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CONTENTS OF VOLUME XIX

1. JANUARY

2. FEBRUARY

3. MARCH

4. APRIL

5. MAY

6. JUNE

7. OCTOBER

8. NOVEMBER

9. DECEMBER

SOIL COLLOIDS AND THE SOIL SOLUTION[1]

BY FRANK K. CAMERON[2]

To no branch of modern scientific inquiry does there pertain a more confusing literature than to soil chemistry. In this confusion there has been developed a special terminology founded on misconceptions and false analogies, but retained with an amazing perversity.

For instance, the addition of lime either as calcium hydrate or as carbonate, to most soils, induces conditions especially favorable to the growth of certain types of plants, such as the clovers, alfalfa, etc. Again, most soils when wetted and brought into close contact with blue litmus paper redden the paper. Hence, it appears, judging from current literature, that the vast majority of soils are "acid," in spite of the facts: (1) that some soils to which lime has been added sufficiently to induce good growth of clover will yet appear to redden litmus paper more vigorously than other soils which will not support the clover effectively; and (2) that the reddening of the litmus paper is, in most cases, a rather obvious phenomenon of selective absorption; and (3) that these same "acid" soils yield aqueous extracts, which, when boiled to expel carbon dioxide, are more often alkaline than neutral and quite rarely acid. The term "acid" soil being appropriated then to mean a soil which better supports certain crop plants after being limed, how may one with propriety designate that soil occasionally encountered whose aqueous extract shows the actual presence of a soluble acid, *i. e.*, responds to the test for a hydrogen ion?

It has long been the fashion with many writers on soil chemistry to ascribe the power shown by soils in absorbing potassium from aqueous solutions of potash salts more rapidly relatively than they absorb sodium and certain other bases,

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[1] A paper prepared for the symposium on colloid chemistry during the Montreal meeting of the American Chemical Society.

[2] Scientist in Charge, Soil Laboratory Investigations, Bureau of Soils, U. S. Department of Agriculture, Washington, D. C.

to the formation and presence of zeolites in the soil. There appears to be geological and petrographical evidence that zeolites are, or may be, deposited at ordinary temperatures from aqueous solution. But as has been shown elsewhere, the concentration of "free" alkali in the solution from which such a deposition might conceivably take place, must be far higher than could ever exist in a soil fit for the production of crop plants;[1] and furthermore, no reputable observer has ever yet reported actually seeing a zeolite in a soil, although many hundred soil samples have now been examined by trained microscopists with this special purpose in mind. By some it has been claimed that the soil zeolites are sub-microscopic, and exist in the clay particles only, and since the assumption of colloids in soils has become common nowadays, it is even postulated that the soil zeolites are in the "colloid condition," which is clearly a mere juggling of terms with a confusion of ideas.

It is to be feared that the term colloid, as commonly used in soil literature, is not entirely free from the same character of objection applying to acid soils and soil zeolites. Professor Remsen once designated basic salts as a "sink of iniquity into which we cast compounds we do not understand." Acid soils, soil zeolites, and soil colloids appear to be such sinks, and the colloid sink to be the deepest of them all.

While, with a large proportion of the writers on soil topics, colloids seem to be nothing more or less than a sufficient if *dernier ressort* to explain things when they are not ingenious enough to devise some other explanation, the subject has been approached seriously. It will be well, before proceeding, to call attention to some of the arguments which are usually advanced to demonstrate the existence of colloids in soils.

Van Bemmelen,[2] because of the numerous apparent

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[1] Proceedings of the Eighth International Congress of Applied Chemistry, New York, 1912, Vol. XV, pps. 43–48.

[2] Landw. Versuchs St., 35, 67–136 (1888); 37, 347–73 (1890); Zeit. anorg. Chem., 22, 313–79 (1899); 23, 321–72 (1900); 42, 265–324 (1904); 46, 322–57 (1910).

parallelisms between the properties of soils and colloids, considered the only rational explanation to be the presence of colloids in soils. As supporting this conclusion, he extracted a number of Dutch soils and some of foreign origin with aqueous solutions of acids of various concentrations. In a similar way, he examined mechanical separates of soils. From these data he classified the soils according to the ratio of reacting weights of alumina to silica or to some of the bases extracted by the acids. Because, in general, these ratios were not whole numbers, he concluded that many of the soil components, especially in the finer state of division, could not be definite compounds; hence, they must be something else, *i. e.*, colloids.

As further proof of the existence of colloids in the soils, van Bemmelen advanced the results of experiments on the rate of evaporation of water from wet soils, which rates he found to be but little different from the rate obtaining with a surface of free water.

Cushman[1] found that on wet grinding of a silicate, the grains were coated with a gel, colloid or "pectoid" which could be dyed. Sjollema[2] considers that practically all the soil components, excepting quartz grains and undecomposed mineral fragments, are colloids because they are colored by organic dyes.

Atterberg considers the physical properties of the soil to be the properties of colloid more or less modified by the presence of coarse particles. He maintains that the colloid properties give the only rational basis for soil classification, and has devoted[3] much energy to developing methods for measuring the colloid properties.

Russell, who stands deservedly in the first rank of present-day investigators of soil phenomena, takes very strong ground. He regards the clay fraction of a soil as a colloid because of

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[1] Bull. No. 92, Bureau of Chemistry, U. S. Dept. of Agric., 1905.

[2] Landw. Versuchs St., 53, 67 (1905).

[3] See for instance, II Agrogeologen Konferenz, Stockholm, 1911, p. 5, et seq.; Kolloid Chem. Beih., 6, 55-89 (1914).

its plasticity, a fact also noted by van Bemmelen and numerous other writers. He also notes that, in some clay suspensions Brownian movements can be observed, and that clay suspensions are markedly affected by the addition of small amounts of electrolytes and some other substances, showing flocculation and deflocculation phenomena. The wetted soil shows the very similar, if not identical phenomena, of "crumbing" on the one hand and "puddling" on the other.

Russell[1] holds that the "clay" particles of the soil form "compound particles" which are responsible for most of the inherent characteristics of a soil, the properties of these compound particles being the properties of colloids. In discussing the medium from which plants derive their sustenance, he says it "is a colloidal complex of organic and inorganic compounds, usually more or less saturated with water, that envelopes the mineral particles; it is, therefore, analogous to the plate of nutrient jelly used by bacteriologists, while the mineral particles serve mainly to support the medium and control the supply of air and water and to some extent the temperatures." Russell even goes so far as to divide modern soil chemists into two schools on the basis of a belief in the existence of soil colloids, to wit: "(1) the nature of the colloidal substances in the soil; these are supposed by van Bemmelen and his school to be decomposition products of weathered silicates, and by Whitney to be particles of any composition, provided the size is sufficiently small; (2) the constitution of the soil solution, van Bemmelen supposing it to be in equilibrium with a solid solution or colloidal complex, and, therefore, to depend as to its concentration on the masses of its constituents present in the complex, while Whitney supposes it to be in equilibrium with definite silicates and to be constant in concentration."

Throughout the literature, even the most recent, there seems to be an implication that colloids are possessed of mys-

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[1] "Soil Conditions and Plant Growth," by Edward J. Russell, Dr. Sc., (Lond.), Longmans, Green & Co., London, etc., 1912, pp. 56–9, 75–7, 110.

terious, almost "uncanny" properties. The term "colloid" in soil work, at least, has tended to promote a confusion of ideas, make against clear thinking, and all too frequently has been an excuse for mental laziness. The time has now come, and especially because of the prominence given to colloids in Russell's very important monograph, when the situation must be faced frankly.

If Professor Bancroft's definition of a colloid is accepted as simply "a phase sufficiently divided"[1] there can be no argument that colloids exist in the soil. A soil contains particles of all mechanical sizes, down to below recognition by the microscope and towards an indeterminate minimum.[2] Thus the amount of surface exposed in the soil is very large, even enormous, as compared with the mass of the components. Surface effects, especially adsorptions, crumbing (possibly flocculation) and puddling (possibly deflocculation) are very pronounced, and the chemistry of the soil, as has been pointed out elsewhere, is to a large extent the chemistry of surface phenomena.[3] If it be recognized, therefore, that the distinctive properties of colloid are surface properties, then there can be no objection to calling soil chemistry a branch of colloid chemistry. In the soil the amount of the surface exposed is not only very great in the aggregate, but is probably very large for all three types of solids, *viz.*, definite compounds, solid solutions, and adsorption complexes.

As far down the gradient of size as it is possible to trace the soil particles, definite compounds in the form of the well-

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[1] Jour. Phys. Chem., 18, 549 (1914).

[2] For convenience, the mechanical separates of soils are usually obtained between arbitrary limits and are designated as sands, silts, and clays. Thus the term silt does not necessarily mean, in soil literature, that the material has been deposited from a water suspension, neither does the term clay imply the composition of the material is that of kaolin or kaolinite, nor even that these definite compounds are present. Fletcher and Bryan: Bull. No. 84, Bureau of Soils, U. S. Dept. Agric., 1912.

[3] Cameron and Bell: Bull. No. 30, Bureau of Soils, U. S. Dept. Agric., 1905; "The Soil Solution," by Frank K. Cameron, The Chemical Publishing Co., Easton, Pa., 1911, pp. 67–9.

known rock and soil forming minerals have been recognized. It seems reasonable to suppose that they still persist as such beyond the limits of positive identification, even perhaps to extreme attenuation. Together with this mineral mixture of definite chemical individuals, the results of degradation agencies, there is always present a more or less indefinite mass of indeterminate compounds, in extreme state of comminution in which *apparently* oxides of aluminum, of iron (ferric) and organic residues (humus) predominate. There is very good reason to believe that some of the components of this "clay" are solid solutions—for example, the so-called basic phosphates of iron and alumina. And there are equally good reasons for believing in the presence of adsorption complexes. In fact it is a well sustained generality that potassium and certain other normal constituents of the soil tend to segregate in the clay separates, which admit of no other explanation than that of selective adsorption.

The minerals of the soil are continually reacting with water, by hydrolysis, and very often with secondary reactions which yield products in the colloid condition. For example, consider the comparatively simple case of orthoclase, assuming for simplicity in presentation, that it has actually the theoretical formula $K.AlSi_3O_8$. Then $K.AlSi_3O_8 + HOH \rightleftarrows KOH + H.AlSi_3O_8$. So far as is known the acid $H.AlSi_3O_8$ does not exist; but as fast as formed, there is a "splitting off" of silica SiO_2, perhaps progressively, with the formation of $H.AlSi_2O_6$ (pyrophylite), $H.AlSiO_4$ (kaolinite), and $H.AlO_2$ (diaspore).

It seems probable that the silica and alumina thus formed, at least for a time, and possibly even for a time also, the other products of hydrolysis, persist in the colloid condition, either as true gels or colloidal solutions.[1] Similarly ferruginous gels, and even perhaps gels of magnesium hydroxides are formed and more or less temporarily affect the constitution of the soil complex. But while admitting the possibility or

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[1] See Van Hise: U. S. Geol. Surv., Monograph No. 47, p. 333, 1904, and Kahlenberg and Lincoln: Jour. Phys. Chem., 2, 77–90 (1898).

even probability of such gels being formed from *a priori* considerations as well as laboratory manufacture, it must also be admitted that there is no satisfactory direct evidence of their presence in a soil under field conditions. The principal evidence for their presence cited in the current soil literature, are the results obtained in the selective absorption of dyes by soils. But no case has been brought forward which cannot be satisfactorily explained by the fact merely that the soil particles present a large surface for absorbent action.[1] Nevertheless, the importance of this gel formation is considered, among soil investigations usually, to be very important as affording a protective coating to the soil grains. This protective coating is generally assumed to prevent solvent action of soil water upon the coated particles, obviously an incorrect assumption, since diffusion must necessarily proceed through the gel as through water. Of course, such a coating might mechanically slow up the rate of solvent action on the soil particles. The ordinary ferruginous-humus-clay mass, because it sticks so persistently to the coarser particles, is frequently supposed to prevent solvent action. This material can, however, be separated quite effectively from the coarser particles, merely by shaking in water to which a little ammonia has been added to deflocculate the soil aggregates. Here again there seems to be possible nothing more than a mechanical slowing up of the rate of solvent action.

Another role popularly assigned by soil investigators to the supposed gel formed on the surface of soil particles is the making possible of adsorption effects. Here there is an astonishing amount of misinformation current. At a recent meeting of a scientific organization, an agricultural chemist of recognized distinction, in discussing a paper which had just been read, made the startling statement that there could be no such thing as an adsorption of potassium by a soil because potassium is not a colloid and it is a well-known fact(?) that

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[1] See, for instance, Seki: Landw. Versuchs St., 79-80 (dem Andenken Oskar Kellner gewidmet), 873, and the literature there cited.

colloids alone can be adsorbed and then only by other colloids. He even went so far as to deny the probability of Patten's observations on the adsorption of methylene blue by powdered quartz,[1] although admitting them as possible if the quartz grains had a coating of colloidal silica; their only importance, he claimed, would be in showing methylene blue to be a colloid.

Finally, it is to this protective coating of colloid material that most teachers of soil physics ascribe the formation of aggregates of soil particles so important in determining the highly desired "crumb" structure of soils and so important for good tilth, "good heart," the textural relations, water holding capacity, and adaptability to types of crops and crop rotations; in fine, to soil physics and soil management in general. Unfortunately, however, there is no positive evidence one way or the other for the existence of these gel coatings. The phenomena of crumbing and of puddling, while very similar to, if not identical with, the phenomena of flocculation and deflocculation, the phenomena of plasticity, etc., seem to be accounted for readily enough by the presence of the fine clay particles, and there is no obvious necessity for assuming the presence of any gel, much less that it is a protective coating.

Practically, there is a serious difficulty in applying observations on ordinary suspensions, gels and colloid solutions to the interpretation of soil phenomena. In a soil containing the optimum, or somewhat less than the optimum water content for plant growth, it appears that practically all the water (soil solution) is spread out over the grains or crumbs, in films.[2] This film water is held to the soil under stresses of such magnitude as may considerably affect the solvent power of the water, although direct proof that such is the case is wanting. It is very probable that the liquid-gas surface

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[1] Trans. Am. Electrochem. Soc., 10, 67–74 (1906).

[2] Cameron and Gallagher: Bull. No. 50, Bureau of Soils, U. S. Dept. Agric., 1908. No mechanical means has yet been devised for extracting this soil solution or separating it from the solid phases, hence we do not yet know what its composition actually is and can only make inferences from indirect methods of experimentation.

tension affects appreciably the liquid-solid surface tension, although in what manner and to what extent it is yet impossible to say. Consequently, great reserve must be exercised in attempting to apply to soil phenomena the reasoning developed from observations on gels and ordinary suspensions. Certainly the water films in the soil are continually changing in thickness; there must be a consequent change in the distribution of solutes between absorbent and solvent, and probably two changes of surface tension at least.

Just how to correlate these several factors and especially in view of the fact that they are each and all continually undergoing change, no man yet knows. Until a clearer vision of the interrelation of these factors is gained, it is vain to look for any correlation of the agricultural importance of a particular soil with arbitrary measurements of its supposed colloidal properties.

Of the necessary consequences of the colloidal constitution of the soil as described in the foregoing paragraphs very much the most important, theoretically and practically, is the concentration of the soil solution, at least with respect to those constituents derived from the soil minerals. From what has been said above, it will be correct and convenient to classify the soil components as follows:

1. Definite compounds, or chemical individuals.
2. Indefinite complexes, but homogeneous, *i. e.*, solid solutions.
3. Indefinite complexes, but not homogeneous, *i. e.*, adsorption complexes.

