia point is brought further to the left, thus indicating greater speed. It is evident that the *gammas* must also be taken into consideration, *and true intensification* only attributed to a substance which shows an increase *in* speed when its H and D curve has the same slope or the *same gamma* as the control. In fact, this is the only result which could be considered in accordance with the present theory of latent image intensification—namely, that the action of the peroxide raises the developability level of *all* grains. True intensification has been effected, then, when the speed ratio shows an increase and when the *ratio of the gamma of the control plate to the gamma of the peroxide-treated plate is* 1. The only peroxide investigated which meets both these requirements is m-chlorbenzoyl peroxide.

4. *Summary.*

1. Water treatment prior to development has two effects:
    - (a). that of facilitating the penetration of the developing solution, as suggested by Wightman and Quirk, which hastens development; this effect shows itself, however, when the concentration of the developing agent is sufficiently high to supersede the
    - (b). dilution effect in which the action of the developing agent is retarded by dilution due to water already in the gelatin, thus

causing a lowering of the gamma below that which would normally be obtained for a given development time with an untreated plate.

2. In view of further data obtained in these experiments it would appear that latent image intensification by means of hydrogen peroxide is dependent to a considerable extent on the developer used.
3. It would seem that a plate has undergone true intensification only when it not only shows an increase in H & D speed but when its H & D curve has the same slope or the same gamma as the curve of the control plate.

5. *Acknowledgment.*

The authors are indebted to Professor C. B. Neblette of the Texas A. and M. College for suggesting work along the line of latent image intensification and to the Pilot Laboratories for the rare organic peroxides used in these experiments. They are also indebted to Prof. Arthur C. Hardy and Prof. A. G. Hall of the Massachusetts Institute of Technology for the use of apparatus with which data for the curves were obtained.

Bates College, Lewiston, Maine.

THE DECOMPOSITION OF SODIUM HYPOCHLORITE—AN ION REACTION

BY W. FRED UNDERWOOD AND EDWARD MACK, JR.

Several studies have recently been made by J. R. Lewis,[1] Howell[2] and Chirnoaga[3] of the decomposition of sodium hypochlorite solutions in the presence of metal oxide catalysts, and some investigations have been reported on the uncatalyzed decomposition. The evidence regarding the mechanism of the reaction is far from satisfactory. For example, Chirnoaga states that his stock solutions of sodium hypochlorite, during decomposition over a time of 317 days, followed closely the unimolecular law. Giordani,[4] however, reports a second order reaction, and Bhaduri's[5] results permit various deductions regarding the order of the reaction. These ambiguous results, together with the well-known fact (emerging from industrial experience with bleach) that the decomposition of sodium hypochlorite is speeded up by the presence of neutral salts, have led us to suppose that the uncatalyzed decomposition is an ion reaction which might be amenable to Brönsted's general type of treatment.

Since the behavior of sodium hypochlorite solutions on electrolysis indicates clearly the presence of the ions Na^+ and ClO^-, it seems natural to suppose that one, at least, of the mechanisms by which sodium hypochlorite changes into sodium chloride and oxygen gas, might be represented as:

$$2\,Na^+ + 2\,ClO^- \rightarrow 2\,Na^+ + 2\,Cl^- + O_2 \qquad (1)$$

or,

$$2\,ClO^- \rightarrow 2\,Cl^- + O_2 \qquad (2)$$

The free energy[6] of formation at 25° of ClO^- is −6500, and of Cl^- is −31,367 cals. Thus the free energy decrease in the reaction is about 49,700 cals., and indicates that the equilibrium in Reaction (2) is displaced strongly toward the right.

In our experimental study we have confined our observations to the initial stages of the reaction, in fact to that stage which includes not more than about the first 1% of the total reaction. Later stages of the reaction seem to be considerably more complicated and involve the probable formation of ClO^-_3 and possibly other ions. We have noted, for example, that under

---

[1] Lewis: J. Phys. Chem., 32, 243 (1928).

[2] Howell: Proc. Roy. Soc., 104A, 134 (1923).

[3] Chirnoaga: J. Chem. Soc., Part II, 1693 (1926).

[4] Giordani: Gazz., 54, 844-60 (1924).

[5] Bhaduri: Z. anorg. Chem., 13, 383 (1897).

[6] Lewis and Randall: "Thermodynamics," p. 607 (1923).

the conditions of our experiments, oxygen gas which has been given off at the beginning may be partially re-absorbed by the system in its later life.

On the hypothesis, then, that Reaction (2) occurs during the initial stages, we may apply the Brönsted theory in terms of the equation,[7] $h = kC_A.C_B.10^{z_Az_B\sqrt{\mu}}$, where h represents the reaction velocity, k the velocity constant, C_A and C_B the molar concentrations of ions A and B, z_A and z_B the valence of ions A and B, and μ the ionic strength of the solution. Since the reacting ions A and B are each ClO^-, we would predict a positive salt effect, that is, increasing reaction velocity with increasing salt concentration, and also predict a slope of +1 for the curve representing the plot k_0, the ordinary velocity constant, against $\sqrt{\mu}$. These predictions are borne out by experimental test.

Experimental

Preparation of Sodium Hypochlorite.—In order to prepare a sample of sodium hypochlorite free from sodium chloride, R. B. MacMillin's[8] method was employed, and modified somewhat for our purpose. A 30-35% aqueous solution of sodium hydroxide of Grade B quality (not more than 0.003% heavy metals) was added to 40% of its own volume of tertiary butyl alcohol. Through this mixture kept at 0° and well-stirred, chlorine gas was passed until a sample of the aqueous solution became acid, and showed only a slight effervescence upon being treated with neutral hydrogen peroxide solution. The chlorine was stopped at this point, since free chlorine reacts with tertiary butyl alcohol to form butyl chloride. The hypochlorous acid which is formed reacts with the alcohol to give tertiary butyl hypochlorite, a yellow colored liquid layer resting above the sodium chloride solution. This layer was then removed and washed first with a 2% solution of sodium hydroxide to remove possible traces of free chlorine, and then with distilled water (to remove traces of sodium chloride), and was finally treated, while stirring vigorously, with slightly more than the theoretical amount of a 40% aqueous solution of Grade A sodium hydroxide (0.000% heavy metals) to obtain sodium hypochlorite. For the purpose of calculating the correct amount of sodium hydroxide to be added, the concentration of the tertiary butyl hypochlorite was determined by the usual iodometric method for sodium hypochlorite.

The sodium hypochlorite solution was separated by decantation, washed with ethyl ether to remove dissolved butyl alcohol, and separated by decantation from the ether. The solution was then cooled to 0° and seeded with a few crystals of sodium hypochlorite, formed by supercooling a small portion of the solution with carbon dioxide snow. The pure crystals of hydrated sodium hypochlorite, $NaClO.5H_2O$, came out rapidly in long pale lemon-yellow needles. They were filtered off in a Jena glass filter and washed with

---

[7] For a good account of Brönsted's theory and the derivation and application of his equations, reference may be made to Brönsted's own lecture, Theory of Velocity of Ionic Reactions, in "Contemporary Developments in Chemistry," Columbia University Press, (1927).

[8] MacMillin: U. S. P. 1,632,483; 1,632,484; 1,632,485.

TABLE I

Rate of Evolution of Oxygen from a Neutral 1.0 Molar Sodium Hypochlorite Solution, containing 2.0 Molar Sodium Chloride.

Volume of Sample = 200 cc. Thermostat Temperature = 45° ± .01

Elapsed Time (mins.)	Total cc. Oxygen evolved Experiment A	Total cc. Oxygen evolved Experiment B	Total cc. Oxygen evolved Average	Total cc. Oxygen evolved Corrected x	$(a-x)$	$k_o \times 10^{-9}$	Barometric Pressure (mm. Hg)
0	0	0	0	0	2240.00	—	744.7
5	0.40	0.40	0.40	0.30	2239.70	11.96	
10	0.80	0.80	0.80	0.61	2239.39	11.56	
15	1.25	1.20	1.23	0.93	2239.07	12.76	
20	1.60	1.60	1.60	1.22	2238.78	11.57	
25	2.10	1.90	2.00	1.52	2238.48	11.98	
31	2.35	2.30	2.33	1.77	2238.23	8.32	
35	2.65	2.60	2.63	2.00	2238.00	11.49	
40	3.00	2.95	2.98	2.26	2237.74	10.38	
45	3.40	3.30	3.35	2.55	2237.45	7.60	
50	3.60	3.65	3.63	2.76	2237.24	8.39	
55	4.00	4.00	4.00	3.04	2236.96	11.18	
60	4.40	4.30	4.35	3.31	2236.69	10.78	
65	4.75	4.65	4.70	3.57	2236.43	10.40	
70	5.05	5.00	5.03	3.82	2236.18	10.00	
75	5.45	5.40	5.43	4.13	2235.87	12.40	
80	5.82	5.80	5.81	4.42	2235.58	11.60	
85	6.05	6.10	6.08	4.62	2235.38	8.00	
90	6.40	6.35	6.38	4.85	2235.15	9.23	
95	6.80	6.70	6.75	5.12	2234.88	10.00	
100	7.15	7.00	7.08	5.38	2234.62	10.41	
110	8.05	7.70	7.88	5.98	2234.02	12.02	
116	8.35	8.10	8.23	6.25	2233.75	9.02	
120	8.65	8.40	8.53	6.48	2233.52	11.52	
125	9.00	8.65	8.83	6.71	2233.29	9.22	
130	9.35	9.00	9.18	6.97	2233.03	10.42	
135	9.65	9.40	9.53	7.24	2232.76	10.82	
140	10.00	9.75	9.88	7.50	2232.50	10.42	
145	10.40	10.10	10.25	7.78	2232.22	11.24	
150	10.75	10.50	10.63	8.08	2231.92	12.40	
155	11.05	10.80	10.93	8.30	2231.70	8.82	
160	11.45	11.20	11.33	8.61	2231.39	12.42	
165	11.75	11.45	11.65	8.85	2231.15	9.64	
170	12.05	11.90	11.98	9.10	2230.90	10.04	
175	12.35	12.25	12.30	9.34	2230.66	9.64	
180	12.70	12.60	12.65	9.62	2230.38	11.25	
185	13.05	12.95	13.00	9.88	2230.12	10.46	

TABLE I (Continued)

Rate of Evolution of Oxygen from a Neutral 1.0 Molar Sodium Hypochlorite Solution, containing 2.0 Molar Sodium Chloride.

Volume of Sample = 200 cc. Thermostat Temperature = 45° ± .01

Elapsed Time (mins.)	Total cc. Oxygen evolved						
	Experiment A	Experiment B	Average	Corrected x	$(a-x)$	$k_o \times 10^{-9}$	Barometric Pressure (mm. Hg)
190	13.45	13.40	13.43	10.20	2229.80	12.87	743.2
200	14.05	13.80	13.93	10.58	2229.42	7.65	
205	14.45	14.20	14.33	10.80	2229.20	8.86	
210	14.75	14.50	14.63	11.12	2228.88	12.87	
215	15.10	14.85	14.98	11.38	2228.62	10.46	
220	15.35	15.25	15.30	11.63	2228.37	10.06	
225	15.80	15.65	15.73	11.95	2228.05	12.90	
230	16.16	15.95	16.05	12.20	2227.80	10.07	
235	16.35	16.15	16.25	12.35	2227.65	6.04	
240	16.65	16.60	16.63	12.64	2227.36	11.72	
245	16.95	16.80	16.88	12.82	2227.18	11.70	
255	17.65	17.10	17.38	13.20	2226.80	7.66	
260	18.05	17.90	17.98	13.65	2226.35	18.17	
265	18.40	18.25	18.33	13.92	2226.08	10.90	
270	18.75	18.65	18.70	14.21	2225.79	11.70	
275	19.15	19.00	19.08	14.50	2225.50	11.70	
280	19.45	19.30	19.38	14.72	2225.28	8.88	
285	19.75	19.65	19.70	14.96	2225.04	9.70	

Average Barometric Pressure.................................744.0 mm.
Vapor Tension of Water at 45.00° = 71.4 mm.

$$\ldots\text{Gas Volume Correction Factor} = \frac{(744.0 - 71.4)}{760} \times \frac{(273)}{(273 + 45.00)}$$

$$= 0.760$$

Average bimolecular velocity constant for the period starting 30 minutes after the zero time point and from interval to interval for the next 180 minutes = 10.41×10^{-9}.

distilled water. It was found possible to store the crystals at 0° for as long as 48 hours without detectable decomposition. It was necessary to wash the crystals repeatedly with distilled water to remove traces of sodium hydroxide, and in fact we found it advisable, before making up the solutions, for the experimental work, to add enough hydrochloric acid to neutralize the traces of hydroxide. The sodium chloride formed in this way was taken into account when salts were later added to the solution.

Experimental Procedure.—Aqueous solutions (generally 200 cc.) containing the desired concentration of freshly prepared sodium hypochlorite and of added salts were made up and placed in pyrex glass reaction vessels kept in a thermostat. The solutions were stirred with motor driven stirrers, through mercury seals, and the escaping oxygen gas was collected over water in water-jacketed burettes, which were kept at the same temperature as the thermostat (45° ± .01). The burettes were provided with manometers to assist in measuring the oxygen volume at atmospheric pressure. The volume of the oxygen was read at 5-minute intervals and was multiplied by a factor which corrected for aqueous tension, and to standard temperature and pressure. Every determination was run in duplicate.

Under the conditions of our experiments the rate of evolution of oxygen is fairly slow, and to speed it up we kept the temperature of the system at 45°. Table I presents the data for a typical run in the presence of added salt. The data are in duplicate, A and B, Columns 2 and 3.

In Column 5 is given x, the corrected average volume (in cc.) of oxygen evolved; and in Column 6, $a-x$, the total volume of oxygen that would be evolved on complete decomposition of the hypochlorite minus x the volume actually evolved at the various time intervals. In Column 7 is given k_0, the velocity constant, calculated from time interval to interval by the usual bimolecular equation, $k_0 = \frac{1}{t}\frac{x}{a(a-x)}.$ It will be observed that the value of k_0 are fairly constant. To obtain an average value for k_0 it was our uniform practice in all of the runs to neglect the initial period of 30 minutes and to average k_0 over the next succeeding 180 minutes.

Table II presents a summarizing list of the average velocity constants of the decomposition of sodium hypochlorite solutions containing various concentrations of neutral salts.

In Fig. 1 the value of log k_0 for Runs I-VIII in Table II are plotted, as solid black circles, against the respective values of $\sqrt{\mu}$. The points are grouped very well along the line corresponding to a slope of +1, with the exception of the two points VII and VIII for $CaCl_2$ at high values for $\sqrt{\mu}$. The results clearly bear out the prediction of the Brönsted equation for the slope. It is very surprising, however, that the equation holds so well for the salt effect at the higher ion concentrations. Ordinarily, in previous studies[7] of the salt effect, the linear relationship between log k_0 and $\sqrt{\mu}$ breaks down at relatively low values of $\sqrt{\mu}$.

No determinations of velocity constants at small sodium hypochlorite concentrations were made because of the extreme slowness of the decomposition. That the sodium hypochlorite itself exerts a salt effect is indicated by the consistency of the results obtained by including the sodium hypochlorite in the calculation of μ; and is indicated directly by a comparison of the velocity constant obtained in Run I, where 1.0 molar hypochlorite was used, with the constant of Run II, where 2.0 molar hypochlorite was employed.

TABLE II

Summary of Velocity Constants (All at 45°)

	Molar conc'n. hypochlorite	Salt added	Molar conc'n. salt added	μ	$\sqrt{\mu}$	Average velocity constant k_o	Log k_o	k_o corrected for comparison with V	Log k_o
I	1.0	NaCl	2.0	3.0	1.73	10.4 × 10^{-9}	1.017−9		
II	2.0	"	2.0	4.0	2.0	12.3 "	1.090−9		
III	1.0	"	0.01075	1.01075	1.005	1.48 "	0.170−9		
IV	1.0	"	0.25	1.25	1.12	1.98 "	0.297−9		
V	1.0	"	1.0	2.0	1.41	4.15 "	0.618−9		
VI	1.0	"	4.0	5	2.24	17.04 "	1.231−9		
VII	1.0	$CaCl_2$ NaCl	5.0 0.07	16.07	4.01	56.25 "	1.750−9		
VIII	1.0	$CaCl_2$	3.5	11.5	3.39	120.0 "	2.079−9		
A	1.0	NaCl	0.96	1.96	1.40	5.39 "		4.15 × 10^{-9}	0.618−9
B	1.0	Na_2SO_4 NaCl	1.0 0.1625	4.1625	2.04	11.08 "		8.53 "	0.931−9
a	1.0	NaCl	1.0	2.0	1.41	23.8 "		4.15 "	0.618−9
b	1.0	$CaCl_2$ NaCl	1.0 0.156	4.156	2.04	48.9 "		8.46 "	0.927−9
c	1.0	Na_2HPO_4 NaCl	1.0 0.09	4.09	2.02	29.7 "		5.17 "	0.713−9

The values of μ, the ion strength, in Table II, are calculated from the equation, $\mu = 1/2\ (m_1z_1^2 + m_2z_2^2)$, where m_1 and m_2 are the molar concentrations, and z_1 and z_2 are the valences of the ions.

The consistency of the values of k_0, calculated with the bimolecular equation, for Run I, in Table I, and also for the other runs, shows that the reaction is bimolecular, at least in solutions of high ion concentrations. This is also indicated by the fact that the time required for 0.005 decomposition in the case of Run I was 216 minutes, and in the case of Run II, with an initial hypochlorite concentration twice as great as in Run I, 90 minutes, a ratio of about 2.4:1. The departure from the theoretical ratio of 2:1 may be attributed to the salt effect of the hypochlorite itself. There is, therefore, good reason for believing that the chemical reaction involved in the decomposition of sodium hypochlorite may be represented, as has previously been stated, by Equation (2).

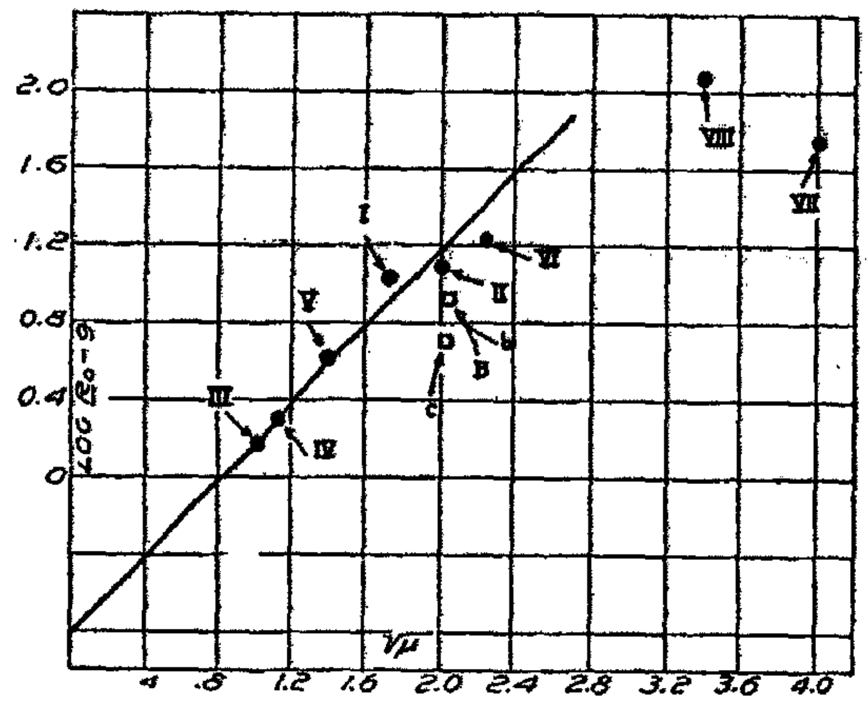


FIG. 1

The results in the lower part of Table II, Runs A, B, a, b, and c, were obtained under experimental conditions somewhat different from those of Runs I-VIII. Different samples of sodium hypochlorite were used and the volume of the reaction solution was 125 instead of 200 cc. Perhaps the consequent different conditions of stirring were responsible for the larger values of k_0 observed in the case of A and a, as compared with V. In order to make the results of A, B, a, b and c comparable with those of I-VIII, the velocity constants for A and a, namely 5.39 and 23.8 × 10^{-9}, respectively, have been arbitrarily changed to 4.15 × 10^{-9} (the same as V). The corresponding value of k_0 for B has been calculated by multiplying 11.08 by the ratio 4.15/5.39 and of k_0 for b and c by multiplying 48.9 and 29.7 by the ratio 4.15/23.8. When, with this treatment, the logs of k_0 are plotted, as squares, against the respective values of $\sqrt{\mu}$ in Fig. 1, the data points of B, b and c, fall in with the rest of the group. It should be pointed out, however, that even if exception be taken to this method of treatment of the data of A, B, a, b and c, the results of I-VIII alone are sufficient to justify the conclusion that Brönsted's theory of ion reactions applies satisfactorily to the decomposition of sodium hypochlorite.

In conclusion the authors wish to allude to an investigation reported in the literature. Clibbens and Ridge, in their study of the bleaching action of sodium hypochlorite solutions[9] upon cotton cellulose, buffered their solutions to various pH values. We suggest that the drastic action which they observed in neutral and near-neutral solutions may be attributed, at least partially, to a salt effect, since these investigators used, for buffering to pH values near 7.0, uni-bivalent salts (potassium sodium hydrogen phosphate and also borax) and on each side of this value, uni-univalent salts.

Summary

The rate of decomposition of aqueous sodium hypochlorite solutions practically free of traces of heavy metals has been studied at 45° in the presence of various salts.

There is a positive salt effect and the slope of the plot of log k_0 against $\sqrt{\mu}$ is $+1$, as predicted from Brönsted's theory, on the assumption that the chemical reaction is $2ClO^- \rightarrow 2Cl^- + O_2$.

The velocity data show that the reaction is kinetically bimolecular in strong salt solutions.

Department of Chemistry,
Ohio State University.

---

[9] Clibbens and Ridge: J. Text. Inst., **18**, T-135 (1927).

2-14-1931

THE THERMAL DECOMPOSITION OF PROPYLAMINE

BY H. AUSTIN TAYLOR AND HAROLD E. ACHILLES[1]

The decomposition of ethylamine recently studied by Taylor[2] was shown to be a homogeneous unimolecular reaction, no deviation from this being observed down to pressures of 50 mms. By comparison with corresponding work on ethers it seemed probable that a more complex amine might show deviations from unimolecularity at higher pressures and thus afford additional data whereby the various theories proposed to account for such reactions might be tested. Propylamine was chosen as a more complex though still straight-chain amine.

The pyrolysis of propylamine has been studied by Upson and Sands[3] by a dynamic method, and still more recently that of ethylamine by Hurd and Carnaham.[4] Such a complete analysis of the complex products of decomposition is thus presented that no further analyses have been made. In the decomposition of ethylamine Hurd and Carnahan find hydrogen, acetonitrile, methane, ethane, hydrogen cyanide, ethylene and ammonia. Correspondingly then, one would expect from propylamine, propylene, propane, ammonia, ethyl cyanide, ethane, hydrogen and hydrogen cyanide. The mechanism proposed by these workers for ethylamine pyrolysis involves a primary breakdown of the amine with the formation of an aldiimide:

$$CH_3CH_2NH_2 \rightarrow CH_3CH{=}NH + H_2$$

which subsequently loses hydrogen:

$$CH_3CH{=}NH \rightarrow CH_3CN + H_2$$

At higher temperatures in the neighborhood of 1000°C. the aldimide may yield methane:

$$CH_3CH{:}NH \rightarrow CH_4 + HCN$$

The presence of ethane and ammonia is supposed to be due to reduction of the amine by the hydrogen formed in the primary decomposition. The reaction is written by them as:

$$CH_3CH_2NH_2 + 2H \rightarrow CH_3CH_3 + NH_3$$

although there is no comment indicating whether some especially active form of hydrogen would be necessary for this reaction.

Upson and Sands had suggested in the initial breakdown of the amine, the formation of ammonia and the ethylidene radical, a reasonable assumption in view of the possible dehydration of the corresponding alcohol. Failing to find, in the decomposition of benzylamine, appreciable amounts of stilbene

---

[1] Abstract from a thesis presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy at New York University.

[2] J. Phys. Chem., 34, 2761 (1930).

[3] J. Am. Chem. Soc., 44, 2306 (1922).

[4] J. Am. Chem. Soc., 52, 4151 (1930).

which would be expected from the combination of two phenylmethylene radicals, Hurd and Carnahan see no necessity for the postulation of the ethylidene radical in ethylamine. The similarity of the decomposition products from both alkyl and aryl amines is alone judged as evidence of a similar decomposition mechanism. According to the Hurd mechanism the only method whereby ethane, which was observed, might be produced by decomposition of ethylamine is by reduction of the amine. That this reaction does not occur may be inferred from the absence of any effect of added hydrogen found by Taylor. Evidence also is presented in the following work that the effect of added hydrogen on the decomposition of propylamine is no more than that of a similar amount of helium or nitrogen. It seems preferable to assume then in the case here studied that propane and ammonia would be formed by reactions subsequent to the alternative split into propylene and ammonia, particularly since the temperatures here used are considerably lower than those employed by Hurd, from whose data even the percentage of unsaturated hydrocarbon is largely increased by a decreased time of contact.

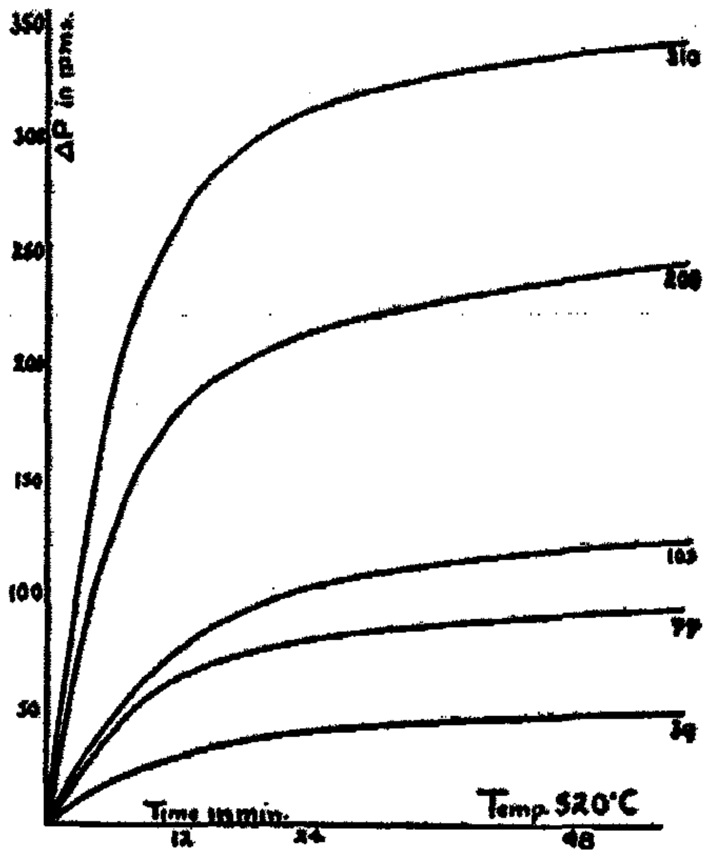


Fig. 1

The apparatus for and method of determination of the rate of decomposition were similar to those used previously by Taylor, with the exception that the reaction vessel was of quartz sealed by a graded seal to the pyrex manometer capillary tubing. The propylamine was redistilled from an Eastman sample and boiled at 48.5-49.5°C. During the reactions only small amounts of a black tarry deposit were observed in the capillary tubing just above the furnace. The reaction bulb itself was always perfectly clean.

The decomposition was studied at four temperatures at 520, 540, 560 and 580°C. The results are shown graphically in the accompanying figures, the pressure increase being plotted against time for different initial pressures. The pressure increase was on the average only slightly greater than the initial pressure, the ratio of the total pressure to the initial pressure lying between 2.1 and 2.2. This additional pressure increase is easily accountable on the basis of subsequent reactions. Actual tests made with propylene itself always showed decomposition evidenced by an increase in pressure.

To demonstrate the homogeneity of the reaction, quartz tubing was added to the reaction bulb sufficient approximately to double the surface.

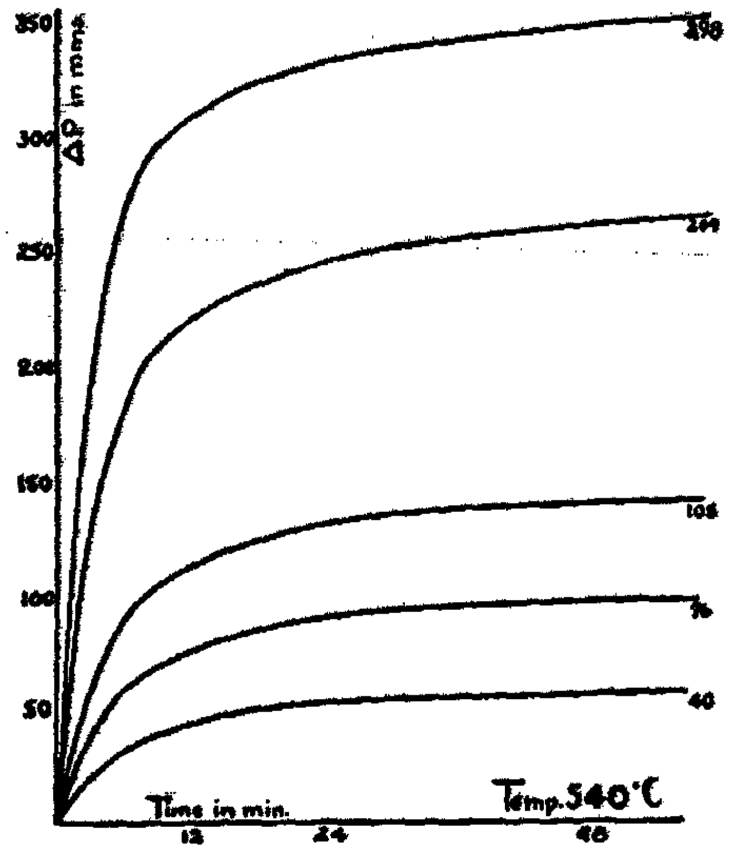


Fig. 2

Table I contains comparative results between determinations carried out in the empty bulb and with increased surface. Data obtained using a pyrex bulb are included.

TABLE I

Temperature 580°C

Initial Pressure Time in mins.	Quartz Bulb 209 ΔP	Double Surface 206 ΔP	Pyrex Bulb 213 ΔP
0.5	80	81	80
1.0	40	39	40
1.5	24	22	23
2.0	14	16	18
3.0	20	17	19
4.0	10	9	11
6.0	9	10	10
8.0	7	6	8

The similarity of the rates of pressure change is indicative of the absence of any heterogeneity.

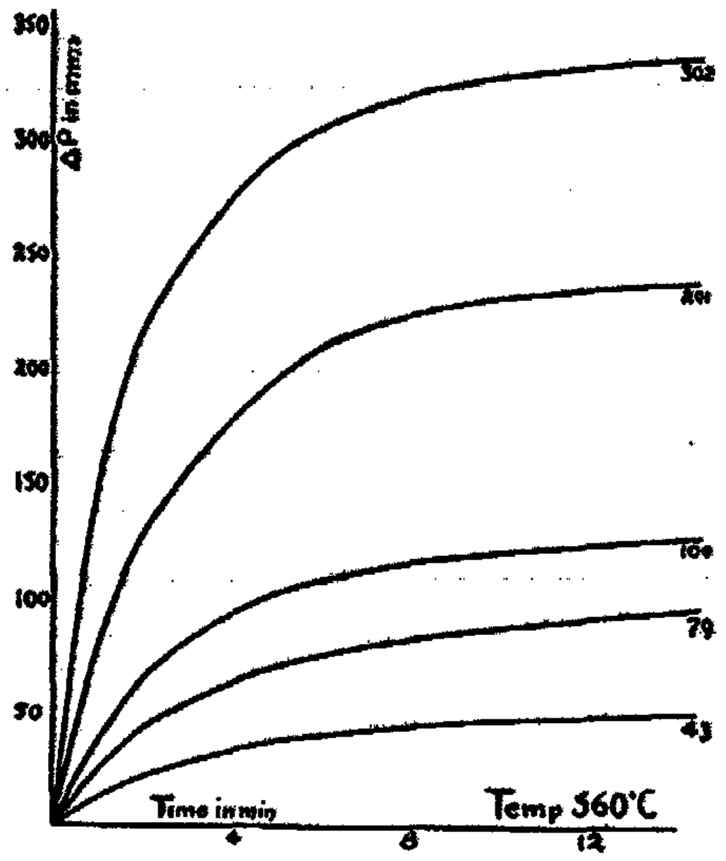

350
300
250
200
150
100
50
ΔP in mms
302
79
43
Time in min
Temp 560°C
4
8
12

Fig. 3

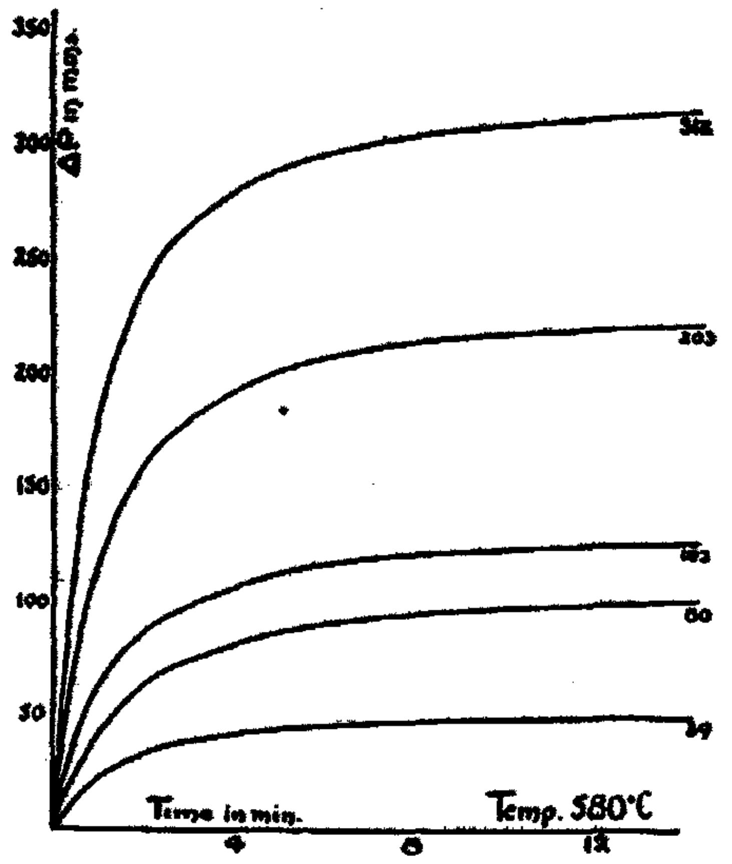

350
300
250
200
150
100
50
ΔP in mms.
312
203
80
49
Time in min.
Temp. 580°C
4
8
12

Fig. 4

The order of the reaction was inferred from an inspection of the times of 25, 50 and 75 per cent decomposition. Table II gives these values.

TABLE III

Initial Pressure	t_{25}	t_{50}	t_{75} mins.
	Temperature 520°C.		
36	4.2	10.2	18.9
38	3.7	9.2	20.0
76	3.6	7.8	16.4
77	3.35	7.3	15.2
103	3.6	8.8	17.4
105	3.6	8.6	17.5
208	2.82	6.5	16.0
211	2.70	6.1	14.7
307	2.46	5.5	12.7
310	2.44	5.4	12.0
362	2.49	6.3	—
	Temperature 540°C.		
40	2.0	4.9	10.5
76	1.7	4.0	8.8
105	1.5	4.0	10.0
207	1.36	3.1	7.3
298	1.10	2.65	6.2
352	1.10	2.82	7.4
	Temperature 560°C.		
43	0.90	2.27	5.35
79	0.90	2.31	5.30
104	0.87	2.30	5.07
201	0.68	1.79	4.29
301	0.58	1.53	3.60
346	0.52	1.55	4.10
	Temperature 580°C.		
39	0.50	1.16	2.70
80	0.48	1.33	3.30
102	0.43	1.00	2.60
203	0.35	0.90	2.44
305	0.31	0.80	1.95
373	0.31	0.81	—
432	0.32	0.85	—
502	0.32	0.81	—
568	0.31	0.80	—
597	0.32	0.83	—

The approximate constancy of these values over large pressure changes can only be significant of a reaction which is practically wholly unimolecular. The striking feature is that the values appear to decrease with an increase of initial pressure, a decrease which might be considered steady if measurements had not been made at higher pressures. A close analysis of the data at 580°C., at which temperature measurements were made at higher pressures than were used at the other temperatures, reveals the fact that the values of t_{25} and t_{50} are constant over the pressure range from 200 to 600 mms. but that below 200 mms. the times increase with a pressure decrease. Such a behavior is similar to that found in other unimolecular reactions although it should be noted that the rate of falling off at lower pressures is very considerable slower than is observed in the decomposition of the ethers. The times of three-quarter decomposition do not exhibit the same degree of constancy that the other values show, presumably since after that time the amounts of secondary decompositions such as of propylene or ethyl cyanide are appreciable in comparison with the primary reaction, the order of these subsequent reactions being uncertain. That this explanation is substantially correct is seen from the effects of foreign gases on the reaction as a whole, where for example at smaller pressures of added diluent an effect only becomes noticeable towards the end of the reaction.

In Table III are presented the rates of pressure change observed using various amounts of hydrogen and nitrogen added initially to the amine.

Table III

A = initial pressures of amine
B = initial pressures of hydrogen
C = initial pressures of nitrogen
Temperature 580°C.

A	203	208	205	198	210		202
B	0	52	105	205	302		406
Time	Pressure Change						
0.5	78	79	78	59	51		45
1.0	119	120	116	87	73		65
1.5	143	143	130	104	85		76
2.0	159	158	143	114	93		82
3.0	181	175	157	124	100		88
4.0	193	183	164	130	105		93
6.0	205	191	171	135	108		96
8.0	213	195	—	137	110		98
A	203	214	207	196	199	202	200
C	0	50	105	206	207*	302	400
0.5	78	80	76	59	56	50	44
1.0	119	120	115	91	88	76	65
1.5	143	143	137	[illegible]	109	89	76
2.0	159	158	152	123	122	101	85
3.0	181	174	170	139	137	109	93
4.0	193	184	181	148	146	115	97
6.0	205	192	190	155	152	120	102
8.0	213	197	196	160	156	123	105

* Helium.

It can be seen therefore that at the lower pressures of foreign gas no effect is observed until the decomposition is over 75 per cent complete. Further, the effects of hydrogen and nitrogen are similar, except when large excesses are used, when hydrogen has a somewhat greater effect than nitrogen. Finally the effect of helium is seen to parallel that of nitrogen at the same pressure.

The absence of an effect of added diluent at lower pressures corroborates the previous evidence for the unimolecular nature of the reaction. The effects in slowing the rate of reaction at higher pressures of diluent might be indicative of inelastic collisions with activated propylamine molecules. Such a behavior by hydrogen however is contrary to the general results obtained in numerous other unimolecular reactions where hydrogen is generally found to have the effect of increasing the rate. The alternative and more probable explanation of the effect of the diluents in decreasing the rate must lie in the secondary decompositions subsequent to the primary unimolecular split of the amine. These secondary reactions will be at least bimolecular, the probability of their being unimolecular at least early in the reaction is small since they are then present only in small amounts. The effect of added gas therefore would be to reduce the rate of these reactions. That perceptible amounts of these reactions do occur even early in the reaction can be seen from the falling value that is obtained for the velocity constant an example of which is given in Table IV.

TABLE IV

Temperature 580°C.

Time	Pressure Change	k	Time	Pressure Change	k
0.5	119	0.729	6.0	340.5	0.344
1.0	187	0.653	8.0	352.5	0.308
1.5	231	0.600	12.0	365	0.229
2.0	259	0.546	16.0	371	0.196
3.0	296	0.475	24.0	378	0.139
4.0	318	0.423			

The constants were calculated using the extrapolated limiting pressure increase as proportional to the initial concentration of amine. If the secondary reactions are inhibited by added gases the values calculated for the velocity constants from the pressure change in presence of added gases should be more nearly constant. This is actually the case. Although the constants still show a decided drift, the extent of it is by no means as great as that above.

Regarding the energy of activation, since, it will be recalled, the quarter and half lives are not constant over the full pressure range studied, the logarithms of these values for a given initial pressure were each plotted against the reciprocals of the absolute temperatures. In this way graphs were obtained at initial pressures of about 40, 80, 100, 200 and 300 mms. The graphs were in all cases straight lines and the parallelism of the lines may be judged from the similarity of the values of the energies of activation calculated from their slopes and given in Table V.

TABLE V

Initial Pressure	E in calories	Initial Pressure	E in calories
40	44,600	200	44,900
80	43,500	300	44,900
100	43,900	Mean	44,400

This value is quite similar to the value found by Taylor for the energy of activation of ethylamine namely 43,400 calories and may be significant of a similar primary rupture of the molecule in the two cases. One important feature of the above results is the identity of the energies of activation when calculated for the same initial pressure at different temperatures, proving that the rate at which the reaction deviates from the truly unimolecular course is the same at different temperatures and further that the pressure below which the reaction is no longer unimolecular is approximately the same over this temperature range.

A comparison of the above data with those of other unimolecular reactions may be made by means of the ratio of E/RT at temperatures where the reactions have equal velocities. The rather low value of 28.2[1] was found by Taylor at 500°C. for the ethylamine decomposition, whilst from the above quarter and half lives propylamine can be shown to be decomposing at the same rate at approximately the same temperature and would therefore give a value of 28.9.

How relatively low is the energy of activation of propylamine can perhaps best be seen from a comparison of the ratio of effective to total collisions occurring and the value of $e^{-E/RT}$. Taking a velocity constant of 0.00158 sec.$^{-1}$ at 500°C. the number of molecules reacting per cubic centimeter per second is approximately 4×10^{15}. The reaction deviates from its unimolecular course at about 200 mms. at which pressure therefore, (using a molecular diameter of 7×10^{-8} cm.) there will be 3.5×10^{27} collisions per cubic centimeter per second. The ratio is therefore 1×10^{-12} approximately. Using the value 44,400 calories for the energy of activation derived from the simple Arrhenius equation the value of $e^{-E/RT}$ becomes about 3×10^{-13}. Neglecting then, the several small corrections which might be made in these figures there is seen to be a substantial agreement. By analogy with other unimolecular reactions this agreement would suggest that a single vibrational bond, corresponding that is, to two square terms, is alone responsible in the activation process, and since the data for ethylamine and propylamine are so similar it may be concluded that the same bond is involved in both cases. A comparison of the data for the decompositions of dimethyl, diethyl and dipropyl ethers, as also for azomethane and azoisopropane shows marked differences with increasing complexity of the molecules quite unlike the similarity found here between ethyl and propyl amines. A possible explanation suggests itself in that in the ethers and azo compounds the primary rupture probably

---

[1] This value was given in error in the original as 28.9.

occurs deep within the molecule whereas with the amines the rupture is most probably in the C-N bond or at least at the end of the carbon chain. Further work is in progress with more complex amines to determine more precisely this influence of complexity. Sight should not be lost of the fact, however, that the secondary reactions for the amines are extremely complex and that consequently the energies of activation may also be complex.

Summary

The decomposition of propylamine over the temperature range 520-580°C. is shown to be a homogeneous reaction. At pressures above 200 mms. the primary reaction is apparently unimolecular. An energy of activation of 44,400 calories shows similarity to that found for ethylamine.

Nichols Chemical Laboratory,
New York University, New York, N. Y.

THE OXIDATION OF ETHANE

BY H. AUSTIN TAYLOR AND E. W. RIBLETT[1]

The more interesting case of the two types of explosive reaction recently considered from a theoretical standpoint by Semenoff[2] is naturally that due to branched chain reactions. The differentiation of this type from the purely thermal explosion is not however always easy, especially where in highly exothermic reactions a thermal explosion may actually precede the chain explosion. From the evidence already accumulated on the explosions of saturated hydrocarbons in oxygen there seems every reason to suspect that these are at least in part due to chain reactions. The succeeding work is an attempt to show that even the slow, non-explosive oxidation of ethane is probably a chain reaction and that therefore the explosive oxidation may be so considered also. The latter conclusion is verified by a study of the critical explosion pressures at different temperatures.

During the progress of the work there appeared a publication by Bone and Hill[3] on the same subject with conclusions similar to those just stated. Stress however had been laid particularly on the slow reaction and of this, the induction period received special attention. They showed that the induction period could be reduced by traces of several compounds such as water, alcohol and iodine. The elimination of the induction period is extremely helpful in the study of the rate of the slow reaction but it seems doubtful whether the mechanism of the reaction in its absence, is necessarily precisely the same as when the induction inhibitors are absent. As Semenoff has shown in the sulphur oxidation the addition of small amounts of ozone is alone required to start chains which in its absence would never occur at the particular temperature. Bone and Hill further claim that no oxidation of the ethane occurs within the induction period and that there is an inconsiderable peroxidation if any during the slow reaction immediately following the induction period. That absolutely no reaction occurs during the induction period is difficult to maintain unless some cause for its sudden initiation is forthcoming. What would seem more plausible is that reactions do occur to extents that are not measurable analytically or alternatively from a pressure-change standpoint mutually balance each other. In the reactions here described ethane was shown to decompose with an increase in pressure at a rate that was much less than the oxidation rate. A simultaneous addition of oxygen to the ethane molecule with a corresponding pressure decrease might easily account for the absence of any total pressure change during the

---

[1] Abstract from a thesis presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy at New York University.

[2] Chemical Reviews, 4, 347 (1929).

[3] Proc. Roy. Soc., 129A, 434 (1930).

induction period in an ethane-oxygen mixture. It is true that the temperatures of Bone and Hill's experiments were considerably lower than those used here so that the ethane decomposition would have been much reduced if it occurred at all. Against this however their induction period at 316° C was about thirty minutes whereas the average time found by us at 460°C was about two minutes. This ratio of thirty to two for a 44° temperature difference, corresponding to quite a plausible increase in a reaction rate, would lend credence to the above interpretation of the induction period provided the mechanism of the succeeding reactions involved chains necessitating only small quantities of material as initiators.