For any given temperature, a definite compound has a definite solubility, which is altogether independent of the relative masses of the solid and the liquid. This solubility may be affected by the presence of a third substance, especially if the solutes are electrolytes. In soil solutions the concentrations are so small that mutual solubility effects can be considered negligible, usually, excepting only those due to dissolved carbon dioxide. There are, however, two modifying influences which are probably effective in the case of soil minerals. It has been shown by Ostwald[1] and by Hulett[2] that a very finely comminuted substance may have quite a different solubility than the same substance when in coarse particles. For instance, the solubility of gypsum may be increased a fifth by grinding the solid to very fine particles. The extremely fine mineral particles in the clay portion of the soil may well, therefore, have different solubilities than those minerals in the fine sands, and intermediate solubilities may pertain to the finer silt particles.

Again, many if not most of the soil minerals are salts of strong bases with weak acids. On dissolving, they are more or less completely hydrolyzed, and one of the products of hydrolysis, the acid usually, is so very slightly soluble that its active mass can be considered negligible. Consequently a simple application of the mass law to the reaction:

$$\text{Mineral} + \text{water} \rightleftharpoons \text{unhydrolyzed salt} + \text{base} + \text{acid}$$

shows that the concentration of the base must become very large, relatively, before equilibrium is attained. It is quite improbable that equilibrium is ever actually attained in the soils of humid areas. And it is equally improbable that any of the ordinary rock forming minerals can be synthetized at the concentrations and temperatures ordinarily realized in soils.[3] From these considerations, therefore, it appears that the major part of the definite compounds which dissolve in the soil water, under humid conditions, are hydrolyzed, and that the soil solution never reaches the concentration of the more soluble constituents required for definite equilibrium or "saturation." Practically, therefore, so far as regards

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[1] Zeit. phys. Chem., 34, 496 (1900).

[2] Ibid., 37, 385-406 (1901).

[3] While highly improbable that zeolites are formed under soil conditions by "building up" processes, there is to be admitted the possibility of their formation by some "building down" mechanism not yet explained. Certainly there is geological evidence that zeolites are sometime alteration products of feldspar. On the other hand there is a respectable body of cumulative evidence in geological literature suggesting that concentrations may occur in adsorption films sufficient to induce "building up" processes. Obviously, however, plant roots do not come into contact with solutions of such concentrations.

the definite compounds in the soil, the concentration of the soil solution is not independent of the ratio of the mass of solid to the mass of liquid, although theoretically such a condition should be obtained if the time element, surface effects and like distributing factors did not enter.

Different considerations obtain when the liquid solution is in contact with a solid solution containing a common component. The concentrations of the common component in both liquid and solid phase is dependent upon the relative masses of the phases. Increasing the concentration in one increases (or sometimes decreases) the concentration in the others. There is a distribution of the common component represented by the equation $C = KC_1$, or $C = KC^n_1$, or perhaps by some more complicated expression. Usually, the exponent n is positive; but that it may have a negative value is suggested by the case where lime is added to lime phosphate in contact with water.

A practical example of a solid solution in the soil is where a soluble phosphate has been added, the phosphoric acid being more or less promptly precipitated as a basic (?) phosphate, *i. e.*, solid solution, and it has been shown that it would require the addition of enormous and impracticable amounts of the phosphate to so increase the concentration of the ferro-phosphoric acid alumino-phosphoric acid and lime-phosphoric acid solid solutions to the point where there would be an appreciable increase in the concentration of the liquid (soil) solution.[1]

The third class of soil solids comprises those cases where there is a mineral complex in which a more soluble substance (solute) is condensed or adsorbed on the surface of a much less soluble substance (adsorbent). Here again is a case of distribution and, obviously, again the concentration of the liquid solution is dependent upon the relative masses of liquid and solid; or, more correctly, upon the volume of the liquid and the absorbing surface of the solid. As a case in illustration, prob-

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[1] Cameron and Bell: Bull. No. 41, 1907; Schreiner and Failyer: Bull. No. 32, 1906, Bureau of Soils, U. S. Dept. of Agric.

ably a large part of the potassium in a soil is adsorbed on the surface of the clay particles. Attempts to study experimentally the distribution of a solute between the solid soil particles and the free water in contact with the soil have shown that the equation is of a quite complex character, owing probably to changing aggregation (flocculation or deflocculation) of the soil particles.[1] But whatever the form of the equation, it is beyond doubt that the concentration in the soil solution changes coincidentally with and in the same direction as the concentration in the absorbent. As the effective surface of the soil is continually changing, it follows necessarily that the concentration of the soil solution is continually changing. But with such dilute aqueous solutions as are soil solutions, it requires a relative large increase in the adsorbed solute to produce an appreciable change in the concentration of the liquid phase. The fact has been shown a number of times experimentally with soils and with other absorbents, both by shaking the absorbent with aqueous solutions of the solute and by percolation experiments. It is clear, therefore, that the concentration of the soil solution, resulting from contact with definite compounds, solid solutions and adsorbent films, *i. e.*, from contact with soil colloids, *is* determined by the relative masses of the liquid phase and of the solid phase, in so far as the masses of the solid phases determine their effective surface to solvent action. Since the moisture content of a soil is continually changing, the soil either drying out or getting wetted, and since the effective surface of the soil particles is continually changing, the concentration of the soil solution is continually changing or tending to change. But as the foregoing analysis of the mechanism of the soil solution develops, and from the inherent nature of the soil colloids, small changes in concentration in the liquid phase (soil solution) are induced by relatively large changes in the common constituents in the solid phases (soil colloids), at least with respect to those mineral constituents of recognized importance for plant growth and

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[1] Cameron and Patten: Jour. Phys. Chem., 11, 581–92 (1907).

fertilizer practice. Consequently, under any given climatic conditions, the concentration of the soil solution, with respect to those constituents derived from soil minerals, varies within narrow limits, no matter what may be the relative masses of those minerals in the soil.[1] Obviously, other constituents, organic or inorganic may sometimes vary quite widely in concentration although in all cases the solubility principles just set forth will apply. So much being granted, it follows logically that in the function whatever its form may be, expressing the relation between crop production and the various natural and artificial factors affecting it, fertilizers as well as each and every other factor are dependent variables, and that furthermore, all soil phenomena affecting crop production are dynamic, contrasted with static, in character: that is, they are all involved in continual changes of some kind or other; and, in fine, each soil must be considered as an individual, with its own inherent characteristics, including crop producing powers. Arguments in detail having already been set forth elsewhere, it is not necessary to repeat them here.[2]

In this paper it has been shown:

1. That soil chemistry can be considered a branch of colloid chemistry, provided a colloid is defined as a phase sufficiently divided where surface phenomena are predominant.

2. That the relation of the gas-liquid surface tension to the solid-liquid surface tension is a most important problem requiring investigation for a clear purview of the functions of soil colloids.

3. That it is a necessary consequence of the colloid constitution of the soil, that very small changes in the concentration of the soil solution correspond to relatively large changes in the composition of the solid phases, respecting those constituents derived from the minerals of the soil.

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[1] That difference in climate may make marked differences in the concentration of the soil solution is, of course, well recognized. See for instance, Mooney: "The Bahama Islands," The Geological Society of Baltimore, Johns Hopkins Press, 1905, pp. 153–74.

[2] Jour. Ind. Eng. Chem., 1, 806–10 (1909); 3, 188 (1911), "The Soil Solution."

THE ELECTRICAL CONDUCTIVITY OF SOLUTIONS OF CERTAIN ELECTROLYTES IN ORGANIC SOLVENTS

BY J. N. PEARCE

The study of the electrical conductivity of solutions in organic solvents has brought to light many interesting relations. In many such solvents the same general relation obtains as is found in the case of aqueous solutions, *viz.*, the molecular conductivity increases regularly with increasing dilution. In the great majority of these no limiting value of the molecular conductivity is obtainable, however great the dilution employed.

On the other hand, a large number of instances have been found in which the behavior is apparently just the opposite, the molecular conductivity in these cases increasing as the concentration increases. Instances of this kind are to be observed in the molecular conductivity of solutions of hydrogen chloride in benzene,[1] xylene, hexane, and ether; the alkaline halides in benzonitrile;[2] mercuric cyanide in liquid ammonia;[3] aluminium bromide in ethyl bromide;[4] in all the more concentrated solutions of methyl-, ethyl-, *n*-propyl-, amyl-, and allyl-alcohols; phenol, carvacrol, thymol, α- and β-naphthol and resorcinol in liquid hydrogen bromide;[5] various aliphatic and aromatic acids in liquid hydrogen bromide and hydrogen chloride;[6] solutions of the ammonium bases and non-salt organic compounds in the liquid halogen halides and hydrogen sulphide[7] and solutions of various salts in aniline, methyl aniline, and dimethyl-aniline.[8]

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[1] Kablukoff: Zeit. phys. Chem., 4, 429 (1889); Cattaneo: Real. Accad. Lincei, [5] 2, II, 112 (1893).

[2] Euler: Zeit. phys. Chem., 28, 619 (1899).

[3] Franklin and Kraus: Am. Chem. Jour., 23, 277 (1900).

[4] Plotnikoff: Jour. Russ. Phys. Chem. Soc., 34, 466 (1902).

[5] Archibald: Jour. Am. Chem. Soc., 29, 665, 1416 (1907).

[6] Ibid., 29, 1416 (1907).

[7] Steele, McIntosh and Archibald: Zeit. phys. Chem., 55, 179 (1907).

[8] Sachanov: Jour. Russ. Phys. Chem. Soc., 42, 683 (1910).

Instances are also known in which the molecular conductivity may both increase and then decrease as we proceed from the more dilute to the more concentrated solutions as, for example, solutions of silver nitrate and cadmium iodide in amylamine.[1] Such cases, the authors state, are not to be explained on the basis of the Arrhenius theory. The molecular conductivity of potassium iodide in liquid iodine[2] at first increases with dilution, passes through a maximum and then decreases rapidly. The molecular conductivity of solutions of silver nitrate in methylamine[3] first increases with dilution, then decreases and afterward again increases with further dilution. Solutions of lithium chloride in ethylamine[4] give molecular conductivities which increase with dilution up to about 0.8 *N* and then diminish rapidly with further dilution, while the molecular conductivities of solutions of silver nitrate and ammonium chloride in the same solvent decrease with dilution throughout and finally appear to attain minimum values in the very dilute solutions. Cadmium iodide[5] in certain organic solvents was found to be strikingly abnormal in that its molecular conductivity varies neither with the dilution nor with the temperature.

Many theories have been advanced to explain this apparently abnormal effect of dilution upon the molecular conductivity. Euler[6] explains the increase in the molecular conductivity of solutions in benzonitrile as being due to the presence of the ions. Franklin and Gibbs explain the abnormal results for solutions of silver nitrate in methylamine by means of a slightly modified form of the hypothesis proposed by Lewis for solutions of potassium iodide in liquid iodine. Their hypothesis and explanation is this: "Salts dissolved in a weak ionizing solvent may be expected to give solutions in

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[1] Kahlenberg and Ruhoff: Jour. Phys. Chem., 7, 254 (1903).

[2] Lewis: Proc. Am. Acad. Arts and Sci., 41, 419.

[3] Franklin and Gibbs: Jour. Am. Chem. Soc., 29, 1389 (1907).

[4] Shinn: Jour. Phys. Chem., 11, 537 (1907).

[5] Dutoit and Friderich: Bull. Soc. chim. Paris, [3] 19, 321 (1898).

[6] Loc. cit.

which the self-ionization of the salt shows itself conspicuously. Methylamine dissolves silver nitrate abundantly, forming solutions, which, when very concentrated, are possessed of a high degree of viscosity. The conductivity of the most concentrated solutions, in that they approach the condition of the melted salt, is, therefore, for the most part, due to the auto-ionization of the salt. As the solution is diluted its viscosity diminishes rapidly with the result that the increasing speed of the ions more than counteracts the effect of diminishing auto-ionization, which may be assumed to accompany dilution, and which of itself would cause a diminution of the conductivity. The observed conductivity therefore increases. The viscosity, however, falls off at a rapidly diminishing rate as the dilution increases, so that after a time the opposing effects of viscosity and self-ionization balance each other, when a maximum of the molecular conductivity is reached. From this point on, for a time, increasing dilution is most conspicuous in its effects on the auto-ionization of the salt. The rate at which the auto-ionization diminishes becomes smaller as the dilution continues to increase with the result that, beyond a certain point, the dissociating action of the solvent becomes conspicuous as the curve passes through the minimum and then ascends after the familiar manner of salts in aqueous solution." Cady[1] noted the similarity between the crystalline compounds of water and copper sulphate on the one hand and ammonia and copper sulphate on the other. Experiments proved that the latter pair also give conducting solutions. It might be inferred from this that whenever a solute and solvent are capable of separating from a solution as a crystalline "solvate" solutions of the two components will conduct electricity.

Kahlenberg and Schlundt[2] ventured the idea that the conducting power of a solution is dependent upon a mutual reaction between the solvent and solute resulting in the forma-

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[1] Jour. Phys. Chem., 1, 707 (1897).

[2] Ibid., 6, 447 (1903).

tion of a compound which conducts the current. This solvent-solute compound theory was further apparently confirmed by Walden and Centnerszwer[1] in their work with solutions in liquid sulphur dioxide. Solutions of lithium chloride in pyridine have remarkably low molecular conductivities. Laszczyński and Gorski[2] explain this as due to the formation of the compound, $LiCl.2C_5H_5N$. That such a theory is useful is very evident, since it can be used in explaining phenomena which are of an opposite nature.

According to Steele, McIntosh and Archibald[3] the power to form conducting solutions is a function of both the solvent and the solute. This belief was strengthened by the fact that the amines, alcohols, ether, acetone, etc., which give conducting solutions in the liquid hydrogen halides and hydrogen sulphide, all have the power of forming compounds with these solvents. In their paper they state that it is their object to show that the anomalous behavior of these solutions can be explained upon the basis of the Arrhenius theory, if we assume that the original dissolved substance, of itself incapable of dissociation, may either become polymerized or unite with the solvent to form a compound which can then behave as an electrolyte. For both assumptions, *viz.*, that of polymerization of the solute, or the formation of a solvent-solute compound, they arrive at the general relation,

$$\lambda_v = \alpha K' = \kappa V^n$$

where α represents the degree of dissociation, κ the specific conductance, V the volume, K′ a constant, and n the number of molecules of the solute combining with m molecules of the solvent, or the number of simple molecules of the solute combining to form one molecule of the polymerized solute. Their results when calculated according to this formula show an increase in molecular conductivity with increasing dilution, whereas when calculated according to the relation $\lambda_v = \kappa V$, the molecular conductivity decreases with dilution.

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[1] Zeit. phys. Chem., 42, 432 (1903).

[2] Zeit. Elektrochemie, 4, 290 (1897).

[3] Zeit. phys. Chem., 55, 179 (1907).

Similar results were obtained by Archibald[1] alone for solutions of paraffin and aromatic alcohols in liquid hydrogen bromide and for organic acids in liquid hydrogen-bromide and hydrogen chloride.

Sachanov[2] has made an extended study of the conductivity of solutions in some organic solvents. The solvents used were aniline, methylaniline, dimethylaniline, acetic and propionic acids and a few esters. In all of these solvents, except the esters, the molecular conductivity of the various salts used decreases very rapidly with dilution, and this phenomenon is especially marked in the more concentrated solutions. Walden had previously shown that the dissociating power of solvents is in a high degree independent of their chemical nature and is determined chiefly by the dielectric constant of the solvent. The dielectric constants of the solvents used by Sachanov are small. Those of the amines used, *viz.*, aniline, methylaniline and dimethylaniline, are 4.79, 6.62 and 4.99, respectively. According to him, the chief factor determining the ability to give conducting solutions is the chemical nature of the solvent. He divides solvents in which diminution of the molecular conductivity is observed into two classes: (1) those in which all solutes, independently of their nature, exhibit such diminution, and (2) those few in which the molecular conductivity, as a rule, increases with dilution, but with certain dissolved substances diminishes. In general, solvents with low dielectric constants are characterized by divergence from the Nernst-Thomson rule. He also states that the decrease of molecular conductivity on dilution is as characteristic a property of solvents with low dielectric constants and slight dissociating power as is the increase of molecular conductivity for solvents with high dielectric constants. The electrolytic dissociation does not depend solely upon the magnitude of the dielectric constant, but also upon the formation of solvates and complex ions, *e. g.*,

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[1] Archibald: Jour. Am. Chem. Soc., 29, 665, 1416 (1907).

[2] Jour. Russ. Phys. Chem. Soc., 42, 683, 1363 (1910); 43, 526, 534 (1911); 44, 324 (1912); Zeit. phys. Chem., 80, 13, 20 (1912).

$$Li_2Br_2.xC_6H_7N \rightleftarrows \overset{+}{Li}.yC_6H_7N + \overline{LiBr_2}.zC_6H_7N$$

The formation of such ions favors electrolytic dissociation because the electroaffinity of these ions is greater than that of the primary ions. In solvents with low dielectric constants only complexes which yield ions of greatly enhanced electroaffinity can undergo electrolytic dissociation. The decomposition of these complex solvates and complex ions explains the decrease of molecular conductivity on dilution and also, so he states, why the Nernst-Thomson rule is not applicable for solvents with low dielectric constants.

In his study of the dielectric constants of dissolved salts, Walden[1] finds that the dielectric constant of a weakly ionizing solvent is increased by solution of certain binary electrolytes, and that this increase is apparently dependent upon the constitution of the salt. On the basis of their specific influence he divides the binary salts chosen into two classes, *viz.*, the strong and the weak. Strong salts, *e. g.*, the tetra-alkylated ammonium salts, which are characterized by a great dissociation tendency, possess also a very high dielectric constant. For weak salts, *e. g.*, the mono-alkylated ammonium salts, the reverse is true. They have a slight tendency to ionize and small dielectric constants. The degree of ionization of a salt depends both on the ionizing power of the solvent and the tendency of the solute to ionize. Since both factors increase with the dielectric constant, the highest degree of ionization will be found in a system where both the solvent and the solute possess large dielectric constants. The presence of ions was also found to increase the dielectric constant.

A large number of the solutes cited in the introduction, if not all of them, exhibit a strong tendency to polymerize and this tendency obviously increases with the concentration. Depolymerization resulting from dilution may proceed either in separate steps or directly down to the simplest products. According to Walden, the minimum degradation of the poly-

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[1] Bull. Acad. Sci. St. Petersburg, 1912, 305–32, 1055–86; Translation by H. C. B. Weber: Jour. Am. Chem. Soc., 35, 1649 (1913).

meric molecules will be obtained when we dissolve a binary salt with a low dielectric constant in a solvent, also with a low dielectric constant. In this case the solution will contain an extremely small number of ions, but a very great number of associated salt molecules. The increase in the dielectric constant must, therefore, be due to the presence of the polymerized molecules. These solutions show a weak molecular conductivity. With progressive dilution the dielectric constant falls rapidly and approaches that of the pure solvent. This will result in a rapid decrease in the dissociating power and therewith a simultaneous decrease in the molecular conductivity.

It is a well known fact that for a given temperature the complexity of hydrates and of solvates, whether of molecules or ions, decreases rapidly with increasing concentration. Furthermore, it has been found that the complexity of these solvates decreases also with rise in temperature. On the other hand, the complexity of the solute molecules and ions, due to polymerization, increases with increase in concentration. The effect of temperature would, therefore, appear in the temperature coefficients of the molecular conductivity.

The present work was undertaken with the idea of making a detailed and thorough study of the molecular conductivity of solutions of electrolytes in various organic solvents over the widest possible ranges of concentration and to determine the effect of temperature upon the conductivity. This seemed advisable since the previous investigators have limited their work to one temperature.

Experimental

The conductivity measurements were made by means of the well known Kohlrausch method. The bridge wire was carefully calibrated according to the method of Strouhal and Barus. During the latter part of the work we were fortunate in securing a new Kohlrausch roller bridge of the type devised by Washburn.[1] All of the measuring flasks, burettes, weights

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[1] Jour. Am. Chem. Soc., 35, 180 (1913).

and resistance boxes bore the certificate and stamp of the Bureau of Standards, or of the Reichsanstalt. Four glass-stoppered conductivity cells with sealed-in electrodes were used.

The two cells of larger resistance capacity were standardized against a 0.02 *N* potassium chloride solution at 25°. This solution was prepared from twice recrystallized Kahlbaum's "C. P." potassium chloride and conductivity water having a specific conductance of 1.2×10^{-6}, and the specific conductance of the solution was taken as 2.768×10^{-3}. With the cell constants thus obtained the molecular conductivity of a 0.002 *N* potassium chloride solution was obtained at 25°. The value of λ_{600} found was: Cell *2 = 147.64, Cell *3 = 147.60. The constants of the two cells of small capacity were then determined against the 0.002 *N* solution, and the constants of all four cells checked against a 0.01 *N* acetic acid solution at 25°.

The temperatures chosen for the work were 0°, 25°, and 35° or 50°. The zero-bath consisted of clean, finely crushed ice, moistened with distilled water. Large water thermostats, electrically heated and electrically controlled, gave temperatures constant to 25° ± 0.01, 35° ± 0.02 and 50° ± 0.02, respectively.

An attempt was made to use only those salts which are very soluble in the solvent used, in order to get the greatest possible range in concentration, but unfortunately the number of typical salts are few. The salts used were either Kahlbaum's C. P. (best grade) or they were specially prepared. In every case they were carefully purified and dehydrated by the methods recommended for the individual salts, and preserved in glass-stoppered weighing bottles over phosphorus pentoxide. The solubility of each salt at 25° was approximately determined and a convenient maximum normality chosen. Whenever possible, the mother solution was made up by direct weighing and then diluted to the concentrations desired, the utmost care being taken to prevent contact with the moisture of the air.

Solutions in Aniline

The aniline used was of an especially good grade from Merck. It had been allowed to stand over fused potassium hydroxide for several weeks. It was then decanted into a clean dry distilling flask and distilled; only the middle portion passing over at 181°–182° (uncorr.) was collected. This portion was then further purified according to the method of Hantzsch. The aniline was refluxed for ten hours with a quantity of pure anhydrous acetone; the acetone was distilled off and the middle portion collected. It was finally twice redistilled from pure, powdered zinc. When first distilled the aniline was practically colorless; its specific conductances at 0°, 25° and 35° were 0.9×10^{-8}, 2.4×10^{-8} and 8.2×10^{-8}, respectively. In spite of all precautions taken in its purification, the aniline gradually darkened on standing, but no noticeable change in the specific conductance was to be observed.

Owing to the extremely high resistances it was found impossible to work satisfactorily with solutions more dilute than 0.005 *N*, while in some cases 0.01 *N* is the highest dilution measurable.

Silver Nitrate

TABLE I—MOLECULAR CONDUCTIVITY

V	λ_0	λ_{25}	λ_{35}
200	0.182	0.372	—
100	0.159	0.349	0.423
40	0.156	0.338	0.414
20	0.194	0.407	0.494
10	0.299	0.650	0.738
4	0.464	0.869	1.418
2	0.725	1.984	2.600

TABLE II—TEMPERATURE COEFFICIENTS

V	$\frac{\lambda_{25} - \lambda_0}{\lambda_0 \cdot 25}$	$\frac{\lambda_{35} - \lambda_0}{\lambda_0 \cdot 35}$	$\frac{\lambda_{35} - \lambda_{25}}{\lambda_{25} \cdot 10}$
100	0.049	0.048	0.021
40	0.047	0.047	0.022
20	0.044	0.044	0.021
10	0.047	0.046	0.021
4	0.055	0.057	0.026
2	0.069	0.078	0.031

Aniline Hydrobromide

Table III—Molecular Conductivity

V	λ_0	λ_{25}	λ_{35}
200	0.159	0.306	0.311
100	0.124	0.213	0.230
40	0.109	0.183	0.185
20	0.123	0.199	0.199
10	0.170	0.263	0.264
4	0.361	0.556	0.564
2	—[1]	0.971	1.009

Table IV—Temperature Coefficients

V	$\frac{\lambda_{25}-\lambda_0}{\lambda_0 \cdot 25}$	$\frac{\lambda_{35}-\lambda_0}{\lambda_0 \cdot 35}$	$\frac{\lambda_{35}-\lambda_{25}}{\lambda_{25}^{\circ} \cdot 10}$
200	0.037	0.027	0.001
100	0.029	0.025	0.008
40	0.027	0.019	0.008
20	0.025	0.017	0.000
10	0.022	0.016	0.000
4	0.022	0.016	0.001
2	—[1]	—[1]	0.003

Aniline Hydrochloride

Table V—Molecular Conductivity

V	λ_0	λ_{25}	λ_{35}
40	0.051	0.085	0.098
20	0.048	0.079	0.088
10	0.056	0.087	0.95
4	0.095	0.143	0.154
2	—[1]	0.265	0.286

Table VI—Temperature Coefficients

V	$\frac{\lambda_{25}-\lambda_0}{\lambda_0 \cdot 25}$	$\frac{\lambda_{35}-\lambda_0}{\lambda_0 \cdot 35}$	$\frac{\lambda_{35}-\lambda_{25}}{\lambda_{25} \cdot 10}$
40	0.026	0.025	0.014
20	0.025	0.024	0.012
10	0.021	0.019	0.009
4	0.020	0.017	0.007
2	—[1]	—[1]	0.008

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[1] Solidified.

Monoethyl-aniline Hydrochloride

TABLE VII—MOLECULAR CONDUCTIVITY

V	λ_0	λ_{25}	λ_{35}
100	0.064	0.112	0.119
40	0.048	0.092	0.102
20	0.021	0.079	0.093
10	0.053	0.084	0.089
4	0.083	0.125	0.134

TABLE VIII—TEMPERATURE COEFFICIENTS

V	$\frac{\lambda_{25}-\lambda_0}{\lambda_0 \, . \, 25}$	$\frac{\lambda_{35}-\lambda_0}{\lambda_0 \, . \, 35}$	$\frac{\lambda_{35}-\lambda_{25}}{\lambda_{25} \, . \, 10}$
100	0.030	0.024	0.006
40	0.037	0.032	0.011
20	0.109	0.097	0.018
10	0.023	0.020	0.007
4	0.020	0.018	0.007

Mercuric Iodide

TABLE IX—MOLECULAR CONDUCTIVITY

V	λ_0	λ_{25}	λ_{35}
10	0.0033	0.0076	0.0097
2	0.0014	0.0036	0.0046
1	0.0012	0.0032	0.0046

TABLE X—TEMPERATURE COEFFICIENTS

V	$\frac{\lambda_{25}-\lambda_0}{\lambda_0 \, . \, 25}$	$\frac{\lambda_{35}-\lambda_0}{\lambda_0 \, . \, 35}$	$\frac{\lambda_{35}-\lambda_{25}}{\lambda_{25} \, . \, 10}$
10	0.053	0.053	0.027
2	0.063	0.066	0.025
1	0.069	0.084	0.043

Ammonium Sulphocyanide

TABLE XI—MOLECULAR CONDUCTIVITY

V	λ_0	λ_{25}	λ_{35}
100	0.187	0.258	0.312
40	0.130	0.251	0.291
20	0.164	0.313	0.366
10	0.267	0.506	0.806
4	0.647	1.271	1.502

Tetraethylammonium Iodide

TABLE XII—MOLECULAR CONDUCTIVITY

V	λ_0	λ_{25}	$\frac{\lambda_{25} - \lambda_0}{\lambda_0 . 25}$
200	0.910	2.021	0.0488
100	0.850	1.910	0.0498
40	0.964	2.195	0.0510
20	1.234	2.842	0.0521
10	1.689	3.943	0.0534
4	2.244	5.631	0.0603
2	2.650	6.849	0.0633
1	1.801	5.445	0.0809
0.8	1.334	4.477	0.0942

Summary of the Results in Aniline Solutions

As might be expected from the nature of the solvent all of the salts used give poor conducting solutions. In respect to the molecular conductivity these salts may be divided into three classes. In the first class which includes by far the larger number are silver nitrate, aniline hydrobromide, aniline hydrochloride, methylaniline hydrochloride, ammonium sulphocyanide and lithium iodide. With these the molecular conductivity decreases with dilution in the concentrated regions passes through a minimum and finally increases normally with further dilution. Mercuric iodide, whose molecules usually exhibit a great tendency to polymerize, gives values for the molecular conductivity which apparently increase normally with the dilution. For tetramethylammonium iodide on the other hand, the molecular conductivity first increases with the dilution to a maximum, then decreases rapidly, passes through a minimum and finally again increases normally with the dilution. The behavior of tetraethylammonium iodide is similar to that found by Franklin and Gibbs[1] for solutions of silver nitrate in methylamine. Of the salts studied tetraethylammonium iodide gives the best and mercuric iodide the poorest conducting solutions.

The effect of temperature varies with the nature of the dissolved salt. The temperature coefficients of the molecular

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[1] Jour. Am. Chem. Soc., 29, 1389 (1907).

conductivity of solutions of silver nitrate, aniline hydrochloride, and aniline hydrobromide decrease with dilution in the concentrated regions and pass through a minimum in those solutions which give the minimum value for the molecular conductivity. Methylaniline hydrochloride, on the contrary, gives a maximum temperature coefficient in that concentration which gives the minimum molecular conductivity. Although but three concentrations of mercuric iodide were studied the temperature coefficients show a distinct increase with increasing dilution, while for tetraethylammonium iodide the temperature coefficients decrease throughout with increasing dilution, the decrease being most rapid in the regions of greatest concentration.

Solutions in Quinoline[1]

Schuchardt's chemically pure, synthetic quinoline was allowed to stand over fused potassium hydroxide for several weeks and then twice redistilled. Only that portion passing over at 227°–229° C was used in the work. In order to make the effect of the temperature greater, the molecular conductivities were determined at 50° instead of at 25° as in the case of aniline. The specific conductivities of the quinoline at 0°, 25° and 50° were found to be 1.6×10^{-8}, 2.2×10^{-8} and 7.4×10^{-8}, respectively.

Rough determinations of the solubility of many salts in quinoline showed that only a very few are sufficiently soluble to make work with them worth while. Of these the four chosen were aniline hydrobromide, silver nitrate, copper bromide and cobalt chloride.