Experimental. The ethane was prepared by the Grignard method from ethyl bromide. Dibutyl ether was used as solvent because of its high boiling point and could therefore be more easily removed from the ethane. The ethane was purified by passage through a coil immersed in a freezing mixture and stored over water. When required for use it was drawn through two towers of sulphuric acid. Oxygen was taken directly from cylinders of the compressed gas.

The reaction system was composed of a pyrex bulb attached to a capillary manometer whereon the pressure changes during experiment could be followed. The manometer was heated throughout its length to avoid condensation of products during an experiment. The gases were admitted to the reaction system from an auxiliary holder serving also as a mixing chamber. The latter had its own manometer for use in preparing known mixture of ethane and oxygen. The reaction vessel was heated in an electric furnace, the temperature of which was measured by a platinum resistance thermometer. The evacuation of the reaction system was made by means of a mercury diffusion pump backed by a hyvac oil pump, the former being necessary for reproducibility of results.

Determinations were made of the rate of reaction as measured by the rate of pressure change for various mixtures of ethane and oxygen at a series of different temperatures. It would be impossible and useless to list here the results of the hundreds of observations made. Typical results are given therefore to illustrate the salient features only. Fig. 1 gives some of the results obtained for a fifty per cent mixture at 470°C. It will be observed that reaction does not begin immediately after the admission of the gases into the reaction vessel, that is, no pressure change is observed. It is this period to which the term induction period has been applied and in all the cases examined here varied up to four or five minutes being as stated on the average about two minutes. This induction period is followed by a period of slow reaction which however gradually develops in rapidity in a manner typical of an autocatalytic reaction, until completed. The duplication of the rate curves is extremely difficult since the induction period and the rate of development in the early part of the reaction seem to be excessively sensitive to traces of foreign substances including reaction products. Two reactions may be carried out at exactly the same pressure and temperature with the same composition of mixture and yet the time of development to rapid

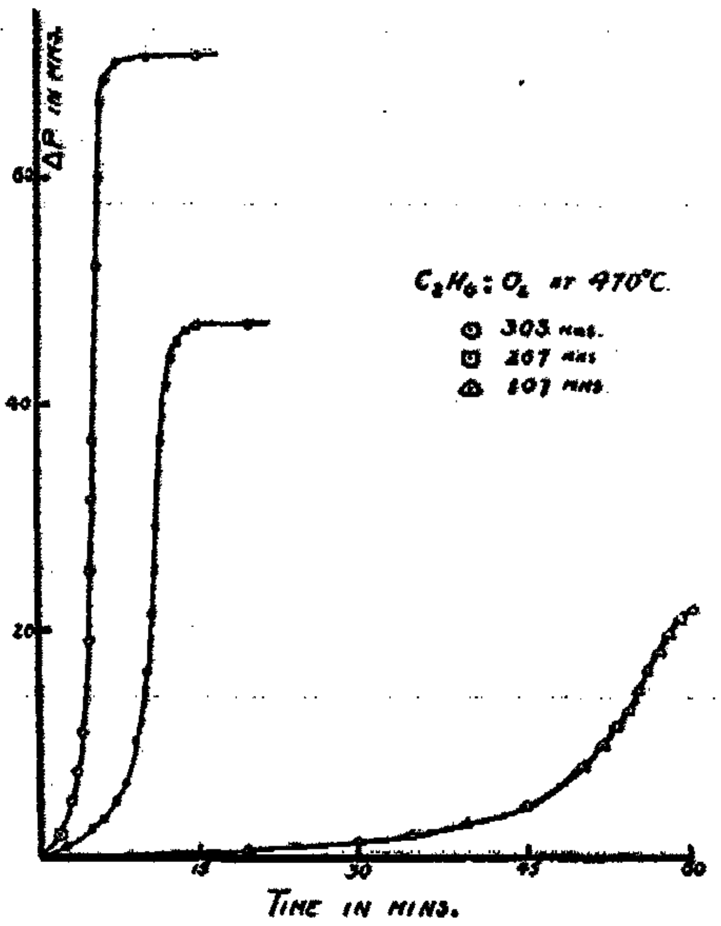

ΔP in mms.
60
40
20
15
30
45
60
Time in mins.
$C_2H_6 : O_2$ at 470°C.
303 mms.
207 mms
107 mms

Fig. 1

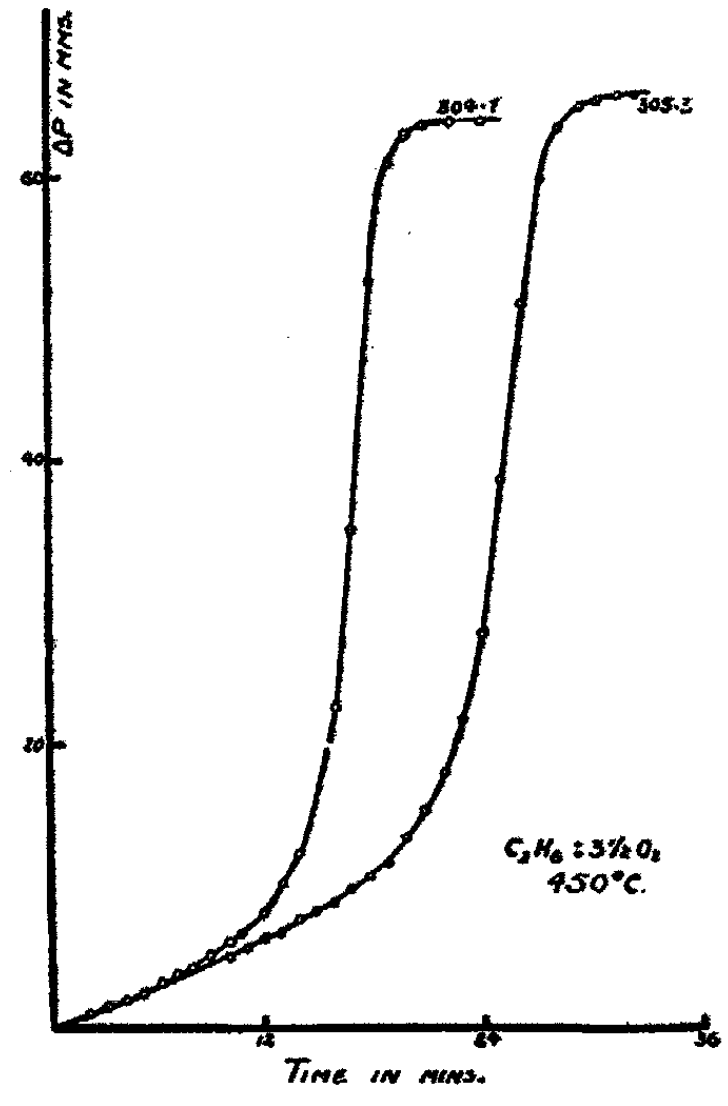

ΔP in mms.
60
40
20
12
24
36
Time in mins.
304·7
305·3
$C_2H_6 : 3\frac{1}{2}O_2$
450°C.

Fig. 2

reaction may vary by as much as one hundred per cent if extreme care is not taken in a thorough evacuation of the reaction vessel. It was observed however that despite this fact, the rate of the rapid reaction is almost constant. Fig. 2 will illustrate the point in that the slopes of the two curves in their steepest portions are the same, whilst the times for total reaction differ by almost fifty per cent. As Bone has shown, whatever happens during the early part of the reaction, oxidation certainly occurs during the rapid reaction and one is enabled therefore to judge comparatively of the effects of pressure, temperature and composition by a study of the rapid reaction rate.

Effect of Pressure. A comparison of the slopes of the rapid portions of the rate curves for given mixtures at fixed temperatures shows in general that the ratio of these is proportional to the ratio of a power of the pressures lying between two and three, a result which does not seem to be affected by a change in temperature or by a change in composition even if one reactant be in large excess. Thus at 470°C. a C_2H_6:5O_2 mixture gave for pressures o 429, 449, 471 and 493 mms. slopes in the ratio of 1:1,2:1,3:1.4 whilst the ratio of the squares of the pressures is 1:1,11:1,22:1.33.

With regard to the effect of pressure on the total pressure change during the reaction for a given mixture the ratio of total is initial pressure is always constant. Thus in the data just given the total pressures developed during reaction were 479, 504, 528 and 552 mms. The ratio of each of these to its initial pressure is 1.12. It is probable then that a change of initial pressure does not affect the composition of the end products for a given mixture. It should be mentioned here that at no time during the experiments was a deposit of carbon observed, the reaction vessel being quite clean even after numerous runs had been made, indicating a clean oxidation to gaseous products which could be pumped out.

Influence of Temperature. Assuming for the present that the reaction is a chain reaction, definite evidence will be given later, the energy of activation calculated from the observed temperature coefficient will be a composite quantity since the total rate of reaction is a function not only of the number of chains initiated but also of the chain length. The effect of pressure on the latter will depend on the cause of the breaking of chains, that is, whether it occurs chiefly in the gas phase or on the surface. Assuming that the majority of chains are broken on the surface an increase of pressure would be expected to increase the chain length, an increase of temperature on the other hand might shorten it, with the result that the energy of activation would decrease with an increase of pressure. Such is what is actually found here. For a C_2H_6:3½O_2 mixture the energy of activation calculated from the ratio of the maximum rates is found to be at 200 mms. pressure, 43,000 calories, at 215 mms. 38,000 calories and at 300 mms. 32,000 calories. From the general magnitude of these values it would seem probable that the actual chain length is not great.

Effect of Composition. In drawing conclusions regarding the effect of composition on the reaction rate it should be fully realized at the outset that such will only be approximate since there is no criterion that exactly the same reactions are occurring under the different conditions. The fact that the total pressure change per unit initial pressure is approximately constant for different mixtures may be taken as evidence of the absence of at least drastic differences in reaction. Thus a $3C_2H_6:O_2$ mixture gives a ratio of total pressure developed to initial pressure of 1.16, a $C_2H_6:O_2$ mixture gives a ratio of 1.23, a $C_2H_6:3\frac{1}{2}O_2$ mixture a ratio of 1.22 whilst a $C_2H_6:5O_2$ mixture gives a ratio of 1.12, all at 470°C. The ratios are all of the same order but too much reliance cannot be placed on this fact since theoretically the complete combustion of ethane to carbon dioxide and water would yield a ratio of 1.11 whilst if equal amounts of carbon monoxide and dioxide are produced along with the water the ratio is only 1.25. It is very possible therefore that quite different reactions may be occurring with different compositions.

The specific effects of oxygen and ethane however are sufficiently different to warrant their statement even if slight differences in reaction do occur with changing composition. The general effect of oxygen appears at first sight to be approximately proportional to its pressure when in excess. Thus at 450° C, 80 mms. C_2H_6 and 280 mms. O_2 react in their rapid range at 27 mms. per minute, whilst 80 mms. C_2H_6 and 400 mms. O_2 react at 40 mms. per minute. As was pointed out previously however an increase of total pressure increases the rate proportional to the second or third power of pressure. An increase in rate proportional to the first power of the oxygen therefore actually corresponds to a retardation when oxygen is in excess. This effect parallels that of nitrogen mentioned later and may also be true of ethane when present in large excess as shown later in the study of explosion limits. The latter however is not so definite probably because of the possible pyrolysis. The accelerating effect of ethane at constant oxygen pressure is much more pronounced, so much so that it is difficult to avoid explosion unless small pressures of oxygen are used when the reaction is extremely slow. Thus at 460°C, 126 mms. of each gas reacted at 28 mms. per half minute whilst with 128 mms. of O_2 and 385 mms. ethane the reaction was extremely rapid corresponding to more than 100 mms. per half minute although no flash or sound typical of explosion could be seen or heard. Such results are typical of many that were obtained.

Evidence for Chain Characteristics. Chain reactions are characterised by (1) extraordinary sensitivity to traces of foreign substances (2) marked negative wall effect (3) explosive possibilities (4) specific effects of diluent gases (5) induction period. Ethane oxidation shows all these characteristics. The period of induction has already been discussed in part. It seems fairly certain that it is a very definite part of the reaction although it may be markedly affected by impurities including the reaction products. Even after extreme purification of the system however it is still present. As pointed out previously the variation in the length of the period with temperature, if comparison between the present work and that of Bone and Hill is reliable, is of the same order as the increase in reaction rate with temperature as found by us. This would suggest that during this period there is a gradual accumulation of some substance which is required for the complete oxidation reaction. As will be seen from the later work on the critical explosion pressure, the induction period together with some slow reaction always precedes the explosion. In other words for explosion it is not at all necessary that the mixture react immediately on admission to the reaction vessel.

Fig. 3 illustrates the sensitivity of the reaction to foreign substances and also shows the negative wall effect. In the diagram the normal reaction at 450° C is seen to be complete in about 85 seconds, which means that it is just below the explosive point. With fifteen per cent nitrogen the reaction is slower taking about three minutes for completion. The addition of glass powder to the reaction vessel changes the time for reaction to almost five minutes, whilst if the powdered glass is coated with potassium chloride the reaction is almost completely inhibited and at 55- C. is still incomplete after forty minutes. In all of these cases there is evidence from the changing total pressure increase of differences of mechanism under the different conditions, a result shown definitely by Pease[1] in the oxidation of propane and the butanes.

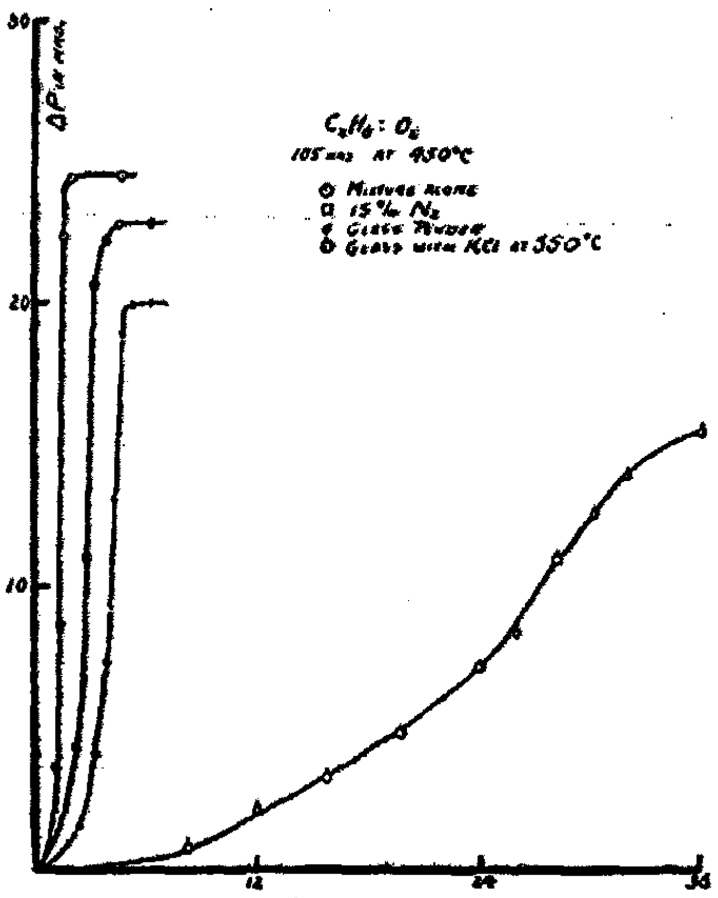


Fig. 3

An attempt to induce reaction by the addition of ozone, used by Spence and Taylor[2] in the oxidation of ethylene, was not entirely successful in that explosion completely destroyed the apparatus each of the several times trials were made. The explosions were however significant. The method for the experiment was to flow ethane and oxygen at equal rates into a Y tube and thence through a furnace at temperatures ranging from 200 to 400°C. Under such conditions the amount of oxidation was almost negligibly small. Upon

---

[1] J. Am. Chem. Soc., 51, 1839 (1929).

[2] J. Am. Chem. Soc., 52, 2399 (1930).

exciting the ozonizer in the oxygen line explosion occurred. Visibly, the explosion seemed to occur in the Y tubes where the gases met and would strike back away from the tube in the furnace. The actual temperature of the Y tube could not have been much above room temperature, yet the remains after explosion could not be found despite the fact that the tube in the furnace always remained intact. It seems quite definite therefore that ozone will induce explosion in ethane-oxygen mixtures at temperatures very considerably lower than those necessary in its absence.

Explosive Limits. The reaction of ethane and oxygen may lead to an explosion at any of the temperatures studied provided the initial pressure of the reactants is large enough. Semenoff, as mentioned, has suggested that the critical pressure above which a reaction is explosive is a function of the temperature given by the equation

$$\log p = A/T + B$$

The magnitude of B depends on the composition of the mixture, dimensions of the apparatus and the presence of foreign substances. The constant A is independent of these but for its interpretation the precise type of explosion must be known. For a purely thermal explosion A is directly proportional to the energy of activation whilst for a chain explosion it is solely a function of the energy necessary to cause the branching of chains.

In the determination of the minimum explosive pressures the temperature of the reaction vessel was kept constant and a series of experiments carried out at different pressures for a given mixture. The pressures were so varied that the limits in which explosion did or did not occur gradually approached each other. Thus the minimum explosive pressure could be determined with an accuracy of from one to four millimeters. The data obtained are given in Table I.

TABLE I

Temp. °C.	Minimum Pressure for Oxygen Concentrations.							
	83.33	77.78	66.67	60.00	55.00	50.00	40.00	25.00
460	546	—	320	—	—	—	—	—
470	495	—	—	—	—	—	—	—
475	390	—	257	—	—	—	—	—
480	367	334	238	193	186	182	191	235
484	—	309	—	—	—	—	—	—
500	266	248	—	—	—	—	—	—
520	211	187	133	108	104	103	110	150
540	164	145	—	—	—	—	—	—
560	—	112	—	—	—	—	—	—
580	—	91	64	53	—	50	—	—
600	—	67	54	—	—	—	—	—

The values of the logarithms of these pressures when plotted against the reciprocals of the corresponding absolute temperatures all yield straight lines which are parallel giving therefore a value of A of 4022 which is independent of the composition. To show that the value is also independent of the dimensions of the apparatus the cylindrical vessel previously used was replaced by a spherical one with a correspondingly smaller surface. The slope of the log $p - 1/T$ line was unchanged although on account of the decreased surface the actual pressures for the spherical vessel were lower than those for the cylindrical, as would be expected from the negative wall effect.

The value of A interpreted as for a purely thermal reaction would yield approximately 40,000 calories for the energy of activation of the reaction. Comparison with the figures given above shows this to be of the order of magnitude actually found. The reaction however is most certainly a chain reaction and a value of A of 4022 for a pure chain explosion would correspond with an energy of about 10,000 calories to cause chain branching. The measured temperature coefficient of the slow reaction may possibly be a composite of this latter value and a true energy of activation which could conceivably be very much larger. The previous agreement might therefore be merely fortuitous. On the other hand the time taken for a given mixture to explode after its admission to the reaction vessel was sometimes of the order of five or six minutes though more frequently around one or two minutes. Such a long period as five minutes would suggest that an acceleration of rate due to heat accumulation in the system was probably preceding the true explosion eventually caused by increased chain length. In such an event the value of A cannot be readily interpreted at all.

In a similar study to the above by Sagulin[1] a value for A of 4900 was obtained, which changed abruptly to 7000 as the temperature was raised above 680°C. The temperatures used by Sagulin were all above 600°C. In view of the complexity of reactions possible, as shown by Pease for propane this abrupt change is quite plausible since dissociation plays a more important part at higher temperatures. A pure oxidation to carbon monoxide and other oxidized products is the more important reaction at lower temperatures, whilst the formation of unsaturated compounds due to partial oxidation is intermediate between the two. It would not be surprising then if a second change of slope should occur at lower temperatures than the one observed by Sagulin. It is certain that the curve for a $C_2H_6:5O_2$ mixture shows a break at about 470° C, which can be seen from the data in Table I. The high pressure necessary for explosions at still lower temperatures, disregarding their violence, precluded the possibility of determining the slope of the new curve.

Finally an examination of Table I will show that there is at each temperature a particular composition of mixture which possesses the smallest minimum explosion pressure. The minimum is not particularly sharp when plotted but can be seen to be in the neighborhood of the fifty per cent mixture.

---

[1] Z. physik. Chem., 1B, 275 (1928).

Furthermore this value is independent of temperature over the range studied. Taken in conjunction with the fact that the ratio of pressure increase to initial pressure is at its highest value in this region it would appear that the oxidation was more efficient for such a mixture.

Summary

The oxidation of ethane has been studied by a static method and shown to be a homogeneous chain reaction. The effects of pressure, temperature, composition, surface and diluents have been shown to substantiate this. The critical explosion pressures determined are shown to be in agreement with Semenoff's theory but seem best explained as chain explosions preceded by thermal accelerations.

Nichols Chemical Laboratory,
New York University, New York, N. Y.

THE OXIDATION OF HYDROGEN SULPHIDE

BY H. AUSTIN TAYLOR AND ERNEST M. LIVINGSTON[1]

The significance of reaction chains in explaining the kinetics of many exothermic reactions has been treated theoretically by Semenoff[2] especially under the conditions where the reaction becomes explosive. Two types of explosion are discussed. In the first, termed thermal explosions, the rate of loss of heat by the system is less than its rate of production by the reaction whereby the temperature of the system continually increases, the reaction becoming explosive. In the second type, the reaction has definite chain characteristics becoming explosive when the chain length becomes infinite and frequently accompanied by chain branching due to secondary activation of more than one reactant molecule. A property common to both types of explosion is the existence of a minimum critical pressure p above which an explosion will occur and below which no explosion occurs, which is related to the temperature of the system by the equation

$$\log p = A/T + B$$

where A and B are constants. For thermal explosions the constant A is directly related to the energy of activation E of the reaction, whilst for chain explosions A is a function only of the energy necessary to cause the branching of chains and otherwise independent of the true energy of activation of the reaction.

The experimental confirmation of the above equation in an explosive reaction cannot therefore be judged as a sufficient criterion of either type of explosion. The proof of a chain mechanism or its absence must be added. The existence of these chains has been demonstrated in one or more of three ways, by studying the unusual kinetics of the reaction, by introducing some active material or "trigger" to start the chains, or by measuring the quantum yield in photochemical experiments. One significant feature of the unusual kinetics is frequently found in the effect of traces of foreign substances. Hinshelwood[3] has pointed out that a chain mechanism is the logical explanation of the general phenomenon of 'trace catalysis,' and more specifically of intensive drying.

It is well known[4] that a number of reactions of hydrogen sulphide are markedly affected by the presence of small amounts of water vapor and also that its oxidation may under suitable conditions become explosive. It was

---

[1] Abstract from a thesis presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy at New York University.

[2] Z. physik, 46, 109 (1927); 48, 571 (1928).

[3] "Kinetics of Chemical Change," pp. 167-187 (1929).

[4] Randall and Bichowsky: J. Am. Chem. Soc., 40, 368 (1918); Taylor and Wesley: J. Phys. Chem., 31, 216 (1927).

deemed advisable therefore to investigate this latter reaction in the light of the foregoing remarks.

The preliminary study of the kinetics of the oxidation reaction was made by a static method whereby the rate of pressure change of known mixtures of hydrogen sulphide and oxygen could be observed at each of several temperatures. The reaction vessel, a pyrex bulb of 300 ccs. capacity was fitted by means of a mercury sealed ground joint to a capillary manometer and pump. The bulb was maintained at constant temperature in an electrically heated furnace, the temperature being controlled by a rheostat in series with the furnace. A nitrogen-filled thermometer was used to indicate the temperature since the experimental conditions necessary were all in the neighborhood of 300° C. Hydrogen sulphide was prepared from pure calcium sulphide and stored over water; the oxygen being taken from cylinders of the compressed gas.

In the early experiments definite amounts of the two gases dried by passage over phosphorus pentoxide were let into the evacuated reaction vessel successively. Exceedingly erratic results followed, the reaction rate at times being slow but frequently explosive. This condition was not improved by preliminary mixing of the two gases in an auxiliary vessel at room temperature before admission to the reaction bulb. The cause of the lack of reproducibility was finally located in the different degrees of drying to which the gases were subjected. Gases which had been dried for long periods of time were found to react consistently at an excessively slow rate. Instead therefore of drying the gases to a high degree, and the production of a uniformity of this is difficult, the gases were saturated with water vapor at 21°C, yielding mixtures which reacted at reproducible measurable rates. Even under these conditions it was necessary to clean the reaction vessel thoroughly with boiling nitric acid after each experiment. The smallest traces of reaction products seemed capable of inducing explosion.

Analysis of the products from the slow reactions showed the presence, along with unchanged reactants, of sulphur, sulphur dioxide and sulphuric acid. The reaction is evidently not the simple one according to the equation:

$$2H_2S + 3O_2 = 2H_2O + 2SO_2$$

This was further substantiated by the observed pressure decrease during the reaction which was always slightly greater than that demanded by the above equation. It should be noted that the manometer was heated sufficiently to maintain all the water, initially present and formed by reaction, in the vapor phase. The additional pressure decrease may be accounted for by subsequent reactions as:

$$2H_2S + SO_2 = 2H_2O + 3S$$

or to the formation of H_2SO_4 or the solubility of the SO_2 in the liquid sulphur formed.

In view of this lack of a simple relation for the pressure change only a few typical results out of some hundreds obtained need be quoted to emphasize the main points observed.

The general course of the reaction is typified by the data in Table I.

TABLE I

$2H_2S:3O_2$ Initial Pressure 386 mms. Temp. 201.8° C.

Time in mins.	Pressure Change in mms.	Time in mins.	Pressure Change in mms.
3	0.5	180	33.0
5	2.5	283	41.5
6	4.0	373	48.0
9	6.0	780	61.5
25	11.0	985	66.0
55	17.0	1053	66.5

The reaction shows a small induction period and at this temperature is seen to be still incomplete after eighteen hours. The effect of a change of pressure will be considered later.

The data quoted in Table II were obtained with approximately the same initial pressure of gases using however an increased reaction surface, the bulb being packed with pieces of pyrex tubing the surface of which had been etched.

TABLE II

$2H_2S:3O_2$ with increased surface Pressure 387 mm. Temp. 202°C.

Time in mins.	Pressure change in mms.	Time in mins.	Pressure change in mms.
3	2.0	7	8.0
4	5.0	9	11.5

The rate of reaction therefore is almost doubled showing some heterogeneity. The increase of surface however must have been considerably more than two and in all probability the greater part of the total reaction is homogeneous. If the reaction is a homogeneous chain reaction an increase of surface would be expected to decrease the rate due to a shortened chain length. The observed increase in rate may therefore be complex, a decrease being more than balanced by an increase due to heterogeneity.

Norrish and Rideal[1] in a study of the rate of formation of hydrogen sulphide from hydrogen and sulphur found the reaction to be partly homogeneous and partly heterogeneous. Oxygen was found to act catalytically for both reactions, the effect being greater for the heterogeneous reaction. Since the surface acts catalytically in the formation of hydrogen sulphide it must also catalyse its decomposition particularly since in this case an excess of oxygen is present.

It is possible therefore that the primary reaction is a decomposition of hydrogen sulphide followed by subsequent oxidation. Judging from the

---

[1] J. Chem. Soc., **123**, 696, 1690, 3202 (1923).

susceptibility of the whole reaction to traces of reaction product especially water, this latter oxidation may well be of a chain type. It consequently follows that the energy of activation measured for these slow rates should be most significant of the primary reaction. The data quoted in Table III in conjunction with those previously given allow a calculation of this energy to be made.

TABLE III

$2H_2S:3O_2$ Initial Pressure 400 mms. Temp. 209.3° C.

Time in mins.	Pressure Change	Time in mins.	Pressure Change
2	0	6	10
4	7	9	13
5	9	14	15

The calculation however will only be approximate, for since the initial rate of pressure change is approximately linear, the temperature coefficient is given by the ratio of the pressure changes after a given short interval of time. Taking nine minutes as a convenient period the pressure ratio is 13/6 giving an energy of activation of 47,000 calories. Since the reaction is complex being partly heterogeneous, this value is undoubtedly lower than the true value for the homogeneous reaction. Norrish and Rideal find a value of 52,400 calories for the energy of activation of the homogeneous formation of hydrogen sulphide. Since the heat of formation is 2,730 calories the energy of activation of the decomposition would be 55,130 calories. Bearing in mind that the 47,000 calories obtained above is a minimum value, not only because the reaction is probably heterogeneous but also since some oxidation has proceeded, and Norrish and Rideal find still lower energies for the direct union of oxygen and sulphur, the difference between the 47,000 calories obtained herein and that calculated for the pure homogeneous decomposition namely 55,000 calories would not appear too great to detract from the plausibility of the assumption that the primary reaction may be a decomposition of hydrogen sulphide.

Attempts to justify this assumption by determining the order of the reaction met with difficulties owing to the tendency of the system to explode. To find the order by conventional methods it would be necessary to determine the relative rates of reaction for different gas mixtures at different total pressures. As will be seen later the pressure necessary for the reaction to proceed at a conveniently measurable rate with one mixture caused explosion with a different mixture, or alternatively a rate of reaction too slow to measure. A complete treatment would necessitate therefore, the study of a series of very slow rates at pressures so low that no mixture would explode. It might be suggested that the reaction rates could be increased by an increase in the temperature of the system. Succeeding work will show that the possibilities here are also considerably restricted, since the pressure below which the reaction is not explosive for a given mixture is itself an exponential function of the temperature. To work at pressures and temperatures only just below the lowest explosion limits of various mixtures would require an extremely uniform temperature throughout the reaction vessel and a temperature control excessively sensitive. The determination however, of the critical limits for explosion and their dependence on pressure, temperature and composition is found to furnish added evidence on the nature of the reaction.

The apparatus for these measurements was essentially the same as that used in the earlier work. Mixtures of known composition were made up in a storage vessel and saturated with water vapor at 21°C. The reaction vessel was evacuated by means of a mercury vapor pump backed by a hyvac oil pump, the high vacuum being found necessary to remove completely the reaction products after explosion. Frequent cleaning with nitric acid was also still found necessary. The furnace being brought to constant temperature a definite quantity of mixture, measured on the manometer, is let into the reaction bulb. The occurrence of an explosion is plainly visible or at the smaller percentages of hydrogen sulphide can be observed from the oscillations of the manometer. By repetition of this process the minimum pressure, for each temperature and for each mixture, above which explosion occurs and below which no explosion takes place can be determined.

Among the products after explosion, hydrogen sulphide, oxygen, sulphur dioxide, water, sulphur trioxide and sulphur were identified in varying quantities depending on the composition of the mixture used. A period of induction of from one half to two minutes was noted in each case of explosion. Neither a change in the dimensions of the reaction vessel nor in the extent of surface by introducing powdered pyrex had any effect on the slope of the pressure-temperature curve. The critical limits observed are given in Table IV.

TABLE IV

Per cent H_2S	°K	Minimum Pressure in mms.	Per cent H_2S	°K	Minimum Pressure in mms.
5	540.8	153	40	523.5	147
10	523.5	138	40	559.1	92
10	545.2	97	40	595.2	62
15	506.3	162	50	523.5	185
15	523.5	118	50	545.2	141
15	539.7	94	50	566.3	109
15	559.1	74	50	595.2	76
20	505.2	160	60	566.9	169
20	531.9	107	60	595.2	122
20	545.2	91	60	624.7	88
20	566.3	67	60	659.9	61
30	523.5	128		Increased Surface	
30	545.2	97.5	50	566.3	158
30	566.3	73	50	595.2	119
40	501.7	213	50	624.1	82

The accompanying Fig 1 shows that these results satisfy the Semenoff equation

$$\log p = A/T + B$$

the logarithms of the minimum pressures for each gas mixture plotted against the reciprocals of the absolute temperatures yielding straight lines which are parallel, having a slope A = 1735. Fig. 2 shows the curve obtained when the minimum pressures are plotted against composition, the temperature being constant. The form of the curve is typical of such explosive reactions as shown by Semenoff and his co-workers, there being a particular gas mixture which has the lowest minimum pressure for explosion at a given temperature.

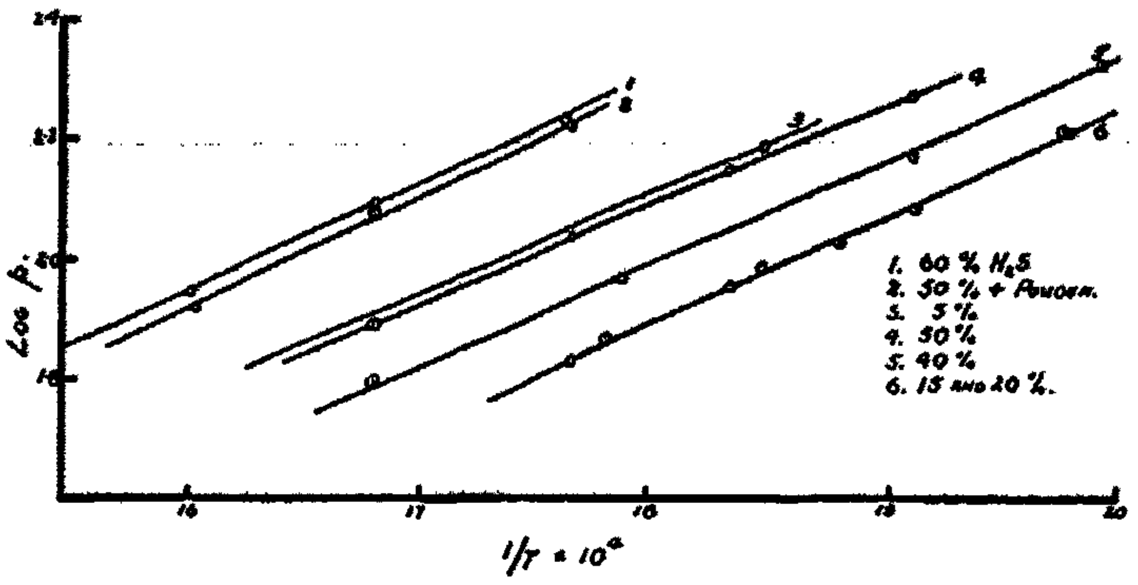


Fig. 1

In this case the mixture contains approximately 18 per cent of hydrogen sulphide. Such a result is found for purely thermal explosions as well as for those resulting from chain reactions.

In order to differentiate between the two types of explosion as was mentioned previously additional evidence for chains or their absence is necessary. In this case the extreme sensitivity of the reaction to traces of product especially water would suggest the possibility of a chain mechanism. The effect of an increased surface as a test for chain characteristics has been shown to be vitiated since the reaction is somewhat heterogeneous.

The possibility of a measurement of the quantum yield of the photochemical reaction was considered. A mixture of hydrogen sulphide and oxygen in a quartz flask was exposed for several hours at room temperature to the full radiation from a quartz mercury vapor lamp. The only change observed in the system was a deposit of sulphur on the flask, the pressure remaining unaltered. The absence of the higher frequency radiation due to air absorption apparently prevented oxidation of the hydrogen which must have been formed along with the sulphur. It seems significant however that the reaction which did occur was the hydrogen sulphide decomposition.

Semenoff has shown that the addition of some active material or "trigger" which would start chains could be used as a criterion for their presence.

Ozone was used by him in the sulphur oxidation. The addition of ozone in this case could not therefore give a conclusive result since the chains if observed might be due solely to the sulphur from a primary decomposition of the hydrogen sulphide.

The evidence adduced so far therefore is not at all conclusive and there remains only the interpretation of the slope of the log p — $1/T$ curve. In the case of a purely thermal explosion this slope as has been stated should be directly proportional to the energy of activation of the reaction. Semenoff has shown this relation to be

$$E = 9.9\,A$$

whence if A is 1735, E should be 17,180 calories, a value which is widely different from the observed energy of activation. It would appear then that the explosion cannot be purely of the thermal type. The value of A for a chain reaction explosion however does not depend on E as such but is a function of the energy necessary to cause the branching of chains, the proportionality factor depending on some power of the pressure according as the chains are ended on the surface or in the gas phase. Thus if U is the energy necessary to cause the branched chains

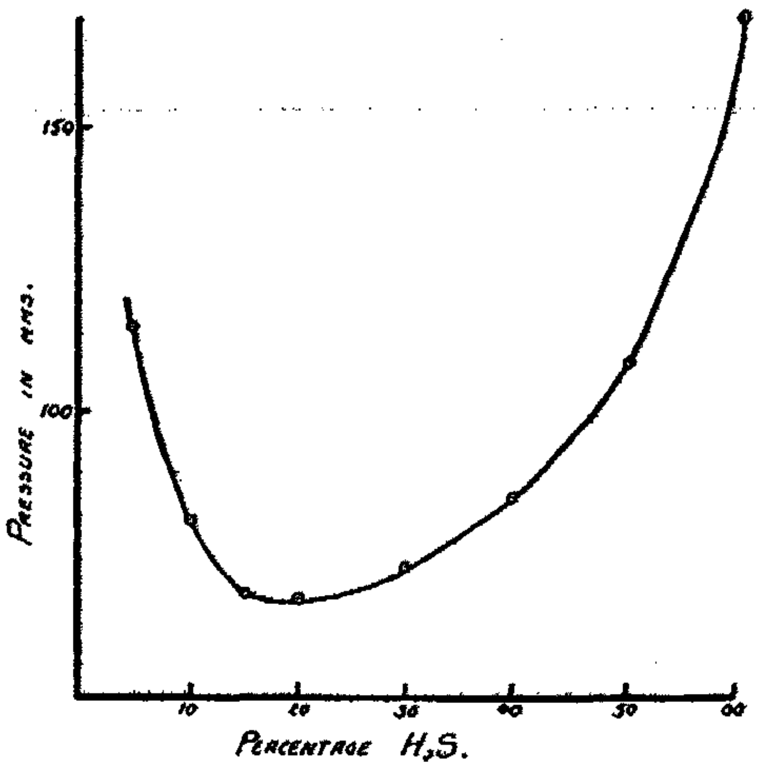


Fig. 2

$$A = U/nR$$

where R is the gas constant and n is the power of the pressure referred to, which in oxidation reactions will probably lie between 0 and 2. Hence U will have a value of the order of 2000 to 3000 calories, a value which could not possibly be the whole energy of activation for the reaction and must hence be an additional quantity requisite to maintain chains which have already started.

The actual possibilities for the source of chains are many. Evidence has been presented from the earlier work that the primary reaction may involve a decomposition of the hydrogen sulphide. The induction period in the explosions might be accounted for on that basis and the photochemical decomposition shows it to be a relatively simple reaction. The system would thus contain hydrogen, sulphur and oxygen. Hydrogen and oxygen as Hinshelwood[1] has shown combine according to a chain mechanism, Pease[2] having definitely identified hydrogen peroxide as an intermediate product. Pease bases the explosiveness of the reaction on the "possibility that a freshly formed peroxide molecule is subjected to dissociation yielding atomic oxygen." The more recent explanation of Alyea[3] attains the same end of both straight and branched chains by means of hydroxyl groups. The presence of atomic oxygen in a system containing free sulphur, Semenoff has shown, leads to sulphur oxidation by a chain mechanism. There are therefore numerous possibilities for both straight and branched chains and the conclusion that the hydrogen sulphide oxidation proceeds by a chain mechanism seems inevitable.

Summary

1. The slow reaction between hydrogen sulphide and oxygen studied by a static method is shown to be partly homogeneous and partly heterogeneous, the former predominating.

2. The critical explosion pressures for various gas mixtures at different temperatures have been measured and shown to agree with the Semenoff theory.

3. Evidence is presented to show that the oxidation must proceed by a mechanism involving both straight and branched chains.

Nichols Chemical Laboratory,
New York University, New York, N. Y.

---

[1] Proc. Roy. Soc., 119A, 591 (1928); 122A, 610 (1929).

[2] J. Am. Chem. Soc., 52, 5106 (1930).

[3] J. Am. Chem. Soc., 53, 1324 (1931).

GUANIDINE AND NITROUS ACID. I*

BY WILDER D. BANCROFT AND BURTON C. BELDEN

1. Introduction

Organic chemists apparently have little idea and very little information as to what compound is formed when one removes a nitrogen atom from guanidine by the action of nitrous acid. This seems rather surprising in the light of the number of investigations which have dealt with guanidine and nitrous acid,[1] and also in view of the fact that the guanidine molecule is certainly not a large one (one carbon, three nitrogen, and five hydrogen atoms) and its two-nitrogen derivative must be a reasonably simple compound.

The only definite information, as far as the authors are aware, which the literature affords on this point, is in the work of Pellizzari,[2] which is reported in Chemical Abstracts as follows:[3] "By addition of one mol ammonium hydroxide, cyanamide is converted into guanidine and dicyanodiamide into biguanide. The only known reaction in the opposite sense is the transformation of o-phenylenediguanide into β-cyano-o-phenyleneguanidine by treatment of nitrous acid. This treatment is now being extended to other compounds and it is found that nitrous acid converts diguanide into cyanoguanidine (dicyandiamide) and guanidine similarly yields a small proportion of cyanamide." In the data which Pellizzari presents to show the conversion of guanidine to cyanamide, the highest yield which he obtained appears to be 0.37 grams silver cyanamide per gram guanidine carbonate. This weight of silver cyanamide is equivalent to about 0.13 grams guanidine carbonate; the conversion to cyanamide has thereby been 13% complete.

This seemed hardly a proper way to leave the matter. If cyanamide is the two-nitrogen derivative of guanidine, when one nitrogen has been removed by the action of nitrous acid, it should be possible to obtain a much higher yield of cyanamide. It should be possible to obtain nearly 100% conversion to cyanamide and to find the remaining few percent as unchanged guanidine. This then is the purpose of the present investigation: to show that cyanamide is the principal product formed when nitrous acid removes one nitrogen from guanidine (and not perhaps the product of a side reaction, as the 13% yield of Pellizzari might indicate).

---

* This work is done under the programme now being carried out at Cornell University and supported in part by a grant from the Heckscher Foundation for the Advancement of Research established by August Heckscher at Cornell University.

[1] Krall: J. Chem. Soc., **107**, 1396 (1915); Hale and Vibrans: J. Am. Chem. Soc., **40**, 1059 (1918); Plimmer: J. Chem. Soc., **127**, 265 (1925); Hynd and MacFarlane: Biochem. J., **20**, 1264 (1926).

[2] Gazz., **51 I**, 224 (1921); Atti Accad. Lincei, **30 I**, 171 (1921).

[3] Chem. Abstracts, **15**, 3982 (1921).

Professor Tenney L. Davis[1] suggests that nitrous acid, in an acid solution, acting on a guanidine salt, might produce nitrosoguanidine. In this case[2] the nitrosoguanidine would "dearrange" to form cyanamide and nitrosoamide. He suggests also that if nitrosoguanidine is not so formed, the guanidine itself might "dearrange" to form cyanamide and ammonia, the ammonia reacting with nitrous acid to yield nitrogen gas.

2. Experimental Study

For the qualitative analysis of nitrogen compounds of the cyanamide and related types there is available the very satisfactory procedure of Buchanan,[3] whereby these compounds can be readily identified: ammonia and its salts, cyanamide, hydrocyanic acid and its salts, dicyandiamide, guanidine and its salts, guanylurea and its salts, thiourea, and urea. Of these we are interested in the test for cyanamide (precipitation of pale yellow silver cyanamide on the addition of ammoniacal silver nitrate), dicyandiamide (precipitation from slightly acid solution of the white silver compound of dicyandiamide which is moderately soluble at 60°), and guanidine (precipitation on addition of alcoholic picric acid). The picric acid would also precipitate melamine, a polymer of cyanamide, and guanyl urea. In the first case, however, the precipitate consists of very characteristic, canary-yellow, needles which no one would ever confuse with guanidine picrate. In this investigation guanyl urea almost certainly would be arrived at through the formation of dicyandiamide, for which this compound is a test, and in the absence of any positive test for dicyandiamide we will conclude that none of our picrate precipitate results from the presence of guanyl urea. Dicyandiamide, incidentally, is a polymer of cyanamide formed when cyanamide is heated, and one might expect some dicyandiamide to be found in this present study. We need, finally, a qualitative test for urea and instead of using the method suggested by Buchanan (the conversion of urea to ammonia by the ureolytic enzyme in soy-bean flour) we will employ the Fosse method of precipitation by xanthydrol.[4]

The quantiative determination of guanidine was made according to the method of Vozarik.[5] The precipitating agent consists of 8 grams ammonium picrate and 5 cc NH_4OH (Sp. G. 0.91) in a liter of water, plus 0.075 grams guanidine picrate to compensate for the solubility of the latter in the precipitating reagent. To 5 cc of the guanidine solution (containing not more than 1 gram guanidine per 100 cc) is added 20 cc of the precipitating reagent and 0.5 cc concentrated NH_4OH. After standing ten minutes, the solution is filtered through a Gooch crucible, and the residue washed with further precipitating reagent, dried, and weighed. To duplicate conditions which

---

[1] Private communication.

[2] Davis and Abrams: Proc. Am. Acad., 61, 443 (1926).

[3] Ind. Eng. Chem., 15, 637 (1923).

[4] Werner: "The Chemistry of Urea," 188 (1923).

[5] Z. angew. Chem., 15, 670 (1902).

will appear later in this paper, this quantitative test was tried also in the presence of sodium sulphate (about two grams in 100 cc guanidine solution); the presence of the salt was found to have no interfering action on the determination.

Our quantitative determination of cyanamide was essentially that of Perotti.[1] A 5 cc sample of cyanamide solution (containing not more than one gram cyanamide per 100 cc) is diluted to 100 cc, made alkaline with 2 cc concentrated by NH_4OH, and standard N / 10 silver nitrate solution added in excess. The precipitated silver cyanamide is filtered out on a Gooch crucible and washed with very dilute NH_4OH. The final step is the titration of the silver remaining in the filtrate. Titration with standard ammonium thiocyanate with ferric alum indicator was unreliable under the conditions of the experiment (probably due to the presence of considerable sodium sulphate). Titration with standard sodium chloride with 5% potassium chromate indicator proved a satisfactory procedure, provided care was taken to have the pH of the filtrate between 6.5 and 7.2. The exact procedure, then, was to neutralize the filtrate with sulphuric acid, using brom thymol blue as indicator, add a measured excess of standard sodium chloride solution, and back titrate the filtrate with further standard silver nitrate in the presence of the potassium chromate.