Aniline Hydrobromide

TABLE XIII—MOLECULAR CONDUCTIVITY

V	λ_0	λ_{25}	λ_{50}
1000	0.596	0.918	1.319
500	0.480	0.760	0.988
200	0.340	0.528	0.666
100	0.267	0.416	0.527
20	0.207	0.324	0.412
5	0.264	0.464	0.642

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[1] The data for solutions in quinoline was obtained by Mr. E. H. Conroy.

TABLE XIV—TEMPERATURE COEFFICIENTS

V	$\frac{\lambda_{25} - \lambda_0}{\lambda_0 . 25}$	$\frac{\lambda_{50} - \lambda_0}{\lambda_0 . 50}$	$\frac{\lambda_{50} - \lambda_{25}}{\lambda_{25} . 25}$
1000	0.0216	0.0243	0.0175
500	0.0236	0.0212	0.0151
200	0.0221	0.0192	0.0105
100	0.0233	0.0195	0.0107
20	0.0266	0.0198	0.0109
5	0.0303	0.0286	0.0153

Silver Nitrate

TABLE XV—MOLECULAR CONDUCTIVITY

V	λ_0	λ_{25}	λ_{50}
1000	2.327	—	—
500	2.158	3.254	4.101
200	1.951	3.115	4.005
100	1.669	2.574	3.178
20	1.443	2.273	2.842
10	1.397	2.246	2.896
5	1.270	2.275	3.197

TABLE XVI—TEMPERATURE COEFFICIENTS

V	$\frac{\lambda_{25} - \lambda_0}{\lambda_0 . 25}$	$\frac{\lambda_{50} - \lambda_0}{\lambda_0 . 50}$	$\frac{\lambda_{50} - \lambda_{25}}{\lambda_{25} . 25}$
500	0.0204	0.0180	0.0104
200	0.0239	0.0210	0.0114
100	0.0217	0.0181	0.0094
20	0.0231	0.0194	0.0100
10	0.0244	0.0215	0.0116
5	0.0317	0.0303	0.0162

Cobalt Chloride

TABLE XVII—MOLECULAR CONDUCTIVITY

V	λ_0	λ_{25}	λ_{50}
266.6	0.104	0.193	0.311
500	0.253	0.464	0.599
1000	0.293	0.499	0.653

TABLE XVIII—TEMPERATURE COEFFICIENTS

V	$\frac{\lambda_{25} - \lambda_0}{\lambda_0 \cdot 25}$	$\frac{\lambda_{50} - \lambda_0}{\lambda_0 \cdot 50}$	$\frac{\lambda_{50} - \lambda_{25}}{\lambda_{25} \cdot 25}$
266.6	0.0342	0.0398	0.0245
500	0.0334	0.0274	0.0116
1000	0.0281	0.0246	0.0123

In view of the fact that quinoline has a higher dielectric constant than aniline we should expect that solutions in it should give higher molecular conductivities. This is found to be true for silver nitrate and aniline hydrobromide. The minimum of molecular conductivity is displaced toward the region of higher concentration and the molecular conductivity increases rapidly with the dilution. The temperature coefficients pass through a minimum, but at dilutions which are greater than those which give the minimum molecular conductivity. Owing to the rather slight solubility of the cobalt chloride only three concentrations of this salt were studied. In these the molecular conductivity increases with dilution, while the temperature coefficients decrease under the same conditions.

Solutions in Pyridine[1]

Merck's best grade of pyridine was allowed to stand over fused potassium hydroxide for several months, then decanted and twice redistilled. Only the middle portion passing over at 115°-115.1° and 745 mm was retained for the work. Its specific conductances at 0°, 25° and 50° were found to be 0.57×10^{-7}, 0.74×10^{-7} and 1.2×10^{-7}, respectively. Lincoln found the specific conductance of the pyridine which he used to have the much higher value of 7.6×10^{-7}.

Those salts which do not show hygroscopic properties were weighed directly, transferred to a certified volumetric flask and made up to volume, but for those salts which do absorb moisture the method of weighing by difference was used.

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[1] The data for the pyridine solutions is a part of an unfinished thesis begun by Mr. E. X. Anderson some years past. Since the completion of that thesis appeared doubtful, it was thought advisable to include the data in this paper.

The pyridine was added directly to the flask from a specially devised filling apparatus whose open ends were always protected by phosphorus pentoxide tubes. The dilute solutions were made by diluting the mother solution, the utmost care being taken to prevent contact with the moisture of the air.

Silver Nitrate

Table XIX—Molecular Conductivity

V	λ_0	λ_{25}	λ_{50}
1	1.05	1.53	2.01
2	14.77	19.38	23.28
10	20.68	25.38	27.25
20	22.38	27.05	29.17
100	27.80	34.49	37.92
500	37.31	47.63	55.10

Table XX—Temperature Coefficients

V	$\frac{\lambda_{25}-\lambda_0}{\lambda_0 . 25}$	$\frac{\lambda_{50}-\lambda_0}{\lambda_0 . 50}$	$\frac{\lambda_{50}-\lambda_{25}}{\lambda_{25} . 25}$
1	0.0149	0.0123	0.0121
2	0.0125	0.0115	0.0081
10	0.0091	0.0064	0.0029
20	0.0084	0.0061	0.0031
100	0.0096	0.0073	0.0040
500	0.0111	0.0095	0.0063

The molecular conductivity increases at first very rapidly with slight changes in dilution in the concentrated regions and then more slowly at higher dilutions. The temperature coefficients show a very rapid decrease in the concentrated solutions.

It will be seen that the molecular conductivities at first increase very rapidly with slight increase in dilution and then less rapidly with further dilution for all three temperatures. The values for λ_{25} agree very closely with those given by Lincoln[1] for the same salt at 25°. The temperature coefficients show

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[1] Jour. Phys. Chem., 3, 457 (1899).

a distinct minima, the effect of temperature upon the conductivity being greatest in the concentrated solutions.

Although solutions of silver nitrate in pyridine possess a relatively high molecular conductivity, Walden and Centnerszwer[1] have found that the molecular weights of silver nitrate in dilute solutions of pyridine are normal, while in the concentrated solutions the molecular weights are greater than normal, thus indicating association. By the same method Schmuilow[2] found that this salt is apparently non-ionized, but, since transference experiments made by Neustadt and Abegg[3] showed that both the $\overset{+}{Ag}$ ion and the NO_3 radical migrated toward the cathode, it was assumed that, if ionization does take place, it does so according to the equation,

$$2AgNO_3 = \overset{+}{Ag_2NO_3} + \overset{-}{NO_3}.$$

It is obvious that if the amount of polymerization just compensates for the effect due to ionization, the total number of dissolved particles will be the same as they would be if neither polymerization nor ionization had occurred. The molecular weights obtained by the boiling point method should be normal. As the concentration is increased, on the other hand, polymerization rapidly increases, while the degree of dissociation decreases, a result which is interpreted by some to indicate the presence of polymerization and the absence of ionization. That the simple $\overset{+}{Ag}$ ions are also present even in the concentrated solutions is not to be doubted.

Lithium Chloride

The pure salt was heated at 160° for several days; it was frequently pulverized in a hot agate mortar and the heating continued until the tendency to cake had ceased. It was then transferred to a weighing bottle and heated to constant weight.

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[1] Zeit. phys. Chem., **55**, 321 (1906).

[2] Zeit. anorg. Chem., **15**, 18 (1897).

[3] Zeit. phys. Chem., **69**, 486 (1910).

TABLE XXI—MOLECULAR CONDUCTIVITY

V	λ_0	λ_{25}	λ_{50}
0.58	0.143	0.199	0.239
1.0	0.218	0.264	0.282
2.0	0.254	0.290	0.299
10.0	0.279	0.322	0.346
100.0	0.519	0.573	0.613
1000.0	1.470	1.600	1.680

TABLE XXII—TEMPERATURE COEFFICIENTS

V	$\frac{\lambda_{25} - \lambda_0}{\lambda_0 . 25}$	$\frac{\lambda_{50} - \lambda_0}{\lambda_0 . 50}$	$\frac{\lambda_{50} - \lambda_{25}}{\lambda_{25} . 25}$
0.586	0.0160	0.0135	0.0079
1.0	0.0083	0.0058	0.0028
2.0	0.0056	0.0035	0.0012
10.0	0.0061	0.0047	0.0030
100.0	0.0041	0.0036	0.0028
1000.0	0.0037	0.0029	0.0020

Lithium chloride is at best a very poor conductor and is but slightly dissociated at all dilutions and temperatures. In other solvents it shows a high tendency to polymerize and doubtless does so in pyridine solutions. The molecular conductivities do increase gradually with increasing dilution throughout the whole range of concentration. The values found by Laszczynski and Gorski[1] for the same solution are about four times larger, due perhaps to the presence of traces of moisture. The temperature coefficients decrease with dilution throughout, the greatest changes being in the most concentrated solutions.

Lithium Bromide

The anhydrous salt was prepared in a manner similar to that used for lithium chloride.

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[1] Zeit. Elektrochemie, 4, 290 (1897).

TABLE XXIII—MOLECULAR CONDUCTIVITY

V	λ_0	λ_{25}	λ_{50}
0.977	—[1]	1.29	1.65
2.0	0.98	1.72	1.98
10.0	2.29	2.44	2.40
100.0	5.43	5.34	4.89
1000.0	13.68	14.15	13.58
10000.0	24.80	28.70	29.90

TABLE XXIV—TEMPERATURE COEFFICIENTS

V	$\frac{\lambda_{25} - \lambda_0}{\lambda_0 . 25}$	$\frac{\lambda_{50} - \lambda_0}{\lambda_0 . 50}$	$\frac{\lambda_{50} - \lambda_{25}}{\lambda_{25} . 25}$
0.97	—	—	0.0109
2.0	0.0298	0.0202	0.0061
10.0	0.0026	0.0009	—0.0006
100.0	—0.0007	—0.0020	—0.0030
1000.0	0.0013	—0.0001	—0.0016
10000.0	0.0063	0.0041	0.0017

For all temperatures the molecular conductivity increases steadily throughout with increasing dilution, but not at all dilutions with a rise in temperature, there being at certain dilutions a decrease in conductivity with increase in temperature. The temperature coefficients are in all except the most concentrated solutions very small. They pass through a minimum of negative value.

Lithium Iodide

This salt after several months' standing over phosphorus pentoxide was heated for nearly one week at 150°.

TABLE XXV—MOLECULAR CONDUCTIVITY

V	λ_0	λ_{25}	λ_{50}
1.00	4.40	7.04	9.82
2	7.79	10.98	13.82
10	12.76	16.40	18.62
100	18.34	23.35	25.98
1000	27.10	35.99	42.65
10000	31.20	44.4	50.50
∞	(31.2)[2]	(44.9)	(50.5)

[1] Solidified.

[2] Extrapolation.

TABLE XXVI—TEMPERATURE COEFFICIENTS

V	$\frac{\lambda_{25} - \lambda_0}{\lambda_0 . 25}$	$\frac{\lambda_{50} - \lambda_0}{\lambda_0 . 50}$	$\frac{\lambda_{50} - \lambda_{25}}{\lambda_{25} . 25}$
1	0.0224	0.0246	0.0158
2	0.0164	0.0155	0.0103
10	0.0114	0.0092	0.0054
100	0.0109	0.0083	0.0045
1000	0.0131	0.0115	0.0074?
10000	0.0169	0.0124	0.0055

From Table XXV it will be observed that lithium iodide is a good conductor. The molecular conductivity increases very rapidly for slight dilution in the concentrated regions and then more slowly, but steadily up to a maximum at ten thousand liters. The temperature coefficients pass through a minimum at a dilution of one hundred liters.

Sodium Iodide

TABLE XXVII—MOLECULAR CONDUCTIVITY

V	λ_0	λ_{25}	λ_{50}
1.33	0.11[1]	0.70	0.84
5	10.0	11.14	11.20
10	14.56	16.15	15.80
100	21.66	23.81	22.87
1000	32.99	39.53	41.28
10000	42.20	56.70	63.20

TABLE XXVIII—TEMPERATURE COEFFICIENTS

V	$\frac{\lambda_{25} - \lambda_0}{\lambda_0 . 25}$	$\frac{\lambda_{50} - \lambda_0}{\lambda_0 . 50}$	$\frac{\lambda_{50} - \lambda_{25}}{\lambda_{25} . 25}$
1.33	0.2084[1]	0.1279[1]	0.0076
5	0.0046	0.0024	0.0002
10	0.0044	0.0017	—0.0009
100	0.0040	0.0011	—0.0016
1000	0.0079	0.0050	0.0018
10000	0.0137	0.0099	0.0046

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[1] Solid phase present.

Sodium iodide solutions in pyridine are good conductors at all dilutions except those near the point of saturation where the molecular conductivities are very small at all temperatures. By extrapolation λ_∞ was found to be 43.3 at 0°. Laszczynski and Gorski[1] obtained 44.32 for the value of λ_∞ at 18°. For 25° and 50° no limiting values of the molecular conductivity could be found; at these temperatures the conductivity continues to increase with dilution more rapidly than at 0°. The temperature coefficients exhibit well defined minima with negative values appearing for temperatures between 25° and 50°.

Potassium Thiocyanate

The sample was recrystallized from absolute alcohol, washed with the alcohol and dried at 95°. This salt differs from the others that have been studied in that its solubility in pyridine decreases as the temperature rises.

TABLE XXIX—MOLECULAR CONDUCTIVITY

V	λ_0	λ_{25}	λ_{50}
7	5.97	7.12	7.75
14	7.20	8.45	9.00
70	11.40	13.36	14.54
140	14.17	16.77	18.14
1400	27.32	33.70	38.31
14000	42.86	58.51	71.30
∞	46.5[2]		

TABLE XXX—TEMPERATURE COEFFICIENTS

V	$\frac{\lambda_{25} - \lambda_0}{\lambda_0 \cdot 25}$	$\frac{\lambda_{50} - \lambda_0}{\lambda_0 \cdot 50}$	$\frac{\lambda_{50} - \lambda_{25}}{\lambda_{25} \cdot 25}$
7	0.0077	0.0060	0.0035
14	0.0069	0.0050	0.0026
70	0.0070	0.0055	0.0035
140	0.0073	0.0056	0.0033
1400	0.0093	0.0081	0.0055
14000	0.0146	0.0133	0.0087

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[1] Loc. cit.

[2] By extrapolation.

Apparently the conditions which tend to produce a decrease in solubility with rise in temperature are those which have to do with rapid increase in conductivity at higher temperatures. The temperature coefficients here also pass through a minimum.

Ammonium Thiocyanate

The anhydrous salt was prepared in the same manner as was the potassium salt.

TABLE XXXI—MOLECULAR CONDUCTIVITY

V	λ_0	λ_{25}	λ_{50}
0.33	2.10	4.46	7.43
1.00	8.21	11.70	15.12
2.00	10.45	13.76	16.53
10.00	11.96	14.56	16.29
100.00	17.00	20.33	22.18
1000.00	33.57	41.80	47.76

TABLE XXXII—TEMPERATURE COEFFICIENTS

V	$\frac{\lambda_{25} - \lambda_0}{\lambda_0 . 25}$	$\frac{\lambda_{50} - \lambda_0}{\lambda_0 . 50}$	$\frac{\lambda_{50} - \lambda_{25}}{\lambda_{25} . 25}$
0.33	0.0451	0.0508	0.0266
1.00	0.0170	0.0169	0.0117
2.00	0.0127	0.0116	0.0081
10.00	0.0087	0.0072	0.0048
100.00	0.0078	0.0061	0.0036
1000.00	0.0098	0.0085	0.0057

The molecular conductivity curves for ammonium thiocyanate are peculiar in that they rise rapidly with slight increase in dilution, then rise slowly for a considerable change in dilution, and finally increase rapidly as the dilution is further increased. The values for λ_v are considerably larger than those found by Laszczynski and Gorski. Working up to dilutions of 2080 liters these men calculated the value of λ_∞ at 18° to be 40.22. In the curves for the above tables it is clearly seen that the 0°-curve gives promise of a limiting value for λ_0, but the 25°- and 50°-curves give no sign of such a behavior.

The initial rapid increase in the molecular conductivities and decrease in the temperature coefficients are undoubtedly due to a rapid decrease in the viscosity of the concentrated solutions with slight increase in dilution. The concentrated solutions here used are very viscous.

Mercuric Chloride

TABLE XXXIII—MOLECULAR CONDUCTIVITY

V	λ_0	λ_{25}	λ_{50}
0.5	0.009[1]	0.036	0.045
1.0	0.019	0.025	0.030
2.0	0.016	0.021	0.025
10.0	0.016	0.021	0.027
100.0	0.037	0.061	0.067
1000.0	0.130	0.260	0.400?

TABLE XXXIV—TEMPERATURE COEFFICIENTS

V	$\frac{\lambda_{25} - \lambda_0}{\lambda_0 . 25}$	$\frac{\lambda_{50} - \lambda_0}{\lambda_0 . 50}$	$\frac{\lambda_{50} - \lambda_{25}}{\lambda_{25} . 25}$
0.5	0.1176[1]	0.0793	0.0104
1.0	0.0136	0.0119	0.0076
2.0	0.0126	0.0105	0.0065
10.0	0.0126	0.0141	0.0119?
100.0	0.0260	0.0162	0.0139
1000.0	0.0400	0.0415	0.0215

Mercuric Bromide

TABLE XXXV—MOLECULAR CONDUCTIVITY

V	λ_0	λ_{25}	λ_{50}
0.5	0.012[1]	0.034	0.043
1.0	0.020	0.026	0.032
2.0	0.018	0.023	0.026
10.0	0.017	0.023	0.028
100	0.031	0.047	0.053
1000	0.130	0.280	0.290

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[1] Solid phase present.

Mercuric Iodide

TABLE XXXVI—MOLECULAR CONDUCTIVITY

V	λ_0	λ_{25}	λ_{50}
0.5	—[1]	0.013	0.018
1.0	0.009	0.013	0.018
2.0	0.008	0.012	0.015
10.0	0.013	0.019	0.024
100.0	0.069	0.102	0.117
1000.0	0.266	0.364	0.448

The conductivities of the mercuric halide salts are extremely poor conductors. With increase in dilution the molecular conductivity varies but little and only begins to show an appreciable increase at a dilution of one hundred liters. All three of the salts show faint but distinct minima in the molecular conductivity. Since the molecular conductivities are so small, any slight errors in them will be highly magnified in the temperature coefficients. The values of the latter are all of the same order of magnitude as those given for mercuric chloride and all three salts give minima for temperature coefficients.

The values for λ_v for mercuric iodide are much smaller than those obtained by Lincoln[2] at 25°.

Copper Chloride

Kahlbaum's C. P. cupric chloride was heated for several hours in a stream of pure dry hydrogen chloride at 160°, then heated in a stream of dry hydrogen and cooled in a current of the latter; lastly, it was quickly transferred to a weighing bottle and further heated in an air bath at 160°.

TABLE XXXVII—MOLECULAR CONDUCTIVITY

V	λ_0	λ_{25}	λ_{50}
25	0.053	0.062	0.074
50	0.066	0.076	0.086
100	0.088	0.098	0.111
200	0.130	0.146	0.171
500	0.203	0.216	0.216?
1000	0.302	0.365	0.410

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[1] Solid phase present.

[2] Loc. cit.

TABLE XXXVIII—TEMPERATURE COEFFICIENTS

V	$\frac{\lambda_{25} - \lambda_0}{\lambda_0 . 25}$	$\frac{\lambda_{50} - \lambda_0}{\lambda_0 . 50}$	$\frac{\lambda_{50} - \lambda_{25}}{\lambda_{25} . 25}$
25	0.0073	0.0082	0.0076
50	0.0059	0.0059	0.0052
100	0.0045	0.0053	0.0055
200	0.0050	0.0063	0.0063
500	0.0027	0.0014	0.0000
1000	0.0084	0.0072	0.0049

The molecular conductivities for all temperatures increase steadily with increase in dilution. While more or less irregular the temperature coefficients exhibit a minimum value in the dilute regions.

Kohlschuetter[1] states that cupric chloride dissolved in pyridine gives a blue solution and since its molecular weight as determined by the boiling point method is normal, its color may be attributed to that of the undissociated cupric chloride. Naumann[2] has also observed this blue color in his work and assumes it to be due to the presence of the complex, $CuCl_2.2Pyr$. All of the cupric chloride solutions used in this work gave a beautiful, deep green color without the least indication of a bluish tint and, furthermore, the solutions remained green for several months. On the other hand, in making one of the trial solubility tests an attempt was made to weigh the salt directly. The salt absorbed moisture so rapidly that this was impossible. Although it was noticed that the edges of the salt mass had taken on a greenish blue color, it was quickly transferred and dissolved in pyridine and, as might be expected, the solution was perfectly blue. When however, the salt was quickly weighed by difference, a deep green solution was always obtained. It is evident, therefore, that the blue solutions reported by Kohlschuetter and Naumann owe their blue color to traces of water.

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[1] Ber. deutsch. chem. Ges., 37, 1153 (1904).

[2] Ibid., 37, 4609 (1904).

Copper Nitrate

A 0.1 *N* solution of silver nitrate was treated with an excess of finely divided, reduced metallic copper and allowed to stand until the solution gave no test for silver.

Table XXXIX—Molecular Conductivity

V	λ_0	λ_{25}	λ_{50}
10	9.68	12.94	14.96
20	5.00	7.21	8.88
40	8.57	11.60	14.16
100	12.08	16.43	20.43
1000	16.41	23.88	39.71
10000	19.42	27.24	45.71

Table XL—Temperature Coefficients

V	$\frac{\lambda_{25} - \lambda_0}{\lambda_0 . 25}$	$\frac{\lambda_{50} - \lambda_0}{\lambda_0 . 50}$	$\frac{\lambda_{50} - \lambda_{25}}{\lambda_{25} . 25}$
10	0.0135	0.0109	0.0062
20	0.0176	0.0155	0.0093
40	0.0142	0.0131	0.0088
100	0.0144	0.0138	0.0097
1000	0.0158	0.0162	0.0119
10000	0.0161	0.0168	0.0124

Copper nitrate gives far better conducting solutions than does the chloride.

Cobalt Chloride

The pure salt was first partially dehydrated by long standing over phosphorus pentoxide and then subsequently treated according to the method employed for copper chloride. The final product was of a pale blue color. Reitzenstein[1] prepared the compound $CoCl_2.4Pyr$. Pearce and Moore[2] found that within their respective temperature limits we may have the three compounds, $CoCl_2.6Pyr$, $CoCl_2.4Pyr$, and $CoCl_2.2Pyr$.

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[1] Ann. Phys. Chem., 43, 839.

[2] Am. Chem. Jour., 50, 231 (1913).

Cobalt chloride dissolved in pyridine gives a red solution at 0°, a violet at 25°, and a deep purple at 50°. These color changes at different temperatures are doubtless closely associated with changes in the amount of pyridine combined with the salt, since the colors of the solid phases in contact with the saturated solutions at these temperatures are approximately the same as those of the solutions.

TABLE XLI—MOLECULAR CONDUCTIVITY

V	λ_0	λ_{25}	λ_{50}
10	0.009[1]	0.012	0.021
20	0.015	0.015	0.022
40	0.021	0.020	0.024
100	0.042	0.045	0.041
1000	0.220	0.230	0.310
10000	0.600	1.000	—

TABLE XLII—TEMPERATURE COEFFICIENTS

V	$\frac{\lambda_{25} - \lambda_0}{\lambda_0 \cdot 25}$	$\frac{\lambda_{50} - \lambda_0}{\lambda_0 \cdot 50}$	$\frac{\lambda_{50} - \lambda_{25}}{\lambda_{25} \cdot 25}$
10	0.0148[1]	0.0293	0.0319[1]
20	0.0019	0.0101	0.0174
40	—0.0021	0.0028	0.0082
100	0.0028	—0.0005	—0.0036
1000	0.0018	0.0082	0.0139

Cobalt chloride in pyridine gives at best exceedingly poor conducting solutions. By some its solutions are considered as non-conductors. Consequently, slight errors are highly magnified. The results obtained show a continuous increase in molecular conductivity with dilution for all temperatures. Lincoln's values for λ_v at corresponding dilutions are very much higher than the values here given. The temperature coefficients, although subject to error, show definite minima at which negative coefficients are observed. As is evident from Table XLII the effect of temperature is greater between 25° and 50° than at the lower temperatures. This is

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[1] Solid phase present.

no doubt due to the greater instability of the solvated ions at higher temperatures.

Cadmium Nitrate

The solution of the pure salt was prepared by displacing the silver of a 0.1 *N* solution of silver nitrate by means of pure metallic cadmium.

TABLE XLIII—MOLECULAR CONDUCTIVITY

V	λ_0	λ_{25}	λ_{50}
10	0.141	0.160	0.122
20	0.322	0.348	0.288
40	0.402	0.433	0.340
100	0.694	0.733	0.630
1000	2.370	2.310	2.440
10000	7.400	8.600	9.800

TABLE XLIV—TEMPERATURE COEFFICIENTS

V	$\frac{\lambda_{25} - \lambda_0}{\lambda_0 . 25}$	$\frac{\lambda_{50} - \lambda_0}{\lambda_0 . 50}$	$\frac{\lambda_{50} - \lambda_{25}}{\lambda_{25} . 25}$
10	0.0052	—0.0028	—0.0095
20	0.0033	—0.0021	—0.0070
40	0.0031	—0.0031	—0.0086
100	0.0023	—0.0018	—0.0056
1000	—0.0010	0.0006	0.0023
10000	0.0065	0.0065	0.0056

Solutions of cadmium nitrate would be classed as poor conductors; the values of λ_v increase with dilution throughout. For the concentrated solutions increase of temperature above 25° produces a rapid decrease in conductivity and, as the temperature coefficients show, this decrease is greater between 25° and 50° than between 0° and 25°. An explanation for this phenomenon will be given in the discussion.

Summary of the Results in Pyridine Solution

The molecular conductivities of fourteen salts and their temperature coefficients have been determined in pyridine solutions. These salt may be divided into two classes, the strong and the weak. Among the former are silver nitrate, lithium iodide, sodium iodide, potassium and ammonium thiocyanates and copper nitrate. The values for λ_v of these salts are very small in the most concentrated solutions, but they increase rapidly with slight initial dilutions and then more slowly with further increase in dilution. All of them give minima in the temperature coefficients, except copper nitrate whose temperature coefficients seem to increase steadily with dilution.

The weak salts are lithium chloride, lithium bromide, the three mercuric halides, copper chloride, cobalt chloride and cadmium nitrate. Only the mercuric salts give minimum values for λ_v; the molecular conductivity of the others increases slowly with increasing dilution. All but one salt of this group give minimum values for the temperature coefficients, those of lithium chloride decrease with dilution. Negative temperature coefficients have been found for solutions of sodium iodide, lithium bromide, cobalt chloride and cadmium nitrate.

Discussion

The molecular conductivity of a solution of an electrolyte is dependent first upon the nature of the solvent and primarily upon its dielectric constant, or specific inductive capacity. According to the Nernst-Thomson rule, the dissociating power of a solvent will be greater, the greater is its dielectric constant.

Walden[1] has found that the dielectric constants of solvents of feeble ionizing power is increased by dissolving in them certain binary salts. The amount of this increase depends upon the constitution of the salt used. According to him salts may be divided into two classes, the strong and the weak. Strong salts exhibit a great tendency to ionize and possess large dielectric constants, while in a weak salt both of these are small. The degree of ionization of a salt depends both on the ionizing power of the solvent and the tendency of the salt to ionize.

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[1] Bull. Acad. Sci. St. Petersburg, 1912, 305–332.

As both of these factors increase with the dielectric constant the highest degree of ionization will be found in a system where both the solvent and the solute possess large dielectric constants.

The molecular conductivity also depends upon the degree of dissociation of the electrolyte, the nature of the ions, their speeds and the viscosity of the solutions. The degree of dissociation depends upon the magnitude of the electroaffinities of the ions formed. It will also be more or less affected by the degree of solvation of the molecules and ions present, since, doubtless, the energy content of the simple and polymerized molecules, as well as the electroaffinities of the ions must be somewhat modified by combination with the solvent. If degradation of energy accompanies an increase in electroaffinity, then, as Sachanov[1] states, the electroaffinity of the ions must increase with solvation and, for a given electrolyte, will be greater, the more dilute the solution is.

The speeds of the ions, if they have the power of combining with the solvent, must also be greatly affected by solvation; the greater the amount of solvation, the greater will be their mass, or volume, and, therefore, the smaller will be their migration velocities. Since, according to the Law of Mass Action, the degree of solvation of the ions must increase with increasing dilution, the effect of solvation upon the ionic velocities will be greatest in the most dilute solutions.

The stability of the solvated ions (also molecules) decreases with rise in temperature. If we consider solutions which are dilute with respect to a given ion, we should expect to find the effect of temperature to increase with dilution. That this is true may be seen from a study of the temperature coefficients given in this paper.

According to Noyes and Coolidge,[2] the molecular conductivity of aqueous solutions for a given concentration, increases steadily with rise in temperature up to 306°, the increase

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[1] Loc. cit.

[2] Zeit. phys. Chem., 46, 323 (1903).

being due chiefly to a steady decrease in viscosity. The rate of decrease in dissociation of the salt is small between 18° and 100°, but becomes much larger for higher temperatures. This decrease is evidently due to a change in the nature of the solvent, *i. e.*, a decrease in its degree of association and, hence, in its dissociating power.

If the formation of ions depends to any extent upon the power of these ions to combine with the solvent, an increase in temperature should be accompanied by a decrease in ionization and likewise in molecular conductivity. It has been noted that lithium bromide, sodium iodide, cobalt chloride and cadmium nitrate in pyridine give negative temperature coefficients. For lithium bromide the value of λ for a 0.01 N solution decreases slowly from 0° to 25° and then more rapidly up to 50°, while the same values for the other three salts increase up to 25° and then decrease with rise in temperature. All of these show a tendency not only to form polymeric molecules in pyridine, but also the power to form pyridine-solute complexes. The effect of temperature on these solvates is clearly indicated by the color changes in the cobalt chloride solutions. These salts also have the power to form complex ions which, doubtless, also have a great tendency to form solvates. It will be observed also that these negative temperature coefficients are those of minimum value. They are likewise found in those concentrations in which the concentration of the complex ions is least and hence most highly solvated. The effect of temperature upon the unstable solvent-ion complexes will, therefore, be greatest at this point. If, again, the formation of these ions depends upon their power to combine with the solvent, then the degree of ionization should decrease with rise in temperature. This assumption agrees perfectly with the results obtained.