Our first idea was to treat a guanidine sample with nitrous acid in a Van Slyke apparatus (in the presence of a strong mineral acid) until nitrogen gas equivalent to one nitrogen atom of the guanidine had been liberated, and then remove the contents of the apparatus, neutralize, and test at least qualitatively to determine what nitrogen compound or compounds had been derived from guanidine. However, the amount of guanidine which can be properly used in a Van Slyke apparatus (5 cc of a 1% solution, or about 50 milligrams guanidine) is so small in comparison to the several inorganic substances also present (sodium nitrite, acetic acid, and sulphuric acid) that the qualitative tests are badly interfered with, if not completely masked.

The next move was to take a one-gram sample of guanidine carbonate in a beaker, make strongly acid with sulphuric acid, place in an ice bath, and add dropwise and with constant stirring a solution of sodium nitrite. This should yield the decomposition product of guanidine in large enough amounts to be readily detected and perhaps estimated. This proved a rather ineffective means of treating guanidine with nitrous acid, for in the course of an hour perhaps 5% of the original guanidine would have disappeared. However, in every qualitative examination of the results of such treatment cyanamide was found to be present and urea and dicyandiamide absent. This appears to be at least approximately the method used by Pellizzari in obtaining the results reported above.

The final step was to treat acidified guanidine solutions with nitrogen trioxide produced according to the method described in Houben-Weyl.[2]

---

[1] Gazz., 35 II, 228 (1905).

[2] "Die Methoden der organischen Chemie," 4, 595 (1924).

In this procedure 25 grams of arsenic trioxide is treated with 25 cc nitric acid (Sp.G. 1.35) in a generator flask. After a rather slow start, this reaction proceeds rapidly enough at room temperature for fifteen or twenty minutes, producing a brown gas which contains nitrogen trioxide. When this gas is passed into an ice-cold water solution, the solution becomes greenish-blue as nitrous acid is formed. It became quickly apparent that by this treatment guanidine could be converted rapidly (that is, within a few minutes) into its two-nitrogen derivative. In fact, it required rather careful attention to stop the reaction with an 80 or 90% conversion of the guanidine, which was what we wanted. This is the method followed in obtaining the data reported below.

In this work Eastman Kodak Company best-grade guanidine carbonate was used. It so happened that the sample we received was far from "best-grade," for the quantitative precipitation of guanidine by the picrate method outlined above showed the sample to be 79.7% guanidine carbonate. When a difficulty soluble portion of the sample has been removed by filtration, the guanidine carbonate content was raised to 84.0%. Inasmuch as the 20% impurity did not appear to interfere with our experiments, the guanidine carbonate was used as received.

Our procedure was this: take a one-gram sample of guanidine carbonate, add a solution of 18 cc water and 2 cc concentrated sulphuric acid (whereupon the carbonate is decomposed with the evolution of carbon dioxide), cool the solution in an ice-salt bath, bubble a stream of gas from the nitrogen trioxide generator through the solution for a given number of minutes, allow to stand for an additional number of minutes, and then neutralize the solution with

TABLE I

	No. 1	No. 2	No. 3
Weight guanidine carbonate	1.000 gr.	1.000 gr.	1.000 gr.
Volume conc. H_2SO_4	2 cc.	2 cc.	2 cc.
Treatment with N_2O_3	5 mins.	6 mins.	6 mins.
Allowed to stand	5 mins.	8 mins.	12 mins.
Qualitative:			
guanidine	considerable	slight	nil
cyanamide	slight	considerable	considerable
Quantitative:			
guanidine (calculated as guanidine carbonate)		159 mgr.	nil
cyanamide (calculated as guanidine carbonate)		585 mgr.	545 mgr.
guanidine carbonate in the original sample (79.7% pure)		797 mgr.	
% guanidine unchanged		20.0%	
% guanidine converted to cyanamide		73.4	
% guanidine unaccounted for		6.6	

sodium hydroxide solution to halt the action of nitrous acid. The resulting solution is made up to 100 cc in a volumetric flask and is ready for qualitative and quantitative examination.

The data for three typical runs are given below in Table I. It will be noted that the first run did not permit a sufficient conversion of the guanidine to its two-nitrogen derivative, while in the third run all the guanidine was consumed. The second run is approximately what we wanted.

It should be stated that the time for "treatment with N_2O_3" is of course somewhat dependent upon the speed with which the generator is operating. Further, the rate of the reaction of guanidine with nitrous acid naturally increases as the solution becomes more saturated with the gas, so that the interval between the fifth and sixth minutes is of more consequence in the reaction than the first minute.

Sample No. 2 was also tested qualitatively for the following compounds, none of which was found to be present: urea, cyanide, and dicyandiamide.

The conclusions we draw from this investigation are these:—

1. An effective method for removing one nitrogen from guanidine by the action of nitrous acid (other than in the Van Slyke apparatus) is to treat the cold, acidified solution with nitrogen trioxide.

2. When guanidine is so treated, cyanamide is the two-nitrogen compound formed.

Cornell University.

CATALYTIC DECOMPOSITION OF KEROSENE*

BY E. W. KANNING[1] AND O. W. BROWN[2]

Introduction

Hydrocarbons, when subjected to rather high temperatures, decompose giving a wide variation of products. The hydrocarbon may decompose in such a manner to produce hydrocarbons lower in the series, unsaturated compounds, or hydrocarbons higher in the series. It is also possible that in the case of paraffin hydrocarbons, aromatic compounds result from the thermal decomposition. In most cases hydrogen and carbon are among the various products. The complete decomposition of any hydrocarbon would, of course, give hydrogen and carbon as the sole products.

In the case of methane a rather high temperature is required for its complete decomposition. Methane starts to decompose at 650-700°C.[3] and has been found to completely decompose in a porcelain tube at 780-980°C.[4] Since high temperature is necessary to bring about the decomposition of hydrocarbons, the use of catalysts has been studied to a great extent with the aim of lowering the temperature of decomposition and of studying the effect of catalysts on the products of the decomposition of various hydrocarbons. Use has been made of catalysts in the petroleum industry for the purpose of cracking the high-boiling fractions of petroleum to more valuable low boiling fractions. Much investigation in this particular field has resulted in the production of a larger total volume of gasoline from the same volume of crude petroleum.

Schenck, Krägeloh, Eisenstecken and Klas[5] have studied the decomposition of methane over iron and cobalt catalysts and have found that over iron, methane starts to decompose at 350°C. and at 740°C. 89.6% decomposition was attained. Over cobalt, the decomposition began at 310°C. and reached a maximum of 89.15% at 740°C. Sabatier[6] has reported the decomposition of methane starting at 320° C. over a nickel catalyst.

With paraffin hydrocarbons higher in the series, the initial decomposition temperature is lower. For example, ethane starts to decompose with the aid of catalysts at 485°C. and the decomposition is quite rapid at 700°C. The decomposition products become more complex also as hydrocarbons higher in the series are decomposed.

---

*This paper is constructed from a dissertation presented by Eugene William Kanning to the Faculty of the Graduate School of Indiana University in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry.

[1] Instructor of Chemistry, Indiana University.

[2] Professor of Chemistry, Indiana University.

[3] Egloff, Schaad and Lowry, Jr.: J. Phys. Chem., 34, 1623 (1930).

[4] Bone and Jerdan: Chem. News, 84, 7 (1901); Proc. Chem. Soc., 17, 164 (1901).

[5] Schenck, Krägeloh, Eisenstecken: Z. anorg. allgem. Chem., 164, 313-325; Schenck, Krägeloh, Eisenstecken and Glas: 145-85 (1927); Stahl Eisen, 45, 671-675 (1926).

[6] Sabatier and Senderens: Ann. Chim. Phys., (8) 4, 435 (1905).

The effect of catalysts on the decomposition of hexadecane is reported by Gault and his co-workers.[1] In this work Gault studied the effect of temperature and catalysts on the properties of the products obtained. The volume of gas, volume of liquid, per cent saturated and unsaturated hydrocarbons, the density of the liquid and the composition of the gaseous products were noted. The results obtained point to many interesting facts. With an increase of temperature the volume of the gas, per cent hydrogen in the gas, per cent liquid below hexa-decane and the yield of unsaturated and aromatic hydrocarbons increased. The volume of the liquid products accordingly decreased with a rise in temperature. Gault and his co-workers also found that the carbon deposited on the catalyst at low temperature renders the catalyst less active, while that deposited at higher temperature seems to have no effect on the catalyst.

Of the most common catalysts which have been studied for the decomposition of hydrocarbons, cobalt, iron and nickel have probably been most successful in lowering the initial decomposition temperatures.

The following investigation was undertaken to determine the most suitable temperature for the decomposition of a fraction of kerosene which boils between 200 and 230°C. when passed over cobalt, iron, manganese or nickel catalysts. The effect of change of temperature on the volume and composition of gaseous products was studied. The per cent of hydrogen, methane, higher paraffin hydrocarbons and unsaturated hydrocarbons was determined in the gaseous product obtained at different temperatures. The volume, density and iodine number of the liquid hydrocarbon produced was also determined. In each instance the weight of carbon deposited on the catalyst from a given volume of kerosene was ascertained. With the cobalt catalyst, the relation between the rate of flow of kerosene over the catalyst, and the volume and composition of the gas produced was studied.

Apparatus

The apparatus shown in the sketch, Fig. 1, was used in all the experiments throughout this investigation.

In Fig. 1 the capillary tube, E, is welded to the glass tube, D, and is bent so as to extend into the iron pipe, F, about three inches. The junction between the iron pipe and the capillary tube is made gas tight by means of a small piece of heavy rubber tubing. The glass tube, D, having a volume of about 12 cubic centimeters, holds the liquid to be introduced into the reaction chamber and the rate of flow of this liquid is regulated by raising and lowering the mercury leveling tubes, A. The glass tube, D, and the mercury leveling tubes, A, were made from broken burettes and the graduations were found to be quite convenient in adjusting the mercury level and regulating the rate at which the liquid was passed through the capillary tube.

---

[1] Gault and Hessel: Compt. rend., 179, 171-173 (1924); Ann. Chim., (10) 2, 318-377 (1924); Gault, Hessel and Altchidjian: Compt. rend., 178, 1562-5 (1924); Gault and Sigwalt: Ann. combustibles liquides, 2, 309-323, 543-84 (1927).

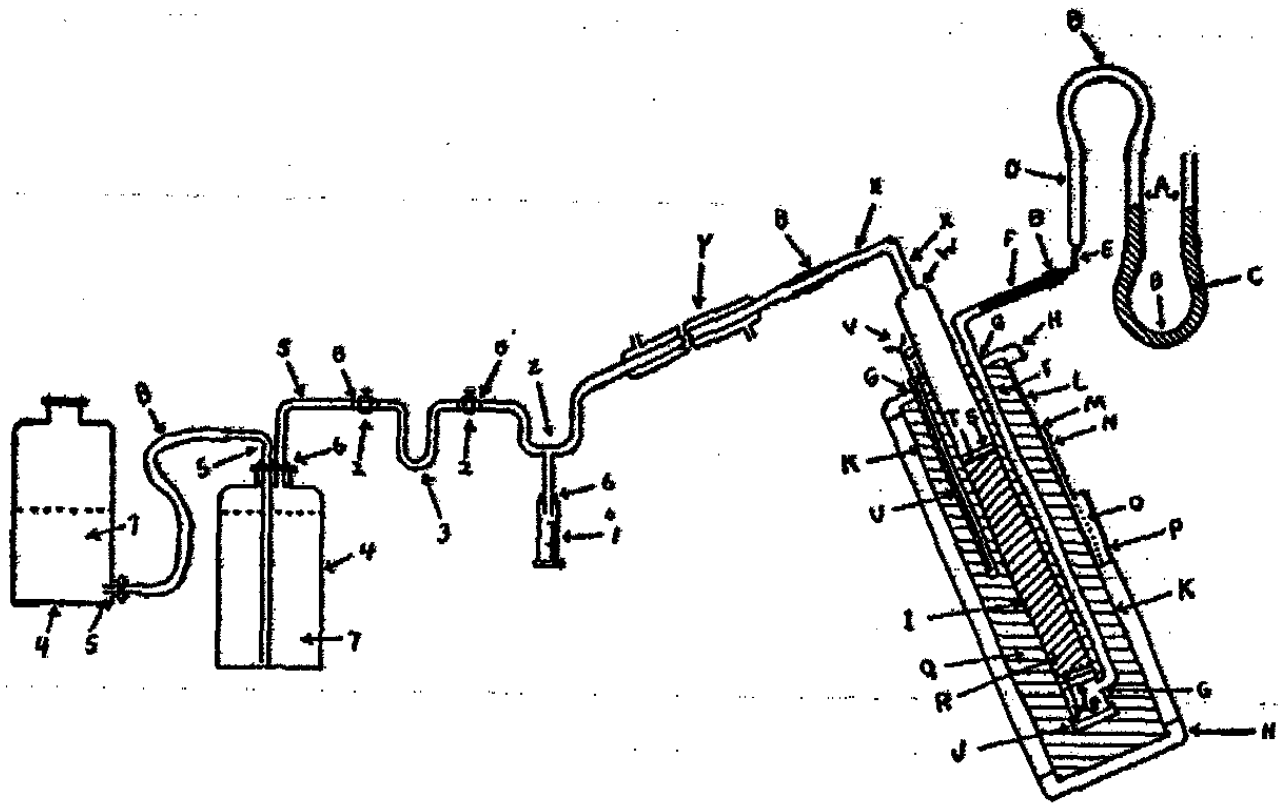


Fig. 1

A—Mercury leveling tubes which furnish pressure for the introduction of liquid into the catalyst tube.
B—Rubber tubing.
C—Mercury.
D—*Glass tube into which the kerosene (B.P. 200°-230° C.) is placed.*
E—Capillary tube welded to D conveying the liquid into the catalytic furnace.
F—Iron pipe ¼ inch diameter, extending into the furnace to the catalyst tube.
G—Gas weld.
H—Iron pipe cap for 3½ inch diameter iron pipe.
I—Catalyst tube, iron pipe 1½ inch diameter and 18 inches long.
J—Iron pipe cap for 1½ inch diameter pipe.
K—Heating jacket, iron pipe 3½ inch diameter and 15 inches long.
L—Single layer of asbestos paper.
M—Layer of alundum cement.
N—Heating element.
O—Layer of alundum cement.
P—Four layers of asbestos paper.
Q—Eutectic alloy of lead and tin.
R—Catalyst.
S—Iron rings.
T—Nickel gauze.
U—Thermocouple well, iron pipe ⅜ inch diameter and 5 inches long.
V—Copper-advance (constantan) thermocouple.
W—Iron pipe reducer, from 1½ inch to ½ inch.
X—Iron pipe ½ inch diameter.
Y—Water condenser.
Z—Glass U tube with a glass tube welded to the bottom of the U, serving as a liquid trap.
1—25 cubic centimeter graduated cylinder.
2—Screw clamp.
3—Glass U tube.
4—Glass bottle, 8 liter capacity.
5—Glass tubing.
6—Rubber stopper.
7—Water.

The mercury pressure necessary to allow the liquid to pass into the catalyst tube at a gradual and constant rate depends upon the size of the capillary tube used.

The upper iron pipe cap, H, is screwed loosely to the heating jacket, K, and contains holes of the necessary size through which the catalyst tube, I, the iron pipe, F, and the thermocouple well, U, extend. These tubes are all gas welded to the iron cap. Therefore, when this upper cap is screwed on to the heating jacket, the three tubes are held securely in place. The lower pipe cap, H, is screwed to the bottom of the heating jacket and is made tight with a lute consisting of red lead, litharge, glycerine and water. This cap forms the bottom of the container of the molten lead-tin bath and must be made tight.

The reaction tube, I, is an iron pipe 1½ inches inside diameter and 18 inches long. This tube extends above the upper pipe cap about three inches and down into the molten bath, Q. The upper end of the catalyst tube is fitted with a pipe reducer, W, which reduces a 1½ inch diameter pipe to one of ½ inch diameter. The lower end of the tube is fitted with a pipe cap, J. Both the reducer and the cap are screwed to the iron tube and are made removable to allow easy changing of the catalysts. They are made gas tight by means of the red lead-litharge-glycerine-water lute. The iron feed pipe, F, which extends down into the molten bath along side of the catalyst tube, is gas welded into a hole in the side of the catalyst chamber one inch from the lower extremity. The liquid entering the furnace through this feed pipe, F, is thus pre-heated to the temperature of the catalyst before it passes over the catalyst.

The catalyst column, R, is about 10 inches long and is held in place by means of a round piece of nickel wire gauze, T, resting on two iron rings, S. These rings have an outside diameter of a little less than 1½ inches so as to afford easy replacement in the catalyst tube which is 1½ inches in diameter. The lower ring is held in place by the tube, F, which extends into the catalyst tube, I, about ¼ inch. The nickel gauze and single iron ring above the column of catalyst are merely to keep the catalyst in its given position while assembling the apparatus. The lower end of the catalyst column is one inch above the point at which the tube, F, enters the reaction chamber.

The upper end of the catalyst tube, I, which is fitted with the reducer, W, extends one inch and then by means of an elbow bends at right angles and extends four inches, where it is connected to the glass condenser, Y, by means of heavy rubber tubing.

The heating jacket, K, is covered with a single layer of asbestos paper, L, which was securely cemented to it with sodium silicate solution. A coating of alundum cement mixed with water and about ¼ inch thick was placed over the asbestos layer. When the cement had dried, twenty-five feet of chromel wire No. 16, B and S gauge, N, Fig. 1, was wound on top of this layer of alundum cement. In starting the winding of the wire, the end was doubled back about two feet and this doubled end was twisted securely around the jacket with about six inches of the end extending out for electrical connection.

This first round of wire does not do any of the heating but merely holds the rest of the coil in place while winding. When the coil of chromel wire has been wound to the other end of the heating jacket, the end is again doubled back. At this point, instead of continuing the winding in the same direction, the doubled wire is bent so as to wind it in the opposite direction. This forms a loop in the wire and the end is brought through this loop, bent back and twisted tightly with one side of the loop, the end extending several inches for electrical connection. This heating coil of chromel wire was covered with a layer of alundum cement, O, which was about 3/8 inch thick. Over this layer of alundum cement were wrapped three or four layers of asbestos paper in order to insure heat insulation. The heating coil was connected to the 110 volt D.C. circuit and the heat regulated by means of an external chromel wire resistance.

The temperature was measured by means of a copper-advance thermocouple described in a previous article from this laboratory.[1] The thermocouple extended into the molten bath of tin and lead in the thermocouple well, U. The temperatures recorded in this investigation are correct within 2-5 degrees Centigrade.

The molten bath, Q, of the eutectic alloy of tin and lead was found to be very suitable for the temperatures employed in the experiments conducted in this investigation.

The glass water condenser, Y, fitted to the iron pipe, X, by means of rubber tubing, is welded to the U tube, Z. This U tube with a short glass tube welded to its lower part serves as a trap for the liquid products which drop into the graduated cylinder, 1, while the gaseous products pass on into the gas-collecting apparatus. The glass U tube, 3, contained a small amount of water through which the gas bubbled. This indicated when the gas was passing into the collector. The screw clamps, 2, were clamped over short pieces of rubber tubing which permitted the removal of the gas collector for the collection of samples of gas for analysis, or for the exchange of gas collectors during the progress of an experiment. The gas-collecting apparatus consisted of two glass bottles of about eight liters capacity. The gas obtained as the product of the catalytic decomposition was collected and confined in one of these bottles while the other, which was fitted with an outlet in the bottom, was used only as a leveling bottle to keep the level of the water, over which the gas is collected, the same in the two bottles. The two bottles were connected as shown in the diagram, Fig. 1, by means of a long rubber tube to allow the raising and lowering of the leveling bottles. Wherever stoppers were needed rubber stoppers were used in order to keep the apparatus gas tight. Care was taken in setting up the apparatus to insure a gas tight construction in order to exclude atmospheric gases from the interior and to keep the interior gas from escaping. The catalytic furnace was tilted about 25° from the vertical position in order to allow the water condenser to assume a slanting position.

---

[1] R. J. Hartman and O. W. Brown: J. Phys. Chem., 34, 2651-65 (1930).

Procedure

Before each experiment was undertaken, the furnace was brought to the desired temperature while a stream of hydrogen was being passed through the catalyst tube at the rate of 14 liters per hour, thus preventing the oxidation of the catalyst. (Hydrogen was also passed over the catalyst while the furnace was cooling). The hydrogen was introduced into the furnace through the tube, F, Fig. 1, the capillary, E, having been removed. By removing the graduated cylinder, 1, the hydrogen was forced out of the vertical glass tube at the bottom of the trap, Z. The end of this tube was immersed in water which partly filled an Erlenmeyer flask and through which the gas bubbled. When the temperature at which the experiment was to be carried out had been reached, the flow of hydrogen through the apparatus was stopped and the capillary tube, E, replaced into the tube, F. The graduated cylinder, 1, was also replaced. Ten cubic centimeters of the kerosene fraction were placed in the glass tube, D, and the rubber hose, B, placed on top. The mercury tube was then raised to generate a slight pressure on the liquid in D and the screw clamps, 2, were opened to allow the gaseous products to pass into the gas collecting bottle. The bottle into which the gas passed and the glass tubing connecting it with the U tube, 3, was previously filled with water. The leveling bottle of the gas-collecting apparatus was so adjusted that the level of the water in it was slightly below that of the water in the bottle into which the gas was passing, thus assuring an unhindered flow of gas into the bottle A constant rate of flow of the kerosene into the reaction chamber was maintained throughout the experiment by means of the mercury leveling tubes, A. After a few cubic centimeters of liquid had been passed over the catalyst, the hydrogen which was contained in the furnace had been replaced by the products of the catalytic decomposition. The U tube, 3, was then disconnected from the gas collecting bottle and connected to a gas burette for the purpose of obtaining a sample of the gaseous product for analysis. The sample having been taken, the U tube was again connected as before and the experiment completed. When all of the liquid had passed into the furnace, the screw clamps, 2, were closed and the graduated cylinder, 1, loosened from the rubber stopper. The capillary tube, E, was then removed from the feed tube, F, and hydrogen passed through the furnace at the rate of 14 liters per hour to wash out all of the liquid products of the reaction. This liquid product was collected and measured in the graduated cylinder.

Estimation of the Products

The gaseous products obtained from the experiments were analyzed by means of absorption and combustion with the use of Hempel gas apparatus. No attempt was made to determine any single hydrocarbon other than methane in the gaseous mixture obtained from the decomposition. The gaseous hydrocarbons higher than methane in the paraffin series were determined by absorption in absolute alcohol. The gas was then passed into an absorption pipette containing a 30% solution of potassium hydroxide to remove any traces of carbon dioxide which it might contain. The unsaturated hydrocarbon gases were determined by passing the gas into a pipette containing saturated bromine water, the bromine fumes being removed by means of the potassium hydroxide pipette. The gas was then passed into a pipette containing a solution of pyrogallic acid in strong potassium hydroxide to determine and remove traces of oxygen. Finally it was passed into a pipette containing ammoniacal cuprous chloride solution to determine carbon monoxide if present. About twenty cubic centimeters of the remaining gas were placed into a Hempel explosion pipette over mercury in order to determine the per cent of hydrogen and methane by the Hempel method. This method affords a relatively accurate determination of these two gases by a single combustion with oxygen.

The accuracy of the determination of the constituents of the gaseous mixtures is within 0.1 to 0.3% for the absorptions, 1% for methane and 1 to 3% for hydrogen.

The total quantity of the gas obtained as a product from the experiments was measured by means of calibrations on the side of the gas-collecting bottle. The hydrogen remaining in the reaction tube and adsorbed on the catalyst before kerosene was passed over the catalyst was found by experiment to be negligible in regard to the accuracy of the measurement of the total volume of the gas collected.

In the experiments where liquid was obtained as a product, the volume of the liquid was measured in the graduated cylinder, 1, Fig. 1. The density of the liquid product was accurately determined by means of a pycnometer. The iodine number of the liquid product and of the kerosene fraction passed over the catalyst was determined in the manner described by Kamm.[1]

The carbon which was deposited on the catalyst was determined by burning with oxygen and absorbing the carbon dioxide in two Geissler potash bulbs connected in series. The oxygen purified from CO_2 and water vapor was passed over the catalyst in the reaction tube at 300° C. The resulting gas containing CO_2 and an excess of oxygen was passed, first through a U tube containing calcium chloride, then through two weighed potash bulbs and finally through a weighed U tube containing calcium chloride. The weight of carbon was calculated from the increase in weight of the two potash bulbs and the last calcium chloride tube. This absorption train was connected to the liquid trap, Z, Fig. 1.

After the determination of carbon, it was necessary to reduce the catalyst with hydrogen before the next experiment was carried out.

Materials used

The kerosene fraction used in all the experiments was obtained from commercial kerosene. The kerosene was shaken with concentrated sulphuric acid three times, separated from the acid by means of a separatory funnel and then fractionally distilled. The fraction used was that which boiled between 200

---

[1] Oliver Kamm: "Qualitative Organic Analysis," page 170.

and 230° C. This liquid was a clear, colorless material having a density of .7879 and an iodine number of 27.6.

The hydrogen used in the reduction of the catalysts was commercial electrolytic hydrogen. Before passing into the furnace, the hydrogen was purified by passing over hot copper, through concentrated sulphuric acid, glass wool and then through a caustic soda tower. This purification removed all traces of oxygen and water vapor.

The oxygen used in the determination of the carbon deposited on the catalyst was commercial electrolytic oxygen. It was purified by passing through concentrated sulphuric acid and over soda lime and calcium chloride. This treatment removed traces of water vapor and carbon dioxide.

The cobalt nitrate from which the cobalt catalyst was prepared was Mallinckrodt's C.P. Quality $Co(NO_3)_2.6H_2O$, containing 0.30% alkali salts, 0.01% chlorine, .002% copper, 0.000% iron, 0.02% lead, 0.60% nickel, 0.01% sulphate and 0.08% zinc.

The ferric nitrate from which the iron catalyst was prepared was Baker's Analyzed $Fe(NO_3)_3.9H_2O$ and contained no copper or zinc, .001% chlorine and .001% SO_3.

The manganese sulphate from which the manganese catalyst was prepared was Coleman and Bell's $MnSO_4.4H_2O$, containing 0.02% calcium, 0.005% chlorine, 0.003% iron, 0.200% magnesium and alkalies, a trace of reducing matter, and 0.05% zinc.

The nickel nitrate used in the preparation of the nickel catalyst was Baker's Analyzed $Ni(NO_3)_2.6H_2O$ and contained .001% cobalt, no copper, .001% iron, .001% chlorine and .001% SO_3.

The pumice stone used as catalyst support was treated in the following manner. Lump pumice stone was crushed in a Blake crusher and sizes ranging from 3/16 to 1/2 inch were used for treatment. The crushed material was boiled in 1:5 nitric acid for four hours. It was then washed free of acid on a Büchner funnel with distilled water and dried in an oven at 105° C. for eight hours. The resulting material was used as the support for all the catalysts in this investigation.

Preparation of the Catalysts

The cobalt catalyst used in this investigation was prepared in the following manner: 247 g. of cobalt nitrate were dissolved in a small amount of water. To this solution, 25 g. of pumice stone were added and the mixture boiled for ten to fifteen minutes to saturate the pumice stone with the solution. Cobalt hydroxide was precipitated with a slight excess of a 15% solution of sodium hydroxide. The precipitate was washed free of alkali on a Büchner funnel with distilled water and dried at 105°C. in an oven for eight hours. The material was reduced in the furnace at 400° C. for two hours in a stream of hydrogen flowing at the rate of 14 liters per hour. The resulting cobalt metal catalyst supported on 25 g. of pumice stone weighed 50 grams.

The iron catalyst was prepared as follows: 361.7 g. of ferric nitrate were dissolved in a small amount of water and boiled for ten to fifteen minutes with

25 g. of the pumice stone. Ferric hydroxide was precipitated with an excess of a 1:1 solution of ammonium hydroxide. The resulting precipitate was washed free of ammonium hydroxide on a Büchner funnel and dried at 105° C. for eight hours. The dried material was reduced for two hours at 415° C. in a stream of hydrogen of 14 liters per hour. The catalyst material consisted of 50 g. of metallic iron supported on 25 g. of pumice stone.

The manganese catalyst was prepared as follows: 202.9 g. of manganese sulphate were dissolved in as little hot water as possible. To this solution, 25 g. of pumice stone were added and the mixture boiled for ten to fifteen minutes. Manganese hydroxide was precipitated by the addition of a slight excess of 1:1 ammonium solution. The precipitate was washed free of ammonium hydroxide and also sulphates on a Büchner funnel and dried for two hours in an oven at 105° C. The dried material was placed in the furnace and reduced for two hours at 435° C. in a stream of hydrogen of 14 liters per hour. The resulting catalyst material consisted of 50 g. of manganese metal supported on 25 g. of pumice stone.

In the preparation of the nickel catalyst, 247.7 g. of nickelous nitrate were dissolved in a small amount of hot water. To this solution 25 g. of pumice stone were added and the mixture boiled for ten to fifteen minutes to impregnate the pumice with the nickel nitrate solution. Nickel hydroxide was precipitated by the addition of a slight excess of a 15% solution of sodium hydroxide. The precipitate was washed free of alkali on a Büchner funnel and dried for eight hours at 105° C. The dried material was reduced at 350° C. for two hours in a stream of hydrogen of 14 liters per hour. The catalyst material consisted of 50 grams of metallic nickel supported on 25 grams of pumice stone.

Cobalt Catalyst

A number of experiments were carried out with a cobalt catalyst prepared in the manner previously described, in order to determine the effect of temperature on the catalytic decomposition of the kerosene fraction. Other experiments were made for the purpose of determining the effect of the rate of flow of the liquid passed over the catalyst. In the experiments carried out at various temperatures, the quantity and rate of flow of the liquid passed into the reaction chamber were kept constant, ten cubic centimeters being passed in sixty minutes. In determining the effect of the rate of flow of the liquid, the temperature and quantity (10 cc.) of the liquid were kept constant.

In the experiments in which the temperature was the variable factor the following determinations were made and recorded: the total volume of gas obtained as product from the ten cubic centimeters of kerosene passed over the catalyst, the volume of liquid product, the per cent of hydrogen and methane in the gaseous product, the per cent of gaseous paraffin hydrocarbons above methane in the series, per cent of gaseous hydrocarbons of the unsaturated series, the grams of carbon deposited by the decomposition and the iodine numbers and densities of the liquid products in those experiments where liquid was obtained.

Table I shows the effect of temperature on the volume and composition of the gaseous product obtained with the cobalt catalyst.

TABLE I

Volume of Kerosene Fraction passed: 10 cc.
Rate of Flow of Kerosene Fraction: 10 cc. per hour.
Catalyst: 50 g. of cobalt on 25 g. of pumice.

Temp. °C.	Volume of gas obtained in cc.	Per cent hydrogen in gas	Per cent methane in gas	Per cent gaseous paraffins above methane in gas	Per cent gaseous unsaturated hydrocarbons in gas
290	495	49.70	37.50	10.80	0.00
305	498	50.70	32.40	9.40	0.00
350	663	56.10	29.20	8.30	0.00
400	1980	61.50	26.40	6.40	0.00
450	4800	65.40	25.60	5.40	0.20
500	9715	68.76	24.47	2.20	0.30
510	9842	68.85	24.47	3.20	0.40
525	9990	69.81	24.26	3.14	0.50
550	10040	69.80	24.00	3.22	0.62

It is most apparent from Table I, that, as the temperature is increased, the volume of gas obtained from 10 cubic centimeters of the kerosene fraction increases greatly. At 550° C. over 1,000 volumes of gas are obtained from one volume of liquid. The following curves, Fig. 2, show the temperature plotted as abscissa and per cent as ordinates. Curve 1 represents the per cent of hydrogen in the gaseous product obtained at various temperatures and Curve 2 the per cent of methane.

From Curve 1, Fig. 2, it is seen that the per cent of hydrogen in the gaseous product increases with the temperature at which the experiment is carried out. When 525° C. is reached the production of hydrogen seems to have reached a maximum since at 550° C. there is no further increase. From Curve 2, Fig. 2, it is seen that the per cent of methane in the gas decreases as the temperature is increased. The per cent of methane approaches a minimum at 525° C. since the curve nearly straightens out horizontally at that point. Therefore, at 525° C. cobalt attains an activity greater than that at any lower temperature studied and there is no marked increase in activity at 550° C. over that obtained at 525° C.

The per cent of paraffin hydrocarbons which are gaseous at ordinary temperature and higher than methane in the series, and all gaseous hydrocarbons which can be absorbed by absolute alcohol, decreased with an increase in temperature up to 525° C., as is seen in Table I. No unsaturated hydrocarbons were found in the gas until 450° C. was reached. At no time was the amount of unsaturated gaseous hydrocarbons sufficiently great to warrant further investigation. The excess of hydrogen present at all times seems to have hydrogenated to a great extent any unsaturated gases which might have been formed.

From 290 to 450° C. inclusive, Table II, it is noted that liquid was obtained as a product when ten cubic centimeters of the kerosene had been passed over the catalyst. No liquid was obtained, however, at 500° C. Whenever liquid did not appear after ten cubic centimeters of the kerosene had been passed into the furnace, an experiment was performed to determine the volume of kerosene which could be passed over the catalyst before a liquid product appeared. At 500° C. it was not until 32.5 cubic centimeters of kerosene had been passed before a liquid appeared as product. At 510, 525 and 550° C. one hundred ten cubic centimeters of kerosene were passed continuously at the rate of 10 cc. per hour without the appearance of a liquid product, but 97,950 cc., 99,800 cc. and 103,500 cc. gas respectively were obtained, or, for

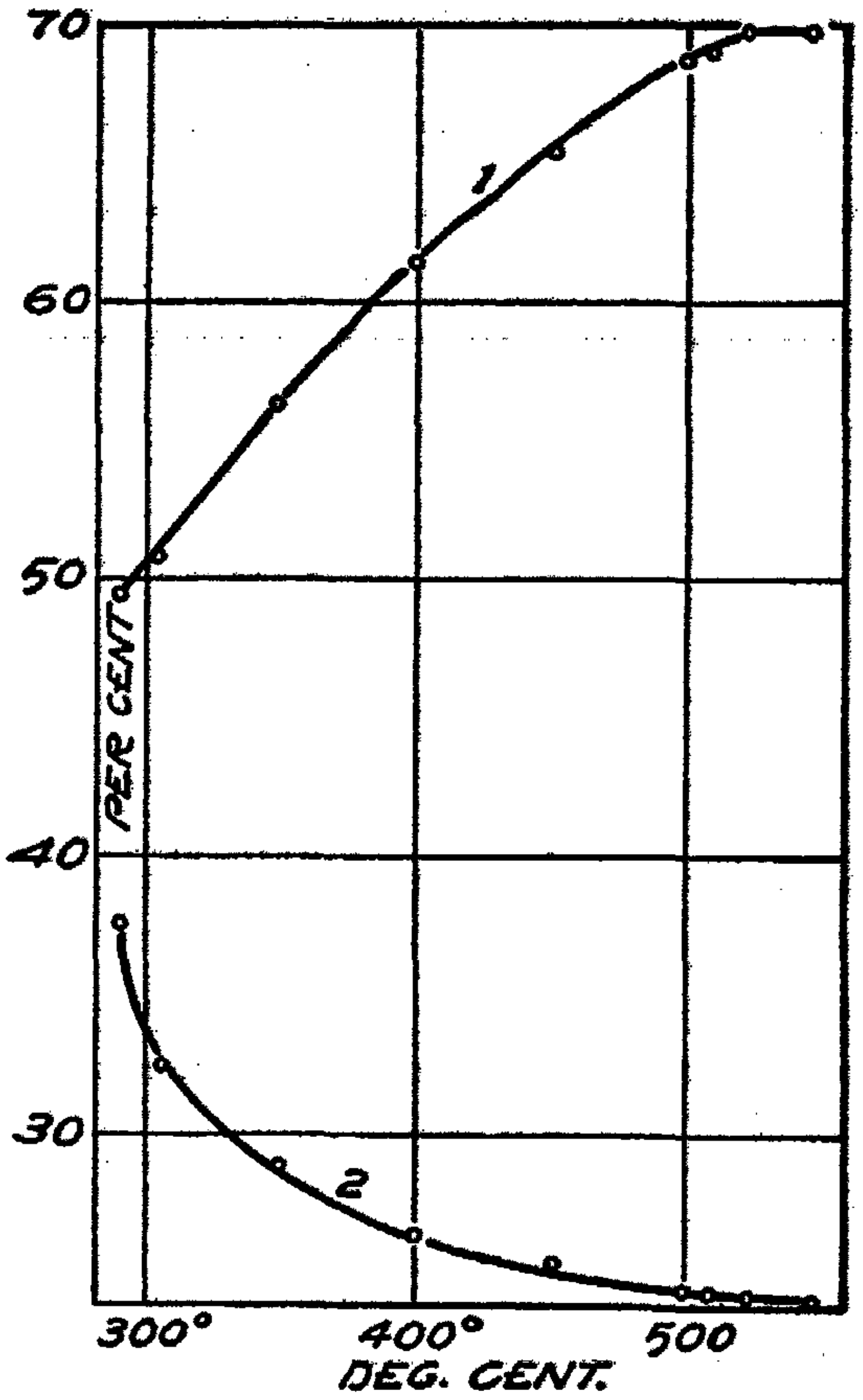


FIG. 2

every 10 cc. of kerosene passed, 8,904, 9,072 and 9,409 cubic centimeters respectively of gas were obtained. These figures agree well with those shown in Table I. In each case when 110 cc. of kerosene had been passed, the catalyst appeared to be still as active as at first but the accumulation of carbon within the catalyst tube mechanically stuffed the tube making it difficult to force more kerosene over the catalyst. At temperatures lower than 500° C. it seemed that the deposition of carbon blanketed the catalyst thereby rendering it less active. A greater quantity of carbon was deposited at temperatures above 500° C., but, as the nature of the carbon deposited at these temperatures was probably less amorphous its blanketing action was much less pronounced. Gault and his co-workers also found that the catalyst was poisoned more readily at the lower temperatures.

TABLE II

Volume of Kerosene passed: 10 cc.
Rate of Flow of Kerosene: 10 cc. per hour.
Catalyst: 50 g. of cobalt on 25 g. of pumice.

Temp. °C.	Grams carbon	Cc. of liquid product	Density of liquid product	Iodine number of liquid product
290	0.1479	9.2	0.7740	—
305	0.1240	9.2	0.7760	28.0
350	— —	9.0	0.7751	29.3
400	0.7736	7.0	0.7815	32.1
450	0.8554	4.5	0.7847	35.4
500	3.0692	0.0	0.7849*	42.1*
510	3.1666	0.0	— —	—
525	3.1879	0.0	— —	—
550	3.2480	0.0	— —	—

*These values were obtained from a liquid product which was produced at 500°C. after 32.5 cc. of the kerosene had been passed over the catalyst. The first 10 cc. did not yield a liquid product.

Table II shows the effect of temperature on the volumes, densities and the iodine numbers of the liquid products obtained. The table also gives the grams of carbon deposited in the catalyst tube by the decomposition of 10 cc. of the kerosene fraction.

From Table II, it can be seen that the volume of the liquid product decreases as the temperature is increased. This shows an increase in the activity of the cobalt catalyst on the decomposition of the kerosene fraction as the temperature is raised. At 500° C., all of the ten cubic centimeters were converted into a gaseous product as no liquid product was obtained. The iodine numbers of the liquid products increased which shows that as the temperature was increased, the liquid product became more unsaturated. It is noticed in Table II that with cobalt as a catalyst the iodine numbers of the liquid products obtained were always higher than that of the kerosene originally passed into the furnace. This indicates that with cobalt as a catalyst there was always a tendency for the liquid to become dehydrogenated rather than hydrogenated, even though there was an excess of hydrogen present at all times. The iodine numbers of the liquid products obtained at the various temperatures are plotted as ordinates and the temperatures as abscissa. The resulting curve for cobalt is Curve 1, Fig. 5, where it is plotted along with similar curves for the other catalysts studied in this investigation.

The densities of the liquid produced can be seen to increase slightly as the temperature at which the reaction is carried out increases. This is probably due to the formation of hydrocarbons of higher carbon content.

The carbon deposited in the catalyst tube from the decomposition is proportional to the quantity of liquid decomposed by the catalyst. Thus it can be seen that the grams of carbon increase with an increase of temperature and also increase with an increase of gas formed.

Table III

Temperature: 500° C.
Quantity of Kerosene passed: 10 cc.
Catalyst: 50 g. of cobalt on 25 g. of pumice.

Time required to pass 10 cc. of kerosene in minutes	Volume of gas in cc.	Volume of liquid in cc.	Per cent hydrogen in gas	Per cent methane in gas	Per cent higher hydrocarbons in gas
45	9,750	none	67.2	25.3	2.4
30	9,550	none	68.1	26.0	2.8
20	6,500	3.5	67.4	25.2	3.0

In order to determine the effect of the rate at which the kerosene was passed over the catalyst, a series of experiments were carried out at 500° C. using a new cobalt catalyst, prepared in the same manner as before. Ten cubic centimeters of the kerosene fraction were passed over the catalyst in each experiment at a definite rate. Table III shows the effect of the rate of flow on the volume of the gaseous products, the volume of the liquid products and the per cent of hydrogen, methane and higher saturated hydrocarbons in the gas.

From Table III it can be concluded that a rate of flow of ten cubic centimeters of the kerosene in twenty minutes was too great for the 50 grams of cobalt catalyst to convert the kerosene into all gas, since liquid product appeared. The analysis of the gaseous products indicated practically no change in the per cent of hydrogen, methane and gaseous paraffins above methane in the series. The volume and analysis of the gaseous products obtained from these experiments compare very closely with those of the gas obtained in the previous experiments at 500° C., Table I. From Table III, it is seen also that thirty minutes is as fast as ten cubic centimeters of the kerosene can be passed over 50 grams of catalyst and still give all gas as product.

Iron Catalyst

An iron catalyst was prepared from ferric nitrate in the manner previously described. Experiments were carried out with this catalyst in the same manner as with cobalt in order to determine the effect of temperature on the following factors: volume of gaseous product, composition of gaseous product, volume of liquid product and its density and degree of unsaturation as indicated by the iodine number. Table IV shows the effect of temperature on the volume and composition of gas obtained. In all the experiments with iron as catalyst the rate of flow of the kerosene fraction was kept constant at 10 cc. per hour.

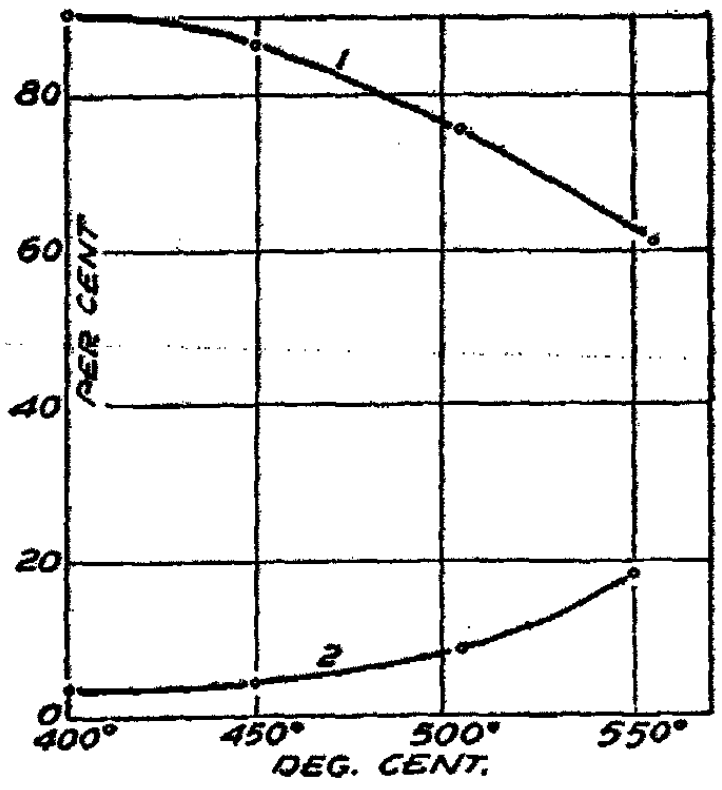


FIG. 3

TABLE IV

Quantity of Kerosene passed: 10 cc.
Rate of Flow of Kerosene: 10 cc. per hour.
Catalyst: 50 g. of iron on 25 g. of pumice.

Temp. °C.	Volume of gas obtained in cc.	Per cent hydrogen in gas	Per cent methane in gas	Per cent gaseous paraffins above methane in gas	Per cent gaseous unsaturated hydrocarbons in gas
300	none	—	—	—	—
350	none	—	—	—	—
400	622	90.5	3.62	0.00	0.00
450	2350	86.9	4.10	0.40	0.00
505	4500	75.9	8.50	8.00	0.00
555	9500	61.6	18.20	11.00	0.00

The curves, Fig. 3, show the temperature plotted as abscissa and per cent as ordinates. Curve I represents the per cent of hydrogen in the gaseous product and Curve 2 represents the per cent of methane. From Curve 1, Fig. 3, it can be seen that the maximum per cent of hydrogen in the gaseous product is obtained at 400° C. The volume of gas obtained at this temperature, Table IV, is, however, considerably less than that obtained at the higher temperatures. From this it is noted that the temperature which yielded the highest per cent of hydrogen in the gaseous product did not yield the greatest volume of gas.

Curve 2, Fig. 3, shows that the per cent of methane in the gaseous product increases with the temperature. It is also noted here that at 550° C., 18.2% methane was obtained while only 59.6% hydrogen was obtained, or, in other words, of all the temperatures used, 550° C. gave the highest yield of methane and the lowest yield of hydrogen, which is quite different from the results obtained with cobalt as catalyst.

The per cent of paraffin hydrocarbons other than methane which are gases at ordinary temperatures, increased with an increase in temperature as shown in Table IV. There were no unsaturated compounds present in the gaseous product with iron as the catalyst.

TABLE V

Quantity of Kerosene passed: 10 cc.
Rate of Flow of Kerosene: 10 cc. per hour.
Catalyst: 50 g. of iron on 25 g. of pumice.

Temp. °C.	Grams of carbon deposited	Cc. of liquid product	Density of liquid product	Iodine number of liquid product
300	0.0000	9.2	0.7667	22.3
350	0.0000	9.0	0.7704	26.0
400	0.1367	8.8	0.7678	32.8
450	0.2923	7.0	0.7645	40.9
505	0.5193	6.0	0.7628	52.2
555	——	0.0	——	—

Table V shows the effect of temperature on the volume of liquid produced, the density and iodine number of the liquid, and, also, the grams of carbon produced by the decomposition.