It was, for a time, believed that the molecular conductivity of an electrolyte in solution must increase with dilution. Then appeared the above cited work in organic solvents which, in the minds of some chemists, completely overthrew the whole electrolytic dissociation theory. In practically all of these cases the molecular conductivity was found to decrease with increasing dilution. Unfortunately, these investigators seem to have stopped too soon. Had they but continued their work at greater dilutions, they would probably have found that in very dilute solutions in these solvents the molecular conductivity behaves normally as in aqueous solutions.

This has been found to be true for solutions in aniline, quinoline and pyridine, without exception. There are also solutes which in these three solvents show increase in conductivity throughout the whole range of dilution.

The three solvents chosen are but slightly, if at all, associated and they have small dielectric constants, *viz.*, aniline = 7.31,[1] quinoline = 8.8,[2] pyridine = 12.4.[2] The ionizing power of the solvents and the conductivity of their solutions increase from aniline to pyridine. Salts dissolved in them give, for the most part, low molecular conductivities and exhibit a great tendency not only to polymerize, but also to combine with the solvent. It is probable that there are present at all dilutions to a greater or less extent, both the simple and polymeric molecules and their ions, as well as the solvated forms of each.

We may represent the condition of equilibrium existing in a solution by the following scheme:

$$\overset{+}{\mathrm{Li}}\cdot\mathrm{S}_1 + \overset{-}{\mathrm{Br}}\cdot\mathrm{S}_2 \rightleftharpoons \mathrm{LiBr}\cdot\mathrm{S}_3 \rightleftharpoons (\mathrm{LiBr})_2\cdot\mathrm{S}_4 \rightleftharpoons \overset{+}{\mathrm{Li}}\cdot\mathrm{S}_1 + \overset{-}{\mathrm{LiBr_2}}\cdot\mathrm{S}_5,$$

where S_1, S_2, S_3, etc., represent the number of molecules of combined solvent. The two molecular forms are in equilibrium with each other and also with their respective ions.

Unfortunately, we have no means of arriving at any conclusions as to the complexity of the solute in these solvents, except by the boiling-point method and this is not applicable in the very dilute solutions. The assertion that simple molecules predominate in the dilute solutions is supported by experiments upon the molecular weights of alcohol, acetic acid

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[1] Turner: Zeit. phys. Chem., 35, 385 (1900).

[2] Schlundt: Jour. Phys. Chem., 5, 157 (1901).

and phenol in benzene. The molecular weights are smallest in the dilute regions and increase rapidly with increase in concentration, *e. g.*,

	Concentration Percent	Mol. weight found	Mol. weight Theory
Alcohol	0.161	46	46
	32.50	318	
Acetic acid	0.465	110	60
	22.8	153	
Phenol	0.34	144	94
	26.8	252	

Most of the salts used in this work show by the boiling-point method either normal molecular weights or slight association. That these solutions contain ions is obvious from the fact that they conduct electricity. It is obvious also that the phenomena of ionization, polymerization and solvation may all exist at the same time and still give normal molecular weights, since the effect due to polymerization of the solute molecules under the conditions need only be just sufficient to counteract the effects due to ionization and solvation.

Returning to our equilibrium equation, it is evident that, if we begin with the most dilute solutions and increase the concentration, there will be a repression of the simple ionization with the formation of simple molecules. The molecular conductivity in the dilute solutions should, and does, decrease with increase in concentration.

With the increase in concentration of the simple molecules there is an accompanying increase in the number of the more easily ionizing polymerized molecules.

Normally, the molecular conductivity of any salt, whether simple or complex, should decrease with increase in concentration, whereas in many solvents the reverse is true. One way of explaining this phenomenon seems to have been overlooked, one which at least seems logical and in harmony with the facts.

Let us take a solution of a salt at a dilution which is far beyond that dilution which just gives complete dissociation or maximum molecular conductivity. If now we begin to remove the solvent (say, by evaporation) the molecular conductivity calculated for the successively increasing concentrations will remain constant up to that concentration which first gives the maximum molecular conductivity. If, however, we should start with that initial great dilution and, while removing solvent, add the ions of the salt sufficiently rapidly, we should find for each successively greater concentration an increase in the molecular conductivity until that concentration is again reached which first gives the maximum value. After this the molecular conductivity must again decrease with increase in concentration.

Since the amount of polymerization of the solute molecules need only be very small in order to compensate for the effect due to ionization, as determined by the boiling-point method, we cannot be far wrong in assuming that the polymerized molecules are highly dissociated and that their ionic product,

$$\overset{+}{\mathrm{Li}}\cdot\mathrm{S}_1 \times \mathrm{Li}\overline{\mathrm{Br}}_2\cdot\mathrm{S}_5 = \mathrm{K},$$

is relatively very large. Furthermore, according to Walden's views upon the dielectric constant, the dissociation should increase with increase in the concentration of the salt. We may consider, therefore, that those dilutions which give minimum values of molecular conductivity are far beyond the dilution at which the polymerized molecules are completely dissociated. Normally, the molecular conductivity of these should remain constant with removal of solvent until that concentration is reached which just gives the maximum value for the molecular conductivity of the polymerized solute. With the increase in concentration of the highly dissociated polymer there is an abnormally rapid increase in the number of ions with the result that from the minimum on the molecular conductivity increases with concentration. If it is possible to exceed the ionic product which the ions of the polymerized molecules would give at the concentration giving the maximum molecular conductivity, then from this point on the molecular conductivity should decrease with further increase in concentration.

Starting then with the most concentrated solutions, the molecular conductivity should first increase with dilution to a maximum, due to an increase in the dissociation of the solute and a decrease in the viscosity of the solution. From the maximum the molecular conductivity decreases abnormally, due to a rapid decrease in the number of ion-forming molecules which in its effect more than counterbalances the effect due to increase in dissociation. At the minimum the influences due to the two kinds of molecules and their respective dissociations just balance each other. From the minimum on the molecular conductivity continues to increase with further dilution due to the ionization of the simple salt.

A curve representing such a phenomenon would have a maximum in the concentrated regions, a minimum at higher dilutions and, if complete dissociation is possible, a second maximum at infinite dilution. The data for the molecular conductivity of tetraethylammonium iodide in aniline when plotted give exactly this form of curve. The same may be said for the data otained by Franklin and Gibbs for solutions of silver nitrate in methylamine.[1] They, however, explain the phenomenon as due to the auto-ionization of the salt.

If, on the other hand, it is not possible to exceed the value for the ionic product at complete dissociation, the molecular conductivity should continue to increase with the concentration up to the concentration of the saturated solution. This should be true unless, perhaps, the viscosity of the solutions at these very high concentrations should be great enough to cause a decrease in conductivity. All of the most concentrated solutions in the solvents studied possess a relatively high degree of viscosity, yet for all, with the single exception of tetraethylammonium iodide, the molecular conductivity

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[1] Jour. Am. Chem. Soc., 29, 1389 (1907).

increases along with the viscosity as the concentration is increased.

Silver nitrate is the only salt that has been used in all three solvents; aniline hydrobromide has been used in aniline and quinoline. While these two can scarcely be considered as a basis for comparison, a study of their molecular conductivities brings out one or two interesting points. It will be observed that as the dielectric constants of the solvents increase the dilution at which the value of the molecular conductivity is a minimum is displaced toward solutions of higher concentration. The tendency for molecular conductivity to increase with concentration, likewise, becomes less. If this tendency is due to the presence of easily dissociating polymeric molecules, then we can say that the tendency of a solute to polymerize in different solvents becomes greater, the smaller the dielectric constant of the solvent. In the dilute solutions the molecular conductivity and hence the dissociation of the solute for a given normality increases with the dielectric constant of the solvent. In so far as these salts and solvents give us a clue, we are justified in saying that the Nernst-Thomson rule does hold for dilute solutions in solvents with low dielectric constants.

This work is to be continued with solutions in other organic solvents.

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THE THEORY OF DYEING, IV

BY WILDER D. BANCROFT

In the first paper of this series tables were given[1] showing that the amounts of tannin taken up by wool[2] and by cotton[3] vary continuously with the concentration of the aqueous solution, no definite compound being formed. Wool takes up more tannin from hot solutions than from cold ones; but the reverse appears to be true for cotton.[4] Since tannin is an acid mordant, the amount adsorbed should be less in alkaline solutions and greater in acid solutions if no other factor comes in. Addition of alkali cuts down the amount of adsorbed tannin almost to zero. Addition of acetic acid[5] increases the adsorption which, however, passes through a maximum[6] when the concentration of the acid becomes high. Sulphuric acid decreases the adsorption of tannin by cotton, and hydrochloric acid has practically no effect at all. These differences with different acids are undoubtedly connected with the relative adsorptions of these acids by cotton and we cannot hope for a complete understanding of the matter until somebody secures data with special reference to this point. The increased adsorption due to salts seems to depend more upon a decrease in the apparent solubility of the tannin than upon any effect due to adsorbed ions, though here again satisfactory data are entirely lacking.

I have been unable to find any quantitative data in regard to the adsorption of oil mordants by cotton. In view of what we know about the adsorption of hydrochloric and sulphuric acids by cotton, there is no reason for assuming the existence of any compounds in the case of oleic acid or sulphonated Turkey red oils.

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[1] Bancroft: Jour. Phys. Chem., 18, 4 (1914).

[2] Pelet-Jolivet: "Die Theorie des Färbeprozesses," 79 (1910).

[3] Sanin: Zeit. Kolloidchemie, 10, 82 (1912).

[4] Knecht and Kershaw: Jour. Soc. Dyers, 1892, 40; Ganswindt: "Theorie und Praxis der modernen Färberei," 2, 216 (1903).

[5] Knecht, Rawson and Loewenthal: "A Manual of Dyeing," 1, 188 (1910).

[6] Dreaper: "The Chemistry and Physics of Dyeing," 161 (1906).

As yet only a few lakes have been studied carefully from the viewpoint of colloid chemistry; but these few cases are enough to clear up matters very much. Biltz[1] has studied the behavior of alizarine with hydrous chromic oxide and hydrous ferric oxide to determine whether chromic and ferric alizarates are formed. In Table I are given the data for alizarine red SW and chromic oxide. To 5.460 cc of chromium hydroxide gel (= 0.1106 g Cr_2O_3) there were added 200 cc aqueous alizarine solution, containing 0.8 percent NaOH; the mixture was boiled for an hour and a half.

TABLE I

Conc. solution g/liter	Grams dye adsorbed per gram oxide	Conc. solution g/liter	Grams dye adsorbed per gram oxide
0.00034	0.175.	0.0188	0.565
0.0031	0.306	0.0341	0.740
0.0052	0.358	0.0500	0.904
0.0078	0.402	0.417	1.50

There is a continuous increase in adsorption with increasing concentration, and the data can be represented fairly well by an exponential formula $(x/m)^3 = 2.1\ c$ where x/m is the amount of alizarine per gram of oxide and c is the equilibrium concentration in the solution. Biltz, therefore, concludes very properly that no chromium alizarate is formed.

The data for alizarine and ferric oxide are given in Table II. To 2.220 cc ferric oxide gel (= 0.1141 g FeO_3) there were added 200 cc of varying amounts of alizarine dissolved in 0.8 percent NaOH. The mixture was shaken for 6–8 hours.

TABLE II

Conc. solution g/liter	Grams dye adsorbed per gram oxide	Conc. solution g/liter	Grams dye adsorbed per gram oxide
0.00114	0.0677	0.00261	0.655
0.00201	0.0964	0.00281	1.01
0.00234	0.134	0.00326	1.695
0.00242	0.308	0.00369	2.57

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[1] Ber. deutsch. chem. Ges., 38, 4143 (1905).

While the concentration in the solid is increasing from 0.134 to 6.01 the concentration of the solution varied only from 0.00234 to 0.00281. Biltz was of the opinion that this was really to be considered as a constant concentration, so he ran another set of experiments with 1.025 cc ferric oxide gel (= 0.05815 g Fe_2O_3). The data are given in Table III.

TABLE III

Conc. solution g/liter	Grams dye adsorbed per gram oxide	Conc. solution g/liter	Grams dye adsorbed per gram oxide
0.00313	0.236	0.0052	3.27
0.00314	0.579	0.0125	4.73
0.00355	1.425	0.0708	6.16
0.00417	2.44	0.159	6.57

From these experiments, Biltz concluded that we really have a ferric alizarate consisting of one molecule Fe_2O_3 to three molecules alizarine. He accounts for the fact that the concentration of the solid phase continues to rise by postulating that the amorphous, hypothetical ferric alizarate adsorbs alizarine. This might be legitimate if the amount of adsorption were small; but it runs to an excess of forty percent of alizarine, stopping there merely because no more experiments were made. The only proper deduction to be made from these experiments is that there is no evidence of the formation of ferric alizarate and that we are dealing with a continuously varying adsorption. This is confirmed by the fact that gelatinous ferric oxide takes up six times as much alizarine as a granular oxide. If we had a definite compound, the granular oxide should have shown it clearly. Of course, I do not intend to deny the possibility of ferric alizarate and chromic alizarate existing under certain conditions but merely that they are not formed under the conditions described. For instance, we do not get any hydrate of ferric oxide under ordinary conditions of precipitation; but van Bemmelen[1] has shown that a monohydrate can be prepared from sodium ferrite.

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[1] "Die Absorption," 174 (1910).

The experiments of Liechti and Suida[1] on ferric alizarate are not convincing either way. They mixed solutions of ferric chloride and ammonium alizarate together according to the equation $Fe_2Cl_6 + 3C_{14}H_6O_4(NH_4)_2 = Fe_2(C_{14}H_6O_4)_3 + 6NH_4Cl$, and a brownish black precipitate of ferric alizarate was thrown down. This in itself means nothing because the precipitate would have to have this composition unless the solution were to become acid or alkaline. If the solution had become either acid or alkaline, some of the alizarine or of the iron would have been dissolved. "If the precipitate is well washed, dried, and extracted with ether, a moderately large amount of alizarine dissolves out and the residue, on re-drying, forms a black powder which, on analysis, gives the formula $Fe_2O_3(C_{14}H_6O_3)_{2.5}$." The extraction of alizarine by ether is not proof that we have or have not a compound. Alcohol will take cupric chloride out of the definite compound $CuCl_2.2H_2O.2KCl$ and will extract adsorbed iodine from charcoal. If the extraction was carried on long enough, the ether ought to have taken out all the alizarine in excess of the next compound supposing there to be any. On that basis the system is behaving like one in which we have adsorption and no compounds.

"If pure ferric hydrate, freshly prepared and well washed, is stirred up with a quantity of alizarine paste and water in proportions corresponding to the formula $Fe_2O_3.3C_{14}H_8O_4$, and the mixture gradually heated to 100°, and then boiled five hours, the water lost by evaporation being replaced, a precipitate is produced which is soluble to some extent in distilled water, giving a violet solution. If this is washed, dried, and then extracted with ether, the ether dissolves out a large quantity of alizarine. The residue, redried and analyzed, has the formula $(Fe_2O_3)_3(C_{14}H_6O_3)_2$. It is more than probable that by the long-continued boiling, a part of the ferric hydrate loses some of its hydroxyl groups as water, thus forming only a very basic compound, which may also be regarded as

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[1] Jour. Soc. Chem. Ind., 5, 523 (1886).

a mixture of a less basic compound with ferric oxide." Since there is no such compound ordinarily as ferric hydroxide, the non-existent hydroxyl groups cannot be lost. If this were ferric alizarate and ferric oxide, both sets of experiments on extraction with ether are grossly inaccurate. We do not have to question the accuracy of Liechti and Suida's experimental work if we postulate adsorption. On heating for five hours, the hydrous ferric oxide coagulated somewhat and had less adsorbing power. Consequently, more alizarine was extracted with ether.