From Table V, it is noticed that as the temperature was increased, the grams of carbon deposited also increased and that the volume of liquid product decreased. The densities of the liquid products did not vary to a great extent as the temperature was raised, but the iodine numbers increased to a marked degree. This shows an increase in unsaturation as the temperature rose. Curve 2, Fig. 5, shows this variation in the iodine number as the temperature of the reaction was varied. The maximum unsaturation was obtained at 555° C. The values for the iodine numbers of the liquid produced at 300 and 350° C. were lower than that of the kerosene passed into the furnace, which was 27.6. This shows that at the lower temperatures a slight hydrogenation of the kerosene took place. Except for this very slight hydrogenation of the liquid, there was very little action on the kerosene at 300 or 350° C., since no gaseous product was obtained in either case.

At 555° C. 80 cubic centimeters of the kerosene were passed over the iron catalyst at the rate of 10 cc. per hour without the appearance of a liquid product. At various intervals during the introduction of the kerosene into the furnace, samples of the gaseous product were collected and analyzed. It was found that the analyses of these samples checked very closely with each other, showing that the gas remained of the same composition throughout the experiment. It was apparent that the kerosene could not be passed over the catalyst faster than 10 cc. per hour, without the formation of a liquid product. The total volume of the gas obtained from the 80 cc. of kerosene was 78,100 cc. which is 9,787.5 cc. per 10 cc. of kerosene. This latter value agrees very well with the volume of the gas obtained at the same temperature as shown in Table IV.

Manganese Catalyst

Experiments with manganese as catalyst, prepared as previously described, were carried out in order to determine the effect of temperature on the various factors which were studied in the case of cobalt and iron. Table VI shows the effect of temperature on the gaseous product resulting from the decomposition of the kerosene fraction over the manganese catalyst.

TABLE VI

Quantity of Kerosene passed: 10 cc.
Rate of Flow of the Kerosene: 10 cc. per hour.
Catalyst: 50 g. of manganese on 25 g. of pumice.

Temp. °C.	Volume of gas obtained in cc.	Per cent hydrogen in gas	Per cent methane in gas	Per cent gaseous paraffins above CH_4 in gas	Per cent gaseous unsaturated hydrocarbons in gas
300	none	—	—	—	—
370	none	—	—	—	—
400	515	76.0	6.6	8.0	0.0
500	1550	68.8	8.1	19.2	0.0
550	2130	15.6	22.9	54.8	0.0

No gas was obtained as product with manganese as catalyst at 300 or 370° C. Gas appeared as a product at 400° C. and increased in volume as the temperature was raised, as shown in Table VI. It is noted also that manganese did not yield large volumes of gas as did cobalt and iron over the same temperature range.

From Table VI is can be seen that with manganese as catalyst the per cent of hydrogen in the gaseous product decreased as the temperature of the reaction was increased. The hydrogen content of the gas is seen to have dropped as low as 15.6 per cent. As the temperature was increased, the per cent of methane in the gaseous product increased and reached a maximum of 22.9 at 550° C. At 550° C. the per cent of gaseous paraffin hydrocarbons above methane in the series was 54.8 which indicates that manganese has the specific activity of producing this stage of decomposition at this temperature. It is seen also from Table VI that no unsaturated gaseous hydrocarbons were obtained, as was also the case when iron was used as catalyst.

Table VII shows the effect of the temperature variation on the liquid product obtained and also the grams of carbon deposited.

TABLE VII

Quantity of Kerosene passed: 10 cc.
Rate of Flow of Kerosene: 10 cc. per hour.
Catalyst: 50 g. of manganese on 25 g. of pumice.

Temp. °C.	Grams carbon deposited	Cc. of liquid product	Density of liquid product	Iodine number of liquid product
300	none	9.7	0.7770	26.53
370	none	9.5	0.7764	27.16
400	0.1862	9.2	0.7780	28.99
500	0.3412	8.5	0.7834	48.10
550	0.3874	5.5	0.7987	73.02

From Table VII, it can be seen that the activity of the manganese catalyst increases with the temperature, as shown by the diminishing volume of liquid obtained as product and the increasing amount of carbon deposited. The iodine numbers of the liquid products, indicating the degree of unsaturation, became larger as the temperature was increased. The density of the liquid rises slightly with the temperature but not to any marked degree. The iodine numbers are plotted as ordinates and the temperature as abscissa, Curve 3, Fig. 5.

Nickel Catalyst

The effect of temperature on the various factors encountered in the decomposition of the kerosene fraction was also studied using nickel as the catalyst, which was prepared as has been previously described. Table VIII shows the effect of temperature on the volume and composition of the gaseous product obtained with nickel.

TABLE VIII

Quantity of Kerosene passed: 10 cc.
Rate of Flow of Kerosene: 10 cc. per hour.
Catalyst: 50 g. of nickel on 25 g. of pumice.

Temp. °C.	Volume of gas obtained in cc.	Per cent hydrogen in gas	Per cent methane in gas	Per cent gaseous paraffins above CH$_4$ in gas	Per cent gaseous unsaturated hydrocarbons in gas
310	none	—	—	—	—
390	1452	46.4	36.40	0.0	8.0
450	1780	57.0	26.20	1.1	6.8
500	2000	59.2	15.80	12.0	5.5
550	3250	38.1	9.04	44.7	1.3

Curve 1, Fig. 4, shows the effect of temperature on the per cent of hydrogen in the gaseous product obtained from the decomposition of the kerosene fraction over nickel catalyst.

The curve shows a maximum production of hydrogen at 500° C. Higher or lower than 500° C. the per cent of hydrogen in the gas decreases quite rapidly. Curve 2, Fig. 4, shows the effect of temperature on the per cent of methane in the gaseous product. The methane content seemed to steadily decrease with a rise in temperature, the minimum per cent of methane being obtained at 550° C. and the maximum at 390° C.

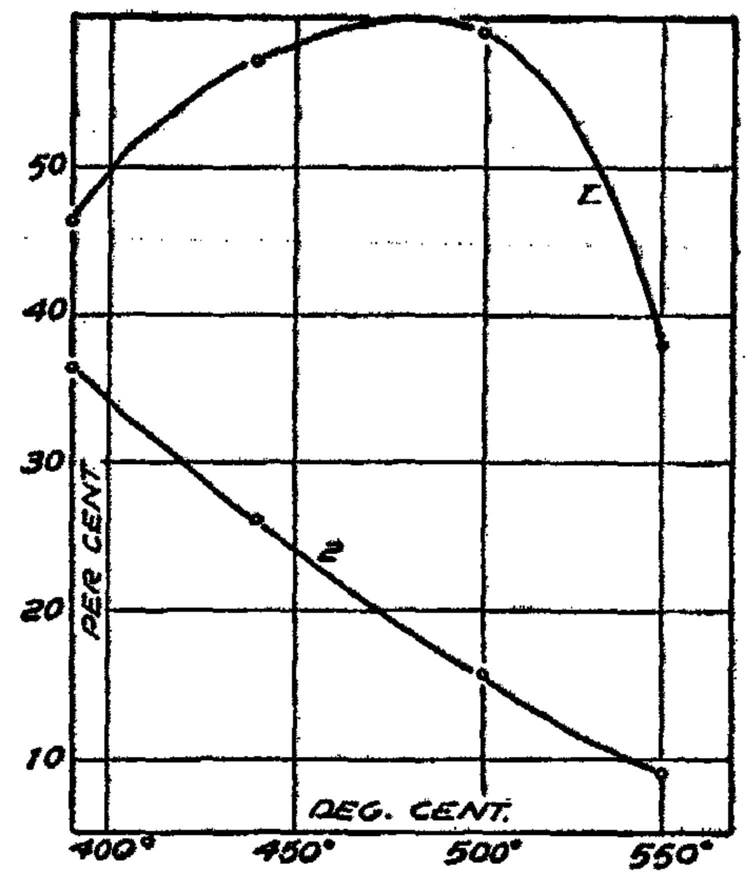


Fig. 4

From Table VIII, it can be seen that, with nickel as catalyst, the per cent of hydrocarbon gases of the paraffin series which are above methane increased as the temperature was raised. A decided increase was found from 500 to 550° C., the per cent of these gases being 12.0 and 44.7 respectively.

Unlike any of the other catalysts, nickel causes an appreciable production of unsaturated gaseous hydrocarbons as is seen in the table. The per cent of these unsaturates decreases with an increase in temperature, from 8.0% at 390° C. to 1.3% at 550° C.

At 310° C. no gaseous product was obtained, but the volume of gas steadily increased as the temperature was raised to reach a maximum of 3,250 cubic centimeters at 550° C. from ten cubic centimeters of kerosene. It is noted that the volume of gas obtained with nickel at 550° C. is considerably less than that obtained with cobalt and iron but not less than that obtained with manganese.

Table IX shows the effect of temperature on the volume, density and iodine number of the liquid products and also the grams of carbon deposited from the experiments with nickel as catalyst.

TABLE IX

Quantity of Kerosene passed: 10 cc.
Rate of Flow of Kerosene: 10 cc. per hour.
Catalyst: 50 g. of nickel on 25 g. of pumice.

Temp. °C.	Grams of carbon deposited	Cc. of liquid product	Density of liquid product	Iodine number of liquid product
310	none	10.0	0.7882	27.10
390	0.0875	8.8	0.7689	28.02
450	0.2764	8.5	0.7742	36.40
500	0.5787	7.5	0.7703	50.76
550	0.1630	3.5	0.8063	70.99

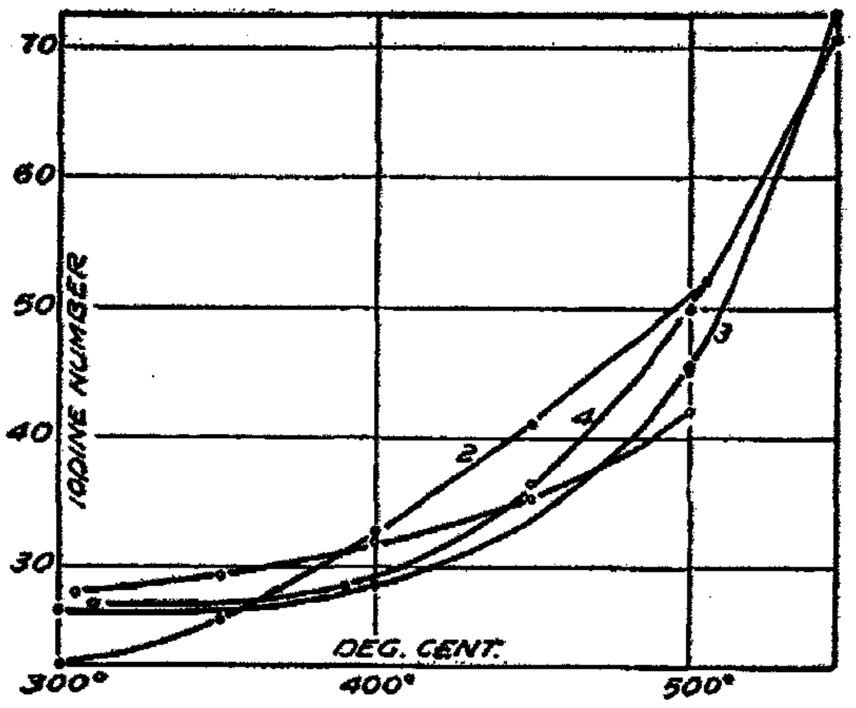


FIG. 5

From Table IX, it is evident that the grams of carbon deposited increased with the temperature until 550° C. was reached. The amount of carbon deposited at 550° C. was less than that deposited at 500° C. probably because a greater per cent of gaseous hydrocarbons was found in the former case. The extent of the decomposition was greater at 500° C. because, in the latter case, nearly half of the volume of the gas produced was composed of hydrocarbons of the paraffin series above methane, Table VIII. The volume of the liquid products decreased as the temperature was raised and as a greater volume of gas was produced.

The iodine numbers of the liquid products increased with the temperature, which shows a higher degree of unsaturation of the liquid products at the higher temperatures. At 310° C. there was apparently no decomposition over the nickel catalyst since the volume, density and iodine number of the liquid product were the same as those of the liquid passed into the furnace. Curve 4, Fig. 5, represent the iodine numbers plotted as ordinates and the temperature plotted as abscissa.

Comparison of the Catalysts

In comparing the activity at the various temperatures of the four catalysts, cobalt, iron, manganeses and nickel, for the decomposition of the fraction of kerosene boiling between 200 and 230° C., the following factors are noted: the volume of gaseous product obtained from ten cubic centimeters of the kerosene, the per cent hydrogen, methane, saturated gaseous hydrocarbons above methane in the paraffin series and unsaturated hydrocarbons in the gaseous product, the volume of liquid product obtained from 10 cc. of the kerosene, and, the density and degree of unsaturation of the liquid product as shown by the iodine number.

The cobalt catalyst appeared to be the most active of those studied. Cobalt was the only catalyst of those studied found to convert 10 cc. of the kerosene to gas in less time than one hour over 50 g. of catalyst without the formation of a liquid product. The volume of gas obtained with all four catalysts from 10 cc. of kerosene increased with an increase in temperature. The maximum volume of gas obtained with each catalyst was at 550° C., the highest temperature used.

With cobalt, the per cent hydrogen in the gaseous product increased as the temperature was raised, while with iron and manganese the per cent of hydrogen steadily decreased with a rise in temperature. When nickel was used as catalyst, the per cent of hydrogen in the gaseous product of the reaction reached a maximum at 500° C. These facts illustrate the specific action of the catalysts and no set rule can be formulated to explain these differences in activity.

The highest per cent of hydrogen in the gaseous product was obtained with iron as catalyst at 400° C. This value was 90.5%, as seen in Table IV. However, the quantity of liquid decomposed under these conditions was low compared with that obtained at the same temperature with cobalt. The per cent hydrogen in the gaseous mixture obtained over cobalt at 400° C. was 61.5. Manganese and nickel are less active at this temperature and are inferior to cobalt and iron for the production of gas. At higher temperatures, all of the catalysts gave more gaseous product from the ten cubic centimeters of the kerosene passed. However, with an increase in temperature the per cent of hydrogen in the gas decreased when iron and manganese were used as catalysts. When nickel was used, the maximum yield of hydrogen in the gas was reached at 500° C. The yield dropped to 38.1% at 550° C. The most suitable catalyst for the production of the gaseous product seems to be cobalt, since the maximum volume of gas was obtained from ten cubic centimeters of kerosene and contained a per cent of hydrogen of 69.8. Iron was found to be second to cobalt for gas production and nickel and manganese, third and fourth, respectively.

With cobalt and nickel, the per cent of methane in the gaseous product decreased as the temperature was raised, while with iron and manganese this factor increased with the temperature. The maximum per cent of methane, 46.4, was obtained with nickel at 390° C., while the highest per cent obtained with cobalt was 37.5 at 290° C. With cobalt and nickel as catalysts the production of methane was greater than with iron or manganese.

In Tables VI and VIII, it is seen that the per cent of saturated hydrocarbon gases above methane was 54.8 and 44.7 over manganese and nickel, respectively. This fact is peculiar to these two catalysts only. In neither the case of cobalt nor iron was there so great a per cent of these hydrocarbon gases obtained. Nickel, unlike any of the other catalysts studied, caused appreciable amounts of unsaturated hydrocarbon gases to be produced, the gas mixture containing 8.0% at 390° C. Cobalt was the only other catalyst giving these unsaturates in the gas produced. The gas obtained at 550° C. contained 0.62%.

With all four catalysts, the volume of liquid products decreased with an increase in temperature. This is the result of a more complete decomposition with rise in temperature. No liquid was obtained above 500° C. with cobalt or at 555° C. with iron, while with manganese and nickel, liquid products were obtained at all the temperatures studied. If the manganese or nickel were used at higher temperature, it would be expected that the products would be all gaseous. The iodine numbers of the liquids obtained increased with the temperature in all cases where liquid products were obtained. This agrees with similar work by Gault and his co-workers.

The highest degree of unsaturation of any liquid produced was obtained at 550° C. with manganese as catalyst. Its iodine number was 73.02. The highest iodine number obtained with nickel as catalyst was 70.99 at 550° C. Fig. 5 shows the iodine numbers plotted as ordinates and the temperature as abscissa for each of the four catalysts.

The carbon deposited by the decomposition of the kerosene which passed over the catalyst was proportional to the temperature employed, the higher the temperature the more carbon deposited. It was found that in all experiments the carbon deposited at low temperature rendered the catalyst inactive, while that formed at a more elevated temperature had little or no effect on the activity. This is especially brought out in the experiments on cobalt. As is noted in Table II, above 500° C. the activity of the catalyst was in no way impaired by the deposition of large quantities of carbon.

Further investigation concerning the catalytic decomposition of hydrocarbons is now being conducted by the writers. In the continuation of this work, other catalysts are being used and the decomposition of hydrocarbon fractions boiling higher and lower than the kerosene used in this investigation is being studied.

Experiments to study the decomposition of commercial gas oil over a cobalt catalyst at 500° C. have been conducted. Gas oil which has a boiling range higher than that of kerosene, when passed over a cobalt catalyst at the rate of 10 cc. per hour, decomposed into a gaseous and liquid product. The volume of gas obtained from 10 cc. of the oil at 500° C. was 6,250 cc. The volume of liquid product was 2.5 cc. The composition of the gaseous product was: 45.2% hydrogen, 32.8% methane and 17.0% higher paraffin hydrocarbons.

This indicates that under the conditions used, gas oil does not decompose as completely as kerosene. It is believed, however, that a slower rate of flow of the oil or a second pass over the catalyst would cause a more complete decomposition.

Conclusion

1. With all four catalysts it was found that an increase in temperature yielded an increase in the quantity of kerosene decomposed which results in an increased volume of gaseous product, a decreased volume of liquid product and an increased deposition of carbon.

2. In the experiments where liquid products were formed, the iodine number increased with the temperature.

3. Carbon deposited at the lower temperatures rendered the catalyst less active, while that deposited at the higher temperatures had little or no effect.

4. Cobalt was shown to be the best catalyst of the four studied for the production of the greatest volume of gas in the shortest time. One gram of cobalt catalyst at 550° C. will convert 0.33 g. of kerosene to 6.3 cc. of gas in one minute.

5. It was found that a continuous conversion of kerosene can be affected over a cobalt catalyst at 500° C. which is 50° C. lower than with iron.

6. As the temperature was increased it was noticed that in the case of cobalt as catalyst, the per cent of hydrogen in the gaseous product increased while the per cent of methane decreased. With manganese and iron as catalysts the per cent of hydrogen decreased while the per cent of methane increased. In the case of nickel the per cent of hydrogen reached a maximum and the per cent of methane decreased as the temperature was raised.

7. Of the four catalysts studied, only nickel gave unsaturated hydrocarbons in the gaseous product to any appreciable extent. Cobalt, however, gave traces.

8. Nickel and manganese at 550° C. favored the production of large quantities of paraffin hydrocarbon gases above methane.

9. Each of the four catalysts exhibited specific catalytic properties with regard to the nature of the products.

10. The four catalysts might be arranged in the following order in regard to their ability to decompose the kerosene fraction boiling from 200° to 230° C.: cobalt, iron, nickel and manganese.

11. The gas having the highest per cent of hydrogen, 90.5, was obtained over iron at 400° C.

12. The gas having the highest per cent of methane, 46.4, was obtained over nickel at 390° C.

Laboratory of Physical Chemistry,
Indiana University, Bloomington.

THE SOLUBILITIES AND SOLUBILITY PRODUCTS OF METALLIC SULFIDES IN WATER

BY I. M. KOLTHOFF

There is tremendous confusion in the literature with regard to the solubilities and solubility products of metallic sulfides. Most text books on inorganic chemistry and qualitative analysis present tables based on the measurements of O. Weigel[1] and of L. Bruner and J. Zawadski[2] which do not show even an order of agreement, differences of more than 10^{10} sometimes being noticed as will be shown below. In their text on qualitative analysis, F. P. Treadwell and W. T. Hall[3] give both sets of figures and mention in a discussion that something must be wrong (p. 462): "Owing to the colloidal nature of each of these sulfide precipitates, it is extremely difficult to determine the true solubility and the values are so small that ordinary methods of measurements will not serve. When shaken with water colloidal solutions of all these substances can be obtained and sometimes, as in the case of copper sulfide, a little sulfate is formed by atmospheric oxidation." "The data given for these solubilities in the German text cited, doubtless represent many hours of careful, accurate and skillful analytical work, but in the case of the sulfide values, there is evidently something wrong if one authority gives the value of 1.25×10^{-6} for mercuric sulfide and another authority the value of 4.6×10^{-26}."

The following table gives a survey of the solubility data of metallic sulfides based on Weigel's and on Bruner and Zawadski's work as may be found in various texts of outstanding reputation.[4] The values derived from the solubility products (Bruner and Zawadski) are usually obtained by neglecting the hydrolysis of the sulfide ion, a considerable error thus being introduced as will be discussed below. However, no correction is made for this in the following table.

It is evident that one of the two sets of figures must be wrong (as a matter of fact they both are) and it is highly desirable to have more reliable data on the solubilities of metal sulfides available. For example, in studies on the fractional precipitation of sulfides one can select any figures to prove or disprove the applicability of the mass action law to the precipitation of sulfides

---

[1] O. Weigel: Z. physik. Chem., 58, 294 (1907).

[2] L. Bruner and J. Zawadski: Z. anorg. Chem., 65, 136 (1909); 67, 454 (1910).

[3] F. P. Treadwell and W. T. Hall: "Analytical Chemistry, Vol. 1 Qualitative Analysis," 7th English Edition, p. 461 (1930).

[4] Comp. e.g. Tables of Landolt-Börnstein-Roth, 5th Edition, (1923); Ergänzungsband (1927); W. Böttger: "Qualitative Analysis," 4th-7th Edition, (1925); Treadwell and Hall l.c.; W. M. Latimer and J. H. Hildebrand: "Reference Book of Inorganic Chemistry." Appendix XI and XIX (1929); H. I. Schlesinger: "General Chemistry," p. 303-308 and p. 783 (1930).

as has been done in the literature. Moreover, it may be mentioned that the problem is not only of chemical but also of great geological importance with regard to a study of ore deposits.[5]

TABLE I

Solubilities of Precipitated Metal Sulfides in Water as found in the Literature (Mols per Liter)

Metal Sulfide	Weigel's Data	Bruner and Zawadski (Neglecting Hydrolysis of Sulfide Ion)
MnS	7.16×10^{-5}	3.8×10^{-6}
ZnS	7.06×10^{-5}	3.5×10^{-12}
FeS	7.01×10^{-5}	3.9×10^{-10}
CoS	4.16×10^{-5}	— — —
NiS	4.00×10^{-5}	1.2×10^{-12}
CdS	9.0×10^{-6}	6.0×10^{-15}
Sb_2S_3	5.2×10^{-6}	— — —
PbS	3.6×10^{-6}	2.0×10^{-14}
CuS	3.51×10^{-6}	9.2×10^{-23}
As_2S_3	2.1×10^{-6}	— — —
Ag_2S	5.5×10^{-7}	3.4×10^{-17}
Bi_2S_3	3.5×10^{-7}	— — —
HgS	5.4×10^{-8}	6.3×10^{-27}

A critical study of the literature on the solubility of metal sulfides reveals the following facts which may be responsible for the present confusion:

a. Weigel's work on the electrical conductance of saturated solutions of metallic sulfides *cannot be correct*. The solubility of most sulfides in water is so small that in many cases the conductivity of the saturated solution is much smaller than that of the purest (ultra pure) conductivity water. At such extremely small solubilities, the conductance measured in the saturated solution in contact with the solid body must be mainly attributed to slight impurities, which are very hard to wash out from precipitates of a colloidal nature and to surface conductance of the solid particles. Another factor which has to be considered is that most sulfides are easily oxidized by the oxygen of the air. In Weigel's work no indication is found that he performed his experiments in the absence of oxygen and, therefore, it is quite possible that he measured the conductance of the metal hydroxides formed by oxidation of the sulfides.

It should be mentioned that Weigel's calculation of the solubility from his conductance measurements is not correct. He assumed that in the saturated solution of the metal sulfide, the hydrolysis of the sulfide ion is complete according to the equation: $S^{=} + 2\,H_2O \rightarrow H_2S + 2\,OH^-$. As may be inferred from computations given further on, Weigel's assumption is not justified as

---

[5] Comp. F. W. Clarke: "The Data of Geochemistry," 5th Edition, (1924); W. H. Emmons: "The Enrichment of Ore Deposits," U. S. Geological Survey, Bulletin 625 (1917). In both monographs, Weigel's data seem to be considered as reliable.

the sulfide ion under his experimental conditions is mainly hydrolyzed to bisulfide HS⁻. However, since Weigel did not work with ultra pure water free from carbon dioxide, it is not possible to calculate from his data the corresponding solubilities. Finally, it may be said that in cases where the metal of the sulfide forms an extremely weak base, it is no longer allowable to assume that the hydroxide formed by hydrolysis is completely ionized (Bi_2S_3; Sb_2S_3; SnS_2). For all the reasons mentioned, Weigel's figures *should no longer be accepted* and *should be omitted in reliable tables of the solubilities of the metal sulfides.* Weigel's[6] attempt to explain the difference between his data and those based on the solubility products does not take into account any of the above objections to his own work and the conclusion is maintained that his figures should be rejected.

b. Weigel's values are supported by measurements of W. Biltz[7] on the sensitivity of the precipitation of metallic sulfides. Biltz mixed a dilute solution of the metal salt with an equimolecular sulfide solution and observed by means of the ultramicroscope at which metal ion concentration particles of the sulfides no longer could be detected. Biltz stated: "Die ultramikroskopische Methode ist bis zu sehr geringen Löslichkeiten brauchbar, sie versagt dann, wenn die gelöste Masse so klein ist, dass ein Bruchteil derselben in aufgelöstem Zustand nicht mehr zur Bildung einer grösseren Anzahl von Submikronen ausreicht." But even assuming that no supersaturation phenomena occur, the optical method can never serve for the direct measurement of the solubility of extremely slightly soluble substances. A minimum number of particles has to be present in order to be visible; this minimum not being constant, but dependent upon the size of the particles formed at a certain method of observation (either ultramicroscopic or Tyndall effect). Suppose that this minimum of visibility corresponds to a concentration of the metallic sulfide equal to v, and that the solubility is equal to s, then the sensitivity, St, found by mixing equivalent amounts of cation and anion (and neglecting the hydrolysis of the anion!) is:

$$St = v + s.$$

Biltz estimated from observations of Zsigmondy[8] on gold sols that with his own arrangement v equals about 10^{-7}.

From the above it is evident that the sensitivity method, though of great practial importance, will never yield good results for s if the latter is much smaller than v and it is just this case we are dealing with in the solubilities of metallic sulfides. Even if the visibility were small with regard to the solubility, which apparently is assumed by Biltz, his reported figures are much too high since he assumed that the metal and sulfide ion concentration in his solutions were the same. (Biltz derived the following solubilities: MnS, 1×10^{-4}; CdS, 6.6×10^{-6}; PbS, 5.5×10^{-6}, CuS, 4.1×10^{-6}; Ag_2S,

---

[6] O. Weigel: Sitzungsber. Ges. Förd. gesamt. Naturw., Marburg, No. 2, 35-50 (1921); Chem. Zentr., 1922, I, 182.

[7] W. Biltz: Z. physik. Chem., 58, 288 (1907).

[8] Zsigmondy: Drudes Ann., 15, 585 (1904).

8.0×10^{-7}. It is more or less accidental that the order of agreement between his figures and those of Weigel is fairly good.)

c. Much better methods for the determination of the solubility of metallic sulfides than the two discussed above are the equilibrium and the potentiometric ones. In the former the solubility of the sulfide is determined at a known acidity and hydrogen sulfide concentration and from the figure obtained the solubility product can be calculated. This has been done by Bruner and Zawadski[2] in their classical work; their figures have been partly supplemented by L. Moser and M. Behr.[9] In the potentiometric method the metal ion concentration in the saturated metal sulfide solution is measured electrometrically at a known sulfide ion concentration. The latter method must be used in all cases where the solubility of the metal sulfide is so small that the chemical (equilibrium) method cannot be applied any longer.

Quite generally one must realize that the solubility of a metal sulfide depends upon its age and manner of preparation. After the particles have grown to a certain size and are present in the stable modification, the solubility represents a constant and the solubility product principle can be applied to the calculation of the solubility under various conditions. Freshly precipitated sulfides as a rule are not present in the stable form and, therefore, exhibit a higher solubility than aged products. S. Glixelli[10] found that freshly precipitated zinc sulfide from alkaline medium (β ZnS) is about 4.6 times more soluble than zinc sulfide precipitated from acid medium (α ZnS). It seems that the so-called β ZnS is amorphous[11] and that on standing it is transformed into the crystalline modification (α ZnS). It seems to the author that β ZnS cannot be considered as a real modification in the chemical sense, its properties (solubility, water content) being dependent upon its age and method of preparation. On ageing it loses water and its solubility decreases gradually until it is completely transformed into the crystalline modification. Therefore, it is hardly possible to speak of a definite solubility of β zinc sulfide since the latter is not of constant composition. The solubilities of nickel and cobalt sulfide also depend on the time of standing after the precipitation.

Frequently, it has been doubted in the literature whether the mass action law holds for the precipitation of metallic sulfides and whether the reaction:

$$Me^{++} + H_2S \leftrightarrows MeS + 2\,H^+$$

is reversible. This question will be considered more in detail in subsequent papers; let it be only said here that the mass action law must hold when equilibrium is attained and the stable solid body is present. The former point has often been overlooked; it is well known that relatively weakly acid solutions of zinc, nickel, cobalt, etc. do not precipitate with hydrogen sulfide though the solubility product has been exceeded considerably. A solution of 0.1 N zinc sulfate in 0.5 N sulfuric acid saturated with hydrogen sulfide, for example, is strongly supersaturated with respect to zinc sulfide; still no

---

[9] L. Moser and M. Behr: Z. anorg. allgem. Chem., 134, 49 (1924).

[10] S. Glixelli: Z. anorg. Chem., 55, 297 (1906).

[11] Comp., J. Böhm and H. Niclassen: Z. anorg. allgem. Chem., 132, 1 (1923).

precipitate is formed after a short time of standing. After a few months, however, zinc sulfide separates out. The conflict with the mass action law, therefore, is only apparent since several authors have applied this principle to cases where equilibrium had not been established. Many metal sulfides show a pronounced tendency to form supersaturated solutions which may be explained by a relatively large difference in solubility between the extremely small nuclei and the crystals of larger size, and by the slow speed of formation of the nuclei. A saturated solution of hydrogen sulfide has an extremely small sulfide ion concentration and it is quite possible that under these conditions the speed of the reaction between the metal and sulfide ions is a marked time reaction. That the speed of separation of the metal sulfide is governed by the mass action law, has been clearly shown by Krishnamurti[12] in the precipitation of cadmium sulfide where the activities of the hydrogen, sulfide and cadmium ions are the determining factors in the speed of precipitation. These supersaturation phenomena are of great importance in the study of the fractional precipitation of metal sulfides as will be shown in forthcoming papers.

The chemical and potentiometric methods mentioned under c, seem to give the most reliable data on the solubility products of metal sulfides. From these figures one cannot calculate the solubility in water by putting,

$$s = \sqrt{L}$$

s being the solubility of a divalent metal sulfide and L its solubility product, as the sulfide ion is strongly hydrolyzed and the metal ion concentration in the saturated solution therefore is much greater than the sulfide ion concentration. As the second ionization constant of hydrogen sulfide and the solubility of most metal sulfides are extremely small, it is evident that the carbon dioxide content of the water used as solvent will have a great influence upon the numerical value of the solubility. In the following pages, simple equations are derived for the calculation of the solubility of metal sulfides in pure water (carbon dioxide-free) and water in equilibrium with the air (carbon dioxide content 1.35×10^{-5} molar). Most data on the solubility products have been determined at 18° and therefore the computations are related to this temperature where $K_w = 10^{-14.18}$. In the equations concentrations are written instead of activities. The uncertainty in the values of the solubility products is so large that this approximation hardly affects the results. The first ionization constant of hydrogen sulfide is equal to 9.1×10^{-8} or $10^{-7.05}$ [13] the second one to 1.2×10^{-15} or $10^{-14.92}$ [14]

---

[12] Krishnamurti: J. Chem. Soc., 1926, 1549.

[13] This is the value given by F. Auerbach: Z. physik. Chem., 49, 217 (1904). Walker and Cormack: J. Chem. Soc., 77, 5 (1900) reported a value of 5.7×10^{-8} at 18°. The figures given by K. Jellinek and J. Czerwinski: Z. physik. Chem., 102, 476 (1922) show a variation between 2.3 and 720×10^{-8} and therefore do not seem to be trustworthy.

[14] J. Knox: Z. Elektrochemie, 12, 477 (1906).

In the derivation of the solubilities of metal sulfides in water, the following equations have to be considered:

$$MeS \rightarrow Me^{++} + S^{=}$$

$$S^{=} + H_2O \leftrightarrows HS^{-} + OH^{-} \quad (1)$$

$$HS^{-} + H_2O \leftrightarrows H_2S + OH^{-} \quad (2)$$

$$S^{=} + 2H_2O \leftrightarrows H_2S + 2\ OH^{-} \quad (3)$$

$$\frac{[HS]\ [OH^{-}]}{[S^{=}]} = \frac{K_w}{K_2} = \frac{10^{-14.18}}{10^{-14.92}} = 10^{0.74} \quad (4)$$

$$\frac{[H_2S]\ [OH^{-}]}{[HS^{-}]} = \frac{K_w}{K_1} = \frac{10^{-14.18}}{10^{-7.05}} = 10^{-7.13} \quad (5)$$

$$\frac{[H_2S]\ [OH^{-}]^2}{[S^{=}]} = \frac{K_w^2}{K_1K_2} = \frac{10^{-28.36}}{10^{-21.97}} = 10^{-6.37} \quad (6)$$

$$[H^{+}]\ [OH^{-}] = K_w = 10^{-14.18} \quad (7)$$

$$[Me^{++}]\ [S^{=}] = L \text{ (Sol. product)} \quad (8)$$

or

$$[S^{=}] = \frac{L}{[Me^{++}]} \quad (9)$$

Weigel[1] assumes that the hydrolysis of the sulfide ion in a saturated solution of the metal sulfide is complete to hydrogen sulfide (equation 3). He reports solubilities between 0.5×10^{-6} (Ag_2S) and 7.1×10^{-5} molar (MnS). In the most favorable case where the solubility is 0.5×10^{-6} molar, we would find then according to Weigel an hydroxyl ion concentration of 1×10^{-6} (equation 3). But at this $[OH^{-}]$, the ratio of $[H_2S]$ to $[HS^{-}]$ according to equation (5) is $10^{-1.13} = 0.075$; in other words, practically all the sulfide is hydrolyzed to bisulfide and only 8% to hydrogen sulfide. Therefore, even if we could accept Weigel's conductivity data his computations should be corrected with the approximated assumption that all the sulfide ions are hydrolyzed to HS^{-} and not to H_2S. However, since it has been shown before that Weigel's data cannot represent the conductance of saturated solutions of pure sulfides in pure water, the recalculation of his figures will be omitted.

Considering a saturated solution of a divalent metal sulfide, it is found that:

$$2\ [Me^{++}] + [H^{+}] = 2\ [S^{=}] + [OH^{-}] + [HS^{-}] \quad (10)$$

If the solubility is equal to x, then $[Me^{++}] = x$. From equations (4), (5), (6), (7), (8) and (10) a relation can be derived between $[Me^{++}]$, $[OH^{-}]$ and L. The final equation is rather complicated and of a higher power and it is much simpler to introduce some approximation. In cases, where the solubility product is extremely small, the solubility in water will be so small that it is much less than the hydrogen and hydroxyl ions formed by dissociation of the water. Therefore, in these cases, it can be assumed that the hydroxyl ion concentration of the saturated sulfide solution is the same as that of the solvent being $10^{-7.09}$ at 18°. Under these conditions, the ratio,

$$\frac{[H_2S]}{[HS^-]} = \frac{10^{-7.05}}{10^{-7.09}} = 10^{0.04} = 1.1 \quad \text{(see equation 5)}$$

If the solubility of the sulfide is x, then

$$x = [Me^{++}] = [HS^-] + [H_2S] = 2.1\,[HS^-]$$

From equations (4), (9) and the last relation, it is found that,

$$x = 10^{4.08}\sqrt{L} \qquad (11)$$

If the metal is monovalent (Ag_2S), it is easily derived that,

$$x = 10^{2.52}\sqrt[3]{L} \qquad (12)$$

In cases where the solubility is so large that the hydroxyl ions formed by the hydrolysis of the sulfide ion can no longer be neglected with regard to the hydroxyl ion concentration of pure water, by first approximation it can be assumed that the hydrolysis takes place quantitatively according to equation (2). In repeating the calculation a correction can be made for this assumption.

If the solubility of the divalent metal sulfide is again x, then

$$x = [HS^-] = [OH^-]$$

and from equations (4) and (9),

$$x = 10^{0.25}\sqrt[3]{L} \qquad (13)$$

If the metal combined to the sulfide is monovalent (Tl_2S) then,

$$x = 10^{0.04}\sqrt[4]{L} \qquad (14)$$

Finally, the expressions should be given for the solubility of the sulfide in equilibrium water; i.e. water in equilibrium with the carbon dioxide of the atmosphere having a pH of 5.8 or a pOH of 8.4. According to equation (5) at this pH:

$$\frac{[H_2S]}{[HS^-]} = \frac{10^{-7.13}}{10^{-8.4}} = 15$$

Therefore, the hydrolysis of the sulfide ion is practically complete to hydrogen sulfide (equation 3); and $[H_2S] = x$. From equations (6) and (9) it is found that

$$x = 10^{5.11}\sqrt{L} \qquad (15)$$

The solubility is 11 times larger than in ultrapure water. Under the same conditions, the solubility of the sulfide of a monovalent metal is,

$$x = 10^{3.21}\sqrt[3]{L} \qquad (16)$$

being five times larger than in ultrapure water. Expressions (15) and (16) hold for sulfides with a solubility much smaller than the ion concentration of the water. If this condition is not fulfilled (MnS; Tl_2S), the following reaction must also be considered:

$$S^{=} + H_2CO_3 \leftrightarrows HS^- + HCO_3^- \qquad (17)$$

and

$$\frac{[HS^-][HCO_3^-]}{[S^=][H_2CO_3]} = \frac{10^{-6.5}}{10^{-14.92}} = 10^{8.42} \qquad (18)$$

since the first ionisation constant of carbon dioxide is $10^{-6.5}$. Assuming that the saturated solution of the sulfide is saturated with carbon dioxide from the atmosphere, ($[H_2CO_3]$ or better $[CO_2] + [H_2CO_3] = 1.35 \times 10^{-5}$), we find

$$\frac{[HS^-][HCO_3^-]}{[H_2S]} = 10^{3.55} \qquad (19)$$

By first approximation, it can be assumed that $[HS^-] = [HCO_3^-]$; the result can be corrected for the hydrolysis of the bisulfide ion to hydrogen sulfide. With this assumption, the solubility of a divalent metal sulfide is:

$$x = 10^{1.18} \sqrt[3]{L} \qquad (20)$$

being eight times larger than in ultrapure water. The solubility of a monovalent metal sulfide (Tl_2S) is:

$$x = 10^{0.74} \sqrt[4]{L} \qquad (21)$$

being five times larger than in ultrapure water. By application of the above set of equations, the data of the solubilities of the various sulfides have been calculated in pure water and in equilibrium water and are reported in the following table.

The data of Bruner and Zawadski[2] on the solubility products of sulfides have been taken from their publication. As a rule the age of the precipitated sulfide has not been indicated by the above authors. The cadmium sulfide samples were prepared by treating cadmium sulfate and cadmium chloride respectively in a sealed tube with hydrogen sulfide for "a long time." Lead sulfide was prepared in a similar way.

Two products of iron sulfide were used, one obtained by precipitation of Mohr's salt with hydrogen sulfide, the second by precipitation in the presence of sodium acetate. In another set of experiments equilibrium was reached by dissolving iron sulfide in acetic acid in a current of hydrogen sulfide. The figures obtained were of the same order of magnitude, though much higher than those of Moser and Behr,[9] who used iron sulfide eighteen hours after precipitation at room temperature. The latter authors precipitated cobalt and nickel at 60°-70° and determined the solubility in 2 N sulfuric acid three hours after the precipitation. In the calculation, it is assumed by the author that the hydrogen ion concentration in 2 N sulfuric acid is equal to one. Moser and Behr precipitated manganese sulfide at a temperature between 60°-70°, waited until the flesh colored precipitate had changed into green, and determined the solubility nine hours after the precipitation. The figure of the solubility product derived from their results is about 10^6 smaller than that reported by Bruner and Zawadski. The latter authors probably used the flesh colored form of manganese sulfide. The thallium sulfide used by Moser and Behr was obtained at room temperature by precipitation of thallous sulfate with hydrogen sulfide, the solubility being determined four hours after the precipitation. The zinc sulfide was precipitated at 60°-70° and was twenty-four hours of age before the solubility was determined. Moser and Behr's figure is in striking harmony with those found by Schaefer[15] and by Glixelli.[10] The data on the solubility of β zinc sulfide as given by Glixelli[10] have also been tabulated though these figures have hardly any exact significance, since the amorphous form has no constant solubility as has been discussed before.

The data on the solubilities of bismuth, copper, silver, mercuric and mercurous sulfide have been calculated from potentiometric measurements, carried out by I. Bernfeld,[16] Cl. Immerwahr,[17] J. Knox,[18] R. Lucas,[19] and K. Jellinek and J. Czerwinski;[20] and they are different from those derived by Bruner and Zawadski. This is especially true for bismuth sulfide, the solubility product given by Br. and Z. being 2.3×10^{-91}, whereas the author calculated a figure of 1.6×10^{-72}. This last number probably is much too low and it is doubtful whether the potentiometric method gives good results in this case. It certainly does not in the case of lead sulfide as may be inferred from the work of G. Trümpler[21] and Jellinek and Czerwinski;[20] the corresponding data, therefore, have been omitted in the table.

The figures on the solubilities of most sulfides in pure water and equilibrium water are so small that it is more than doubtful whether they have any practical significance. It is very hard to prepare those extremely slightly soluble sulfides in such a pure state that the theoretical values of the solubility can be reproduced experimentally. Moreover, it should be considered that traces of oxygen oxidize the sulfides; and also for this reason the experimental figures would not correspond to the theoretical ones..

From practical as well as didactic point of view, it therefore seems desirable to tabulate the value of the reaction constant K in the equation:

$$[\mathrm{Me}^{++}] = \mathrm{K}\,\frac{[\mathrm{H}^+]^2}{[\mathrm{H_2S}]} \tag{22}$$

or (for Ag_2S and Tl_2S):

$$[\mathrm{Me}^{+}] = \sqrt{\mathrm{K}\,\frac{[\mathrm{H}^+]^2}{[\mathrm{H_2S}]}} \tag{23}$$

At known hydrogen ion and hydrogen sulfide concentration, the solubility is directly derived by means of this equation. Assuming that the solution is

---

[15] Schaefer: Dissertation, Leipzig, (1906).

[16] I. Bernfeld: Z. physik. Chem., 25, 46 (1898).

[17] Cl. Immerwahr: Z. Elektrochemie, 7, 477 (1901).

[18] J. Knox: Z. Elektrochemie, 12, 477 (1906).

[19] R. Lucas: Z. anorg. Chem., 41, 193 (1904), from solubility measurements of silver sulfide in potassium cyanide.

[20] K. Jellinek and J. Czerwinski: Z. physik. Chem., 102, 476 (1922).

[21] G. Trumpler: Z. physik. Chem., 99, 9 (1921).

TABLE II

Solubilities and Solubility Products of Metal Sulfides

Metal Sulfide	K(eq. 22 and 23)	[Me]	p L	L	Sol. Water	Sol Eq. Water	Observer
MnS (flesh colored?)	6.3×10^{6}	6.3×10^{7}	15.16	7.0×10^{-16}	$10^{-4.81}$	$10^{-3.87}$	Bruner & Zawadski
MnS (green)	5.6	5.6×10^{1}	21.21	6.2×10^{-22}	$10^{-6.52}$	$10^{-5.49}$	Moser and Behr
FeS	3.4×10^{3}	3.4×10^{4}	18.43	3.7×10^{-19}	$10^{-5.9}$	$10^{-4.96}$	Bruner and Zawadski
FeS	2.4	2.4×10^{1}	21.58	2.6×10^{-22}	$10^{-6.7}$	$10^{-5.7}$	Moser and Behr
Tl_2S	6.4×10^{-1}(?)	2.5	22.16	7.0×10^{-23}	$10^{-5.5}$	$10^{-4.80}$	Bruner and Zawadski
Tl_2S	1.1×10^{-2}	3.3×10^{-1}	23.92	1.2×10^{-24}	$10^{-5.93}$	$10^{-5.23}$	Moser and Behr
αZnS	7.3×10^{-4}	7.3×10^{-3}	25.10	8.0×10^{-26}	$10^{-8.47}$	$10^{-7.44}$	Schaeffer
αZns	4.5×10^{-4}	4.5×10^{-3}	25.3	5×10^{-26}	$10^{-8.57}$	$10^{-7.54}$	Glixelli
αZnS	6.3×10^{-4}	6.3×10^{-3}	25.16	6.9×10^{-26}	$10^{-8.50}$	$10^{-7.47}$	Moser and Behr
βZnS	about 10^{-2}	10^{-1}	23.96	1.1×10^{-24}	$10^{-7.90}$	$10^{-6.87}$	Glixelli
CoS	1.7×10^{-5}	1.7×10^{-4}	26.72	1.9×10^{-27}	$10^{-9.28}$	$10^{-8.25}$	Moser and Behr
NiS	1.0×10^{-5}	1.0×10^{-5}	26.96	1.1×10^{-27}	$10^{-9.40}$	$10^{-8.37}$	Moser and Behr
CdS (from $CdCl_2$)	6.5×10^{-6}	6.5×10^{-5}	27.15	7.1×10^{-28}	$10^{-9.50}$	$10^{-8.47}$	Bruner and Zawadski
CdS (from $CdSO_4$)	4.6×10^{-7}	4.6×10^{-6}	28.29	5.1×10^{-29}	$10^{-10.06}$	$10^{-9.03}$	Bruner and Zawadski
PbS	3.1×10^{-6}	3.1×10^{-5}	27.47	3.4×10^{-28}	$10^{-9.65}$	$10^{-8.62}$	Bruner and Zawadski
Bi_2S_3	3.5×10^{-3}?	3.5×10^{-2}?	71.8 ?	1.6×10^{-72}?			Bernfeld
CuS	6.3×10^{-19}	6.3×10^{-18}	40.16	6.9×10^{-41}	$10^{-16.0}$	$10^{-14.97}$	Immerwahr
CuS	1.1×10^{-20}	1.1×10^{-19}	41.92	1.2×10^{-42}	$10^{-16.88}$	$10^{-15.85}$	Knox
CuS	3×10^{-20}	3×10^{-19}	41.46	3.5×10^{-42} (Av.)	$10^{-16.65}$	$10^{-15.62}$	Jellinek & Czerwinski
Ag_2S	1.6×10^{-29}	4×10^{-14}	49.74	1.8×10^{-50}	$10^{-14.06}$	$10^{-13.37}$	Bernfeld
Ag_2s	2.1×10^{-29}	1.45×10^{-14}	50.64	2.3×10^{-51}	$10^{-14.36}$	$10^{-13.67}$	Lucas
Ag_2S	3.6×10^{-28}	6×10^{-14}	49.41	3.9×10^{-50}	$10^{-13.95}$	$10^{-13.26}$	Knox
Ag_2S	1.1×10^{-28}	3.3×10^{-14}	49.92	1.2×10^{-50}	$10^{-14.12}$	$10^{-13.43}$	Jellinek & Czerwinski
Ag_2S	5.1×10^{-29}	2.2×10^{-14}	50.24	5.7×10^{-51}	$10^{-14.23}$	$10^{-13.24}$	Jellinek & Czerwinski
Average Ag_2S	9×10^{-29}	3×10^{-14}	50.00	1×10^{-50}	$10^{-14.18}$	$10^{-13.5}$	Average
Hg_2S	0.9×10^{-25}	0.9×10^{-24}	47.0	$10^{-47.0}$	$10^{-19.42}$	$10^{-19.39}$	Immerwahr (average)
HgS	2.7×10^{-32}	2.7×10^{-31}	53.5	3×10^{-54}	$10^{-22.67}$	$10^{-21.64}$	Knox

always saturated with hydrogen sulfide, at atmospheric pressure, the following expression is also very useful:

$$[\mathrm{Me}^{++}] = K'[\mathrm{H}^+]^2 = 10\,K\,[\mathrm{H}^+]^2 \qquad (24)$$

or (for Ag_2S and Tl_2S):

$$[\mathrm{Me}^+] = \sqrt{K'[\mathrm{H}^+]^2} \qquad (25)$$

The values of K and K′ have been given in the following table as they are of real practical importance.

K is the reaction constant as given in equations (22) and (23), [Me] representing the metal ion concentration in a solution saturated with hydrogen sulfide and the metal sulfide at a hydrogen ion concentration of one. pL is the negative logarithm of the solubility product L. Sol. water is the solubility in pure water. Sol. eq. water is the solubility in water saturated with carbon dioxide from the atmosphere.

It seems to the author that some facts in the geological literature, which up to the present time were rather confused, can be better interpreted in the light of the recalculated data presented in this paper.

Summary

1. The figures on the solubilities of metal sulfides determined by Weigel and given in most text books are unreliable and should be rejected.
2. A critical survey of the literature on the solubilities of metal sulfides has been made and from the experimental work, the solubilities in pure water and equilibrium water have been calculated. These figures are of small or no practical importance and it is recommended that the relation between the solubility and the hydrogen ion and hydrogen sulfide concentrations be expressed by the reaction constant. The latter expression can only be applied in the state of equilibrium.

School of Chemistry of the
University of Minnesota,
Minneapolis,
March, 1931.

99. 107

A STUDY OF GUM ARABIC

Part I. Viscosity and Adsorption Measurements

BY GEORGE L. RIDDELL AND CECIL W. DAVIES

Introduction

In the course of work relating to the principles underlying lithographic printing, some results have been obtained which we believe may have a wider interest. The experiments to be described had as their object the measurement of the extent of adsorption of gum arabic on surfaces of zinc, aluminum, lithographic stone, and animal charcoal.

As a preliminary, a method had to be found of estimating small changes in the concentration of gum arabic solutions. The ammoniacal copper acetate method recommended by Waters and Tuttle[1] as the best method of estimating the gum arabic proved quite unsuited to our purpose. Errors of 5% were found in trials of the method with pure gum solutions as is shown in Table I:

TABLE I

Wt. of dry gum taken	Wt. of ppt.	Ash	Wt. of gum found
0.2216	0.2748	0.0478	0.2270
0.3796	0.4261	0.0613	0.3648
0.2467	0.3150	0.0595	0.2555
0.2514	0.3378	0.0857	0.2521

Estimation by direct weighing after evaporation was also unsuitable owing to retention of water by the gum. In place of direct methods, therefore, the amount of adsorption was estimated by measurements of the apparent viscosity of the solution, under carefully controlled conditions, before and after contact with the adsorbent.

Materials used

Gum Arabic. Gum arabic is an exudation of the acacia tree and has been classified by Matthews[2] as a colloidal polysaccharide. It contains from 3-4% of ash which consists chiefly of calcium carbonate with small quantities of potassium and magnesium carbonates. Early work on the constitution of gum arabic was carried out by Neubauer,[3] Mulder[4] and O'Sullivan.[5] Norman[6] has recently suggested that it is unlikely that a definite empirical formula can be assigned to gum arabic and states that its general composition is probably a "nucleus acid consisting of a gallactose and a uronic acid, probably galacturonic acid, to which is linked arabinose by glucosidic linkages." Butler and Cretcher[7] suggest that the nucleus acid is an aldobionic acid (d-galactose d-glycuronic acid) to which is attached d-galactose, l-arabinose and rhamnose.

The gum arabic used was a sample similar to that used in lithographic practice and no attempts were made to purify it since the product obtained by the electrodialysis method of Thomas and Murray[8] had markedly different properties from natural gum arabic. That the sample was not entirely uniform was shown by slight variations in colour and by the fact that the pH of a series of one percent aqueous solutions as measured with the hydrogen electrode varied from 3·2 to 5·3. The non-uniformity of gum arabic has been commented upon by Williams.[9] The gum was therefore first crushed and hand-picked to remove foreign particles, and then ground to a powder. The particles passing a 40-mesh wire sieve were bottled and well mixed and all experiments were carried out on this sample. It was impossible to make up a stock solution of gum arabic since after long standing its properties were altered and a grey sludge settled out.

Zinc. The adsorbent surface consisted of strips cut from a "prepared" zinc lithographic plate. This was a sheet of zinc, finely grained on one side, which has been cleaned with caustic soda and distilled water, immersed in a dilute solution of potash alum and nitric acid, and thoroughly washed with distilled water until the washings were free of sulphate ions and showed a pH of 7·6.

Aluminium. The "prepared" plate from which strips were taken was an aluminium sheet grained on one side which had been immersed in dilute sulphuric acid, washed free of acid and dried.

Lithographic stone. The stone used was a uniform sample, buff in colour, which yielded the following figures on analysis:

	CaO	CO_2	H_2O(at 120°C)	MgO	Fe,Al	Insol. HCl
(a) Per Cent	54.63	42.18	0.18	0.31	Trace	2.04
(b) " "	54.77	42.04	0.17	0.32	Trace	2.03

These figures agree well with those of Garden[10] and Merrill.[11] The stone was broken and sieved. The portion passing the 20-mesh but retained by the 30-mesh sieve was washed successively with running water, very dilute nitric acid and distilled water until the washings showed a pH of 8.5. The stone was dried at 105°C some time before use.

Density Measurements

For the viscosity calculations it was necessary to determine, without great accuracy, the densities of gum arabic solutions. These were measured, at 20.00°C, by means of a 10 c.c. pycnometer. The results are shown in Table II:

Viscosity Measurements

The measurements were obtained with a capillary viscometer of the type described by Bingham[12] who claims an accuracy of a tenth of one percent. In this type of viscometer the liquid is blown through the horizontal capillary by air at a constant, measured pressure. The air pressure in our apparatus was supplied by a water pump from which air was forced into a ten-gallon reservoir; the air from this was led past a pressure regulator and a water manometer to two three-way taps, each of which could be connected either to one limb of the viscometer or to air. The pressure regulator consisted of a long side arm opening under water, and the water pump was adjusted so that air escaped from the regulator at the rate of about two bubbles a second. With this simple arrangement, combined with the large reservoir, a constant pressure could be obtained, the value of which was given by the height of the water manometer after applying the necessary temperature correction.[13] The viscometer was rigidly supported by means of a frame in a thermostat at 20.00 ± .02°C. Two interchangeable capillaries were employed in this investigation. One had a diameter of 0.4 mm, and with this in use, the instrument was calibrated by means of freshly distilled dust-free water for which the value n = 1.005 centipoises[14] at 20.00°C was taken. The second, of diameter 0.6 mm. was calibrated by intercomparison with the first using a water-alcohol mixture of which the viscosity was 2.732 centipoises. The kinetic energy correction, the true average pressure correction and the hydrostatic head correction were applied in the manner described by Bingham[15]

TABLE II

Concentration (Per cent)	D_4^{20}
0.00	0.9982
0.10	0.9984
0.50	0.9996
1.00	1.0019
3.00	1.0083
4.76	1.0146
7.00	1.0228
10.00	1.0332
12.00	1.0403
14.00	1.0470
16.00	1.0549
18.00	1.0619
20.00	1.0682

Gum arabic is a lyophilic colloid, and it was therefore to be expected that the apparent viscosity of a gum solution would be dependent on its age and previous history, and on the velocity of the solution flowing through the capillary, and that it would also prove very sensitive to small changes in the pH of the solution. To obtain results that would be reproducible these factors were investigated in turn.

The effect of velocity gradient is shown by the following figures for a 4% solution at 20.00°C.

Driving pressure (gms/sq.cm.)	20.62	30.35	41.20	52.96
Viscosity (centipoises)	3.249	3.220	3.196	3.179

The effect is marked and similar to that found by several workers for colloidal solutions.[16]

In all the measurements to be described a constant driving pressure of 52.30 (±.05) gms. per sq. cm. was used.

To determine the effect of previous history, gum solutions were subjected to various treatments. In one series of experiments a 2.3% solution of gum arabic was made up on a water bath, and a sample, introduced into the clean, dry viscometer showed an apparent viscosity, at 20.00°C and under a driving pressure of 52.30 gms/sq. cm., of 2.421 centipoises. This sample was then discarded, and the viscometer was refilled without rinsing. The second sample, under the same conditions of measurement, gave the value 2.420. Subsequent samples gave the following values: After six hours agitation at 16°C, 2.420; after cooling for five hours at 0°C, 2.419; after ageing for a further twenty-six hours, 2.425. The maximum variation was therefore .20%. In another series of experiments a 1% solution was heated on a water-bath for four hours without a change in the apparent viscosity. These and other experiments all showed that, within 0.2%, the viscosity of a dilute solution of gum arabic is unaffected by its previous treatment. This is in striking variance with the behaviour of gelation and other lyophilic colloids (see, for instance, Sheppard and Houck[17]) and seems to imply that in contrast to them, gum arabic rapidly attains a state of true equilibrium when brought into solution in water.

The effect of pH was next investigated over the range required by the adsorption experiments. Gum arabic solutions in contact with lithographic stone acquire a pH value of 8.5, as shown by comparison with standard buffers, using thymol blue as indicator, and a gum solution adjusted to this pH with dilute alkali is unaffected by prolonged contact with lithographic stone. In the experiments with stone as adsorbent, therefore, the gum solutions were first adjusted to the value pH = 8.5 by adding a known weight (a few drops) of 0.04 N calcium hydroxide. Similarly, for the experiments with zinc the solutions were pre-adjusted to the equilibrium value pH = 6.6 (using brom cresol blue as indicator), and for aluminium the equilibrium value was pH = 7.6, (the indicator in this case being phenol red). For the experiments with animal charcoal the arbitrary value pH = 6.2 was employed and the solutions were adjusted to this value with brom cresol purple.

The viscosity figures at 20.00°C and at the four pH values are included in Table III.

When the viscosity is plotted against percentage concentration, the data of Table III yield four curves lying so close together that within experimental error the viscosity of commercial gum arabic must be regarded as insensitive to small changes in the pH of the solution. The experimental error in these measurements was necessarily large, however, owing to the non-homogeneity of the gum; whereas individual determinations with the same solution always agreed to within 0.2%, and this percentage variation was never exceeded when using the apparatus in preliminary experiments with water and cane sugar solutions, yet the scatter shown by the figures of Table III imply occasional variations amounting to several times this amount.

TABLE III

Before Adsorption		After Adsorption				
Viscosity cp.	Conc. % C_1	Viscosity cp.	Conc. % C_2	Wt. of Soln.	Amount of adsorbent	Wt. of gum adsorbed per unit of adsorbent
Adsorbent = Lithographic Stone pH 8.5 Temp. 20.00 ± .02°C						
1.088	0.144	1.061	0.099	24.7190	1.0000	0.0112
1.350	0.498	1.245	0.300	31.5166	1.0000	0.0626
1.388	0.657	1.241	0.405	30.3250	1.0000	0.0769
1.563	0.927	1.392	0.658	26.8044	0.8914	0.0840
1.628	1.042	1.537	0.882	42.1394	0.9042	0.0897
1.629	1.057	1.538	0.900	37.3468	0.6730	0.0880
1.709	1.293	1.612	1.023	31.1173	1.0000	0.0849
1.888	1.582	1.648	1.200	23.8780	1.0680	0.0798
—	1.732	1.857	1.500	48.8396	2.0100	0.0572
2.088	1.994	1.982	1.800	31.2694	1.2474	0.0497
2.504	2.662	2.392	2.462	36.3190	1.9338	0.0386
3.211	4.049	3.081	3.799	39.1275	3.1682	0.0320
3.696	4.886	3.557	4.636	33.7756	3.3000	0.0268
4.243	5.942	4.078	5.663	34.3220	4.0688	0.0249
Adsorbent = Aluminium pH 7.6 Temp. 20.00 ± .02°C						
1.165	0.232	1.129	0.173	26.7962	9	0.0018
1.271	0.380	1.180	0.230	22.0880	9	0.0037
1.345	0.491	1.271	0.310	22.4130	9	0.0046
1.390	0.565	1.300	0.420	28.0351	9	0.0044
1.429	0.637	1.371	0.540	33.1679	9	0.0036
1.516	0.766	1.461	0.675	29.3230	9	0.0030
1.572	0.881	1.520	0.790	27.4878	9	0.0028
1.831	1.411	1.800	1.335	24.4013	9	0.0021
2.140	1.098	2.104	2.000	25.3620	12	0.0021
Adsorbent = Zinc pH 6.6 Temp. 20.00 ± .02°C						
1.305	0.518	1.238	0.410	30.8125	9	.0037
1.534	0.856	1.446	0.705	31.1305	9	.0053
1.663	1.100	1.560	0.921	28.7263	9	.0058
1.723	1.243	1.635	1.070	27.4316	9	.0053
1.926	1.626	1.874	1.514	31.4982	9	.0040
2.200	2.333	2.131	2.095	30.9575	12	.0030
2.477	2.882	2.434	2.780	33.2687	12	.0029
Adsorbent = Bone Charcoal pH 6.2 Temp. 20.00 ± .02°C						
1.148	0.247	1.123	0.217	22.7833	1.0000	0.0069
1.472	0.718	1.454	0.690	29.1170	0.5040	0.0167
1.784	1.237	1.678	1.050	29.4300	3.0000	0.0185
1.733	1.182	1.699	1.120	31.2392	1.0000	0.0195
1.936	1.525	1.859	1.375	32.2725	5.5000	0.0156
2.012	1.714	1.951	1.620	32.0851	3.0000	0.0102
2.309	2.287	2.293	2.270	31.8570	1.0000	0.0056
2.697	3.005	2.660	2.930	33.2741	5.0000	0.0051

Adsorption Measurements

A fresh solution of gum arabic was made up by weight for each determination, and its pH adjusted, as described, to the necessary value. A weighed portion was allowed to remain in contact with a known quantity of the adsorbent in the thermostat for fifteen or more hours, by which time, according to preliminary experiments, equilibrium had been established. The flask was then thoroughly shaken, some of the liquid was withdrawn, and its viscosity was measured. A viscosity measurement was also made on the untreated portion of the solution. The amount of gum adsorbed was then

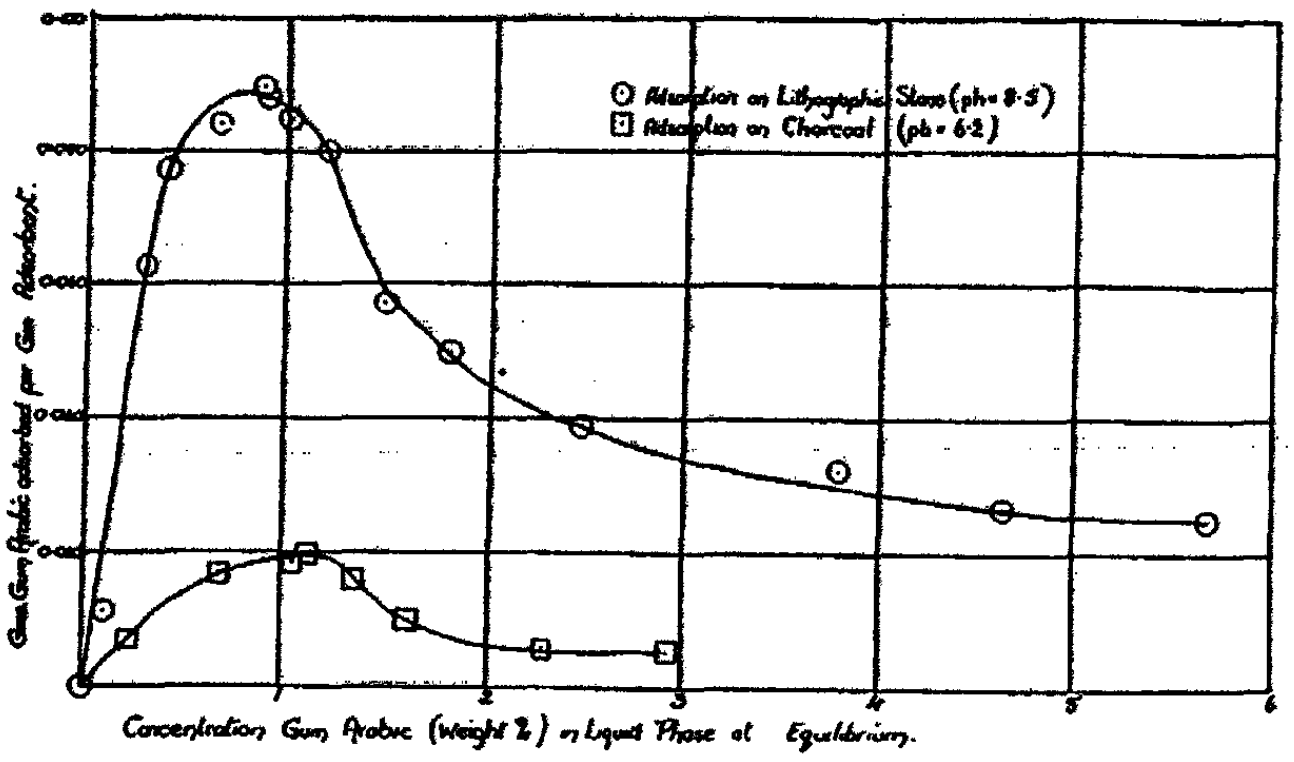


FIG. 1

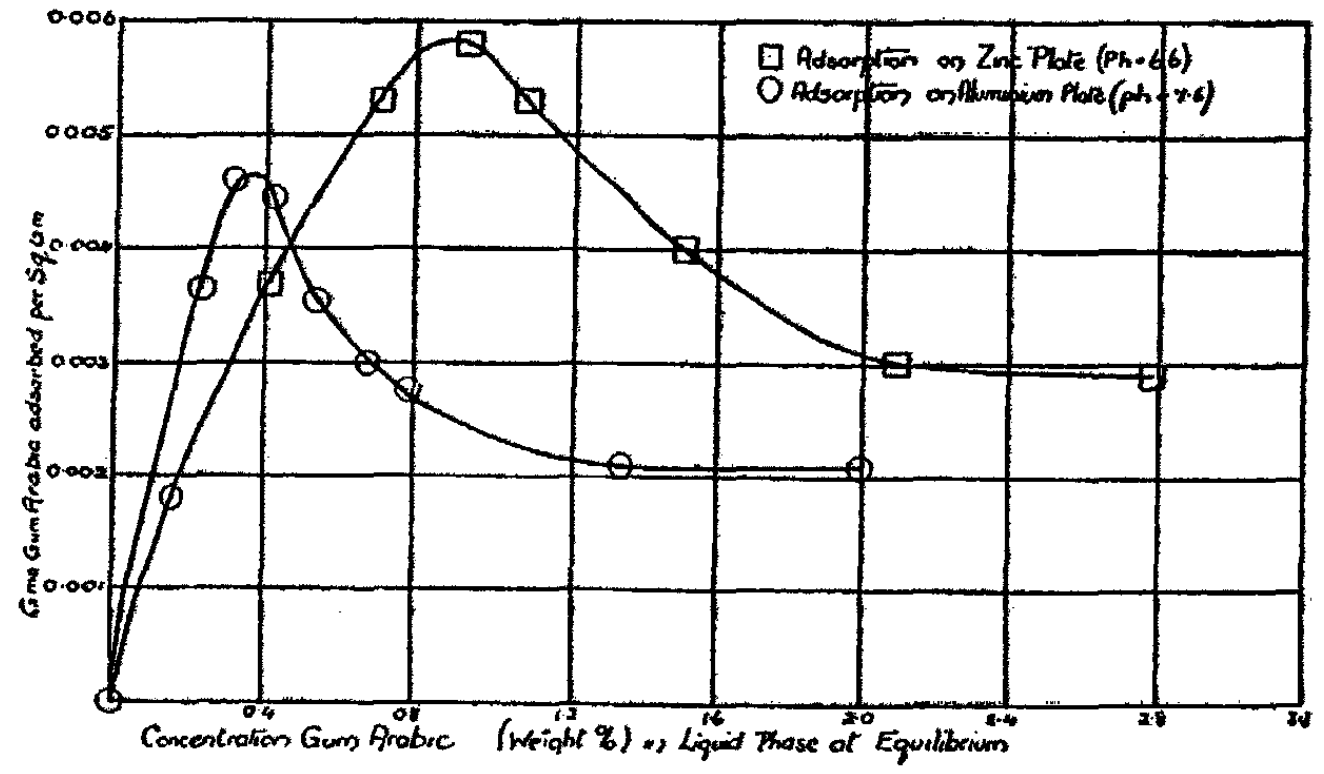


FIG. 2

calculated from the observed decrease in viscosity, combined with the known slope of the concentration-viscosity curve. The results of the measurements are shown in Table III and Figs 1 and 2. The amount of adsorbent shown in Column 6 of Table III represents the weight in gms. for the stone and charcoal series, and the area of "prepared" surface in sq. cms. for the zinc and aluminium series.

It will be seen that the adsorption curves are of unusual form; the adsorption first increases very rapidly, but before saturation is reached a second effect intervenes, with the result that the amount adorbed diminishes on further increasing the concentration and soon appears to be approaching a constant value. This abnormal type of curve is reminiscent of that obtained by Schofield and Rideal[1] from an application of the Gibbs' adsorption equation to the adsorption of alcohol at the surface of alcohol-water mixtures. It should be borne in mind, however, that the maximum adsorption of gum appears at concentrations of 1% or less, while with alcohol-water mixtures the maximum adsorption occurs at a concentration of alcohol of 40-50%.

The true explanation of the anomalous adsorption must probably be sought among the following possibilities:

(i) the decrease in adsorption is real, and due to a diminution in the thickness of the adsorbed layer.

(ii) the decrease is real, and due to a change in the molecular condition of the gum arabic.

(iii) the decrease is apparent only, being due to simultaneous adsorption of the water in varying amounts.

(iv) the decrease is due to preferential adsorption of a minor constituent of the gum, which eventually attains a sufficiently high concentration to displace the main constituent from the surface of the adsorbent.

The further possibility, that some change is induced in the surface structure of the adsorbent, is inherently improbable and may be dismissed on the ground that the abnormality is shown in the animal charcoal experiments; that is, when using the adsorbent upon which our views of the "normal" adsorption curve are mainly founded.

Explanation (iii) may also be dismissed, since the maxima in the adsorption curves lie at concentrations of 1%, or less, of gum. This explanation would therefore imply that after a critical concentration had been reached, any further adsorption of gum would be accompanied by an adsorption of more than a hundred times its weight of water. Such a possibility need not be considered, except in so far as a change in the relative adsorption of water might accompany the change suggested under heading (ii).

With regard to the thickness of the adsorbed layer, it is of course impossible to speak definitely. For the charcoal experiments the estimates of Lowry and Hulett,[19] Harkins and Ewing[20] and others would lead to an area that might amount to as much as one hundred square metres per gram of adsorbent. Now the maximum adsorption on charcoal was found to be 0.019 grams of gum arabic per gram of adsorbent so that a continuous adsorbed film of gum arabic of density 1.4 would, on this basis, have a thickness of only $\frac{0.019}{1.4 \times 10^6}$ cms; that is, about 1.5Å. This would correspond to a unimolecular layer that was far from complete, and although the actual surface is probably smaller, and the thickness greater, than is given by this estimate, it is evident that on a charcoal surface the adsorbed layer of gum arabic need not be regarded as more than one molecule thick. If this is the case, a general explanation of the anomalous adsorption curves cannot be found in the assumption of a multimolecular layer of changing thickness; in any event, an abrupt change in thickness could only be an accompaniment to the change suggested under heading (ii).

The fourth possibility, that of preferential adsorption, cannot, perhaps, be definitely dismissed; but it is difficult to reconcile such an explanation with the abrupt change in slope which occurs at the maximum points.

We believe, therefore, that the correct explanation of the anomalous adsorption curves must probably be found in a change in the molecular condition of the gum arabic. The shape of the curves can further indicate the nature of this change. It has been pointed out by McBain that for the equilibrium $nA \leftrightarrows A_n$, where simple molecules of a substance A unite to form a complex A_n, the transition from simple to complex will be the more abrupt the greater the value of n. Whereas the equilibrium point in a chemical change involving only two or three molecules is but gradually altered by change in concentration, for a polymerisation in which the factor n is large there is a critical concentration below which only simple molecules exist, but at which the proportion of polymerised form begins to increase very rapidly. The soaps[21] and butyric acid[22] form systems of this type, and the sudden transformation which is found in gum arabic solutions must presumably be attributed to a change of the same sort. If this is so, it may be that gum arabic exists as a simple electrolyte at concentrations of less than 0.5%, and as a colloid at concentrations greater than 2%. The point below which no micelles are present, and which has been called by Bury,[23] the critical concentration for micelles, lies at a concentration of 0.4-1.0%, and depends to some extent on the hydrogen ion concentration of the solution; the optimum pH value for micellar association appears to be close to 7.6. A further possibility which cannot be ignored is that a similar abrupt transition may occur from one type of colloidal particle to another of much greater complexity. It is hoped that work now in progress will indicate which of these hypotheses is the correct one.

In the light of these suggestions the viscosity concentration curves of gum arabic are of interest. They are unusual in being concave to the axis of concentration at low concentrations; so far as it is possible to speak from our figures, the region of maximum curvature can be identified with the region of decreasing adsorption. Apparently, then, the change in the molecular condition of the gum leads to a relative diminution in the viscosity of the solution.

There remains for consideration the interesting fact that with all four adsorbents the amount of gum adsorbed from concentrated solutions is much less than from the dilute solutions. The figures are as follows:

Adsorbent	Wt. in gms. of gum adsorbed per unit quantity adsorbent	
	Maximum value	Saturation value
Lithostone	0.0890	0.0260
Aluminium	0.0047	0.0021
Zinc	0.0058	0.0029
Charcoal	0.0192	0.0051

A constant ratio is not found between corresponding "maximum" and "saturation" values, nor is one to be expected, since the maximum values have no particular significance, saturation by the simpler molecules not having been reached. But it is evident that the saturated surface in equilibrium with a dilute solution of gum arabic must retain several times the amount of gum associated with a surface saturated by a more concentrated gum solution. Any explanation advanced for this great difference will necessarily be highly speculative. It may be argued that the particles present in concentrated solution are more heavily hydrated and have a very much greater bulk and cross section (per unit weight of gum) than those in dilute solution. Alternatively, it may be suggested that at the critical concentration a reorientation of the adsorbed molecules takes place to give an adsorbed film in which each molecule is more firmly bound and occupies a greater area of the surface of the adsorbent, through the interaction at the surface of the same forces which in the liquid phase lead to an aggregation of the gum particles. In this connection another fact may be noted. Technical experiments conducted by one of us at the London School of Printing have shown that the film of gum deposited on lithographic plates from more concentrated gum arabic solutions, is more retentive of water and to a marked extent more grease-repellent than is the film produced by solutions of less than the critical concentration.

This work was commenced with the aid of a grant to one of us (G. L. R.) from the Department of Scientific and Industrial Research, and we wish to place on record our thanks for this financial assistance.

Battersea Polytechnic
London.
March 25, 1931.

References

[1] U. S. Bur. Standards Tech. Paper, 67 (1916).
[2] "Physiological Chemistry," Chap. II (1916).
[3] J. prakt. Chem., **62**, 193.
[4] Bull. de N. 167 (1838).
[5] J. Chem. Soc., **45**, 41 (1884); **57**, 59 (1889).
[6] Biochem. J., **23**, 524 (1929).
[7] Science, **68**, 116 (1928); J. Am. Chem. Soc., **51**, 1519 (1929).
[8] J. Phys. Chem., **32**, 676 (1928).
[9] Chem. News, **58**, 224; Z. anal. Chem., **28**, 732 (1889).
[10] Privately communicated.
[11] "The Non-metallic Minerals," 2nd. Ed. (1910).
[12] "Fluidity and Plasticity," Chap. V (1922).
[13] "Fluidity and Plasticity," p. 299 (1922).
[14] "Fluidity and Plasticity," p. 340 (1922).
[15] "Fluidity and Plasticity," Appendix A (1922).
[16] Phil. Mag., **6**, 374 (1903); Dissert. Heidelberg, (1903); Kolloid-Z., **27**, 154 (1920); **13**, 88 (1913); **40**, 53 (1926); **43**, 187 (1927); Proc. Phys. Soc. London, **28**, 274 (1916).
[17] J. Phys. Chem., **34**, 273 (1930).
[18] Proc. Roy. Soc., **109A**, 57 (1925).
[19] J. Am. Chem. Soc., **42**, 1393 (1920).
[20] J. Am. Chem. Soc., **43**, 1798 (1921).
[21] Rept. Brit. Assoc., **1922**, p. 360.
[22] Phil. Mag., **4**, 841 (1927); J. Chem. Soc., **1929**, 679.
[23] J. Chem. Soc., **1930**, 2263.

THE DISSOCIATION OF ACID-BASE INDICATORS IN ETHYL ALCOHOL WITH A DISCUSSION OF THE MEDIUM EFFECT UPON THE INDICATOR PROPERTIES

BY I. M. KOLTHOFF

1. At the suggestion of Professor Wilder D. Bancroft, J. Waddell[1] studied the influence of organic solvents upon the color of nine acid-base indicators in acidic and basic medium and concluded from the effects observed whether the indicator behaved as an acid or a base. According to W. D. Bancroft and H. L. Davis[2] the method of Waddell seems to be trustworthy and to offer a solution to this problem. Bancroft and Davis[3] state: "The reasoning back of this work was that; if an indicator is an acid and one adds a weak alkali such as ammonia to the solution of an indicator in an organic solvent, in which the free indicator acid is readily soluble and the salt presumably not readily soluble, some of the free acid will pass into the organic liquid and will give the color of the undissociated acid. In the presence of acetic acid the indicator of course will show its acid color in the organic solvent. The same sort of thing will be true of an indicator base in the presence of acetic acid or ammonia in an organic solvent—the color shown will be that of the undissociated indicator base." Though it must be admitted that Waddell's method as a rule will give qualitative information on the point as to whether the indicator is an acid or a base, it should be emphasized that the above generalization is too wide and that the phenomena observed will be dependent upon the acid and basic properties of the solvent used and its influence upon the dissociation of the acid-base system and the type of indicator added. From a quantitative point of view, the kind of acid-base system used is of great importance (strong acid, weak uncharged acid or cation acid, or a buffer mixture). In his experiments with methyl orange, Waddell mentions "that it is very hard to realize color changes when hydrochloric acid or sulfuric acid are taken as acids." Moreover, it should be considered that Waddell did not exclude the presence of water in his organic solvents. As will be shown later on in this paper even traces of water may exert a tremendous influence upon the color equilibrium of an indicator in an organic medium. For the reasons mentioned, it is of importance to investigate the relations more from a quantitative point of view. The following study gives some quantitative information upon the properties of some acid-base indicators in ethyl alcohol as a solvent and the influence of small amounts of water on the color equilibrium of the indicator under various conditions.

---

[1] Waddell: J. Phys. Chem., 2, 171 (1898).

[2] W. D. Bancroft and H. L. Davis: J. Phys. Chem., 34, 1797 (1930).

[3] Ref. 2, p. 1803.

2. *Theoretical discussion. Pure alcohol as a solvent.* According to the conceptions of J. N. Brönsted[4] an acid is a substance with a tendency to split off protons and correspondingly a base is a substance which takes up protons:

$$\underset{\text{acid}}{A} \leftrightarrows \underset{\text{base}}{B} + \underset{\text{proton}}{H^+}$$

The acid and basic strengths are determined by the acidity constant K_{acid} and basicity constant K_{base}.

$$\frac{C_B}{C_A} a_{H^+} = K_{acid} \tag{1}$$

$$\frac{C_A}{C_B} \cdot \frac{1}{a_{H^+}} = K_{base} \tag{2}$$

C_B and C_A represent the concentrations (or better the conventional activities) of the base and the acid respectively in the specific solvent and a_{H^+} denotes the proton activity, the absolute value of which is unknown. Conventionally, for the sake of comparison, the proton activity in water can be put equal to the activity of the hydrated hydrogen ions $a_{H_3O^+}$.

Brönsted predicted the direction of the change of the acidity and basicity constants if instead of water an organic solvent with a lower dielectric constand is used. If the acid is a neutral molecule (or anion) the acidity constant will decrease going from water as a solvent to alcohol since as a rule the absolute activity of the monovalent anions (B^-) will be greater in alcohol than at the same concentration in water. Moreover, if we are dealing with organic acids the activity of the undissociated form (A) in alcohol as a rule is smaller than in water at the same concentration. The change of the constant cannot be calculated quantitatively as the individual character of the acid and base are of great significance.

The degree of dissociation of an acid (or a base) as determined by the dissociation constant (ionization constant) according to Brönsted depends upon two factors, namely, the acidity constant of the acid (or basicity constant of the base) and the basic character (acid character respectively) of the solvents.

$$\begin{array}{l} A \leftrightarrows B + H^+ \\ \underline{H^+ + S \leftrightarrows SH^+} \\ A + S \leftrightarrows B + SH^+ \text{ (dissociation)} \end{array} \tag{3}$$

The dissociation constant $K_{diss.}$ is

$$\frac{[B]\,[SH^+]}{[A]} = K_{diss.} \tag{4}$$

---

[4] Comp. J. N. Brönsted: Chem. Rev., 5, 232 (1928), where a general discussion of the theory and the literature has been given.

S being the solvent and SH^+ the combination of the proton with the solvent. Further on:

$$\frac{[SH^+]}{[aH^+]} = K_{\text{conv.bas.solv.}} \qquad (5)$$

$K_{\text{conv.bas.solv.}}$ is the conventional basicity constant of the solvent, assuming that the activity of the solvent itself is equal to one. From the above it is evident that the dissociation constant of an acid in a solvent is equal to the product of its acidity constant and the conventional basicity constant of the solvent.

$$K_{\text{diss.}} = K_{\text{acid}}\, K_{\text{conv.bas.solv.}} \qquad (6)$$

Therefore, the ratio of the acidity and dissociation constants in two different solvents is given by the ratio of the basicity constants of the solvents. It is easily shown that,

$$\frac{K_{\text{acid (water)}}}{K_{\text{acid (alc.)}}} = \frac{K_{\text{diss.(water)}}}{K_{\text{diss.(alc.)}}} \cdot \frac{K_{\text{conv.bas.alc.}}}{K_{\text{conv.bas.water}}} \qquad (7)$$

in which $K_{\text{acid(water)}}$ is the acidity constant in water, $K_{\text{acid(alc.)}}$ the same in alcohol, etc. H. Goldschmidt[5] with his collaborators have made careful investigations of the dissociation of various acids in 100% ethyl alcohol at 25°. The dissociation constants have been derived from conductance measurements in the classical way, some of them having been corrected by E. Larsson[6] for the difference between ion concentrations and ion activities. These differences as a rule are very small. Larsson, moreover, has determined the dissociation constants of some acids in ethyl alcohol at 25° by potentiometric measurements. As a rule, his data are in fair agreement with those of Goldschmidt.

L. Michaelis and M. Mizutani[7] by potentiometric measurements, have determined the acidity constants (not the dissociation constants) of various acids in mixtures of water and ethyl alcohol of varying composition. Their figures can be graphically extrapolated to 100% ethyl alcohol, though, of course, this procedure makes the result somewhat uncertain. Moreover, it should be mentioned that quite consciously Michaelis and Mizutani introduced some approximations in their calculations and neglected the difference between activities and concentrations. The latter point will be taken up in the discussion of the figures in Table I.

Denoting the negative logarithm of the dissociation constant as $pK_{\text{diss.}}$ and the negative logarithm of the acidity constant as pK_{acid}, it is found from equation (7) that:

$$pK_{\text{diss.alc.}} - pK_{\text{acid alc.}} = pK_{\text{conv.bas.alcohol}} - pK_{\text{conv.bas.water}} \qquad (8)$$

---

[5] H. Goldschmidt: Z. physik. Chem., **89**, 129 (1914); **91**, 46 (1916); **99**, 116 (1921); E. Mathiesen: **119**, 439 (1926); Goldschmidt and F. Aas: **112**, 423 (1924).

[6] E. Larsson: Untersuchungen über die elektrolytische Dissoziation einiger Elektrolyte in aethylalkoholischer Lösung; Thesis, Kopenhagen, (1924).

[7] L. Michaelis and M. Mizutani: Biochem. Z., **147**, 7 (1924); Z. physik. Chem., **116**, 135; Mizutani: 350 (1925).

TABLE I

Dissociation of Uncharged Acids and Monovalent Cation Acids in Water and in Alcohol.

Acid	$pK_{diss.w.}$	$pK_{diss.alc.}$ Goldschmidt	$pK_{diss.}$ alc.corr.	$pK_{diss.alc.}$ Larsson	$pK_{diss.alc.}$ average	$pK_{diss.alc.} - pK_{diss.w.}$	pK_{acid} M.M.	$pK_{diss.} - pK_{acid}$	Average Difference
Uncharged Acids									
Acetic	4.73		10.8	10.26	10.6?	5.9	7.5	3.1	3.05
Formic	3.70	9.15			9.15	5.45	5.95	3.2	
Trichloroacetic	0.88	5.83	5.96	5.68	5.8	4.9			
Trichlorobutyric		6.98	7.08	7.05	7.05				
Benzoic	4.2	10.43	10.4	10.13	10.25	6.05	7.4	3.05	
Salicylic	3.0	8.67	8.73	8.73	8.7	5.7	5.8	2.9	
p. Nitrophenol	7.1			11.2	11.2	4.1	9.2	3.0	
Monovalent Cation Acids									
NH_4^+	9.4			10.5		1.1	8.35	2.15	2.27
Aniline H^+	4.7	5.7				1.0	3.6 ±0.1	2.1	
Methylaniline H^+	4.86 4.3	4.9				0.04 0.6	2.4	2.5	
Dimethyl aniline H^+	4.0 5.17	4.4				+0.4 −0.67	2.2	2.2	
o. Toluidine H^+	4.50	5.6				1.1	3.2	2.4	
m.Toluidine H^+	4.8	5.9				1.1	3.5	2.4	
Pyridine H^+	5.2	4.7				−0.5	2.6	2.1	

since conventionally in water the dissociation constant is put equal to the acidity constant.

In Table I is given a comparison of some data found by Goldschmidt, Larsson and some extrapolated figures of the results of Michaelis and Mizutani. In the column $pK_{diss.w.}$ the negative logarithms of the classical dissociation constants in water are reported: $pK_{diss.alc.Goldschmidt}$ denotes the negative logarithm of the dissociation constant in pure alcohol according to Goldschmidt (conductivity measurements); $pK_{diss.alc.corr.}$ the same corrected by Larsson for the ionic strength effect; $pK_{diss.alc.Larsson}$ the same as determined by Larsson by potentiometric measurements; whereas $pK_{diss.alc.average}$ represents the average value of $pK_{diss.}$ in alcohol. Under the head $pK_{water} - pK_{alc.}$ the differences between the negative logarithm of the ionization constant in water and in alcohol are reported. $pK_{acid\,M.M.}$ represents the extrapolated value of the acidity constant in alcohol according to measurements of Michaelis and Mizutani; $pK_{diss.alc.} - pK_{acid\,alc.}$ the difference between the negative logarithm of the dissociation constant and acidity constant in alcohol, whereas the last column gives the average difference for uncharged acids and monovalent cation acids.

From the results in the table, it is seen that the difference between the dissociation constant in water and in alcohol is not a constant; if the acid is an uncharged molecule the constant in alcohol is of the order of 10^4 to 10^6 times smaller than in water. If the acid is a monovalent cation, the difference is much smaller as might be expected from the postulates of Brönsted.[4]

The values of the dissociation constants of monomethyl anilinium ion and dimethyl anilinium ion in water are rather uncertain. For the latter Goldschmidt reports a pK value of 5.17, potentiometrically Mizutani found 5.12. According to these figures the dissociation constant of dimethyl anilinium ion is about five times larger in alcohol than in water. M. Bourgeaud and A. Dondelinger[5] found from hydrolysis measurements that $pK_{diss.water}$ is 4.0. However, it seems doubtful whether this figure is correct. Goldschmidt reports for the monomethyl anilinium ion a pK_{water} of 4.24, Bourgeaud and Dondelinger of 4.3, Mizutani on the other hand of 4.86.

More interesting for the present problem is the difference between the dissociation constant and acidity constant in alcohol, the negative logarithm of which has been given in the last column. This figure should be constant as it represents the difference between the negative logarithms of the conventional basicity constant of alcohol and of water. The average difference for acids behaving as neutral molecules is 3.05, on the other side the average for monovalent cation acids is 2.27. It should be remembered, however, that the data of Michaelis and Mizutani have not been corrected for the difference between ion activities and ion concentrations. In most cases, Michaelis and Mizutani measured a system containing 0.01 N of a uni-univalent salt. If f is the activity coefficient of the monovalent cation or anion, then in alcohol according to Larsson,[6] the expression holds:

M. Bourgeaud and A. Dondelinger: Bull., 37/38, 277 (1925).

$$-\log f = 2\sqrt[3]{c}$$

$$\text{For } c = 0.01 \qquad\qquad -\log f = 0.43$$

If Michaelis and Mizutani's data are corrected for the difference between ion activity and ion concentration, all pK_{acid} values of uncharged acid molecules are increased by 0.43, thus decreasing the average difference in the last column to $3.05 - 0.43 = 2.62$. On the other hand all pK_{acid} values of monovalent cation acids are decreased by 0.43, making the average in the last column $2.27 + 0.43 = 2.7$.

Therefore, there is a satisfactory agreement between the two series, the average difference being 2.65. According to direct potentiometric measurements made by Larsson[6], $pK_{conv.bas.alc.} - pK_{conv.bas.water}$ is 2.52. Considering the uncertainty in both sets of figures, the agreement is very gratifying and it may be assumed that $pK_{conv.bas.alc.} - pK_{conv.bas.water.}$ is 2.6 ± 0.1, or water is about 400 times as strong a base as ethyl alcohol.

Change of dissociation by addition of small amounts of water to alcoholic solutions of acids.

It has been shown before that the degree of dissociation of an acid is governed by its acidity constant and the conventional basicity constant of the solvent:

$$A \rightleftarrows B + H^+ \tag{9}$$

$$\underline{H^+ + C_2H_5OH \rightleftarrows C_2H_5OH\ H^+} \tag{10}$$

$$A \quad + C_2H_5OH \rightleftarrows B + C_2H_5OH\ H^+ \tag{11}$$

Since water is a much stronger base than alcohol, it can be expected that addition of small amounts of water to an alcoholic solution of an acid will qualitatively have the same effect as the addition of a weak base, say ammonia to an aqueous solution of a weak acid; in other words, addition of water to an alcohol solution of a weak acid will increase the dissociation. There will be a competition between the two bases, water and alcohol, to combine with the proton split off by the acid A. Quantitatively the effect will be governed by the equilibrium constant K of the reaction:

$$C_2H_5OH\ H^+ + H_2O \rightleftarrows H_2OH^+ + C_2H_5OH \tag{12}$$

$$\frac{[C_2H_5OH\ H^+]\,[H_2O]}{[H_2OH^+]} = K \tag{13}$$

(the concentration of alcohol in the alcoholic solution can be considered as a constant.) K represents the distribution coefficient of the proton between alcohol and water. Instead of concentrations, activities should be written, but no correction has been applied here for this difference.

From conductivity measurements, H. Goldschmidt[5] (1914) found that:

$$\frac{[C_2H_5OH\ H^+]\,n}{[H_2OH^+]} = 0.0583 = K\ (25°) \tag{14}$$

in which n represents the concentration (normality) of the water in the alcoholic solution.