Pelet-Jolivet[1] has made some experiments on the dyeing by crystal ponceau of wool mordanted with alum. The data are given in Table IV.

TABLE IV

2 grams wool mordanted with alum
Volume of solution = 200 cc
A = crystal ponceau (sodium salt)
B = crystal ponceau + 0.25 g $Na_2SO_4.10H_2O$
Time = 5 days at room temperature

Total dye milligrams	Dissolved dye A milligrams	Adsorbed dye A milligrams	Dissolved dye B milligrams	Adsorbed dye B milligrams
113.8	37.8	76	42.2	71.6
189.8	107.4	82.4	116.4	73.4
303.6	214.8	86.8	220.8	82.8
417.5	—	—	329.3	88.2
569.3	—	—	479.9	89.4

These results are perfectly normal. It is a clear case of adsorption and the sodium sulphate cuts down the amount of dye taken up, which is what it should do. Quite different results were obtained at 90°. The data are given in Table V. In this case the amount adsorbed is practically independent of the concentration in the bath and it seems probable that a definite compound is formed, though one would have liked to have seen some experiments made with less than 140 milligrams of crystal ponceau. Pelet-Jolivet succeeded in preparing

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[1] "Die Theorie des Färbeprozesses," 213 (1910).

a crystalline aluminum salt of crystal ponceau. It is evidently a definite compound and it may very likely be formed under the conditions of the experiments at 90°.

TABLE V

2 grams wool mordanted with alum
200 cc solution of crystal ponceau
Time = 2 hours at 90°

Total dye milligrams	Dissolved dye milligrams	Adsorbed dye milligrams
182.7	42.3	140.4
292.3	154.7	137.6
401.9	261.1	140.8
548.1	413.7	134.4
730.8	592.4	138.4

A somewhat similar phenomenon seems to have been observed by Bayliss[1] with alumina and Congo red. "If to a solution of Congo red an excess of hydrochloric acid be added, the blue free acid is precipitated; but if the precipitate be suspended in water and dialysed, a deep blue colloidal solution is formed, as described in a previous paper.[2] Freshly precipitated and well-washed aluminum hydroxide is suspended in water, and a small quantity of the blue acid colloid is added. A dark blue precipitate falls, which can be washed by decantation, best with the aid of the centrifuge, and again suspended in water. It remains dark blue, and might hastily be supposed to be merely an aggregated portion of the acid colloid. That this is not so, and that the body contains also aluminum hydroxide, is shown at once by its behavior on warming. When this is done, a red solution is rapidly formed, which, on cooling, deposits flakes of a red substance, while the solution itself becomes pale in color. The same change occurs at room temperature, but very slowly. It is evident that we have here, in the adsorption compound formed at first, acid and base existing side by side but uncombined.

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[1] Proc. Roy. Soc., 84B, 81 (1911).

[2] Ibid., 81B, 270 (1909).

On heating, chemical combination takes place with the formation of the aluminum salt of Congo red, which, like all the salts of this acid, is of a red color. Congo red is a convenient body for the present purpose, since the salts are of a color which is so different from that of the acid.

"The precise manner in which combination is caused to take place by the action of heat does not immediately concern us; the most important fact is that a body can be prepared containing acid and base uncombined. The mode of formation of the adsorption compound is, it will be noticed, to all intents and purposes a case of the mutual precipitation of electropositive and electronegative colloids, in this case, aluminum hydroxide and Congo-red acid, respectively.

"The dry preparation of aluminum hydroxide supplied by Kahlbaum can be used, but, owing to the large size of the grains, it is not very effective. It is important that, whatever preparation be used, no free caustic alkali must be present, otherwise the red salt of the dye with this alkali is formed at once. The adsorption compound, if formed at all, only exists for an infinitesimally short time, owing to the rapidity of the chemical reaction.

"In order to obtain as large a relative surface of the hydroxide as possible I have made various hydroxides in colloidal solution, prepared by dialysis of solutions of salts which are hydrolytically dissociated. Ferric chloride, aluminum acetate, zirconium and thorium nitrates have been treated in this way. With ferric hydroxide, although the result of the experiment is quite distinct, the change of color on heating is not so obvious as with a colorless hydroxide. Aluminum hydroxide is good, but is unstable when sufficiently dialysed. The best of all those with which I have worked are the colloidal hydroxides of zirconium and thorium, which are beautifully clear and colorless solutions. The clearness is of course an indication of the minute size of the suspended particles. Like all solutions prepared in the way described, they still contain, even after prolonged dialysis, traces of the original acid. If this is present in too large a proportion, no red salt is formed even on heating the adsorption compound. This fact was shown in a striking way in my first preparation of zirconium hydroxide, which had been insufficiently dialysed. In this case, although the adsorption compound was duly precipitated, it did not become red on heating. When the adsorption compound was suspended in water and subjected to further dialysis, it was noticed to be turning slightly reddish at room temperature; on boiling, the change to the red salt is immediate. The compound with thorium hydroxide seems to require heating for a longer time before combination occurs than do the others; but this may be merely owing to the presence of more acid in the particular preparation."

It is clear that the blue lake is not a definite compound. Bayliss assumes that the red lake is the aluminum salt adsorbed by alumina but the only proof of this that he offers is the color—presumably because it did not occur to him that anybody would question the conclusion. On the assumption of the formation of an aluminum salt, I do not see why the presence of a trace of free acid should have so much effect. As long as there is a sufficient excess of alumina, one would expect a portion of the excess to combine with the Congo red. This difficulty disappears if we assume, as Blucher and Farnau[1] do that "the red Congo acid, although instable in aqueous suspension, is stabilized by the hydrous aluminum oxide." This is in accord with the stabilization of rosaniline and other color bases by wool or silk.[2]

Gilbert[3] has recently made a study of the copper lakes of eosine. He found that a definite, crystalline copper eosinate could be prepared; but that it was a different substance from the so-called copper eosinate prepared by a metathetical reaction between sodium eosinate and copper sulphate. Although the lake is fairly constant in composition when prepared in this way, it always contains an excess of copper when an excess of copper salt is employed. When hydrous copper

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[1] Jour. Phys. Chem., 18, 634 (1914).

[2] Bancroft: Ibid., 18, 128 (1914).

[3] Jour. Phys. Chem., 18, 586 (1914).

oxide is treated with ether solutions of eosine in varying amount the typical adsorption curve is obtained and there is no indication of a definite compound. Under these conditions the total amount of eosine taken up is only about one-tenth of the amount necessary to form copper eosinate. A wider range of concentrations was obtained by starting with colloidal hydrous copper oxide and colloidal eosine (free acid). The ratio of copper to eosine was varied between two molecules of copper to one of eosine and two molecules of eosine to one of copper. All these lakes behave like the lake with the copper and eosine in equivalent quantities and all can be carried into colloidal solution. In presence of ether small amounts of certain salts cause decomposition of the lake into hydrous copper oxide and eosine. This seems to be analogous to Bayliss' results with Congo red and alumina where small amounts of acid prevent the development of the red color.

With magnesia and eosine solutions the typical form of adsorption curve is obtained. The evidence is convincing that none of the ordinary eosine lakes are compounds at all and that lead eosinate, for instance, does not exist under the ordinary conditions of precipitation.

Davison[1] found that the acid dyes, Fast Green, Acid Green, Acid Violet, Croceine Orange, Alizarine Yellow, and Fast Blue were adsorbed less by alumina when sodium sulphate was present in the bath than when it was not. This is what happens when wool is substituted for alumina and has been discussed in detail in the first paper of this series.

Pelet-Jolivet[2] has shown that methylene blue is adsorbed by silica, the amount taken up varying with the previous treatment of the silica in a manner quite similar to that observed by Liechti and Suida with iron and alizarine. Dreaper[3] believes that magenta and tannin form a definite compound; but he gives no proof for this and he admits that one hundred parts of the alleged magenta tannic acid compound will ad-

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[1] Jour. Phys. Chem., 17, 748 (1917).

[2] "Die Theorie des Färbeprozesses," 71, 205 (1910).

[3] "The Chemistry and Physics of Dyeing," 244 (1906).

sorb at least up to 160 extra parts of tannic acid if the latter be present in excess. It is, therefore, safe to consider the case of magenta and tannin as one of adsorption.

Sanin[1] considers that the basic dyes form definite compounds with tannin when the dye is in excess, but admits that tannin is adsorbed when the tannin is in excess. He gives no proof for the existence of a definite compound at any time except the fact that he can write a formula for the product and Gilbert's work with the copper-eosine lakes shows how little reliance is to be placed on that test. The mordanting of basic dyes with acid dyes and *vice versa* is of course nothing but a case of adsorption.

Though the data are not as complete as one would like, it seems to me that they are sufficient to justify the conclusion that in general the dye is adsorbed by the mordant and does not form any definite compound with it. We have next the problem of the fixing agents. Sodium phosphate is used for fixing alumina, sodium arsenate for iron, lime for alizarine and alumina, tartar emetic for antimony. Putting it more broadly we can say that phosphates, arsenates, silicates, oleates, and tannin are used as fixing agents for the metallic mordants while the metallic mordants act as fixing agents for tannin and the oleates. Are we dealing with definite compounds in these cases or do we have the precipitation of a positive by a negative colloid and *vice versa?*

Mecklenburg has studied the case of tin phosphate[2] and ferric arsenate.[3] He found that a regular adsorption curve was obtained when stannic acid was treated with phosphoric acid and that there was no evidence of any formation of stannic phosphate under the conditions of the experiment. He also found that different samples of stannic acid took up different amounts of phosphoric acid from which he was inclined to deduce the existence of five stannic acids; but that of course was absurd. It would have been easy to have pre-

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[1] Zeit. Farbenindustrie, 10, 97 (1911); Zeit. Kolloidchemie, 13, 305 (1913).

[2] Zeit. anorg. Chem., 74, 207 (1912).

[3] Zeit. phys. Chem., 83, 609 (1913).

pared twenty stannic acids if this were the only test. This is merely another instance of the general phenomenon that the degree of the adsorption varies with the conditions under which the adsorbing agent is prepared. Exactly similar results were obtained with ferric oxide and sodium arsenate. In all cases adsorption curves were obtained, but the degree of adsorption varied with the previous history of the ferric oxide preparation. In these two cases, which have been studied, we find that tin phosphate and ferric arsenate are not formed. It is, therefore, probable that when a corresponding study of aluminum phosphate, stannate, and silicate[1] shall have been made, it will appear that these are also cases of adsorption. This does not preclude the formation of these substances as definite compounds under certain conditions. As a matter of fact crystallized aluminum orthophosphate has been prepared by de Schulten[2] and crystallized ferric arsenate by Hautefeuille and Margottet.[3] Wislicenus and Muth[4] have studied the action of tannin solutions on fibrous alumina. They find that the amount of tannin taken up increases rapidly at first with the concentration of the solution and then reaches a practically constant value. They deduce from this the existence of an aluminum tannate, but this is hardly justifiable. They have merely found what others have found in undoubted cases of adsorption that the adsorption apparently reaches a limiting value.[5] Experiments with differently prepared samples of alumina would undoubtedly have given different figures.

It is not possible at present to account satisfactorily for the action of lime in the case of alizarine with iron or alumina mordant. Liechti and Suida[6] believe that definite compounds are formed; but their experiments were done at a time when

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[1] Cf. Stremme: Jour. Chem. Soc., 94 II, 1041 (1908); 100 II, 406 (1911).
[2] Comptes rendus, 98, 1853 (1884).
[3] Ibid., 106, 135 (1888).
[4] Zeit. Kolloidchemie, 2, XVIII (1908).
[5] Schmidt: Zeit. phys. Chem., 74, 699 (1910).
[6] Jour. Soc. Chem. Ind., 5, 525 (1886).

that was the only possible explanation. "If normal calcium alizarate is mixed with perfectly clear lime-water in a closed vessel, and allowed to stand for some time, a portion of the calcium alizarate dissolves, forming a ruby-red solution. If this solution is then boiled for only a short time, a brownish red precipitate separates, whilst the supernatant liquid becomes quite colorless, and contains much free lime. This precipitate is soluble on continued washing with water, forming a violet solution. On analysis, it proves to be a basic calcium alizarate, having the formula $CaO.C_{14}H_6O_3.CaO$.

"This is the compound originally dissolved in the lime-water, the behavior of which solution, on warming, points to the existence of a much more basic calcium alizarate in the cold solution. Experiment shows, indeed, that about 5 mols CaO can hold in solution 1 mol of the basic calcium alizarate."

There is nothing in this to show that we do not have a peptonization by lime with coagulation on boiling. The statement that the precipitate is soluble on continued washing with water sounds as though peptonization were taking place as the coagulating agent was washed out.

"The compound ($Al_2O_3.CaO(C_{14}H_6O_3)_4$) is readily produced as a fine dark red precipitate by the action of calcium acetate and aluminum acetate on ammonium alizarate. This lake is soluble on continued washing with water, and is also partially soluble in ammonia. The ammoniacal solution, when filtered and evaporated to dryness, leaves a residue which, according to analysis, possesses the formula $Al_2O_3(C_{14}H_6O_3)_4$, while the portion insoluble in ammonia is found to have the formula $Al_2O_3.CaO(C_{14}H_6O_3)_3$, the original lake having the formula $Al_2O_3.CaO(C_{14}H_6O_3)_4$. It appears, therefore, that ammonia dissolves out alizarine and normal aluminum alizarate, leaving behind an aluminum calcium alizarate, which is more basic than the normal alizarin red." These experiments are open to the same criticisms that were made to the experiments on the iron alizarates. In their present form they are of no value whatsoever. It is also not quite clear how aluminum alizarate can be removed from an aluminum calcium alizarate and leave the ratio of alumina to lime the same as before.

It has been noticed[1] that caustic alkalies do not redissolve hydrous aluminum oxide or hydrous chromium oxide if the precipitation has been made in presence of a magnesium salt. There is nothing to show whether a similar result is obtained in presence of a calcium salt; but it seems to me that experiments along this line would be profitable.

Sanin[2] has made some measurements on the reaction between tannin and antimony salts. He claims to find three different salts depending on the conditions of the experiment. In dilute solutions with no excess of potassium antimony tartrate, there is precipitated the salt $(C_{14}H_9O_9)_2SbOH$. If an excess of the antimony salt is taken the salt has the composition $C_{14}H_9O_9.SbO$. At 80°–90° the precipitate analyzes to $(C_{14}H_9(SbO)O_9)_2SbOH$. It is admitted that it is difficult to obtain any of these salts pure, but Sanin prefers to consider the products as mixtures of two of these definite compounds rather than as substances of continuously varying composition. He considers that the first of these three salts is one that is formed in the fabric. In a later paper Sanin[3] rather weakens on this point. He admits that adsorption does occur when tannin and potassium antimony tartrate are mixed and all that he claims now is that it is also possible to get definite compounds if one observes certain conditions. One cannot object to this though one would like more definite proof that compounds are formed at all. The difficulty is that Sanin claims that the technical conditions for dyeing cotton with basic dyes are exactly those which lead to the formation of definite compounds and that is by no means proved. It seems to me that Sanin's experiments are precisely analogous to those of Gilbert where he found that a lake of fairly constant

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[1] Knecht, Rawson and Loewenthal: "A Manual of Dyeing," 2, 222, 240 (1910).