If the dissociation constant of the acid in pure alcohol is K_o, then

$$K_o = \frac{[C_2H_5OH\,H^+][B]}{[A]} = \frac{[C_2H_5OH\,H^+]^2}{[A]} \qquad (15)$$

in a solution of the acid in pure alcohol. Assuming that this constant does not change upon addition of small amounts of water, it is found from (14) and (15) that the dissociation constant of the acid K_n in alcohol with a concentration of n of water

$$Kn = \frac{\{[C_2H_5OH\,H^+] + [H_2OH^+]\}\,[B]}{[A]} = \frac{[C_2H_5OH\,H^+]\,[B]}{[A]}\;\frac{(K+n)}{K} \qquad (16)$$

or

$$K_n = K_o\,\frac{K+n}{K} = K_o\,\frac{(0.0583+n)}{0.0583} \quad (25°) \qquad (17)$$

assuming that the acid is weak enough to put [A] in both cases equal to the analytical concentration of the acid. Goldschmidt found that expression (17) holds to a water concentration of 0.1. At higher water concentrations the empirical relation.

$$K_n = K_o\,\frac{K+n}{K}(1 + 0.9\,n + 0.3\,n^2) \qquad (18)$$

expresses quantitatively the influence of water upon the dissociation constant of an acid in alcohol. If the influence of the water were expressed in its concentration instead of in its activity, equation (17) probably would hold to higher concentrations.

For monovalent cation acids, Goldschmidt[5] (1921) concluded that the dissociation constant does not change appreciably upon addition of small amounts of water. However, there seems to be some confusion in Goldschmidt's excellent work here; he probably means that K_o is not changed by addition of small amounts of water[9].

Experimentally Goldschmidt[10] showed that:

$$K_{o\,\mathrm{Solvolysis}} = \sqrt{\frac{K_{o\,\mathrm{diss.cation\ acid}}}{K_{o\,\mathrm{diss.uncharged\ acid}}}} \qquad (19)$$

in which $K_{o\,\mathrm{Solvolysis}}$ being the alcoholysis constant of the salt of a weak acid and a weak base in pure alcohol is only slightly affected by the addition of small amounts of water (concentration n). He found that the solvolysis constant $K_{n\,\mathrm{Solvolysis}}$ in the presence of a concentration of water equal to n is approximately:

---

[9] H. Goldschmidt: Z. physik. Chem., 99, 120 (1921); "Dieses Resultat zeigt auch, dass bei den genannten Basen eine Veränderung der Affinitätsgrösse K_n (in Brönsted's terminology Kdiss. alc. of cation acid) durch etwaige Bildung eines Wasserumlagerungsproduktes nicht in erheblichem Grade eintritt."

[10] Ref. 9: comp. also H. Goldschmidt and G. V. Mathiesen: Z. physik. Chem., 119, 43 (1926).

$$K_{n\ \text{Solvolysis}} = \sqrt{\frac{K_{o\ \text{diss.cation acid}}}{K_{o\ \text{diss. uncharged acid}}\ (1 + 0.9\,n + 0.3\,n^2)}} \qquad (20)$$

From (18) and (20) it is found that:

$$K_{n\ \text{diss.cation acid}} = K_{o\ \text{diss.cation acid}}\ \frac{(0.0583 + n)}{0.0583} \qquad (21)$$

an expression similar to (17). From Goldschmidt's experimental work, it may be inferred that equation (21) only holds to water concentrations of 0.1 to 0.2; at higher water contents an empirical factor should be introduced, somewhat similar to the one in equation (18) for uncharged acids.

3. *Application of the theory to the properties of acid-base indicators in pure and water containing alcohol.*

Indicators behaving as uncharged acids or monovalent anion acids will have a dissociation constant in alcohol much smaller than that in water. On the other hand, if the monovalent cation of the indicator behaves like an acid (or the uncharged form as a base) it may be expected that the difference will be much smaller and that cases may occur where the dissociation constant in alcohol is greater than the same in water.

It is of interest to consider the influence of small amounts of water upon the color of an indicator in a pure alcoholic solution. The effect of the addition of water will depend upon the kind of the acid-base system present in the alcohol.

Suppose an indicator shows an intermediate color in an alcoholic solution containing a trace of a strong acid (like hydrochloric acid).

$$\frac{[\text{Basic form}]\,[C_2H_5OH\ H^+]}{[\text{Acid form}]} = K_{o\ \text{diss.ind.}} \qquad (22)$$

$K_{o\ \text{diss.ind.}}$ represents the dissociation constant of the indicator in pure alcohol. In the presence of a concentration n of water it is found that

$$K_{n\ \text{diss.ind.}} = \frac{[\text{Basic form}]\{[C_2H_5OH\ H^+] + [H_3OH^+]\}}{[\text{Acid form}]} =$$

$$= K_{o\ \text{diss.ind}}\cdot \frac{(0.0583 + n)}{0.0583}\ (1 + 0.9\,n + 0.3\,n^2) \qquad (23)$$

Since it was assumed that the alcohol contained a strong acid, it is found that the sum of $[C_2H_5OH\ H^+]$ and $[H_3OH^+]$ is constant and equal to the total acid concentration. From equations (22) and (23) it is seen that:

$$\left\{\frac{[\text{basic form}]}{[\text{acid form}]}\right\}_n : \left\{\frac{[\text{basic form}]}{[\text{acid form}]}\right\}_o = \frac{K_n}{K_o} = \frac{0.0583 + n}{0.0583}\,(1 + 0.9\,n + 0.3\,n^2) \qquad (24)$$

or approximately at small water content:

$$\left\{\frac{[\text{basic form}]}{[\text{acid form}]}\right\}_o : \left\{\frac{[\text{basic form}]}{[\text{acid form}]}\right\}_n = 1 + 16\,n \qquad (25)$$

Equations (24) and (25) show that any acid-base indicator, independent of the acid or basic character of the uncharged form, will decrease its sensitivity very much for strong acids upon addition of traces of water to the alcohol. From the above it can be calculated that in 98.2% alcohol ($n = 1$) the sensitivity of an indicator for a strong acid is about 17 times less than in pure alcohol. Upon addition of larger quantities of water individual differences between various types of indicators will occur. The above postulates are supported by experimental work (see section 4).

If the original solution of the indicator in pure alcohol contained a weak acid instead of a strong one, it can easily be shown that:

$$\left\{\frac{[\text{basic form}]}{[\text{acid form}]}\right\}_n : \left\{\frac{[\text{basic form}]}{[\text{acid form}]}\right\}_o = \sqrt{\frac{K_n}{K_o}} = \text{approx.} \sqrt{1 + 16n} \qquad (26)$$

Therefore, in such a solution, the color of the indicator changes much less to the alkaline side upon addition of water than if a strong acid were present. Finally, if the original solution of the indicator in alcohol contains a buffer mixture, the addition of small amounts of water will not affect the color of the acid-base indicator at all. From the above it is evident that the type of acid-base system present in the alcohol is the only determining factor of the effect of addition of small amounts of water on the color of an acid-base indicator; the individual indicator properties are immaterial unless the indicator behaves as a pseudo-base.

4. *Experimental.* Use can be made of the fact that the color of an indicator in an alcoholic buffer solution is not affected by the addition of traces of water. If the ratio of the concentrations of the basic and the acid forms of the indicator is an alcoholic buffer solution containing a trace of water is experimentally determined, the dissociation constant of the indicator in pure alcohol is calculated by means of the equation:

$$K_{o\ \text{diss. ind. alc.}} = \frac{[\text{basic form}]}{[\text{acid form}]} \cdot \frac{[A]}{[B]} \cdot K_{o\ \text{diss. acid alcohol}} \qquad (27)$$

$[A]:[B]$ is the ratio of the concentrations of the acid and its salt in the buffer mixture and $K_{o\ \text{diss. acid alc.}}$ is the dissociation constant of the acid form of the buffer in pure alcohol. Actually activities should be written instead of concentrations; however, the corrections have been omitted as they are rather uncertain and moreover the correction for the activities of both forms of the indicator is counterbalanced by those of the acid and the base in the buffer solution, if the uncharged form of the indicator is an acid. In many cases, it was shown that the color of the indicator hardly changed, if the buffer solution was ten to fifty times diluted with pure alcohol. The ratio of the acid to basic form of the indicator was determined by the wedge method or the Gillespie test tube method, completely acid or basic solutions of the indicator in pure alcohol being used for comparison.

The alcohol was dehydrated by refluxing for five days over finely powdered lime, distillation over calcium and finally over sulfanilic acid to remove traces of basic impurities. The strength was obtained from the specific gravity (to fifth decimal place). The various fractions used contained between 99.94 to 100.00% alcohol. Sodium ethylate was prepared by dissolving pure sodium in alcohol at 0°. If prepared at higher temperature the solution assumes a yellow color and is less stable. The concentrations of acids and bases used were determined according to standard methods. The acids, salts and indicators were purified by recrystallization and dried in a proper way to remove traces of water. The solutions of most indicators in pure alcohol are not stable for an indefinite time, probably on account of ester formation. The solutions used were not older than fourteen days. The following buffer solutions were used: salicylic acid + sodium salicylate; benzoic acid + sodium benzoate (prepared from benzoic acid and sodium ethylate); trichloroacetic acid and its sodium salt (prepared as sodium benzoate); diethyl barbituric acid (veronal) and its sodium salt. The dissociation constant of veronal in pure alcohol is not given in the literature and, therefore, was determined in a colorimetric way; it was found to be equal to 4×10^{-14} ($pK = 13.6$) at 25°. The results are given in Table II. In the column preceding the last one, the negative logarithms of the dissociation constant of the indicators in water[11] are reported and in the last column (Δ) the difference between $pK_{\text{ind. alcohol}}$ and $pK_{\text{ind. water}}$.

The procedure is demonstrated by the following example in which bromophenol blue was used as an indicator. Mixture containing 0.05 molar salicylic acid and 0.05 molar sodium salicylate. The dissociation constant of salicylic acid in alcohol is 2×10^{-9}, or $pK = 8.7$,

$$\text{Ratio:} \frac{[\text{basic}]}{[\text{acid}]} = \frac{[\text{blue}]}{[\text{yellow}]} = \frac{31}{69}$$

therefore,

$$K_{\text{diss. Br.P.B}} = \frac{31}{69} \times 2 \times 10^{-9} = 9 \times 10^{-10} \; pK_{\text{diss. alc.}} = 9.05$$

In the same buffer solution ten times diluted with alcohol:

$$\text{Ratio :} \frac{[\text{basic form}]}{[\text{acid form}]} = \frac{29}{71}$$

corresponding with a $pK_{\text{diss. alc.}}$ of 9.09. In the original buffer solution with a water normality equal to one:

$$\text{Ratio :} \frac{[\text{basic form}]}{[\text{acid form}]} = \frac{28}{72}$$

showing the slight effect of a small concentration of water upon the acidity constant of the indicator in alcohol. In a buffer mixture containing 0.02 N salicylic acid and 0.08 N sodium salicylate:

---

[11] Comp. I. M. Kolthoff: J. Phys. Chem., 34, 1466 (1930).

$$\text{Ratio}: \frac{[\text{basic form}]}{[\text{acid form}]} = \frac{62}{38}$$

corresponding to a $pK_{\text{diss.alc.}}$ of 9.09. As an average value of $pK_{\text{diss.alc.}}$ of 9.1 is reported in the table.

Discussion. The sulfonphthaleins in their color change from the yellow to the alkaline form have a dissociation constant in alcohol which is 10^5 to 10^6 times smaller than the same in water, the difference being of the same order as that of benzoic acid, salicylic acid and phenol. This is somewhat surprising since the last three acids are monobasic acids. Extrapolating some of Mizutani's[12] data and correcting for the difference between the acidity constant and dissociation constant, it is found that the second dissociation constant of malonic acid in alcohol is $10^{6.3}$, that of succinic acid $10^{6.4}$ times and that of phthalic acid about 10^7 times smaller than the same in water.

The figures in the table have only an approximate significance and the investigations should be continued by spectrophotometric measurements, taking the difference between activities and concentrations into account.

A surprising result was obtained for the dissociation constant of the cation of pentamethoxy triphenyl carbinol in alcohol. This constant is about 10^4 times smaller in alcohol than in water, whereas a much smaller difference was expected (see Table I; dissociation constants of cation acids).

The large difference must be attributed to the pseudo basic character of this substance. This property also accounts for the following fact: The addition of small amounts of water (up to $n = 1$) has only a slight influence upon the color of an indicator in an alcoholic buffer solution; with penta methyoxytriphenyl carbinol as an indicator the color changes very strongly to the basic side by addition of a little water. The ratio of the basic to acid (colorless to red) form of the indicator in a buffer containing 0.05 molar trichloroacetic acid and 0.05 molar sodium trichloroacetate in alcohol was found to be 0.54; if sufficient water was added to make the concentration about 1 molar, the ratio changed to 11.5. Therefore, a strong interaction must take place between the pseudo base and the water.

The change of the dissociation constants of the indicator bases methyl orange and dimethylamino azobenzene is of the expected order. From the figures reported (which in this case are not very accurate) it is seen that the sensitivity of methyl orange for strong acid is of the same order in pure alcohol as in water. This conclusion is supported by some older measurements[13] in which it was shown that the sensitivity of methyl orange for strong acid in pure alcohol is very much decreased by the presence of traces of water. The change of the sensitivity can be calculated on the basis of Goldschmidt's equation:

$$K_{n_{\text{M.O.}}} = K_{o_{\text{M.O.}}} \sqrt{\frac{n + K}{K}}\,(1 + 0.9\,n + 0.3\,n^2),$$

---

[12] Mizutani: Z. physik. Chem., 118, 318 (1925).

[13] I. M. Kolthoff: Pharm. Weekblad, 60, 227 (1923).

TABLE II

Dissociation Constants of Acid Forms of Indicators in Pure Alcohol

Indicator	Kind of Buffer Solution	[A]:[B] in buffer	$K_{diss.acid}$ in pure alcohol	$K_{diss\ ind.}$ in pure alcohol	$pK_{ind.alc.}$	$pK_{ind.}$ water	Δ
Thymolblue	Trichloroacetic acid	0.05 : 0.05	1.6×10^{-6}	1.8×10^{-6}	5.7	1.65	4.05
		0.02 : 0.08		2.4×10^{-6}			
2.4.2′4′2″ Pentamethyoxy triphenylcarbinol	"	0.05 : 0.05	"	8.6×10^{-7}	6.0	1.86	4.1
		0.02 : 0.08		10.1×10^{-7}			
Dimethylamino azobenzene	"	0.095 : 0.005	"	6.5×10^{-5}	(5.20)	3.25	(1.95)
		0.09 : 0.01		6×10^{-5}			
Methylorange	"	0.0975 : 0.0025	"	1.4×10^{-3}	2.9—	3.46	—0.45
		0.095 : 0.005		1×10^{-3}	3.0		
Bromophenolblue	Salicylic acid	0.05 : 0.05	2×10^{-9}	9×10^{-10}	9.1	4.10	5.0
		0.02 : 0.08		8×10^{-10}			
Bromocresolgreen	Benzoic acid	0.09 : 0.01	5.6×10^{-11}	6×10^{-11}	10.3	4.90	5.4
		0.05 : 0.05		4.5×10^{-11}			
Bromocresolpurple	"	0.01 : 0.09	"	3×10^{-12}	11.5	6.4	5.1
Bromothymolblue	Veronal	0.09 : 0.01	4×10^{-14}	1.5×10^{-13}	12.8	7.3	5.5
Phenolred	"	0.05 : 0.05	"	6×10^{-14}	13.4	8.0	5.4
α Naphtholphthalein	"	0.05 : 0.05	"	1.5×10^{-14}	13.8	8.3	5.5
Thymolblue (alk.range)	"	0.005 : 0.095	"	7×10^{-16}	15.15	9.2	5.9
Phenolphthalein	"	0.005 : 0.095	"	(5×10^{-16})	(15.3)	(9.3)	(6.0)?

which appeared to hold for water concentrations up to 1.5 molar. From the older sensitivity measurements, it was computed that the sensitivity of methyl-orange for strong acid in pure alcohol is of about the same order as in water. Experiments have also been made with methyl red as an indicator. In aqueous medium this substance behaves as an hybrid ion, having a red color. The anion is yellow, the cation red. It seems that in pure alcohol methyl red is mainly present in the amino acid form, having an orange color. This color is stable over a wide range of hydrogen ion concentration in alcoholic medium, the change from orange to red taking place at about the same hydrogen ion concentration as that of methyl orange (in the latter case from pure yellow to red), the change from orange to yellow takes place in the vicinity of a pH of 10. No exact study has been made, though interesting information may be expected from a study of such an ampholyte in alcoholic medium.

Finally, it should be stated that the values of the dissociation constants of alpha naphtholphthalein and of phenolphthalein (the latter is a dibasic acid) in water have no exact significance; they are only given for approximate comparison.

5. *Addition of alcohol to aqueous solutions.* It has been shown before that the dissociation constant of an indicator increases very much upon addition of water to an alcoholic solution. This was explained by the fact that water on account of its stronger basic properties has a larger affinity for protons than alcohol has. It may be expected that addition of traces of alcohol to an aqueous solution will not materially affect the color. With larger concentrations the conditions may change, depending upon the acid-base system present and the type of indicator used.

The dissociation of a strong acid in water is not affected by addition of large amounts of alcohol. If we are dealing with a weak acid (uncharged form is an acid) the dissociation constant will decrease upon addition of alcohol on account of decrease of the dielectric constant of the medium (medium effect; change of the activity coefficients of the components). On the other hand, it may be predicted that the dissociation of a cation acid will increase upon addition of alcohol to an aqueous solution (Brönsted).[4]

TABLE III

Influence of Alcohol upon Dissociation Constants (pK) of Indicators in Water

Vol. % Alcohol	M.O.	D.Y.	Trop. oo	Dimethylanilinium (Michaelis & Mizutani)
10	−0.10	−0.11	−0.06	
20	−0.22	−0.24	−0.24	−0.16
30	−0.48	−0.48	−0.56	
40	−0.90	−0.90	−1.1	−0.52

	B.P.B.	Acetic acid
10	+0.06	+0.09
20	+0.21	+0.24
30	+0.35	+0.42
40	+0.38	+0.68

In Table III the influence of alcohol upon the dissociation constant of some indicators is given:[14] methyl orange (M.O.); dimethylamino azobenzene (D.Y.) and Tropeolin 00 (Trop. 00) behave like acid cations (indicator bases); bromophenolblue (B.P.B.) as an acid anion. For comparison, the change of the constants of dimethylanilinium ion and of acetic acid[15] are given.

With this general information it is possible to compute the influence of alcohol upon the color of an indicator in any acid-base system in water. The color of an indicator acid (e.g. bromophenolblue) changes to the acid side upon addition of alcohol to an aqueous solution of a strong acid, since:

$$\frac{[I^-]}{[HI]} = \frac{[\text{basic form}]}{[\text{acid form}]} = \frac{K_{Ind}}{[H_2OH^+]} \tag{28}$$

and K_{Ind} decreases with increasing alcohol concentration. The color of an indicator base (like methyl orange) on the other hand will change to the alkaline side as the dissociation constant increases.

If the alcohol effect were studied in a solution of a weak acid instead of in that of a strong acid, it would be found to be less in the case of an indicator acid. The dissociation constant of the acid and indicator acid change in the same direction:

$$[H_2OH^+] = K_{acid}\frac{[A]}{[B]} = \sqrt{K_a[A]} = K_{Ind.}\frac{[HI]}{[I^-]} \tag{29}$$

$$\frac{[I^-]}{[HI]} = \frac{K_{Ind}}{\sqrt{K_{acid}[A]}} \tag{30}$$

If the dissociation constant of the weak organic acid (uncharged form is an acid) and that of the indicator acid change in the same ratio upon addition of alcohol, it is found by comparing equations (28) and (30) that the ratio of the basic to acid form decreases in porportion to the decrease of K_{Ind} in solutions of a strong acid and only with the square root of the change of $K_{ind.}$ in a solution of a weak acid. In a similar way it can be shown that upon addition of alcohol the color of an indicator base changes more strongly in a solution of a weak acid than in the same of a strong acid:

$$\frac{[IH^+]}{[I]} = \frac{\sqrt{K_{acid}[A]}}{K_{ind.cation}} \tag{31}$$

Again if $K_{ind.cation}$ increases in the same ratio as K_{acid} decreases upon addition of alcohol, it is found that in a weak acid:

$$\frac{[IH^+]}{[I]} \text{ changes with } \sqrt{\left(\frac{K_{ind.cation\ water}}{K_{ind.cation\ water\ +\ alcohol}}\right)^2} \tag{32}$$

---

[14] Derived from earlier experiments: I. M. Kolthoff: Rec. Trav. Chim., 42, 251 (1923).

[15] Compare L. Michaelis and M. Mizutani: ref. 7.

$$\text{and in a strong acid with } \frac{K_{\text{ind. cation water}}}{K_{\text{ind. cation water + alcohol}}} \tag{33}$$

Still more striking is the difference in the behavior between an indicator acid and an indicator base if the alcohol effect is studied in a buffer solution of a weak acid and its salt.

$$\frac{[\text{HI}]}{[\text{I}^-]} = \frac{K_{\text{acid}}}{K_{\text{ind. acid}}} \quad \frac{[\text{A}]}{[\text{B}]} = \frac{K_{\text{acid}}}{K_{\text{ind. acid}}} \text{ . const.} \tag{34}$$

Assuming again that K_{acid} and $K_{\text{ind. acid}}$ decrease in the same ratio upon addition of alcohol, it is found from expression (34) that the color of the indicator acid in the buffer solution is not affected by addition of alcohol. On the other hand, for an indicator base, it is shown that:

$$\frac{[\text{IH}^+]}{[\text{I}]} = \frac{K_{\text{acid}}}{K_{\text{ind. cation}}} \text{ . const.} \tag{35}$$

With the same assumption as above, it is found that,

$$\frac{[\text{IH}^+]}{[\text{I}]} \text{ changes with ratio } \left(\frac{K_{\text{ind. cation water}}}{K_{\text{ind. cation water + alcohol}}}\right)^2 \tag{36}$$

Summarizing the above results, it is found that the color of an indicator acid changes to the acid side upon addition of alcohol to an aqueous solution of a strong acid; the change is less in a weak acid and no effect is noticed in a buffer solution. The color of an indicator base is shifted to the alkaline side upon addition of alcohol to an aqueous solution of a strong acid, the effect is more marked in a solution of a weak acid and the strongest effect is noticed in a buffer solution of a weak acid and its salt. This alcohol effect, therefore, offers a simple method of deciding whether the indicator in its uncharged form is an acid or a base.

The above semiquantitative conclusions were confirmed by some experiments. The color of methyl orange (indicator base) in 0.01 N acetic acid is red-orange; upon addition of 40% alcohol the color is yellow. On the other hand, the color of tetrabromophenol tetrabromo sulfonphthalein (bromophenolblue cannot be used on account of its changing dichromatism) changes slightly to the acid side (dilution of the acid counteracts the effect) upon addition of alcohol.

The colors of methyl orange, dimethylamino azobenzene, and hexamethyoxy triphenylcarbinol in an acetate buffer of pH of 3.8 changed strongly to the alkaline side upon addition of alcohol; the greenish color of tetrabromophenol tetrabromosulfonphthalein in the same buffer changed only slightly to more intense green upon addition of alcohol. The behavior of bromocresolgreen in an acetate buffer of pH of 5.0 is similar to that of the latter indicator; in 50% alcohol the color was only slightly more alkaline than in water.

6. *Titrations in alcoholic medium.* A few words may be said about acid-base titrations in alcoholic medium though it is beyond the scope of this paper to treat this subject in an exhaustive way.

Potentiometric titrations of various acids and bases in alcohol have been made by E. R. Bishop, E. B. Kittredge and J. H. Hildebrand.[16] The jump in potential at the equivalence point in the titration of a strong acid with a strong base is much greater in alcohol than in water. This is to be expected since the ionization product of alcohol ($C_2H_5OH\ H^+$] [$C_2H_5O^-$] is $4 \times 10^{-20} = 10^{-19.4}$ (Larsson[6] at 25°) and that of water 10^{-14}. The ionization product of alcohol is about $10^{5.4}$ times smaller than that of water. The dissociation constants of uncharged weak acids and acid anions are decreased in the same order. Therefore, the alcoholysis (in alcohol) of the sodium salts of these acids is of the same order as the hydrolysis (in water). For this reason the titration of uncharged weak acids or acid anions in alcohol offers no advantages over the same in water. If an uncharged acid is too weak to be titrated in aqueous medium it cannot be expected that better results will be obtained in alcohol. Experimentally this has been proved to be true. On the other hand, if we consider the titration of cation acids like ammonium salts with sodium hydroxide, it may be expected that such "replacement titrations" can be carried out in alcoholic medium in cases where the base formed is too strong to permit the titration in water. In Table I, it is seen that the dissociation constant of ammonium and other cation acids is only ten times or less smaller in alcohol than in water. Empirically applications of this fact have been made already; e.g. in the titration of ammonium salts, amino acids, polypeptides, alkaloid salts, in alcoholic medium with sodium ethylate (or sodium hydroxide) as a titrant using phenolphthalein, thymolblue or thymolphthalein as an indicator.

Since the dissociation constant of cation acids in alcohol is of the same order as that in water, it can be predicted that the titration of weak uncharged bases with hydrochloric acid in alcoholic medium has no advantages over the same procedure in water. On the other hand, replacement titrations of salts of weak acids with hydrochloric acid can be made in alcoholic medium, which do not give good results in aqueous medium. Suppose that sodium benzoate is titrated in alcoholic medium using hydrochloric acid as a titrant, and that at the equivalence point the concentration of the benzoic acid is equal to 0.1. The pH (p $C_2H_5OH\ H^+$) then is 5.9. At this pH methyl orange has still its alkaline color, its change to red starts at a pH of 4.;. For this reason salts of formic, acetic, benzoic, salicylic acid, etc. can be titrated in alcoholic medium using an alcoholic solution of hydrochloric acid as a titrant and methyl orange as an indicator. Experimentally this has been confirmed. Still the applicability of this type of titrations is rather limited as most salts are only slightly soluble in alcohol. Though this difficulty can be overcome by adding an excess of hydrochloric acid and back titrating with sodium ethylate, there is still another difficulty which makes the method impracticable, namely, that

---

[16] E. R. Bishop, E. B. Kittredge and J. H. Hildebrand, J. Am. Chem. Soc., 44, 135 (1922).

traces of water in the alcoholic solution make the indicator much less sensitive for an excess of strong acid. In 100% alcohol the sensitivity of methyl orange is of the same order as that in water; in 99% alcohol it is about sixteen times and in 95% alcohol about 125 times less sensitive for strong acids. The influence of traces of water upon the dissociation of acids in alcohol is extremely large (comp. paragraph 3) and must be considered in practical cases.

Summary. 1. From the work of H. Goldschmidt, Larsson and Michaelis and Mizutani, it has been calculated that ethyl alcohol is about 400 times as weak a base as water.

2. The dissociation constants of some indicators in pure alcohol have been determined.

3. The influence of the addition of traces of water upon the color of an indicator in alcoholic solutions of various types of acid-base systems has been discussed and investigated.

4. The color of pentamethoxy triphenylcarbinol in an alcoholic buffer solution changes very much toward the alkaline side by addition of traces of water. This exceptional behavior is explained by the pseudo-base character of the indicator.

5. The influence of alcohol upon the color of an indicator in aqueous solutions of various acid-base systems has been discussed and investigated. The color of an indicator acid in an aqueous buffer solution of an uncharged acid and its salt is hardly affected by alcohol, whereas the color of an indicator base changes strongly to the alkaline side. This behavior offers a simple method of deciding whether an indicator is an uncharged acid (or acid anion) or an uncharged base (cation acid).

6. The titration of weak uncharged acids or bases in alcoholic medium has no advantages over the titration in aqueous solution. On the other hand, salts of uncharged bases which are too strong to be titrated in aqueous medium can be titrated in alcoholic solution. Similarly salts of acids which are too strong to permit a titration in aqueous solution can be titrated in alcohol using an alcoholic solution of hydrochloric acid as a titrant and methyl orange as an indicator. The effect of traces of water upon the increase of the dissociation of weak acids in alcohol limits the practical applicability of this type of titration.

School of Chemistry,
University of Minnesota.
Minneapolis, March 1930.

A STUDY OF THE ZINC ELECTRODE

BY FREDERICK H. GETMAN

In our previous studies of the copper[1] and cadmium[2] electrodes it has been shown that single crystals of each of those metals function as constant and reproducible electrodes when immersed in solutions of their respective salts. The investigations of Anderson[3] and Straumanis[4] on the electrochemical behavior of single crystals of zinc have revealed a similar constancy and reproducibility in the electrode potential of that metal. Straumanis also pointed out that when a single crystal of zinc is split so as to expose definite cleavage planes to the solution in which it is immersed, the resulting difference of potential is identical with that which is developed when a polycrystalline electrode of pure zinc is immersed in the same solution.

Having previously used single crystals of copper and cadmium to determine the normal electrode potentials of those metals, it has seemed of interest to determine the electrode potential of zinc in a similar manner.

Relatively few determinations of the normal electrode potential of zinc have been made. Among the first to measure the electromotive force of zinc cells was Jahn[5] who studied the galvanic system,

$$\mathrm{Zn(amalgamated),\ ZnCl_2,(M)\ AgCl,\ Ag,}$$

in which the concentration of zinc chloride ranged from 0.556 to 2.22 M. Cells of the type,

$$\mathrm{Zn,\ ZnCl_2(M),\ AgCl,\ Ag,\ AgCl,\ ZnCl_2(M'),\ Zn,}$$

were investigated by Goodwin,[6] the concentrations of the zinc salt ranging from 0.001 to 0.2 M.

The first accurate determination of the normal electrode potential of zinc was made by Horsch[7] who made use of cells of the type,

$$\mathrm{Zn,\ ZnCl_2(M),\ AgCl,\ Ag,}$$

the concentration of zinc chloride ranging from 0.0003 to 0.01 M. Basing his calculations upon the best available conductivity data for solutions of zinc chloride he found the normal electrode potential of zinc to be 0.758 ± 0.002 volt at 25°C.

Quite recently the electromotive force of a similar cell has been measured by Scatchard and Tefft[8] at 25° with concentrations of zinc chloride ranging from 0.003 to 1.5 M. From their measurements they find for the cell

---

[1] Getman: J. Phys. Chem., 34, 1454 (1930).

[2] Getman: J. Phys. Chem., 35, 588 (1931).

[3] Anderson: J. Am. Chem. Soc., 52, 1000 (1930).

[4] Straumanis: Z. physik. Chem., 47, 161 (1930).

[5] Jahn: Wied. Ann., 28, 21, 491 (1886).

[6] Goodwin: Z. physik. Chem., 13, 577 (1894).

[7] Horsch: J. Am. Chem. Soc., 41, 1787 (1919).

[8] Scatchard and Tefft: J. Am. Chem. Soc., 52, 2272 (1930).

$$ZnHg(2\ phase),\ ZnCl_2(M),\ AgCl,\ Ag,$$

$E_0 = 0.9834$ volt. On combining this value with Cohen's value of 0.0006 volt for the difference of potential between pure zinc and the two-phase amalgam[1] and Scatchard's value of −0.2224 volt for the potential of the silver-silver chloride electrode,[2] they obtained for the normal electrode potential of zinc,

$$Zn,\ Zn^{++},\ E_0 = 0.7616\ \text{volt}.$$

In the present investigation the cells employed were set up according to the scheme

$$Zn,\ ZnCl_2(M),\ Hg_2Cl_2,\ Hg,$$

with concentrations of zinc chloride ranging from 0.002 to 1.0 M. Relatively few measurements of the electromotive force of this particular galvanic combination appear to have been made.

Experimental

Materials. The single crystals of zinc were prepared for the writer by Mr. J. H. Dillon of the physics department of the University of Wisconsin according to the method which he has developed for the preparation of single crystals of metals of relatively low fusibility.[3] The zinc used in making these crystals was of a high degree of purity.

The polycrystalline electrodes were made either from very pure zinc supplied by Merck, or from a sample of so-called "spectroscopic" zinc kindly furnished the writer by Mr. H. M. Cyr of the research staff of the New Jersey Zinc Co. and guaranteed to be 99.999% pure.

The granulated zinc from which the zinc chloride was prepared was obtained from Merck and was of the grade supplied for forensic analysis.

All of the other materials employed in making up the cells were prepared as described in our previous papers treating of the copper and cadmium electrodes.[4]

Preparation of Electrolyte. The mother solution of zinc chloride was prepared by dissolving Kahlbaum's granulated zinc in a solution of pure hydrochloric acid. The latter was prepared by slowly dropping pure concentrated sulphuric acid into a solution of pure hydrochloric acid and absorbing the resulting gaseous hydrochloric acid in conductivity water until an acid of approximately 0.5 molal was obtained. An excess of granulated zinc was then added to the acid and the mixture warmed gently on the water-bath until the metal ceased to dissolve. The solution was then filtered to remove the remaining particles of zinc and diluted to a concentration approximating 1 M. After transferring to a glass-stoppered flask, the solution was allowed to stand for some days in contact with a small piece of zinc to insure against excess

---

[1] Cohen: Z. physik. Chem., 34, 612 (1900).

[2] Scatchard: J. Am. Chem. Soc., 47, 2098 (1925).

[3] Dillon: Rev. Sci. Inst., 1, 36 (1930).

[4] Loc. cit.

acidity. The concentration of the solution was finally established by gravimetric determination of its chlorine content as silver chloride and volumetric determination of its zinc content by means of standard potassium ferrocyanide The concentration thus determined was found to be 1.0375 molal.

Apparatus. The apparatus employed was the same as that used in our previous studies of electrode potentials and the same experimental procedure was followed in setting up the cells and measuring their electromotive force.

Electromotive Force Measurements

The cells were immersed in an electrically heated and controlled thermostat bath, set at 25° ± 0.02°, and sufficient time was allowed for the establishment of thermal equilibrium before any measurements were made. Readings were taken at frequent intervals over a period of six hours, it having been previously observed that no appreciable deterioration of the cells is likely to occur during that interval of time. The tendency to erratic fluctuations in electromotive force which was noted in our study of the cadmium electrode was also observed with polycrystalline electrodes of zinc, but to a less degree. Single crystal electrodes of zinc were, in general, found to resemble single crystal electrodes of copper and cadmium in tending to give rise to a greater difference of potential than the corresponding polycrystalline electrodes. The difference, however, was of the same order of magnitude as the experimental error and therefore, no attempt has been made to distinguish between the potentials of the two types of electrode. Cells in which the concentration of the electrolyte was less than 0.005 M were found to deteriorate so rapidly that measurements at lower concentrations could not be made with any degree of satisfaction.

TABLE I

E.M.F. of the Cell, Zn, $ZnCl_2(M)$, Hg_2Cl_2, Hg(25°)

m (mols $ZnCl_2$/1000 g. H_2O)	E′	E
0.00200	1.24497	—
0.00500	1.2244	1.2244
0.01000	1.20350	1.2035
0.01999	1.18000	1.1800
0.03000	1.16765	1.1677
0.05003	1.14743	1.1500
0.10019	1.13077	1.1285
0.15047	1.11717	—
0.20000	—	1.1070
0.25148	1.10085	—
0.35339	1.08960	—
0.50000	—	1.1078
0.50786	1.07816	—
0.76770	1.06489	—
1.00000	—	1.0573
1.0375	1.05679	—

The experimental data are summarized in Table I, where m denotes the concentration in mols per 1000 grams of solvent and where E′ is the electromotive force in volts. As has been pointed out, the differences in the electromotive force of cells with single crystal and polycrystalline electrodes were too uncertain to warrant separate tabulation. The values assigned to E′ in the table represent the mean of forty or more measurements of the electromotive force of a series of cells among which two contained single crystal electrodes.

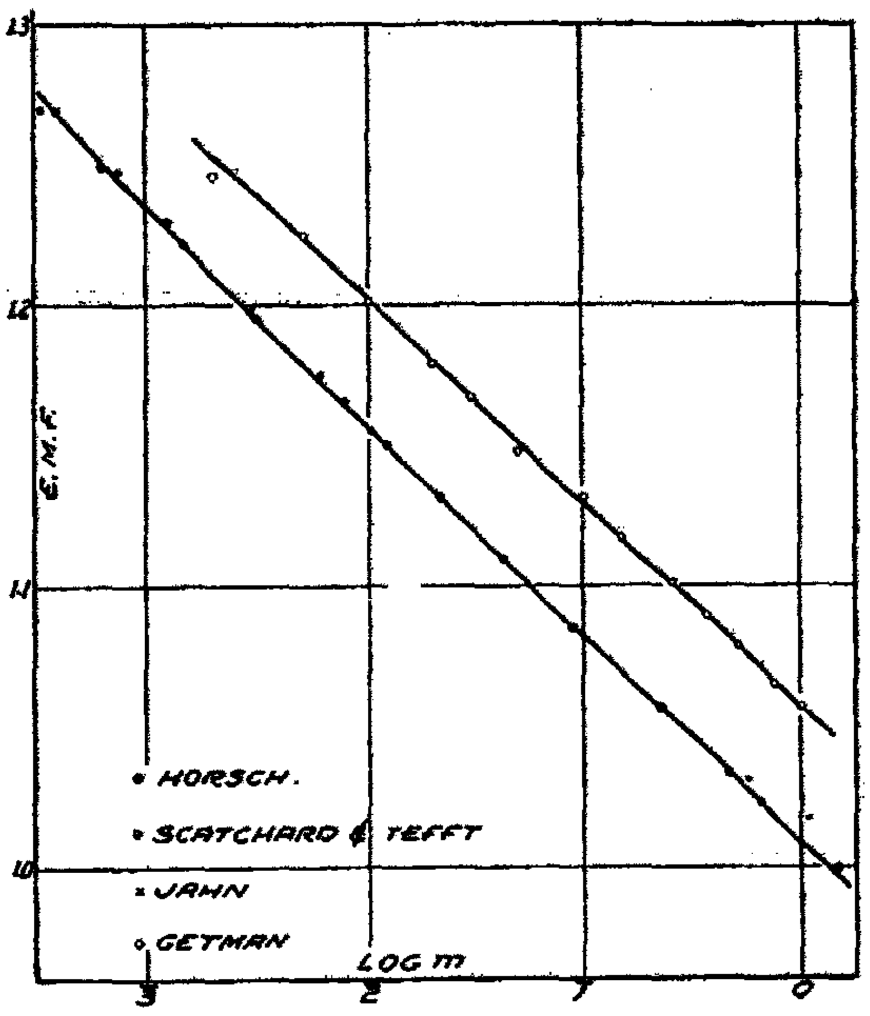


Fig. 1

The values of E′ in foregoing table together with the experimental data of Jahn, Horsch, and Scatchard and Tefft obtained with cells of the type

$$\text{Zn, ZnCl}_2\text{(M), AgCl, Ag(25°)}$$

are shown graphically in Fig. 1. From a similar plot drawn on a large scale the smoothed values of the electromotive force, E, given in the last column were obtained.

Calculation of Results

The electromotive force of the cell

$$\text{Zn, ZnCl}_2\text{(M), Hg}_2\text{Cl}_2\text{, Hg,}$$

is represented by the equation

$$E = E'_0 - RT/nF \ln(4m^3\gamma^3), \qquad (1)$$

where E denotes the measured electromotive force of the cell, E_0' the normal electrode potential of the cell, m the concentration of the electrolyte in mols per 1000 grams of solvent and γ the activity coefficient. The symbols R, T, n and F have their usual significance. On simplifying and transforming to common logarithms (1) becomes

$$E = E_0' - 0.08873 \log (1.588\, m\gamma). \qquad (2)$$

According to Randall[1] equation (2) may be written in the form

$$\log \gamma - \frac{E_0'}{0.08873} = -\left[\frac{E}{0.08873} + 0.2207 + \log m\right], \qquad (3)$$

If the right-hand side of equation (3) is plotted against the square-root of the ionic strength, $\mu^{\frac{1}{2}}$, and the resulting curve is extrapolated to zero-concentration, the value of E_0' can then be readily calculated by means of equation (3).

In order to employ this method, however, it is necessary to know the values of E corresponding to the region of smaller concentrations of the electrolyte where, as has been pointed out, satisfactory results cannot be obtained with the galvanic combination employed. In fact, the only available data for very dilute solutions of zinc chloride are those recorded by Horsch[2] and even those are not of a high order of accuracy. Horsch points out that because of the lack of reproducibility of the electromotive force of cells in which the electrolyte is very dilute he was unable to extend his measurements below 0.0003 molal, and in concentrations below 0.001 molal the deviations of the individual observations from the mean was as much as 0.002 volt.

Applying Randall's method for the determination of E_0' to the measurements of Horsch, the data given in Table II are obtained.

TABLE II

Data derived from Measurements of Horsch

m	$\mu^{\frac{1}{2}}$	E	$E/0.08873 + 0.2007 + \log m$
0.0003478	0.03241	1.2710	11.0660
0.0003995	0.03463	1.2660	11.0702
0.000649	0.04413	1.2497	11.0969
0.000772	0.04771	1.2440	11.1083
0.001253	0.06131	1.2272	11.1286
0.001453	0.06603	1.2219	11.1350

On plotting the figures given in the fourth column against the square-root of the ionic strength, the curve is found to intersect the axis of zero concentration at 11.039. On substituting this value in equation (3) we find $E_0' = 0.9800$. The potential of the silver-silver chloride electrode, as given in the International Critical Tables, is

$$\text{Ag, AgCl, Cl}^-, E_0 = -0.2221 \text{ volt,}$$

---

[1] Randall: Trans. Faraday Soc., 23, 505 (1927).

[2] Loc. cit.

and therefore the normal electrode potential of zinc, as derived from Horsch's measurements, is

$$Zn, Zn^{++}, E_0 = 0.7579 \text{ volt.}$$

As has already been stated, Horsch computed the electrode potential to be $E_0 = 0.758$ volt, making use of conductivity data.

If we accept $E_0 = 0.758$ volt, as the normal electrode potential, as derived from Horsch's data by two different methods, the activity coefficients of zinc chloride may be calculated by means of equation (2), and from these in turn the value of E'_0 for the cell,

$$Zn, ZnCl_2(M), Hg_2Cl_2, Hg,$$

can be computed as shown in Table III.

TABLE III

Evaluation of E'_0 for the Cell, Zn,$ZnCl_2$ (M), Hg_2Cl_2, Hg (25°)
(Activity Data derived from Horsch)

m	E	γ	E'_0	E_0
0.0005	1.2605	0.880	—	—
0.001	1.2356	0.857	—	—
0.002	1.2108	0.797	—	—
0.005	1.2244	0.723	1.0255	0.758
0.01	1.2035	0.680	1.0281	0.761
0.02	1.1800	0.619	1.0286	0.761
0.05	1.1500	0.533	1.0281	0.761
0.1	1.1285	0.486	1.0289	0.761
			Mean	0.760

The values of E_0 tabulated in the last column of the table are derived from the corresponding values of E'_0 in the preceding column by subtracting the potential of the mercury-mercurous chloride electrode.

$$Hg, Hg_2Cl_2, Cl^-, E_0 = 0.2676 \text{ volt,}$$

as given in the International Critical Tables.

In their paper treating of electromotive force measurements with zinc chloride, Scatchard and Tefft[1] have computed the values of the activity coefficients from 0.0001 to 1.5 molal. On substituting their values of γ in in equation (2), together with the corresponding values of E given in Table I, another set of values of E'_0 and E_0 can be computed. In this manner the data recorded in Table IV have been obtained.

The mean value of E_0 calculated from the activity data of Scatchard and Tefft is slightly greater than that derived from data based upon the electromotive force measurements of Horsch.

---

[1] loc. cit., p. 2281.

TABLE IV

Evaluation of E_0' for the Cell, Zn, Zn Cl_2(M), Hg_2Cl_2, Hg (25°)
(Activity Data derived from Scatchard and Tefft)

m	E	γ	E_0'	E_0
0.005	1.2244	0.767	1.0279	0.760
0.01	1.2035	0.708	1.0297	0.762
0.02	1.1800	0.642	1.0300	0.762
0.05	1.1500	0.556	1.0297	0.762
0.1	1.1285	0.502	1.0301	0.762
0.2	1.1070	0.448	1.0319	0.764
0.5	1.0780	0.376	1.0314	0.764
1.0	1.9573	0.325	1.0309	0.763
			Mean	0.762

In a discussion of the available methods for the extrapolation of electromotive force data to infinite dilution, Randall and Young[1] have emphasized the experimental difficulties involved in securing reproducible measurements in extremely dilute solutions and have suggested that the solubility of the glass of which the cells are made is probably sufficient to vitiate all electromotive force data pertaining to extremely dilute solutions. To overcome this difficulty, Hitchcock[2] has recently proposed a method for the extrapolation of electromotive force data to unit ionic activity based upon a partially expanded form of the familiar Debye-Hückel equation.

According to this method when $E_0' - 0.155\sqrt{c}$ is plotted against $\sqrt{m}$, where c denotes the molar concentration, the resulting curve should approach a straight line asymptotically in the region of small concentrations. Hence, if a straight line is thus obtained over the range of concentrations where experimental data are trustworthy, a linear extrapolation to zero concentration may be made with considerable confidence. Employing the interpolation formula

$$c/m = 0.99707 - 0.0134\ m - 0.0129\ m^2 + 0.0288\ m^3,$$

derived by Scatchard and Tefft from the density tables given in the International Critical Tables, to compute the values of c corresponding to the values of m given in Table IV, and plotting the values of $E_0' - 0.155\sqrt{c}$ against $\sqrt{m}$, the value of E_0' at infinite dilution was determined as shown in Fig. 2. The value of E_0', as read from the plot, is 1.300 and, therefore, the value of E_0 is

$$E_0 = 1.0300 - 0.2676 = 0.7624 \text{ volt}.$$

This value will be seen to agree substantially with the mean value of E_0 given in Table IV. Taking the average of the latter with the two preceding calculated values for E_0 we obtain as the normal electrode potential of zinc.

$$\text{Zn, Zn}^{++},\ E_0 = 0.7613 \text{ volt}$$

---

[1] Randall and Young: J. Am. Chem. Soc., 50, 989 (1928).

[2] Hitchcock: J. Am. Chem. Soc., 50, 2076 (1928).

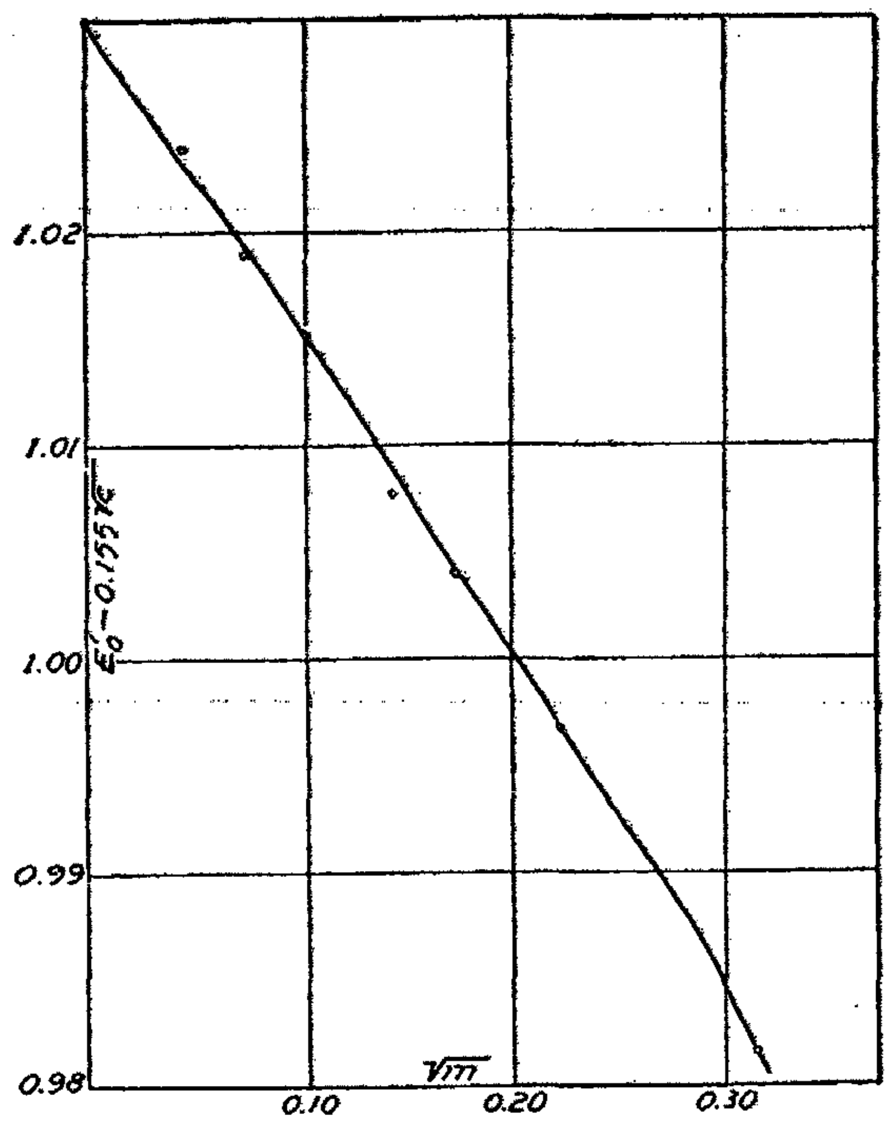


Fig. 2

Summary of Results

(1) The electromotive force of the cell

$$\text{Zn, ZnCl}_2\text{(M), Hg}_2\text{Cl}_2\text{, Hg (25°)}$$

has been measured with concentrations of zinc chloride ranging from 0.002 to 1.0 M.

(2) Electrodes of pure zinc in the form of both single crystals and polycrystalline aggregates have been employed.

(3) The single crystal electrodes were found to resemble single crystals of copper and cadmium in exhibiting a tendency to develop a difference of potential toward the electrolyte slightly greater than that developed by the polycrystalline electrodes. The differences, however, being of the same order of magnitude as the experimental error no attempt has been made to differentiate between them.

(4) The normal electrode potential of zinc has been computed from the electromotive measurements of the cell by three different methods as follows:

(a) By substituting the values of γ derived from the measurements of Horsch in the equation

$$E = E' - 0.08873 \log (1.588\, m\gamma),$$

the resulting value of E_o being 0.760 volt;

(b) By substituting the values of γ derived by Scatchard and Tefft in the same equation, the resulting value of E_o being 0.762 volt;

(c) By plotting $E_o' - 0.155\sqrt{c}$ against $\sqrt{m}$, as proposed by Hitchcock, and noting the value of E_o determined by the intersection of the resulting curve with the axis of zero concentration. This was found to be 0.762 volt.

(5) The average of these three results has been taken as representing the probable value of the normal electrode potential of zinc as derived from electromotive force measurements of the cell employed, viz.,

$$Zn, Zn^{++}, E_o = 0.7613 \text{ volt.}$$

Hillside Laboratory,
Stamford, Conn.

THE CALCULATION OF EQUILIBRIUM CONCENTRATIONS IN ADSORPTION FROM LIQUIDS

BY WM. ROGERS, JR. AND M. D. SCLAR

The Freundlich adsorption isothermal is

$$x/m = kc_2^n \qquad (1)$$

x = amount of solute adsorbed

m = mass of adsorbent

c_2 = equilibrium concentration of solute

k and n are empirical constants for a given solute, solvent and adsorbent.

In the above form the adsorption isothermal does not provide for a calculation of c_2 and x in the case of a solution of known initial concentration, c_1, volume, V, and m.

Freundlich has suggested the use of the following equation for this purpose:

$$\lambda = \frac{V}{m} \log \frac{y}{y - x} \qquad (2)$$

y = number of millimols of solute in solution before adsorption

x = number of millimols of solute adsorbed

λ = an empirical constant

There are objections to the use of equation (2) in calculating equilibrium concentrations.

First, λ is a constant for only one given initial concentration, that is, it varies with the initial concentration, y/V, and is connected with it by the equation, $\lambda = B\ (y/V) - 1/p$ where B and $1/p$ are empirical constants for a given system.

Secondly, Freundlich says that equation (2) holds because n in equation (2) is generally only slightly different from 0.5 and because the experiments are performed in such a way that about 50% of the solute is adsorbed. However, the average n of 26 systems, in which the solutes are non-dissociated, is 0.37.[1] Also the average n of 23 systems, in which the solvent is water, and the solute an electrolyte, is 0.25.[2] In addition, the use of equation (2) is too limited if the application must be confined to cases in which 50% adsorption takes place.

Mecklenburg's method of calculating the equilibrium concentration from the initial concentration[3] requires a different isothermal for each combination

---

[1] Freundlich, translated by Hatfield: "Colloid and Capillary Chemistry," 3rd Ed., p. 175, Table 59.

[2] Freundlich, translated by Hatfield: "Colloid and Capillary Chemistry," 3rd Ed., p. 202, Table 71.

[3] Freundlich, translated by Hatfield: "Colloid and Capillary Chemistry," 3rd Ed., p. 178.

of volume and amount of adsorbent. Hence, this method is even less general than the method involved in equation (2).

Our object is now to describe a general method by which the Freundlich isothermal may be used, for any case which the isothermal describes, to calculate the equilibrium concentration of the solute in a solution, and therefrom to calculate the amount of solute adsorbed, when the initial concentration of the solute, the volume of solution, and mass of adsorbent are known. The general method of transformation of the isothermal into the final form in which it will be used is independent of the units used in the isothermal. The details will vary with the particular set of units used. A representative transformation will now be shown.

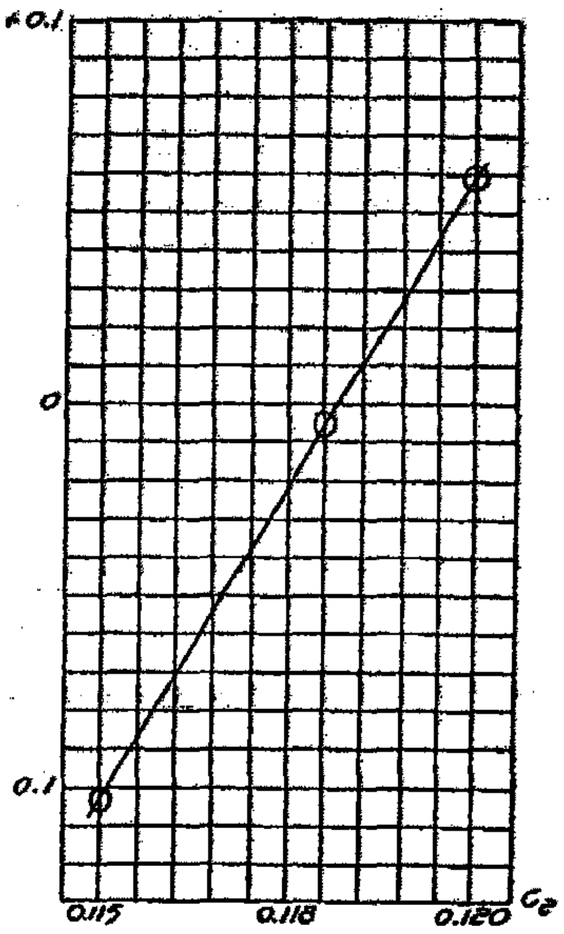


Fig. 1
Calculation of Equilibrium Concentrations in Adsorption from Liquids

$$x/m = kc_2^n \dots\dots (1)$$

If x is expressed in millimols, m in grams, V in liters, and c_1 and c_2 in mols per liter,

$$x = V(c_1 - c_2)\ 1000 \dots\dots (3)$$

Substituting this value of x into equation (1)

$$\frac{1000\ V\ (c_1 - c_2)}{m} = kc_2^n$$

or

$$\frac{1000\ V}{mk}\ (c_1 - c_2) = c_2^n$$

But $\frac{1000\ V}{mk}$ is composed of known factors and is constant for each experiment. Represent it by A. Then

$$A(c_1 - c_2) = c_2^n$$

and

$$Ac_1 - Ac_2 = c_2^n$$

and

$$c_2^n + Ac_2 - Ac_1 = 0 \dots\dots (4)$$

To solve equation (4) for c_2 set the left hand member of (4) equal to z. Assign values to c_2 (the upper limit of c_2 being c_1) and find the corresponding values of z. Plot these data, taking abscissas for c_2 and ordinates for z. Where the curve cuts the c_2 axis, z equals zero. Hence this value of c_2 satisfies equation (4) and thus is the equilibrium concentration. The construction is facilitated by the fact that the curve is a straight line. Equation (3) may now be used to get x.

The validity of equation (4) is seen in the following data in which observed and calculated equilibrium concentrations are compared. The data covers both non-dissociated and dissociated solutes and various combinations of units. The graph used in calculating c_2 (Table I) is pictured in Fig. 1.

TABLE I[1]

Adsorption of Benzoic Acid in Benzene on Blood Charcoal

$k = 3.243$ $n = 0.396$ $t = 25°$

V	m	c_1	c_2 (observed)	c_2 (calculated)
0.1 l	1.0 g	0.1321 mol/l	0.1177 mol/l	0.1182 mol/l

TABLE II[1]

Adsorption of Acetic Acid in Water on Blood Charcoal

$k = 2.630$ $n = 0.425$ $t = 25°$

V	m	c_1	c_2 (observed)	c (calculated)
0.051	1.234 g.	0.13035 mol/l.	0.10420 mol/l.	0.1054 mol/l

TABLE III[2]

Adsorption of Benzene in Ethyl Alcohol on Pure Carbon

$k = 9.79$ $n = 0.53$

c_1 Mol Frac.	$\frac{H(c_1-c_2)}{m}$ (obs'd) Millimols/g	c_2 (observed) mol. fraction	c_2 (calc'd) mol. fraction
0.00653	0.521	0.00513	0.00496
.02604	1.123	.02289	.0228
.1090	2.022	.1033	.1015

TABLE IV[2]

Adsorption of Ethyl Carbonate in Ethyl Alcohol on Pure Carbon

$k = 4.9$ $n = 0.72$

c_1 mol. frac.	$\frac{H(c_1-c_2)}{m}$ (obs'd) millimols/g	c_2 (obs'd) mol. frac.	c_2 (calc'd) mol. frac.
0.00339	0.084	0.00323	0.00324
.0142	.24	.0136	.0137
.0610	.566	.0596	.0594

The equation used in calculating c_2 in Tables III and IV is

$$c_2^n + Ac_2 - Ac_1 = 0, \text{ in which}$$

---

[1] Data in Tables I and II obtained from Freundlich, translated by Hatfield: "Colloid and Capillary Chemistry," 3rd Ed., p. 175, 176; Tables 57, 58, 59, 60.

[2] Data in Tables III and IV obtained from paper of F. E. Bartell and C. K. Sloan: J. Am. Chem. Soc. 51. 1640-41, (1929), Tables II and III.

$$A = \frac{H}{mk} = \frac{H(c_1 - c_2)}{m} \cdot \frac{1}{k(c_1 - c_2)}$$

This last step shows how the numerical value of A was determined from the data presented in the reference indicated.

The data presented by F. E. Bartell and C. K. Sloan for the system bromonaphthalene, ethyl alcohol, and carbon, was not used because the values for c and x (using their notation) were not consistent in the table given. Apparently the x in this case is Δx.

TABLE V[1]

Adsorption of Calcium Hydroxide by Basic Calcium Phosphate

$k = 0.0226$ $n = 0.31$ $t = 25°$
$m = 0.8614$ g. in each bottle
$V = 224.69$ c.c. in each bottle

c_1 g/l	c_2 (observed) g/l	c_2 (calculated) g/l
0.6706	0.5910	0.5967
.1514	.1130	.1080
.0470	.0207	.0209

TABLE VI[1]

Adsorption of Calcium Hydroxide by Tricalcium Phosphate

$k = 0.0342$ $n = 0.17$ $t = 25°$
$m = 0.3838$ g. in each bottle
$V = 224.69$ c.c. in each bottle

c_1 g/l	c_2 (observed) g/l	c_2 (calculated) g/l
0.2848	0.2388	0.2390
.0699	.0348	.0366
.0188	.0011	.0009

TABLE VII[2]

Adsorption of Sulphuric Acid on Wool

$k = 0.237$ $n = 0.38$
$m = 1$ g. wool in each case
$V = 250$ c.c. in each case

c_1 millimols/250 cc.	c_2 (observed) millimols/250 cc.	c_2 (calculated) millimols/250 cc.
0.16	0.09	0.07
0.23	0.13	0.12
0.61	0.43	0.43
4.60	4.18	4.19

---

[1] Data in Tables V and VI obtained from J. R. Lorah, H. V. Tartar, and Lillian Wood: J. Am. Chem. Soc., 51, 1103, (1929), Table II.
k and n were calculated from the complete data given.

[2] Data in Table VII obtained from W. W. Paddon: J. Phys. Chem., 33, 1107 (1929). Table I.
k and n were calculated from the complete data given.

TABLE VIII[1]

Adsorption of Sodium Hydroxide on Silica Jell

$k = 6.34$ $n = 0.37$

c_1 mols/l	c_2 (obs'd.) mols/l	x/m (obs'd.) millimols/g	m (calc'd.) (g)	c_2 (calc'd.) mols/l
0.0127	0.0000	0.29	43.8	0.0001
0.0264	0.0016	0.58	42.8	0.0016
0.0371	0.0036	0.77	43.5	0.0035
0.1325	0.0447	2.02	43.5	0.0450

Since the volume of solution and mass of adsorbent were not given in the reference from which the date in Table VIII was obtained, the volume was taken as one liter in each case and then the mass of adsorbent necessary to cause the indicated adsorption was calculated from the corresponding value of x/m.

$$m = 1000\,(c_1 - c_2).m/x$$

The constants given in Table VIII are not those given in the reference from which the data was obtained. The former are good when c_1 and c_2 are expressed in mols per liter and x/m in millimols per gram. The latter are good when c_1 and c_2 are expressed in mols per liter and x/m in mols per gram, although x/m in the reference was expressed in millimols per gram.

Summary. A method has been presented for transforming the Freundlich adsorption isothermal to a form in which it may be used to calculate the equilibrium concentration and amount adsorbed in the case of a solution of given initial concentration and with known quantity of adsorbent and known volume. Data have been presented which shows the method of transformation is valid for those systems for which the Freundlich adsorption isothermal holds. The method may be used for any units.

Chemistry Department,
Temple University,
Philadelphia.

---

[1] Data in Table VIII obtained from W. A. Patrick and E. H. Barclay: J. Phys. Chem., 29, 1401 (1925), Table I.

THE EFFECT OF SOME IONS ON THE TRANSFORMATION OF ORANGE ANTIMONY TRISULFIDE TO THE BLACK FORM

BY LEO LEHRMAN

In the course of some work it was noticed that orange Sb_2S_3 which had been kept under water for about five months in a glass-stoppered bottle, had completely changed to a dull black color. The Sb_2S_3 had been prepared by bubbling H_2S through an acid (HCl) solution of $SbCl_3$ until there was no more precipitation. The precipitate was washed by allowing the solid to settle, pouring off most of the clear liquid on top, adding 5% NH_4NO_3 solution, stirring well and after standing long enough for the solid to settle, most of the clear liquid on top was again poured off. This procedure was repeated twice using water, and finally the Sb_2S_3 was suspended in water in a glass stoppered bottle. The solution still contained a small amount of NH_4NO_3 and H_2S. Qualitative tests[1] showed the black substance to be antimony sulfide.

Several investigators[2] had studied the change of orange Sb_2S_3 to the black form.

Under the normal laboratory conditions the orange form of Sb_2S_3 is precipitated by H_2S, but under special conditions[3] or by some further treatment[4] the black compound is formed either directly or from the orange sulfide. Also on standing for some time in the presence of certain substances, as stated above, the orange form changes to the black compound. This indicates that the black Sb_2S_3 is the stable form. This fact apparently explains the occurrence in nature of Sb_2S_3 in the black form as stibnite.

That certain substances can act catalytically in the transformation of the orange to the black form has been shown.[5] However, no study has been made of the effect of various ions on this change. It would be of value to know what ions influence the transformation and how they compare in their effect. It was with this objective that this work was carried out.

Experimental

A definite amount of Sb_2S_3 (orange) was made as stated above and suspended in a known volume of water. The solution still contained a small amount of H_2S and NH_4NO_3. 20 cc. samples of the well shaken mixture

---

[1] Soluble in $(NH_4)_2S_x$ and reprecipitation as the orange sulfide by acidification; soluble in HCl with evolution of H_2S; insoluble in tartaric acid (not antimony).

[2] Vortmann and Metzl: Z. anal. Chem., 44, 525 (1905); deBacho: Ann. chim. applic., 12, 143 (1919); Wilson and McCrosky: J. Am. Chem. Soc., 43, 2178 (1921); Currie: J. Phys. Chem., 30, 205 (1926).

[3] Vortmann and Metzl: Z. anal. Chem., 44, 525 (1905); deBacho: Ann. chim. applic., 12, 143 (1919).

[4] de Bacho: Ann. chim. applic., 12, 143 (1919); Wilson and McCrosky: J. Am. Chem. Soc., 43, 2178 (1921); Currie: J. Phys. Chem., 30, 205 (1926).

[5] deBacho: Ann chim. applic., 12, 134(1919); Wilson and McCrosky: J. Am. Chem. Soc., 43, 2178(1921).

TABLE I

Room Temperature

	Final Concentration of Solution added	Extent of Transformation	Time noted
1.	.1N CH_3COOH	Unchanged	1.5 years
2.	.1N HCl	"	"
3.	.1N H_2SO_4	"	"
4.	.1N HNO_4	"	"
5.	.1N CH_3COONa	"	"
6.	.1N $NaCl$	"	"
7.	.1N Na_2SO_4	"	"
8.	.1N $NaNO_3$	"	"
9.	.1N CH_3COONH_4	"	"
10.	.1N NH_4Cl	"	"
11.	.1N $(NH_4)_2SO_4$	"	"
12.	.1N NH_4NO_3	"	"
13.	Water	"	"
14.	Small amount of $NH_4NO_3+H_2S$	Complete	5 months
15.	Small amount of H_2S	Complete	2 months, 16 days

(equal to 200 mg. Sb as Sb_2S_3) were alternately centrifuged and washed with water till all the dissolved material present had been washed out. This was indicated by a slight turbidity in the top water after centrifuging due to the Sb_2S_3 going into colloidal solution. The washed Sb_2S_3 was put into bottles, a definite amount of solution of known concentration added, the volume made up to 100 cc. and stoppered well. In one set of experiments the bottles were allowed to stand at room temperature while in another series they were put in a Freas oven at 75°C. and the time noted for the orange Sb_2S_3 to change to a black color.

In Experiment 14 the Sb_2S_3 was not washed with water to remove dissolved substances so that it contained a small amount of NH_4NO_3 and H_2S. In Experiment 15 the Sb_2S_3 was only washed with water twice after complete precipitation (see introduction) so that it only contained a small amount of H_2S.

Experiment 29 was carried out, except for the different temperature, exactly as Experiment 15 above.

In all cases the colloidal Sb_2S_3 precipitated after a few days except in the experiments using water (Nos. 13 and 28) which took several days longer. The change in color of all the orange Sb_2S_3 was not sudden. As the black variety forms it sinks to the bottom showing it has a higher specific gravity than the orange form. When most of the orange Sb_2S_3 has become black, the remainder goes through a series of color changes, i.e., orange, reddish brown, dark brown and finally black. This gradual change in color is not apparent when there is a large amount of the orange Sb_2S_3 present. The

TABLE II

75°C.

	Final Concentration of Solution added	Extent of Transformation	Time noted
16.	.1N CH_3COOH	Complete	5 months
17.	.1N HCl	"	4 months, 21 days
18.	.1N H_2SO_4	"	4 months, 26 days
19.	.1N HNO_3	"	4 months, 15 days
20.	.1N CH_3COONa	Unchanged	1 year
21.	.1N $NaCl$	Nearly complete	1 year
22.	.1N Na_2SO_4	Slight change	1 year
23.	.1N $NaNO_3$	Complete	1 year
24.	.1N CH_3COONH_4	Slight change	1 year
25.	.1N NH_4Cl	" "	1 year
26.	.1N $(NH_4)_2SO_4$	" "	1 year
27.	.1N NH_4NO_3	Nearly complete	1 year
28.	Water	Complete	10 months
29.	Small amount of H_2S	"	2 months

color of the black Sb_2S_3 is not always the same; in some cases it was dull while in others it had a slight metallic lustre. In Experiment 15 there were two layers of the black variety, the top was dull black while the bottom had a purplish tinge.

Discussion of Results

It can be seen from a comparison of the results in the two tables that increased temperature hastens the change from the orange to the black form. The change in color is gradual and is not noticeable at first due to the large amount of orange Sb_2S_3 masking the small amount of different colored forms. The result obtained in Experiment 15 suggests the possibility of there being more than one modification of the black form.

If the results obtained using water (Experiments 13 and 28) are taken as a basis for comparison, $S^{=}$ and H^+ hasten the transformation, $S^{=}$ to a greater extent. Similarly, for the other ions there is a retarding effect in the following increasing order for the negative ions: $NO_3^- < Cl^- < SO_4^{=} < C_2H_3O_2^-$., and for the positive ions: $Na^+ < NH_4^+$.

Summary

Increase of temperature hastens the change of orange Sb_2S_3 in contact with water and various ions to the black form.

The change to the black form is not direct but gradual, passing through stages as shown by various colors.

The order in which the ions hasten the change is as follows:

Negative ions; $S^{=} > \text{water} > NO_3^- > Cl^- > SO_4^{=} > C_2H_3O_2.^-$

Positive ions; $H^+ > \text{water} > Na^+ > NH_4^+$

College of the City of New York,
New York City.

NEW BOOKS

A Text-Book of Inorganic Chemistry. *Edited by J. Newton Friend Vol. VII, Part 2. 23 × 16 cm; pp. xxviii + 420. London and Philadelphia; Charles Griffin and Company; J. B. Lippincott Company, 1931. Price: $14.00.* This volume deals with sulphur, selenium and tellurium. In the preface, p. xi, the author says: "Of the three examples dealt with in this volume, two are of comparatively recent discovery, the existence of tellurium being recognised only in 1798 and that of selenium about twenty years later. Sulphur has been known from antiquity, and there is evidence that its inflammable and fumigating properties were made use of 3000 years ago; by the alchemists it was regarded as the 'principle of inflammability' and included as one of their *tria prima*; to the phlogistonists it was a compound of phlogiston and sulphuric acid; Lavoisier, in 1777, however, showed it to be a true element, and to-day it is undoubtedly recognised as one of the most important. . . . Probably in no direction has sulphur influenced the general public more widely and directly than in connection with methods of transport, which have been revolutionised by the introduction of sulphur-vulcanised rubber as a wear-resisting, shock-absorbing material for the equipment of wheels of motor vehicles."

The actual writers of this volume are R. H. Vallance, D. F. Twiss and Miss Annie R. Russell. The chapters are entitled: general characteristics of the elements of group VI, subdivision B; sulphur; compounds of sulphur; selenium; compounds of selenium; tellurium; compounds of tellurium.

"In the free or 'native' condition sulphur is found abundantly in volcanic districts, for example in Sicily, Italy, Louisiana, Mexico, Texas and Alaska; smaller quantities occur in Japan, Greece, Austria, Hungary, Germany, France, Spain and elsewhere. The element occurs sometimes in well-formed crystals, but more commonly is mixed with other mineral matter such as calcium sulphate (gypsum), strontium sulphate (celestine) and rock salt. An orange-red variety of native sulphur peculiar to Japan owes its colour to the presence of small quantities of tellurium and selenium, whilst a black pyritic sulphur containing traces of carbon occurs in Mexico and South Spain, in the latter case being found in fantastic fountain-like formation," p. 8.

"In many coal- and oil-gas works in the Western States of America the Koppers process for the removal of hydrogen sulphide from the gas is employed. This consists of passing the gas up towers filled with wooden hurdles over which a dilute sodium carbonate solution is sprayed. The following reaction occurs:

$$Na_2CO_3 + H_2S = NaHCO_3 + NaHS;$$

the sulphur is then recovered from the solution by agitation in intimate contact with air in an emulsifying machine, a catalyst also being present:

$$NaHCO_3 + NaHS + \frac{1}{2}O_2 = S + Na_2CO_3 + H_2O.$$

The catalyst used is colloidal nickel sulphide. The sulphur is run off from the surface, and after filtering and washing is obtained as a paste containing 55 per cent. of water. After drying, a product is obtained which is more toxic than most other forms of sulphur and is very effective in agricultural work as a fungicide; the particles are almost of colloidal size, most being less than 15μ," p. 11.

"Sulphur is applied, commonly in the powdered form or as 'flowers of sulphur,' to medicinal purposes, and also agriculturally as a dust or dressing to check fungoid diseases of certain plants, especially the vine. The toxic properties of sulphur have not been fully elucidated and are variously ascribed to reduction to hydrogen sulphide, oxidation to polythionic acids, or to the vapour of the element itself, produced by slow vaporisation. If adsorbed pentathionic acid be removed from sulphur by means of ammonia, the sulphur loses its toxicity but regains it if suspended in water and exposed to air.

"The element has a definite fertilising action which is exerted in two ways: (1) It supplies sulphuric acid by bacterial oxidation, the presence of the acid increasing the availability of certain mineral constituents in the soil, such as alkalis, ferric oxide, alumina and phosphates. (2) It facilitates the work of the ammonia and nitrifying bacteria, thus placing larger supplies of nitrogen at the disposal of the plants. But although such action may be beneficial in some soils it is equally harmful in others, and a sulphur should not be applied to a soil already acid," p. 12.

"External evidence is available in confirmation of the remarkable molecular alteration in sulphur vapour. Near the boiling-point sulphur vapour is orange-red, but the colour fades to a straw-yellow as the temperature is raised; indeed, above 1000°C. the vapour is said to become colourless and on reaching 1400°C. to assume a pale blue tint. The absorption spectrum of sulphur vapour has been examined over the range 400° to 1200°C., and it is found that absorption increases as the temperature is raised to about 650°C. but above this temperature it decreases as the vapour becomes more and more transparent. This agrees with the view that the dissociation $S_8 \rightarrow S_2$ is not direct, but that molecules of intermediate complexity and of greater absorptive power than S_2 are formed and in turn dissociated. No further change is observable above 900°C. The fluorescence observable in the vapour under reduced pressures also shows variations indicative of the alteration in molecular condition," p. 15.

"Kellas, however, from measurements of the surface tension of liquid sulphur, maintains that between 115° and 160°C. at least 95 per cent. of mobile sulphur is represented by the formula S_6, and that above 160°C. polymerisation occurs, resulting in the formation of S_{12} or $(S_6)_2$ molecules, which are stable nearly up to the boiling-point," p. 17.

"Octahedral sulphur will form mixed crystals with selenium containing up to 35 per cent. of the latter, although no corresponding crystalline form of pure selenium has been isolated, " p. 22.

"When a concentrated solution of ferric chloride is rapidly mixed with fifty to one hundred times its volume of aqueous hydrogen sulphide solution the liquid assumes a transient blue colour, sulphur subsequently precipitating in the ordinary yellowish-white form. Sulphur with a blue coloration is also obtained in the interaction of carbon disulphide and sulphur chloride, for the preparation of carbon tetrachloride, under the catalytic influence of ferric chloride,

$$CS_2 + 2S_2Cl_2 = CCl_4 + 6S.$$

"By submitting various metallic sulphides, *e.g.* those of bismuth, silver, cadmium or zinc, to the action of a solution of sulphur chloride in benzene or toluene, a greenish-blue precipitate of sulphur is obtainable, but the product invariably contains several units per cent. of mineral impurity. The suggestion that Ultramarine owes its colour to the presence of a blue variety of sulphur appears to have little probability, especially in view of the stability of this substance towards heat, and indeed the true nature of the blue- or green-coloured precipitates of sulphur, obtained by any of the afore-mentioned methods, requires much more experimental investigation before the existence of a blue or green modification of sulphur can be accepted.

"Sulphur, however, dissolves in certain organic liquids, for example, hot glycerol or ethylene glycol, and in pyrosulphuric acid, yielding clear blue solutions. Cryoscopic measurements with solutions in the latter solvent indicate that the sulphur molecules are diatomic, and it is to be assumed that this is also the case with the blue solutions in organic solvents. Thus, in such solutions the sulphur is more highly dispersed than in most organic solvents, in which the molecules are octatomic," p. 29.

"Sulphur sols generally are opalescent, with a yellowish-white to yellow colour; when viewed by transmitted light they commonly appear bluish, but if freshly formed may exhibit successively the colours yellow, green, red, violet and blue. Such colour changes, which depend upon the degree of dispersion of the sulphur, may conveniently be shown by adding a dilute solution of phosphoric acid to $N/25$ sodium thiosulphate solution. The yellow or brown colour produced by sulphur in sodium-calcium silicate glass is not due to colloidal sulphur, but is probably caused by the formation of polysulphides," p. 31.

"At 200°C. sulphur can undergo slow oxidation, manifested by a distinct phosphorescence; oxidation can also occur even at the ordinary temperature, especially with finely divided sulphur in a moist condition. 'Flowers of sulphur,' when stirred with water, usually imparts a feeble acid reaction to the liquid. To this slow oxidation probably is to be attributed any beneficial effects resulting from the customary introduction of lumps of sulphur into dogs' drinking troughs," p. 37.

"A remarkable property of the sulphides of the alkaline earth metals and of beryllium and zinc is their power, when certain impurities are present, to exhibit phosphorescence after exposure to bright light. The phenomenon is not due to slow oxidation and is still observable in samples which have been kept hermetically sealed for years; it is obvious, therefore, that the effect is a physical one and not analogous to the phosphorescence observable with sulphur. The nature and amount of impurity present considerably affect the phosphorescence, chlorides for example causing an increase; some impurities inhibit the action," p. 63.

"It will be noticed that as a general rule, the more basic the character of a metal the more stable is its sulphide towards oxidation; an analogy therefore appears to exist between the function of sulphur in a sulphide and oxygen in an oxide. This analogy extends, in a less marked manner, to the behaviour of the corresponding sulphides and oxides towards alkalis. Just as carbon dioxide, arsenious oxide and the antimony oxides lend themselves to salt formation with alkalis, so carbon disulphide, arsenious sulphide and the antimony sulphides can combine with the alkali sulphides, giving rise to sulphur compounds (*thio-salts*) of analogous composition. Indeed, on treatment with an alkali, such a sulphide generally produces a mixture of the corresponding oxy-salt and the thio-salt. These sulphides can therefore be regarded as "thio-anhydrides." From the similarity in behaviour, it is probable that the sulphides are structurally analogous to the corresponding oxides," p. 64.

"A discovery that certain alkaloids were capable of producing definite crystalline compounds with hydrogen polysulphide unfortunately failed to elucidate the mystery of the composition of the latter, since the compounds produced did not yield unanimous indications. Thus strychnine yielded a hexasulphide, $(C_{21}H_{22}O_2N_2)_2.H_2S_6$, whilst brucine gave two hexasulphides, a red one, $(C_{23}H_{26}O_4N_2)_3.(H_2S_6)_2$, and a yellow one, $(C_{23}H_{26}O_4N_2)_2.H_2S_6.6H_2O$, and also an octasulphide, $C_{23}H_{26}O_4N_2.H_2S_8.2H_2O$. Furthermore, apart from the fact that these additive compounds were not of one type and that their composition was at first wrongly interpreted, there was the additional disadvantage that their indications did not accord well with the earlier views concerning the formula of hydrogen polysulphide," p. 68.

"Sulphur hexachloride is a colourless, odourless and incombustible gas of density 5.03 (air = 1). When solidified it forms a colourless crystalline mass of melting-point −56°C. As the vapour pressure of the solid attains one atmosphere at −62°C. the solid has no melting-point under ordinary pressures but volatilises without melting. The critical temperature is +54°C. The gas is only sparingly soluble in alcohol or water. It is remarkably inert, approaching even nitrogen in this respect. It is unaffected by the silent electric discharge, and even the spark discharge causes only slight decomposition. Mixed with hydrogen it withstands a high temperature, but under the influence of powerful electric sparks formation of hydrogen sulphide and hydrogen fluoride can be effected. At a red heat copper and silver are without action on the gas, although magnesium and sodium effect its decomposition; at lower temperatures, however, it resists even these two metals and sodium can be melted unchanged in an atmosphere of the gas, as also can the hydroxides of the alkali metals. Hydrogen chloride and ammonia are unaffected by sulphur hexafluoride, but hydrogen sulphide reacts rapidly according to the equation:

$$SF_6 + 3H_2S = 6HF + 4S,$$ " p. 73.

"A careful study of the equilibria involved at the freezing-points of the chlorides of sulphur has recently shown that four distinct chlorides are capable of existence, namely

S_2Cl_2, S_2Cl_4, SCl_2, and SCl_4," p. 74. "It has been concluded that the equilibrium of the chlorides of sulphur in the middle regions of concentration is dominated by two simultaneous dissociations of the dichloride, proceeding at very unequal rates, namely:

$$(a)\ \text{(Slow)},\ 2SCl_2 \rightleftharpoons S_2Cl_2 + Cl_2.$$

$$(b)\ \text{(Rapid)},\ 3SCl_2 \rightleftharpoons S_2Cl_2 + SCl_4.$$

This would serve to explain the otherwise puzzling observation that, although an equilibrium mixture having the composition of sulphur dichloride deposits sulphur tetrachloride on freezing, freshly prepared mixtures of sulphur monochloride with an over-chlorinated sample of sulphur dichloride exhibit a maximum freezing-point at the composition SCl_2, which disappears when the mixture is brought to a condition of equilibrium. The rapid initial production of sulphur dichloride, in accordance with the foregoing equation (*b*), is presumably followed by the slower process of destruction indicated by equation (*a*). When chlorine is passed into sulphur monochloride at ordinary temperatures, absorption ceases when the liquid contains about 70 per cent. of chlorine (SCl_2 = 68.9 per cent. chlorine), but at 0°C. absorption continues beyond this point. The reaction proceeds more rapidly in direct sunlight, and is catalysed by antimony pentachloride," p. 75.

"Acetic acid under similar conditions dissolves more than 300 volumes or almost its own weight of the gas. Acetone dissolves about twice its weight or nearly 600 times its volume of sulphur dioxide, whilst camphor also absorbs more than 300 times its volume, forming a liquid solution. In the last two cases chemical combination undoubtedly occurs; the freezing-point curve of camphor-sulphur dioxide mixtures indicates the formation of two unstable compounds, namely, $C_{10}H_{16}O.2SO_2$, m.pt. -45°C., and $C_{10}H_{16}O.SO_2$, m.pt. -24°C.; these are probably active in the preparation of sulphuryl chloride in the presence of camphor. The use of methyl *cyclo* hexanone has been recommended as an absorbing liquid for the recovery of sulphur dioxide from waste gases.

"Sulphur dioxide dissolves in aqueous solutions of inorganic salts frequently more readily than in pure water. With most salts, excluding sulphates, compounds appear to be formed in solution of the general type $MX.SO_2$, where M and X stand for univalent metal and negative radical, respectively. The solubility curve of sulphur dioxide in sulphuric acid of concentration ranging from 55 to 98.5 per cent is interesting. A minimum occurs at 85.8 per cent. acid, and from that point the curve inclines sharply upwards for both increase or decrease of sulphuric acid concentration," p. 109.

"Gaseous sulphur dioxide exhibits a tendency to undergo chemical change with formation of an equilibrium mixture with sulphur trioxide and sulphur:

$$3SO_2 \rightleftharpoons S + 2SO_3.$$

Thus it becomes cloudy when exposed to strong illumination, and the presence of free sulphur in the gas at 1200°C. can be detected by Deville's 'hot and cold tube' method. Light of any wave-length, within the absorption band, if it is of sufficient intensity, is capable of bringing about the decomposition of sulphur dioxide. The change does not take place, however, if the gas is absolutely dry. Slow decomposition as represented by the foregoing equation can also be effected by subjecting the gas to prolonged spark discharge. In all probability this conversion of sulphur dioxide into sulphur and sulphur trioxide is merely a special example of the power of gaseous sulphur dioxide at high temperatures to effect the oxidation of reducing agents such as hydrogen and carbon, the reducing agent or oxidisable substance in this case being part of the sulphur dioxide itself. At 2200° Abs. sulphur dioxide is not appreciably dissociated," p. 114.

"Sulphur dioxide exerts a decidedly toxic effect on plants and animals, and has been used in poison gas warfare; even as little as 0.04 per cent. by volume in the atmosphere will cause symptoms of poisoning in human beings after a few hours; in larger quantities, either gaseous or dissolved, the effect may be fatal. The gas acts as a direct blood poison and also affects the blood circulation. The sulphites are not poisonous," p. 121.

"In order to explain the foregoing behaviour, Smits and Schoenmaker assume that sulphur trioxide consists of a mixture of two different kinds of molecules which not only change one into the other, but combine to give a dissociable compound, the reactions leading to the attainment of an inner equilibrium which may be represented as

$$\left.\begin{matrix} x \\ \upharpoonleft\downharpoonright \\ y \end{matrix}\right\} \rightleftharpoons xy.$$

The various modifications of sulphur trioxide will therefore act as mixtures of these three constituents. In a ordinary preparation the condition of equilibrium is more or less rapidly attained, but in an intensively dried material the velocity of such inner transformation is considerably retarded. On realising this condition, as already shown, both the solid and liquid states behave as mixtures. Exposure to X-rays accelerates the attainment of the inner equilibrium," p. 140.

"With aldehydes and ketones sodium hydrosulphite readily forms additive compounds, the most important being that derived from formaldehyde. This product appears to have the composition $2CH_2O.Na_2S_2O_4.4H_2O$, but is separable by recrystallisation from water into the sodium hydrogen sulphite derivative of formaldehyde, viz. $CH_2O.NaHSO_3.H_2O$, and an analogous compound $CH_2O.NaHSO_2.2H_2O$, a crystalline solid of m.pt. 63°C. to 640°C. The latter is known as *Rongalite* and is of especial commercial importance on account of its stability at the ordinary temperature, although at steam heat it exerts all the reducing power of the hydrosulphites; on this account Rongalite, or sodium formaldehyde-sulphoxylate, is a very convenient form of reducing agent where storage for prolonged periods may be necessary before use. The aqueous solution may be stabilised by addition of a soluble zinc salt. Various other methods have been recommended for the preparation of Rongalite, for example, the interaction of hydrosulphite and formaldehyde in the presence of an alkali:

$$Na_2S_2O_4 + CH_2O + NaOH = CH_2O.NaHSO_2 + Na_2SO_3.$$

and the reduction of sodium hydrogen sulphite solution with zinc dust and zinc oxide in the presence of formaldehyde, recrystallising from water at a temperature not exceeding 70°C. the crystals first obtained," p. 228.

"When sulphur reacts with liquid ammonia at temperatures varying between −38°C. and −11.5°C., the solution obtained is blue in colour and from it red, fern-like leaflets are obtainable, to which the name sulphammonium has been given. Sulphammonium is formed also by the action of hydrogen sulphide on nitrogen sulphide, N_4S_4, dissolved in ammonia at −35°C., and by the action of ammonia and a limited amount of hydrogen sulphide on lead or mercury dithiodi-imide. Red, fern-like leaflets of solid sulphammonium are also produced by submitting a mixture of nitrogen and ammonia at −12°C. to a pressure of 45 atmospheres in the presence of sulphur," p. 237.

"By the action of sulphur dioxide on ammonia three different compounds may be formed, the product depending on the conditions of the reaction. The proportions in which the gases combine depend largely on the extent to which the temperature is allowed to rise, the heat of union being considerable. The product also varies according to which gas is present in excess, unless the temperature is kept very low, in which case ammonium amidosulphinate is formed. When sulphur dioxide is in excess the yellow, crystalline *amidosulphinic* acid, $NH_3.SO_2$ or $NH_2.SO_2H$, is formed. With excess of ammonia the product may be either the white, crystalline salt, *ammonium amidosulphinate*, $2NH_3.SO_2$ or $NH_2SO_2.NH_4$, or *triammonium imidodisulphinate*, $4NH_3.2SO_2$ or $NH_4.N:(SO_2.NH_4)_2$, a red compound, having the same percentage composition as ammonium amidosulphinate but of double molecular weight. That in the molecule of this latter substance three of the nitrogen atoms are placed differently from the fourth is evident from the formation of a silver salt, $Ag.N:(SO_2Ag)_2$, which is also red in colour. Triammonium imidodisulphinate is also obtainable by the action of thionyl chloride on liquid ammonia, a diamide first being formed:

$$2SOCl_2 + 7NH_3 = HN:(SO.NH_2)_2 + 4HN_4Cl.$$

The diamide is hydrolysed by water to $NH(SO_2.NH_4)_2$, which reacts with more ammonia to form the triammonium salt. On evaporation, and digestion of the residue with absolute alcohol at −5°C., a red solution is obtained, which, when evaporated in a vacuum, yields the triammonium salt in the form of red flakes," p. 243.

"Xanthates are used commercially as flotation agents in 'froth flotation' processes for the separation of crushed materials, and their use as vulcanisation accelerators for rubber has already been mentioned," p. 268.

"The thermal decomposition of carbonyl sulphide has been investigated. The products of dissociation may be carbon monoxide and sulphur on the one hand, or carbon dioxide and carbon disulphide on the other:

$$(1)\quad COS \rightleftharpoons CO + CS_2.$$
$$(2)\quad 2COS \rightleftharpoons CO_2 + CS_2.$$

At 800°C. reaction (2) appears to proceed slowly in either direction, while (1) is very rapid. The fact that the degree of dissociation in (1) is independent of the amounts of carbon dioxide and carbon disulphide present, shows that carbon monoxide and sulphur are primary products of the decomposition of carbonyl sulphide and are not formed secondarily from the carbon dioxide and carbon disulphide. At temperatures below 400°C. decomposition according to equation (1) is not evident, while at 900°C. it reaches a maximum (64 per cent.); reaction (2) reaches a maximum at about 600°C., at which point 43 per cent. of the carbonyl sulphide is decomposed in this way and 16 per cent. according to reaction (1). The carbon monoxide equilibrium depends upon the pressure, whilst the carbon dioxide equilibrium does not. Nearly all the reactions involved in the thermal decomposition of carbonyl sulphide depend greatly on catalytic influences. Quartz is a pronounced catalyst for reaction (2), but has little influence on reaction (1). Carbonyl sulphide is comparatively rapidly decomposed in quartz vessels, but is stable when kept in glass apparatus," p. 270.

"When superheated selenium vapour is passed into air-free water, colloidal solutions are formed which are usually rose-coloured, but at first of a blue tint and cloudy. Under the most favourable conditions clear yellowish-red or deep red sols may be obtained, the former being the more highly dispersed. The blue sols after dialysis are extremely stable, but non-dialysed sols decompose after a few days, selenious acid being detected except in the yellowish-red sols. The dialysed sols may be frozen to an almost colourless ice which at the ordinary temperature thaws and decomposes. The sols are negative and are readily coagulated by the addition of chlorides," p. 293.

"Colloidal selenium produced by means of hydrazine hydrate can be frozen to a blue ice which melts with complete coagulation, but the presence in the solution of hydrogen chloride, sodium carbonate or potassium chloride, exerts a protective action which is a maximum at certain definite concentrations," p. 294.

"It was first suggested by Siemens in 1875, and the hypothesis was strongly supported by later investigations, that crystalline selenium exists in two forms "A" and "B," "A" being a non-conductor and "B" a good conductor of electricity. In the dark the equilibrium mixture consists almost entirely of "A"; the equilibrium is displaced in the direction of "B" both by the action of heat and by exposure to light:

$$\text{"A"} \rightleftharpoons \text{"B"}.$$

The isolation of the two modifications was described by Pélabon, but was not confirmed by later investigation. The theory is discounted by the fact that at exceedingly low temperatures the action of light is only slightly diminished, whereas it would be expected that such a transformation would no longer proceed.

"However, Briegleb, from X-ray investigations, maintains that in all the allotropic modifications two such pseudo-components do exist, and that these may be separated in some degree by taking advantage of the fact that although their absolute solubilities in carbon disulphide are almost identical, the rates at which they dissolve are different. By spectroscopic methods evidence has been obtained that the two forms exist in equilibrium in this solution and that the equilibrium varies with the temperature.

"What appears to be a more satisfactory explanation and one largely favoured by physicists is that the phenomenon is an effect of purely electronic character. The actual mechanism of the action is not yet completely understood, but the light appears to cause ionisation at the surface of the selenium, with immediate increase in conductivity. The splitting off of electrons may be not only from the selenium atoms but also from the incident stream. It has also been suggested that the interatomic space occupied by the conducting electrons may be increased. The theory explains why the recovery of the selenium is not immediate when the light is removed, and why after exposure to the more deeply penetrating rays, such as the X-rays, the recovery is even slower," p. 298.

"Molten tellurium solidifies to a brittle, silvery, crystalline mass, which is easily powdered. The crystalline modification can also be obtained by sublimation of the element or by its slow formation, for example in the gradual decomposition of hydrogen telluride or in the slow atmospheric oxidation of an aqueous solution of an alkali telluride. When obtained of appreciable size the crystals are generally found to be prismatic, of the trigonal system, and isomorphous with "metallic" selenium ($a:c = 1:1.3298$; $a = 86.8°$)," p. 353.

"The coagulating powers of various electrolytes for tellurium hydrosols have been determined; the results obtained do not agree with Whetham's law," p. 356.

"When illuminated by an incandescent lamp, tellurium vapour exhibits an intense bluish-green fluorescence. Under the light of a mercury vapour lamp the fluorescence is much less intense. The fluorescence spectrum consists of regularly spaced bands in the visible region," p. 356.

"Tellurium and iodine, in the molten condition, are miscible in all proportions, and the system tellurium-iodine has been examined from the thermo-analytical standpoint, the freezing-point curve giving indications only of the formation of a tetra-iodide, TeI_4, in the fused mixture.

"A tellurium di-iodide has been described by Berzelius as obtained when tellurium and iodine are sublimed together, but its existence as a definite compound appears doubtful. Damiens has shown that the so-called tellurium di-iodide is a mixture of the tetra-iodide and a solid solution of tellurium with the tetra-iodide," p. 378.

The reviewer is sceptical about the statement, p. 181, that the formation of the perdisulphuric [persulphuric] acid in the electrolysis of sulphuric acid is due to the coupling of the discharged HSO_4' ions at the anode." The experiments with ammonium sulphate seem to be conclusive that the real reaction is $2SO_4'' \rightarrow S_2O_8''$.

Wilder D. Bancroft

A Treatise on Physical Chemistry. *Edited by Hugh S. Taylor. Vols. I and II. 22 × 15 cm; pp. xxvii + 1814. New York: D. Van Nostrand Company, 1931. Price: $15.00 the set.* The first edition was reviewed over six years ago (29,351). In the preface to this edition, the editor says, p. ix: "The reception accorded to the first edition of this book was such that a decision had to be reached one year ago as to the advisability of a third printing or a new edition. The rapid developments in several branches of the subject made the decision for a new edition inevitable. A perusal of these volumes will show in what directions progress has been dominant [?]. The chapters dealing with the electrochemistry of solutions, homogeneous and heterogeneous reaction velocities, the application of the quantum concept to the structure of matter and to photochemistry, the use of statistical mechanical methods in chemistry have all called for extended revision by reason of developments in the five-year period which has intervened since the book was first put at the disposal of the advanced student of physical chemistry.

"The opportunity thus offered has been taken to present in this edition a more advanced treatment of the kinetic theory of gases and liquids and also a considerably extended discussion of colloidal systems. As a result of all these changes the size of the book has undergone a somewhat considerable increase necessitating a readjustment of the division of chapters, the first chapter (XII) of the second volume of the old edition now becoming the last chapter of the first volume. The order of presentation of the subject matter remains unchanged."

"Progress in the quantum theory of energy made familiar the concept of units of energy, light quanta, or photons, with the discontinuous structure hitherto characteristic of matter. The reversal of this mode of thought, the concept of material particles with the wave nature of light was proposed in 1924 by Louis de Broglie. It led to the wave mechanics of Schrödinger and to the quantum mechanics of Heisenberg, two aspects of the general problem of wave theory of matter intensively developed in the last years. The wave theory of matter assigns to each material particle a wave of a characteristic wave length bearing the same relation to its mass and velocity as was found in quantum theory for the photons. This relation is expressed in the equation

$$\lambda = \frac{h}{mv},$$

where λ is the wave length of the particle with mass m and velocity v, h being again Planck's constant.

"It is of interest to point out the significance of this equation when applied to the electron, the smallest unit to which material properties have hitherto been assigned. For the electron h/m has the value 7.27. If, then, we consider electrons with velocities in the range of 10^7–10^9 cm. per sec., the equation indicates that such electrons should have wave lengths of the same order of magnitude as X-rays. Herein lay a possibility of experimental test, since the wave lengths of X-rays are determinable by well-known reflection methods from crystals.

"Such a test was applied by Davisson and Germer successfully in 1927. They showed that a stream of electrons emitted from a hot filament was selectively reflected from a single crystal of nickel in a manner entirely analogous to the reflection of X-rays. The intensity of the reflection in a given direction was governed, as with X-rays, by the lattice structure of the crystal. With this experiment, therefore, the fusion of the corpuscular and undulatory aspects of both matter and energy was achieved. It gave a marked impetus to the examination of matter from the standpoint of wave theory.

"Efforts to extend these experiments to particles of atomic dimensions have not attained the decisive success of the Davisson and Germer experiments. There are, however, indications in the experiments of Knauer and Stern, that the reflection of helium atoms may be in accord with wave theory.

"It is, however, in the reconciliation of quantum theory with the facts of chemistry that the most significant advances of the wave theory to the chemist may be anticipated. Mention may be made in this connection of the quantum mechanical treatment of the problem of combination between two atoms and the study, by London, of the homopolar binding as a pairing in a molecule of two electrons, the electrons being unpaired in the atoms from which the molecule was produced. This postulate of the Lewis theory of atomic and molecular structure thus returns again in the new quantum mechanics. The chemical valence of an atom, according to London, is determined by the number of its unpaired electrons.

"That wave mechanics may revolutionize our knowledge even of the elements is evident from the recent predictions by Hund and later by Dennison on the basis of quantum mechanics, of the existence of two forms of hydrogen molecules. The molecules are distinguished from each other by the spin of the two nuclei, the spin being such as to give wave functions symmetric in the one case and antisymmetric in the other. This prediction has now been experimentally confirmed by Bonhoeffer and Harteck who have shown that the equilibrium mixture of the two, predicted by Dennison, at room temperatures (25 per cent Symmetrical:75 per cent Antisymmetrical) is displaced at the temperature of liquid hydrogen in presence of active charcoal towards the direction of the symmetrical (termed by Bonhoeffer, Parahydrogen), so that, at these temperatures, the gas leaving the surface of the charcoal is at least 99.7 per cent para-hydrogen. This form is the lower in energy content. Specific heat measurements of Eucken confirm this. Bonhoeffer and Harteck have examined the properties of para-hydrogen in detail. At the boiling point of ordinary hydrogen, $T = 20.39$°K. it has a vapor pressure of 787 mm. At the triple point, $T = 13.95$°K.

The corresponding vapor pressures are $P_{\text{ord.}} = 53.9$ mm., $P_{\text{para}} = 57.0$ mm. Para-hydrogen at room temperatures and ordinary pressures is quite stable in glass vessels. Its slow return to the equilibrium mixture has been followed over a period of months. In presence of suitable catalysts, notably, platinum black, the para-modification reverts immediately to the equilibrium mixture. At higher temperatures in glass vessels the para-hydrogen becomes less stable and reverts at temperatures in the neighborhood of 1000°C. rapidly to the equilibrium mixture, even in glass tubes. The activation energy of conversion is over 50,000 calories although the heat of conversion of one form to the other is only 329 calories at 0°K. Such modifications in our knowledge of well-known molecular species by reason of the newer developments in the wave theory of matter are sufficient evidence of the importance of the modern developments in theoretical physics for the modern physical chemist," p. 32.

"Recent developments have led to the belief that all forces are to be traced back to electrical phenomena. This trend is exemplified by the explanations of the van der Waals forces. Disregarding ions such as are present in electrically dissociated gases, the molecule regarded as a whole is electrically neutral. There are different types of forces, which neutral particles can exert upon each other. One important group can be explained in the following manner. In spite of their electroneutrality, molecules can exert forces on each other just as two magnetic needles can exert forces on each other even though each is magnetically neutral, i.e. contains just as much positive as negative magnetism. The cause of this latter interaction is the fact that the two magnetic poles are not situated at the same point in the needle so that if one needle is brought up to another, in general one of the two poles will be more closely approached than the other. The situation in the case of molecules which are electrically neutral as a whole is entirely similar. The molecules are neutral because they contain just as many positive charges in the nuclei (Rutherford-Bohr atom) as negative charges (electrons) in the outer parts of the atoms. They exert forces on each other because the positive charges are not situated at exactly the same points as are the negative charges. The law of force depends essentially upon the symmetry of the distribution of the charges. The simplest case is that of a 'dipole' in which one positive charge is separated by a small distance from a negative charge. This system has the symmetry of a magnetic needle in that it has a negative and a positive pole. The fields have the same character in each case and the distributions of the lines of forces are of the same type. Examples of such dipoles are: sodium chloride vapor, which consists of positive sodium ions and negative chlorine ions, all acids, water vapor, and so forth," p. 239.

Frazer repeats on p. 361 the Ostwald perpetual motion proof in regard to the partial pressures of two incompletely miscible liquids, ignoring, as Ostwald did, the action of gravity and giving a drawing which does not represent the facts as to what constitutes equilibrium. The reviewer is of the opinion that van't Hoff and not Ostwald proved that osmotic pressure is independent of the type of membrane. Frazer also repeats Ostwald's generalization that "if any two phases are in equilibrium with a third phase, they are in equilibrium with each other." One wishes that this could be applied to saturated solutions of sodium chloride in alcohol and in water, which are each by definition in equilibrium with solid sodium chloride but which are certainly not in equilibrium with each other.

Professor Arthur E. Hill seems not to have an orderly mind. On p. 151 for fractional distillation, the composition is measured along the abscissas and the temperature along the ordinates. On p. 537 for two-component systems, the composition is measured along the ordinates and the temperature along the abscissas. On p. 569 for the iron-carbon diagram the composition is measured along the abscissas and the temperature along the ordinates.

Partington does not mention audion tubes in the measurement of electrolytic conductivity, p. 646, and adopts the German spelling of kation, while the American writers use the English spelling of cation. The editor passes the buck by not including the word in the index. Harned gives nearly eleven pages to a discussion of over-voltage and passivity and sums up the discussion, p. 852, with the statement that "the conflicting opinions concerning the nature of overvoltage and passivity are in themselves an excellent proof of the obscurity which at the present time veils the true nature of the phenomena involved." Harned is no Charlie Chan.

"An ingenious method has been developed recently for measuring the rates of very rapid reactions in solutions. The method consists in making competition experiments by adding to a mixture of two compounds an insufficient amount of some reagent which reacts with both. A series of such experiments are done in which different amounts of the reagent are added, and by suitable analysis the extent of each reaction is determined; from these the ratio of the two velocity constants can be calculated. It is possible to measure absolute velocities in this way by selecting pairs of competitors, one of which has a velocity slow enough to be measured directly, and from this we can pass to very much faster reactions. This method has been used in a *series of studies on the rate of bromination of aromatic* amino and phenolic compounds in aqueous solutions, and recently the rates of ionic reactions have been measured; it has been shown for example that sodium thiosulfate reacts more quickly with iodine than does sodium bisulfite," p. 981.

"Trautz, Perrin and W. C. McC. Lewis originally proposed the radiation hypothesis; it has been widely discussed, especially since 1919. The essential feature of it is that it provides a mechanism for the Arrhenius hypothesis of activation; this mechanism is activation of a molecule by the absorption of radiation emitted by the surroundings. It is assumed that the energy of activation is equal to $Nh\nu$ per mole where N is the Avogadro number, h is Planck's constant and ν the radiation frequency. This hypothesis was very attractive at the time, for it gave an immediate mechanism for unimolecular reactions; a molecule was assumed to absorb a quantum of light at any instant of its time of free flight and decomposes in a single act. The velocity of the reaction would be proportional to the density of radiation capable of decomposing the molecule and since this density increases exponentially with the reciprocal of the temperature the hypothesis agrees with the experimental facts.

"There are several very definite experimental tests to which this hypothesis may be subjected: (1) the frequency of the activating radiation can be calculated from the measured temperature coefficient of the reaction, and this must agree with an infra red absorption band; (2) the substance at a given temperature can be illuminated with infra red radiation of this frequency or other frequencies to see whether increased reaction results. The hypothesis has failed completely to meet any of these tests. For example, nitrogen pentoxide has an energy of activation corresponding to a wave length of 1.16μ but it has no absorption band in this region. It has, however, a very strong band at about five times this wave length. It was thought that this fact might be significant and that therefore light of this or other infra red wave lengths might be effective in bringing about decomposition. Experiments by H. A. Taylor and by Daniels have shown that this is not true. Moreover, the failure cannot be due to any disturbing effect of collisions. Two experiments, one using pinene and the other using nitrogen pentoxide have shown that a unimolecular reaction does not occur when a molecular beam of these substances is passed through an enclosure containing black body radiation at such a temperature that complete reaction should occur if the absorption of black body radiation alone were the cause of chemical reaction. Briefly, the radiation hypothesis has failed to meet any of the experimental tests of its validity," p. 984.

"The new mechanics involves, of course, a renunciation of mechanical models—such as have been used for over a century by both physicist and chemist. Does this mean that we must no longer conceive of a hydrogen molecule as Lewis and Langmuir would represent it by a 'static model' with shared electrons? The answer in terms of our new theories is that for many purposes we may still think in terms of the older concepts and need only to bear carefully in mind the *limitations* of such models. For after all the *object of any theory is to develop a system of conceptions which will enable us to describe the results of an experience*, and it depends upon the nature of the 'experience' as to how extensive we need to make the theory.

"The most striking feature of the new mechanics is its emphasis on the "Principle of Indeterminism" and the fact that it is impossible with regard to an atomic system to predict individual events; only the probability of occurrence can be stated and furthermore we find that on the basis of the new theories there is a finite probability for certain occurrences, like those of radioactive disintegration, *and so forth*, which were inconceivable on the basis of classical theories," p. 1378.

The chapter on photochemistry has been rewritten and brought up to date. The reviewer wishes that a few words could have been *said about* the usefulness of the views of Grotthuss on depolarization, but he realizes that the advanced student of physical chemistry is not interested in qualitative truths when he can study the theory of indeterminism. In two volumes like these there is no room even for a *suggestion that some* of the chemical properties of water might vary with a displacement of the water equilibrium. In the same way it is taboo to suggest to the unfortunate biologists that their electromotive force measurements do not necessarily give true hydrogen ion concentrations. The bluff that chemical thermodynamics is exact must be maintained at all costs.

The chapter on colloids is written now by E. O. Kraemer and is expanded a good deal over that in the preceding edition.

This book is an admirable one, for people who like this type. For people who are old-fashioned enough to prefer Gibbs, Helmholtz and van't Hoff to Nernst, G. N. Lewis and Debye, it is not so good; but there are not many of the latter, and nobody has ever waxed enthusiastic over Jeremiah or Cassandra.

Wilder D. Bancroft

A Text-Book of Inorganic Chemistry. *Edited by J. Newton Friend, Vol. VI, Part 1. 22 × 16 cm; pp. xxviii + 242. London and Philadelphia: Charles Griffin and Co.; J. B. Lippincott Company, 1928. Price: $10.00.* Through a regrettable oversight for which the reviewer cannot account, this volume on nitrogen, written by E. B. R. Prideaux and Herbert Lambourne was not reviewed at the time of its appearance, though it was read then.

The subject is presented under the headings: introductory; the nitrogen atom; nitrogen; ammonia; hydroxylamine; nitrogen and the halogens; oxy-halogen derivatives of the halogens; hydrides and their derivatives containing two or more nitrogen atoms; hyponitrous acid; the oxides of nitrogen; nitrous acid; nitric acid; nitrogen and sulphur; fixation of nitrogen.

"Nitrogen alone among the common elements is found almost exclusively in the atmosphere, and only to a relatively minute extent in the solid and liquid 'ten-mile' crust. In its mode of occurrence it thus resembles the 'inert gases' of the atmosphere, and, like them, is also found in small quantities in gases which issue from hot springs, and dissolved in the ocean. Actually the proportion of nitrogen in the ten-mile crust with atmosphere and hydrosphere is only 0.03 percent," p. 8.

"There are many compounds, such as the ammonium bases, nitric acid, etc., in which it seems impossible or unnatural to retain the trivalency of nitrogen, and the simplest assumption, on the older ideas, is that of quinquevalent nitrogen. In compounds such as nitric acid, $O_2\equiv N-OH$, nitryl fluoride, $O_2\equiv N-F$, the five negative valencies are the contravalencies of Abegg's system. Ammonium and substituted ammonium salts are clearly of a different type; of the two extra valencies, one is a positive or hydrogen valency of the same kind as the first three, and the second is an electrovalency. A change in the valency of nitrogen is exhibited in the tautomerism of hydroxylamine and its derivatives: $H_2=N-OH \rightleftarrows H_3\equiv N=O$; also in the formation of ammonium bases: $R_3N + R_1 \rightarrow R_3NR_1$; and in the tautomeric change of pseudo-bases into true bases *or baso-forms*:

$$=C(OH)-NR_2 \rightarrow \;=C=NR_2OH.$$

It is now no longer necessary, however, to postulate the existence of quinquevalent nitrogen, since all these changes are satisfactorily expressed by the new valency models based on the electronic structure of the atom. *Indeed, these theories* deny the possibility of quinquevalency of the organic type, *i.e.*, quinque-covalency," p. 12.

"When nitrogen combines with three atoms of hydrogen or chlorine, or with three univalent radicals, it forms three duplet valency bonds, in each of which one electron has been contributed by each element. It thus completes the 'octet' or stable shell, and may be regarded either as a cube, of which the edges form the bonds, or preferably as a tetrahedron, at the angles of which are situated pairs of electrons. The latter method has the advantage of representing in an intelligible manner a trivalent combination (such as HCN and N_2), and of being uniform with the system so successfully adapted to the representation of carbon compounds. The single bond is thus represented by contact at angles, the double by contact along edges, and the triple by contact over faces, of two adjacent tetrahedra. These types will be found in F_2, O_2, and N_2 respectively; and the superior stability or greater inertness of the $N \equiv N$ molecule may be due to this configuration.

"The electronic models of chemical combination have supplied a logical and consistent mode of representing the valencies even of compounds, which could not be so represented by any of the older theories. As nitrogen has always held a central position in the field of discussion, this is perhaps a suitable place in which to summarise the conclusions which have been reached at present. Historically, the idea of electrovalency as combination with or rejection of the electron was first suggested by Thomson and more definitely by Ramsay. The explanation of ordinary valency of the organic type as being due to pairs of shared electrons owes much to G. N. Lewis. Finally, the idea of mixed bonds, which is a logical development of electron theories, was developed by Lowry, and some results were stated in the form of postulates by the author as follows, under (3) below. They are particularly helpful in dealing with co-ordination compounds.

"The three kinds of valency are:

(1) *Electrovalency*, the electrostatic force which unites the ions of a salt, *e.g.*, $Na^+ \ldots Cl^-$ either in solution or in the solid crystal. Of this kind are the oxygen and halogen valencies of the metals.

(2) *Covalency*, which unites the atoms of non-polar compounds of an organic type, *e.g.*, CH_4. Of this kind are the hydrogen valencies of the elements, particularly the non-metals. In this case, each atom shares one or more of its electrons with the other.

(3) *Electro-covalency*, which unites some of the atoms of co-ordinated groups, such as $K_4(Fe(CN)_6)$, $[Co(NH_3)_6](NO_2)_3$. This mixed bond consists of a pair of electrons, but also produces an internal field of force or latent polarity. This kind of valency also probably unites the non-metals with one another, or with oxygen in the oxyacids. In this case, two adjacent atoms share as before two electrons, but both electrons are supplied by one only of the sharing atoms," p. 13.

"A progressive weakening in the tendency to add H^+ or CH_3^+, etc., and to give '-onium' compounds is shown by the series NH_3, NH_2OH, NCl_3. It is due to the opposing pull on the electrons by the increasingly negative substituent, which thus leaves the nitrogen atom more positive and thus with a lesser tendency to combine with positive groups. On NH_3 the nitrogen atom exerts a stronger pull on the common electrons than does a hydrogen atom, as is shown by the fact that in $NaNH_2$ the nitrogen has gained a negative electron with formation of a hydrogen ion, which then gains the electron again from the sodium: $NH_2^- \ldots H^+ + Na = NH_2^- \ldots Na^+ + 1/2\ H_2$. The potentially negative nature of the nitrogen atom thus revealed accounts for the ease with which NH_4^+, ammonium ion, is formed. In NH_2OH the oxygen exerts an opposing pull on the common electrons, the nitrogen is less potentially negative, and consequently hydroxylamine salts are formed to a smaller extent, or are more hydrolysed than ammonium salts. In chloramine, NH_2Cl, the strongly electro-negative chlorine completely destroys the tendency of the nitrogen to attach itself to positive ions," p. 16.

"The emission spectrum of nitrogen has been the subject of much investigation. Both the kathode and anode spectra (Geissler tube) consist of characteristic channels. Deslandres identified three groups of lines and bands which were sharply distinguished under strong dispersion. The first group was in the visible spectrum (λ7000–5000), the second group partly in the visible and partly in the ultra-violet (λ5000–2800), and the third group wholly in the ultra-violet (λ2800–2000). Deslandres attributed the third group to an oxide of nitrogen, as this group disappeared if every trace of oxygen was removed by sodium. The second group was the most intense, and the bands at λ3579 and λ3372 were considered characteristic of nitrogen," p. 34.

In regard to the peculiarities of active nitrogen the authors say, p. 46: "These difficulties may be largely overcome by supposing that active nitrogen contains at least two distinct molecular species:

(1) Metastable molecules with a lower heat of formation.

(2) A much smaller proportion of atoms which combine to form high-level excited molecules with a higher heat of formation.

"The former are responsible for the chemical activity, the latter for the glow. These two manifestations of activity are only related to one another in a complicated manner."

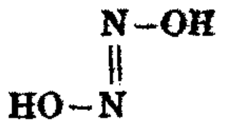
"The fluidity [of ammonia] is much greater (about four times) than that of water, and the surface tension appreciably lower, both being measured at ordinary temperatures. The various physical data lead to the conclusion that ammonia, like water, is probably associated in the liquid state," p. 76.

Hydroxylamine forms $NH_2OH.HCl$, $(NH_2OH)_2.HCl$, and $(NH_2OH)_3.HCl$; but no structural formulas are given for the compounds, p. 111. They are probably considered to be hydroxylamine monohydrochloride with two hydroxylamines of crystallization.

Iodine azide "has been prepared by bringing an aqueous solution of silver azide into contact with an ethereal solution of iodine. On evaporation of the ether in a current of air, colourless crystals are left, which have a penetrating odour similar to that of cyanogen iodide, and which are easily decomposed by explosion into iodine and nitrogen. The compound may be hydrolyzed by water giving azoimide and hypoiodous acid: $N_3I + H_2O = N_3H$ and HOI. The iodine is therefore the electropositive part of the molecule," p. 134.

That hyponitrous acid "contains the diazo-group is indicated by many of the reactions used in its preparation, especially by the hydrolysis of organic compounds known to contain this group. It is in fact a dioxime, as is shown more especially by its preparation from nitrous acid and hydroxylamine.

"The molar weight is decided by the cryoscopic method, and the dibasic character of the acid by the neutralization experiments and conductivities and by the existence of dialkyl derivatives and esters. It has been suggested that hyponitrous acid is the antidioxime



$$\begin{array}{r} N-OH \\ \| \;\;\;\;\;\; \\ HO-N\;\;\;\;\;\; \end{array}$$

the isomeric nitramide being perhaps the syn-compound," p. 141.

The decomposition of nitrous oxide by heat "is one of the few examples of a gas reaction which takes place in the gas phase, at any rate in a silica vessel, as is shown by the fact that increase of surface (by the addition of powdered silica) has no effect on the velocity constant. Since this latter is inversely proportional to the concentration, the reaction is bimolecular," p. 147.

"The absorption of nitric oxide by aqueous solutions of various salts has been the subject of much investigation. In the case of ferrous salt solutions the solubility of the gas increases with the concentration of the solution. The limit is reached when the proportions of iron to nitric oxide are in the ratio 1:1, both in aqueous and alcoholic solutions. It is assumed that unstable chemical compounds are formed of the type $FeSO_4.NO$, $FeCl_2.NO$, etc., but the ready dissociation of such compounds under the influence of heat indicates only a feeble combination. Usher has investigated the freezing-point of such solutions, and finds that neither the freezing-point nor the pressure of the nitric oxide remained constant, and hence no conclusion can be drawn as to the nature of the compound $FeSO_4.NO$. The absorption of nitric oxide by bivalent salt solutions of nickel, cobalt, and manganese is of a similar nature. Ferric salts also absorb nitric oxide readily, as also do many metallic and non-metallic halides. Nitric oxide dissolves in solutions of copper sulphate, producing a violet unstable compound, $CuSO_4.NO$. The solubility of the gas in cuprous halides in various solvents has been determined," p. 152.

"Generally speaking, nitric oxide can be reduced in stages right down to ammonia. Thus, when the gas is mixed with hydrogen and brought into contact with platinum black, or finely divided, nickel or copper, tin, iron, or zinc, ammonia is produced. Stannous chloride reduces nitric oxide to hydroxylamine and ammonia, and also to hyponitrite if the solution is alkaline. Chromous salts produce ammonia in neutral solution and hydroxylamine if the solution is acid. Hydriodic acid reduces nitric oxide to ammonia. Reduction to nitrous oxide is brought about by alkaline pyrogallol, sulphurous acid, phosphine (also some nitrogen), and sulphuretted hydrogen and alkaline sulphides (with some ammonium sulphide)," p. 155.

The general explanation of the formation of ruddy fumes when nitric oxide is brought into contact with air or oxygen is that nitrogen peroxide is formed:

$$2NO + O_2 = 2NO_2.$$

There seems to be little doubt that nitrogen peroxide is the final product, but it is by no means decided whether the above equation truly represents the mechanism of the oxidation. In the first place it would seem that nitrogen trioxide is the sole product when the oxidation is carried out below $-110°$, even with excess of oxygen:

$$4NO + O_2 = 2N_2O_3,$$

and the production of nitrogen tetroxide only occurs above $-100°$:

$$2N_2O_3 + O_2 = 2N_2O_4.$$

"Raschig maintains that at ordinary temperatures a similar intermediate formation of the trioxide occurs, the second oxidation to the peroxide taking a much longer time. According to Lunge, however, the primary product of oxidation is the peroxide, the reaction being of the third order. Further evidence in favour of nitrogen trioxide being the first oxidation product of nitric oxide, is the instantaneous formation of N_2O_3 when nitric oxide and oxygen are mixed in the ratio of 4 to 1 at ordinary temperatures, the product remaining stable. When the proportions of nitric oxide and oxygen are as 2:1, then the N_2O_3 stage is reached very rapidly, then further oxidation to N_2O_4 occurs, 34 percent in 20 seconds and completely in 100 seconds.

"Sanfourche also maintains that the first stage in the oxidation of nitric oxide by dry air is nitrogen trioxide, which occurs instantaneously between $-50°$ C and $525°$ C. The second stage in the oxidation, which results in the formation of nitrogen peroxide proceeds according to the equation

$$2N_2O_3 + O_2 = 4NO_2,$$

and is governed by the temperature. The first oxidation product, even in presence of water, is stated to be the trioxide and not the peroxide. The nitrogen trioxide is then decomposed by water to form nitric acid and nitric oxide," p. 156.

"Nitrous acid resembles nitric acid inasmuch as it shows two kinds of absorption spectra. There is probably an equilibrium between two tautomeric forms:

$$[NO_2]H \text{ and } \left[N\genfrac{}{}{0pt}{}{OH}{O} \right]$$

Thus silver nitrite appears to exist in two forms, one an ionisable salt $[NO_2]$ Ag, and the other a non-electrolyte $\left[N\genfrac{}{}{0pt}{}{O}{OAg} \right]$. This will account for the fact that the productof the reaction between $AgNO_2$ and CH_3I is methyl nitrite, $\left[N\genfrac{}{}{0pt}{}{O}{OCH_3} \right]$, an ester the hydrolysis of which shows that the methyl group is attached to the oxygen atom; and also of nitromethane $[NO_2]CH_3$, a nitro-paraffin the reduction of which shows that the methyl group is attached to the nitrogen atom. The modern valency theory represents the tautomerism of nitrous acid and nitrites as due to the shift of the hydrogen atom from oxygen to nitrogen:

$$NO_2' + NO_2' + H^{\cdot} \leftrightarrows HNO_2,\text{" p. 185.}$$

"Moissan found that pure calcium carbide and nitrogen would not react at 1200°C., but Rothe discovered that nitrification proceeded rapidly if the crude carbide was used. It would appear that some form of catalytic material was necessary for the reaction, and

Polzenius patented the use of calcium chloride in 1901. Thus, whereas with no calcium chloride there was less than 1 per cent. of nitrogen absorbed in twelve to fourteen hours at 730°C., yet under the same conditions with 10 per cent. of calcium chloride 18 per cent. of nitrogen was absorbed (as against 22 per cent. theoretical absorption).

"The disadvantage in the use of calcium chloride, however, is the deliquescent nature of the final product. The action of water is to generate acetylene from the residual carbide and to form dicyanodiamide, $(CN.NH_2)_2$, from the cyanamide, which is deleterious when the cyanamide is to be used for fertiliser purposes. Dicyanodiamide is toxic to plant life, partly because it inhibits the action of nitrifying bacteria.

"In 1906 the use of calcium fluoride, (CaF_2), was suggested in the form of crushed fluor-spar as a catalyst for carbide nitrification, and apparently most modern works now employ this substance," p. 224.

"One hundred weight of these concentrated fertilisers [sodium nitrate or ammonium sulphate] is therefore capable of producing enough food to satisfy a man's bodily requirements for one hundred or more days, or one pound of combined nitrogen properly used in the soil will yield enough food to keep a man going for about five days," p. 230.

"Urea is not toxic to plants even when present to the extent of 1 per cent. It is quickly hydrolysed to ammonia in the soil. The production of this compound from the technical nitrogen compounds mentioned above has been a fruitful field for the chemical inventor. Starting from ammonia, it may be made by the well-known reaction with carbonyl chloride, or the ammonia may be combined with carbon dioxide and the product converted into urea. Urea is also produced from calcium cyanamide by treating a solution with ferric sulphate or various acids under pressure," p. 231.

Wilder D. Bancroft

Chemische Thermodynamik. *By Hermann Ulich. 24 × 16 cm; pp. xvi + 353. Dresden and Leipzig: Theodor Steinkopff, 1930. Price: 18.50 marks, bound 20 marks.* This book is a combination of a treatise on thermodynamics and one on physical chemistry. As such it will probably appeal strongly to chemists. The first chapter deals with the first and second laws of thermodynamics; the second chapter with the thermodynamics of reactions; the third chapter with the application of the thermodynamics of reactions; the fourth chapter with the Nernst heat theorem; the fifth chapter with the special thermodynamics of solutions; and the sixth chapter with surface phenomena, including adsorption. The author uses the German system of letters for chemical values, which is probably unwise.

The following paragraph, p. 8, illustrates the clearness with which the author points out the vagaries in usage. "We denote in future the work done on a system, and measured in any desired units, by A, and the heat taken up by the system by Q. Consequently, the work done by the system on its surroundings is −A, and the heat evolved is −Q. These algebraical signs are those preferred by the physicists; but their use is not general. Nernst, in his handbook on theoretical chemistry, designates the heat taken up by +Q, but calls the work done by the system +A." The author adds, on p. 12, that the thermochemists call the heat evolved +Q.

"It is of course a familiar phenomenon to the chemist that systems, which might undergo chemical changes, may remain for a long time completely unchanged, although they are certainly not in the final state of equilibrium. In such cases, however, the inapplicability of our formulation is often only a delusion caused by the shortness of the time of observation. We may assume, for instance, that we could observe the continuous formation of water from an oxyhydrogen mixture at room temperature, and therefore the continuous drift of the system to its final state of equilibrium, if we had time enough at our disposal or sufficiently sensitive methods of observation. How slowly some of these chemical reactions take place is shown by the continuous thermal change in coal deposits, which seems certainly to occur but which requires geological ages before much alteration can be detected.

"People have introduced the concept of retardation [chemical resistance to change] so as to give a name to the cause for changes, which should theoretically occur, taking place so slowly or not at all. A system which can be retarded in regard to certain possible reactions, can be considered as a system in which those changes cannot take place, provided our observations extend over a sufficiently brief period of time. If the system reaches an equilibrium with reference to other possible changes, one may consider this state as equivalent to a true equilibrium even though the system is far from its final stage with reference to the retarded reactions. In working with such a system, one must of course keep in mind the possibility that the slumbering reactions may become active. It is well known that there are apparently futile additions which in some way may remove the retardations and accelerate the slumbering reaction catalytically. One may therefore consider an oxyhydrogen mixture that has been allowed to stand quite a while, as being under certain circumstances in thermal equilibrium and as a gas mixture which cannot react chemically. Under other circumstances its ability to react may be the important thing," p. 16.

If one works with steam between 300°abs. and 430°abs., the theoretical efficiency is thirty percent, while steam engines do not realize over twenty percent. With the Benson boilers, using superheated steam at about 700°abs., an efficiency of fifty to sixty percent is theoretically possible and thirty-five percent has actually been obtained. With Diesel motors the theoretical efficiency is forty to sixty percent and thirty percent has been obtained practically, p. 35.

On p. 46 the author puts the second law of thermodynamics in the form: "In a closed system a change can take place only when an increase in entropy is possible."

"A peculiar development has caused the avoidance as long as possible of the entropy concept in the presentation of physical chemistry and chemical thermodynamics. The opinion has become widespread that the entropy concept is hard to understand and to apply. It is to be hoped that the presentation in this book will convince people that it is just as easy to form a mental picture of entropy as of energy—in so far as one can speak of mental pictures under these circumstances," p. 51.

Chemical changes can be treated as independent variables only when these reactions are not retarded, p. 64. "Liquid water occurs, as is known, in many modifications, among which we must probably consider $(H_2O)_9$, $(H_2O)_6$, $(H_2O)_3$, $(H_2O)_2$, and H_2O without taking into account the ions H_3O^+ and OH^- and their hydrated forms. The reactions which these molecules undergo are unretarded and no way is known to retard them even in the laboratory. Consequently equilibrium between the different groups of molecules takes place practically instantaneously after each temperature or pressure change," p. 65. This is why liquid water can be treated as a one-component system.

"If we consider now the very surprising retardations in gas reactions, such as the oxyhydrogen gas reaction $2H_2+O_2\rightarrow 2H_2O$, it is evident that before a water molecule can be formed, an H_2 or O_2 molecule or both must be opened up or even destroyed. Since these molecules are very stable, a considerable addition of energy must occur before the very 'energy-rich' reaction of water formation can occur. The system must be pushed over an 'energy-hub' before it can roll down the inclined plane of a decreasing free energy. Catalytically effective are those influences which raise the system over the hub or which lower the hub. The first case occurs when an 'activating energy' is supplied either by heating or by absorption of light quanta. With energy-rich reactions it is only necessary to activate a few molecules in order to start the reaction going in the whole system; for the reaction of the activated molecules sets free such large amounts of energy (either as kinetic energy of the molecules or as radiation) that many of the adjacent molecules acquire sufficient activating energy. If the reaction starts at any point, it runs quickly through the whole system, sometimes in the form of an explosion wave.

"The second effect, the lowering of the energy hub may be accomplished by adding to the retarded system traces of a substance which undergoes an unretarded reaction with one of the reacting substances, giving rise to intermediate products with a lower energy hub. Occasionally, such intermediate products occur as definite chemical compounds, for instance, the formation of nitrosyl sulphuric acid from nitric acid and sulphur dioxide in the chamber process; through its decomposition into nitrous acid and sulphuric acid it is possible to avoid the high activation energy of the direct reaction, $2SO_2+O_2\rightarrow 2SO_3$. More often the intermediate products are molecules adsorbed on solid surfaces, and are deformed and opened up by the unilaterally acting surface forces. It is therefore a very frequent case that gas or solution reactions occur only in adsorption films on solid catalysts, so-called wall reactions," p. 98.

The author calculates, p. 128, that at 2000° abs. it would be easy to convert graphite into diamond if one could work above 40,000 atmospheres pressure.

Although a knowledge of the free energies will show what reactions are possible in any given case, we cannot predict what will actually occur if some of the retardations are removed. Thus acetone might oxidize to acetic acid and formic acid; but it might also go to methane, carbon dioxide, carbon monoxide, and water, p. 147.

Activities and activity coefficients are introduced on p. 168, curiously enough before the mass law, p. 170. On p. 285 it is stated that these merely describe the facts and explain nothing. The differences between the measured electromotive force of the oxyhydrogen gas cell, the theoretical value of that cell, and the decomposition voltage at platinum electrodes are referred to unspecified retardations, p. 175. Substances which have zero entropy at the absolute zero are called Nernst bodies, p. 185. It is recognized that there are substances which have a positive entropy at that temperature. Since ortho and para hydrogen can presumably occur in solid hydrogen, these would represent an unstable system with a finite entropy at the absolute zero, p. 191. On p. 204 the author gives the entropy of liquid water as 15.9 per mol, and 5.3 per gram atom. This latter figure is obtained by dividing the first figure by three, the number of atoms in H_2O. This phrase, entropy per gram atom, seems a very unfortunate one.

"An associated melt is closer to the crystalline state than a non-associated one and, other things being equal, should be formed from the crystals with less increase of entropy. On the other hand, the entropy increase on passing from an associated liquid to an approximately normal vapor phrase should be greater than for a non-associated liquid, and this is usually the case," p. 219. The author then deduces the simple form of Trouton's law, but unfortunately with no reference to Hildebrand.

On p. 224 the author says that the Nernst approximation formula can be used as a guide qualitatively; but should never be taken as the basis for quantitative conclusions.

On p. 305 the author deduces the Nernst distribution law but without mentioning that it can hold strictly only in so far as the mutual miscibility or non-miscibility of the two liquids is unchanged by the addition of the third substance. The distribution law is thereby given a thermodynamic rating to which it is not entitled. There is quite an elaborate discussion of hydration in connection with solutions, p. 313; but very little is said in regard to the effect of approaching non-miscibility on partial pressures. The salting out of a non-electrolyte by an electrolyte is referred to as the increasing of the activity of the non-electrolyte, p. 315. The reviewer believes that it would have been better to have said that it was due to an increase in the chemical potential; but he is grateful to the author for not speaking about a change in the thermodynamic environment.

On p. 343 the author gives Langmuir's equation for the adsorption isotherm and not Freundlich's. While it is quite possible that the Langmuir equation is the more accurate, the Freundlich one is so much easier to work with that it should have been mentioned. Nobody works with the van der Waals equation of state if he can avoid it and nobody but the man who invented it ever works under any condition with any of the more complicated equations of state.

It seems to the reviewer, who is not a thermodynamicist, that this book is probably at least as helpful to the chemist as any of the books on thermodynamics. The reviewer recommends it.

Wilder D. Bancroft

Das kolloide Silber. *By J. Voigt. 22 × 15 cm; pp. iv + 165. Leipzig: Akademische Verlagsgesellschaft, 1929. Price: 10 marks; bound 12 marks.* The conception of this book runs back to 1911 when the author began working on the therapeutic action of colloidal silver. It was planned to write the monograph in 1914; but the war put an end to this.

After the war the author decided that he ought to study the behavior of colloidal silver in the absence of a protecting colloid.

The chapters are entitled: historical; preparation of colloidal silver by electrical sputtering; sol formation by action of light; preparation of colloidal silver by reduction; germ method; effect of other substances on sol formation; colloidal silver with a protective colloid; silver purple of Cassius; physical properties of colloidal silver; colors of the hydrosols; coagulation of colloidal silver; organosols; medicinal and biological; injuries caused by colloidal silver; pharmacological testing of silver sols.

When a colloidal silver sol containing no especial protecting colloid is diluted, there is an increase in the apparent concentration of the silver ions. In a 10 cc sol the apparent mass of silver ions was 3.06×10^{-5}g; when it was diluted with 20 cc water this rose to 6.95×10^{-6}g; reaching a value of 8.34×10^{-6} g when 30 cc water was added to 10 cc if the original sol, p. 44. With the purple of colloidal silver adsorbed by stannic oxide, there is no electrometric evidence of there being any free silver ions, p. 62.

When silver is distilled in a very high vacuum the color varies from yellow through orange, red, and violet to blue. If Canada balsam be poured over the crystals they have less chance to agglomerate, and the color changes relatively little, p. 74. No attempt is made to account for the colors.

Schneider added 5 cc of the organic liquid to be tested to 1 cc of an alcoholic sol of silver. "He obtained immediate coagulation with isopropyl alcohol, normal and secondary butyl alcohols, trimethyl carbinol, heptyl alcohol, octyl alcohol, allyl alcohol, erythrite, octane, amylene, formaldehyde, acetone, ethyl ether, glacial acetic acid, benzene, benzyl alcohol, meta cresol, triethyl amine, methyl aniline, diethyl aniline, and quinoline. Coagulation occurred only after several hours with trimethyl amine and pyridine, while no precipitation occurred on addition of propyl alcohol, isobutyl alcohol, cetyl alcohol (in alkaline solution), tertiary butyl alcohol, ethylene, glycerine, and phenol," p. 86. No explanation is offered for this extraordinary series. The data have never been checked.

"Catalysis by colloidal silver has been studied but very little. Schade showed that collargol had a distinct catalytic action at a dilution of 1:60000. Gross and O'Connor observed that collargol made curare and strychnine more or less ineffective in experiments on frogs. Grumme found that colloidal silver tends to adsorb toxines in the body.... It is surprising that Izar and Ascoli and Izar found that, in their experiments, colloidal platinum and colloidal silver had about the same catalytic activity, while usually platinum has a distinctly greater catalytic action than silver," p. 99.

No general attempt is made to account for phenomena and consequently the value of the book, if any, rests on the facts that it gives. By no stretch of the imagination can the book be recommended.

Wilder D. Bancroft

Allgemeine und physikalische Chemie. *By Hugo Kauffmann. Part II. 16 × 11 cm; pp. 148. Berlin and Leipzig: Walter de Gruyter and Co., 1930. Price: 1.80 marks bound.* The chapters are entitled: valence theory; some more important constitutive properties; heat of reaction; measurement of chemical affinity; electrolytic dissociation; galvanic cells; photochemistry; properties of the atoms.

Evidently the Germans think that it is worth while to cover this amount of ground in 145 tiny pages. Tabloid science does not appeal to the reviewer any more than tabloid newspapers do. It is not very good science at that. On p. 106 we read that "only those wave-lengths which are absorbed by a system can produce chemical changes in it. . . . The converse of this law is not necessarily true for not all rays which are absorbed cause chemical change. Colored glasses cut out certain wave-lengths, which is why they seem colored to us. They are not changed, however, by these rays and the only action of the light is a heating action."

This is true; but it is misleading because it does not bring out the important point, made clear by Grotthuss in 1818, that these wave-lengths tend to decolorize the glasses and will do so if the work necessary is made small enough by the addition of a suitable depolarizer.

Wilder D. Bancroft

Kolloidwissenschaft, Elektrotechnik und heterogene Katalyse. *By Wolfgang Ostwald. 23 × 16 cm; pp. 113. Dresden and Leipzig: Theodore Steinkopff, 1930.* This book is based on two lectures given before the Siemens Company. "The preliminary work for these lectures on colloid chemistry in its bearing on electrochemical work and on heterogeneous catalysis interested the author so much that he has made a further study of the matters in question and has rewritten and enlarged the manuscripts, also tying them together. This amplification has not been confined to the questions of applied colloid chemistry which were immediately under consideration but has resulted in treating some portions of scientific colloid chemistry, particularly the partially dispersed systems, more fully than has been done before. The author has also introduced some new results and points of view, so that the book may be considered as representing an independent investigation in addition to giving a general summary of the situation," p. 1.

The chapters are entitled: states of subdivision of matter—partially and totally dispersed systems—colloidal dimensions; the building up of colloidal particles from smaller units—encolloids; dispersity functions and the optimum colloidal dimensions; general remarks on technical applications of colloid chemistry; insulators from the view-point of colloid chemistry; electrodes and electrical discharges; rectifiers; photo-cells; heterogeneous catalysis; the similarity in construction and method of action of rectifiers, photo-cells and contact catalysts; concluding remarks.

The author classifies filaments and films as partially dispersed systems, p. 4. No explanation is attempted for the colors of colloidal metals, p. 13. On p. 22 the author points out that in dilute glycerol a barium sulphate suspension has a maximum turbidity for a diameter of about 1μ, while the maximum comes at about 0.2μ in concentrated glycerol. With zinc oxide in oil there is a maximum at about 0.3μ. Isobutyric acid and water have a maximum viscosity at the temperature at which the first clouding occurs, p. 25; the one-liquid phase and the two-liquid phases are less viscous than the emulsion. The diameter of d'Herelle's bacteriophage is somewhere between 5 and 50 mμ, p. 34.

Solid insulators are classified as laminar, fibrillar, and corpuscular, p. 39. Mica and varnishes are laminar; asbestos and silk or cotton are fibrillar; paper is considered as primarily fibrillar and secondarily laminar. Porcelain is classed as corpuscular, which is certainly not correct for a glazed porcelain. Wagner finds that the thickness of coherent water on solids is 3-100 mμ, p. 44.

André found that a silver gel in nearly anhydrous sulphuric acid between silver and aluminum-alloy electrodes acted as a rectifier, p. 69. The use of tantalum and aluminum anodes as rectifiers has been known for a long time. The thickness of the active gas film is said to be 4-200 mμ, p. 70.

The author considers that the blue solutions of sulphur in pyrosulphuric acid, glycerol, etc., are not colloidal but consist of bimolecular sulphur in true solution, p. 77. This may be true; but why are the solutions blue?

"In the older theories of contact catalysis we distinguished especially two general variables: surface and adsorption. The walls of the vessel often exert a marked catalytic effect, which is especially noticeable with rough walls. With increasing surface, as with increasing dispersions, the catalytic activity usually increases. It is remarkable, however, that here again there is an optimum effect at intermediate, colloidal, degrees of dispersion, a fact which is not only established experimentally but which is easy to understand theoretically," p. 83. This conclusion is based on the assumption that platinum ions may be considered as finely divided platinum, an assumption which should not be accepted.

Schottky considers that the unipolar conductance of crystals is due to the presence in the crystals of thin films. In Lang's photo-cells the thickness of the total cuprous oxide film—not of the actual rectifying film—is about 70 mμ, p. 112.

There are many interesting things in the book and it is well worth reading. Like all the books by the author, it does not produce the effect that it should, because of a certain haziness of statement as though the author did not think his conclusions quite through. This may seem an advantage to many readers.

Wilder D. Bancroft