[2] Zeit. Farbenindustrie, 9, 2, 17, 49 (1910).

[3] Zeit. Kolloidchemie, 13, 305 (1913).

composition is obtained when copper sulphate and sodium eosinate are mixed.

There seems to be no sufficient reason for the present for denying the existence of definite oleates though it is possible that these substances exist only on sufferance. Knecht, Rawson and Loewenthal[1] say that "the amount of iron which is taken up by the fiber depends less on the strength of the mordanting liquor than on the amount of oil that has already been fixed in the material; the oil attracts the oxide of iron with great energy, so that it is not readily stripped from the fibre, even by comparatively concentrated sulphuric or hydrochloric acid." This is more the behavior that one could expect in case of adsorption than in case we had ferric oleate present. It would not surprise me at all to find that no definite compounds are formed under ordinary conditions between oleic acid and alumina or iron oxide.

The general conclusions are as follows:

1. Tannin is adsorbed by wool and cotton, forming no definite compounds with either. Oil mordants are adsorbed by cotton.
2. Alizarine is adsorbed both by chromium mordant and iron mordant.
3. Alumina adsorbs crystal ponceau, Fast Green, Acid Green, Acid Violet, Croceine Orange, Alizarine Yellow, and Fast Blue.
4. Alumina adsorbs the blue form of Congo red and perhaps stabilizes the red form of the free acid.
5. The eosine lakes are cases of adsorption though definite crystalline compounds can be prepared under certain conditions.
6. Tannin adsorbs basic colors.
7. Silica adsorbs methylene blue.
8. Color lakes are generally cases of adsorption. Definite compounds are formed only under special conditions.
9. The mordanting of basic colors by acid colors and *vice versa* are cases of adsorption.

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[1] "A Manual of Dyeing," 2, 597 (1910).

10. In most cases fixing agents act because they are colloids of the opposite sign from the mordants.

11. Ferric arsenate and tin phosphate are not formed under ordinary conditions of precipitations though both compounds are known. It is probable, though not yet proved, that aluminum phosphate, silicate, oleate, etc., are also not formed under ordinary conditions.

12. No definite statement can be made as to the action of lime on alizarine in alumina mordant; but it seems probable that the lime prevents the peptonization of the alumina.

13. There is certainly adsorption when tannin and antimony salts are brought together and the evidence as to the formation of three definite salts is not satisfactory.

14. The behavior of iron salts with oil mordants appears to indicate adsorption though it is not safe to deny the formation of definite oleates in some cases.

15. The formation of definite compounds plays no important part in the practice of dyeing.

Cornell University

A REDUCTION OF FERRIC SULPHATE IN ACID SOLUTION BY MEANS OF CADMIUM AMALGAM, FOR TITRATION OF IRON AND FREE SULPHURIC ACID

BY J. H. CAPPS AND O. W. BOIES

Within the last few years a knowledge of the composition of mine waters has become of considerable importance.

Mine air generally contains some sulphur dioxide and an abundance of moisture, so that, in the film of water which is everywhere present, there is excellent opportunity for the formation of sulphuric acid. Mine waters as a rule, contain, not only free sulphuric acid, but also ferric and ferrous iron, together with the small amounts of aluminium, sodium, calcium, magnesium, chlorine and silica usually found in the natural waters.

In attempting to determine sulphuric acid volumetrically it has been found that the ferric salt not only began to hydrolyze and liberate more acid as the titration proceeds, but there was also an interference with the color change of the indicator. It was also impossible to determine the end point by means of conductivity measurements or with the hydrogen electrode on account of the effect of the platinized platinum electrode on the ferrous-ferric equilibrium.

The method in use for the determination of sulphuric acid in mine water has been to precipitate the total sulphate ions with barium chloride and to calculate this as sulphates of the various bases present. Any excess of sulphate ions was taken to be free sulphuric acid. As the composition of mine waters varies considerably, this necessitates a great deal of routine analytical work and all the errors fall on the small amount of acid which is determined by difference.

In order to find a simpler and more direct method for getting at this free acid, the following work was done at the Bureau of Mines during the summer vacation of 1913 by Mr. O. W. Boies under the direction of Dr. G. A. Hulett:

Since sulphuric acid can be titrated directly in the presence of ferrous sulphate, the problem resolved itself to one of reducing all iron present to the ferrous state in such a way as to preserve unaltered the concentration of free acid. We attempted to do this electrolytically and first tried a short-circuited voltaic cell with platinum cathode and a soluble anode, using the mine water as the electrolyte. The idea was that the soluble anode would not only prevent oxidation of the electrolyte at the anode, but we could select an anode material with such a potential that the only reaction at the cathode would be $Fe^{+++} \longrightarrow Fe^{++}$, that is, a reduction of the ferric iron but no liberation of hydrogen. We also used a copper voltameter in series with this cell and thus the weight of copper deposited was to be a measure of the ferric iron.

Since this work was undertaken, some work on the electrolytic reduction of iron has been published by H. C. Allen[1] at the University of Kansas and by J. C. Hostetter[2] at the Geophysical Laboratory.

Mr. Allen found that he could reduce iron satisfactorily by using a platinum cathode and a small platinum anode. He also hit upon the idea of a short-circuited cell with amalgamated zinc anode and copper cathode and under these conditions he got a rapid and satisfactory reduction.

Mr. Hostetter got nearly complete reduction of iron by placing his acid ferric sulphate solution in a gold dish which served as cathode and using a small platinum anode suspended in a porous cup with 3 percent sulphuric acid in his anode chamber. After electrolyzing for an hour at between 60° and 80° he added the anode liquid to the main iron solution and continued electrolysis a little longer with fresh anode liquid.

In attacking our problem we covered the same ground somewhat differently. We used a short-circuited cell with a zinc rod as anode and a rotating platinum disk as cathode,

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[1] Jour. Am. Chem. Soc., 36, 937–49 (1914).

[2] Jour. Wash. Acad. Sci., 3, 429–32.

using the mine water as the electrolyte. The reduction was rapid and complete but measurable amounts of hydrogen were also liberated on the platinum. We could select a metal on which the over-voltage of hydrogen is higher than on platinum but chose first to try an anode of saturated cadmium amalgam as its solution pressure is 0.4 volt lower than that of zinc. With this anode there was still a measurable discharge of hydrogen ions on the rotating platinum disk before the iron was completely reduced.

Next we sought for a cathode material with a greater hydrogen over-voltage than that of platinum and tried gold, copper, nickel, and lead. For electrolyte we used a known solution containing ferric sulphate and sulphuric acid. The couple was allowed to act until the iron was completely reduced, as indicated by KCNS. In series with the cell was a copper voltameter. The results showed that hydrogen was liberated in all cases, but least of all on the gold cathode, on which, however, it still came off in analytically measurable quantities. So we decided to try a mercury cathode on which the over voltage of hydrogen is a maximum. It was, however, seen that the process could be much simplified by discarding anode and cathode and merely using a suitable amalgam.

We found that, by vigorously shaking the amalgam and the solution together for a short time, the iron was rapidly and completely reduced and ready for titration. The over-voltage of hydrogen on mercury or cadmium amalgam is so great (0.08 volt greater than on lead) that there was no fear of liberating hydrogen. The work on cadmium amalgam[1] justifies this conclusion. There was, however, to be considered the oxidation of cadmium from the amalgam by dissolved oxygen and the solution of this oxide in the acid.

$$Cd + O \longrightarrow CdO \qquad CdO + H_2SO_4 \longrightarrow CdSO_4 + H_2O.$$

We found that this reaction made a measurable effect on the hydrogen ion concentration so it was necessary to remove the oxygen from the solution.

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[1] Jour. Am. Chem. Soc., 30, 1805 (1908).

The method of procedure was as follows: The acid solution was placed in a small flask provided with a two-holed rubber stopper, through which passed a separatory funnel for the admission of the amalgam, and a tube for connection to the vacuum pump. All the air was pumped out of the flask and likewise that which was dissolved in the solution. The amalgam was then run in, hydrogen admitted to bring the pressure to atmospheric, and the flask shaken until all iron was reduced. The solution was then rinsed out and titrated either with standard sodium hydroxide or permanganate, depending on whether we were determining free acid or total iron. A few runs to find the length of time required to reduce the ferric sulphate showed that, with such concentrations as are found in mine waters, one-half minute to a minute of shaking was sufficient to bring about the complete reduction of the iron.

Experimental Data

Solutions used in this work:

$KMnO_4$ solution	1 cc	0.00556 gram Fe
NaOH solution	1 cc	0.004817 gram NaOH
NaOH solution	1 cc	0.0059 gram H_2SO_4
H_2SO_4 solution	1 cc	0.0017702 gram H_2SO_4

Ferric sulphate stock solution made by dissolving 6.7 grams $(NH_4)_2SO_4Fe_2(SO_4)_3.24H_2O$ in one liter of water. This solution on analysis showed:

0.0008227 gram Fe or 0.002938 gram $Fe_2(SO_4)_3$ per cc

(1) Determination of the degree of reduction obtained with cadmium amalgam:

(*a*) 25 cc alum solution used. Shaken one minute. Required 3.7 cc $KMnO_4$ solution.

25 cc contained	0.002057 gram Fe
3.7 × 0.00556	0.002056 gram Fe
(*b*) Duplicate. 25 cc contained	0.002057 gram Fe
3.7 × 0.00556	0.002056 gram Fe

(2) Determination of the action of the amalgam on the acid:

(*a*) 50 cc of the standard acid solution was shaken with the amalgam for one minute and then titrated with standard NaOH solution.

Aliquot parts of 10 cc were titrated. Required 3 cc NaOH.

H_2SO_4 in 10 cc of solution	0.0177 gram
3 × 0.0059	0.0177 gram

(*b*) Same amounts used but shaken for two minutes. 10 cc required 2.95 cc NaOH.

H_2SO_4 in 10 cc of solution	0.0177 gram
2.95 × 0.0059	0.01748 gram
H_2SO_4 lost	0.00022 gram

(3) Determination of free acid in ferric sulphate solution.

Twenty-five cc of the alum solution was taken, corresponding to 0.002057 gram of Fe^{+++}. To this was added 25 cc of the standard H_2SO_4 solution corresponding to 0.04435 gram H_2SO_4. The resulting solution was then shaken with the amalgam for 30 seconds. 25 cc portions were then withdrawn and titrated with standard NaOH, using methyl orange indicator.

(*a*) 25 cc required 3.9 cc NaOH.

Acid present in 25 cc	0.04435 gram H_2SO_4
3.9 × 2 × 0.0059	0.04602
	0.00167 gram excess

(*b*) 25 cc required 3.85 cc NaOH.

Acid present	0.04435 gram
3.85 × 2 × 0.0059	0.04521 gram
	0.00086 gram excess H_2SO_4

(*c*) 25 cc required 3.8 cc NaOH.

Acid present	0.04435 gram
3.8 × 2 × 0.0059	0.0448
	0.00045 gram excess H_2SO_4

For the next two experiments a fresh H_2SO_4 solution was made up containing 0.002419 gram H_2SO_4 per cc.

(*a*) 25 cc of the alum solution was taken and 10 cc of the acid solution added. This solution was then shaken for 30 seconds and the whole titrated with standard NaOH.

There were required 4.1 cc NaOH.

Acid present in 25 cc	0.02419 gram
4.1 × 0.0059	0.02419 gram
	0.00000

(*b*) 25 cc of the alum solution were taken and 40 cc of the acid solution added. Solution was then shaken for 30 seconds and then titrated. Required 16.3 cc NaOH.

Acid present in 40 cc................	0.09676 gram
16.3 × 0.0059.....................	0.09617
	0.00059 gram lost

The chief difficulty so far experienced with this method has been in catching the end point before it is overrun. Larger amounts of the solution should have been used or else they should have been titrated with a weaker solution of NaOH. The concentration of free acid in natural waters varies from zero to 2.7 grams per liter. The accuracy of this method did not depend upon the amounts of $Fe_2(SO_4)_3$ present, but rather upon how well one could titrate to a very sharp end point.

At this point in the work Mr. Boies left the Bureau of Mines, and in the following winter the investigations were resumed by J. H. Capps in the Physical Chemistry Laboratories of Princeton University, under the direction of Dr. G. A. Hulett, taking advantage of the information already gained on the subject.

The apparatus used was an ordinary Drexel gas-washing bottle, on the central tube of which was sealed a small separatory funnel, and on the other tube a 120° 3-way cock.

Procedure.—The solution was placed in the bottle which was connected with the suction and evacuated. The cock was now closed and the system shaken to equilibrium, most of the oxygen coming out of solution. Next hydrogen was run in and the system again shaken to equilibrium. This process was repeated once or twice and the reducing amalgam run in. The bottle was then shaken vigorously until the reduction of the iron was complete (this generally took about two minutes) and 50 cc of the solution was taken out and titrated with sodium carbonate solution. Another 50 cc portion could be taken out of the same run as a check on the first.

As the color change of the indicator (methyl orange) took place rather slowly during the addition of 2–3 cc of the tenth normal carbonate, it was necessary to have a comparison color with which to match the titration.

Such a comparison color was made and preserved by determining the true end point by conductivity measurements during titration with the indicator present. Just as the end point was reached, the solution was drawn up into a freshly blown, clean sealing bulb and sealed in. This preserved the correct end point color indefinitely and it was found that this color could be matched in actual practice with good accuracy.

We found that the concentration of ferrous sulphate in the solution did not affect the end point of the acid titration.

Mr. Boies was able to titrate free acid in the presence of ferrous iron with sodium hydroxide and phenolphthalein indicator. We could get no satisfactory results in this way, as, in our trials, the precipitation of ferrous hydroxide began before the acid was completely neutralized and the color change of the indicator could not be noted. By using sodium carbonate, however, we could get complete neutralization of the free acid before the formation of ferrous carbonate started.

Experimental Data

Solutions used in this work.

$KMnO_4$ solution.............	1 cc	0.005258 gram Fe
Na_2CO_3 solution.............	1 cc	0.0053 gram Na_2CO_3
Na_2CO_3 solution.............	1 cc	0.0049045 gram H_2SO_4

No stock solutions of either ferrous or ferric sulphate were kept on hand. For each solution made up, weighed amounts of the solid salts ($FeSO_4.7H_2O$ and $Fe_2(SO_4)_3$) were freshly dissolved.

(1) Determination of action of amalgam on free acid:

(*a*) 50 cc H_2SO_4 solution (untreated) required	46.35 cc Na_2CO_3
50 cc H_2SO_4 solution (untreated) required H_2SO_4..............................	46.35 cc Na_2CO_3
(*b*) 50 cc (same solution) shaken with amalgam..........................	46.35 cc Na_2CO_3
50 cc (same solution) shaken with amalgam..........................	46.30 cc Na_2CO_3

When the acid solution has been practically freed of dissolved oxygen and shaken thoroughly with the amalgam, cadmium was found to have gone into solution in every case. Tests for cadmium were made by concentrating the solution and treating with H_2S. However the amount of acid used up by the dissolving of the metal was too small to be determined volumetrically by measuring diminution of acid.

(2) As to the completeness with which the iron was reduced no measurements were taken. Reduction was considered complete when no color appeared on treatment of a drop of the solution with KCNS.

(3) Determination of free acid in solution with $Fe_2(SO_4)_3$.

Solution made (*a*, below) up with 10 cc 9.27 *N* H_2SO_4 and another (*b*, below) with the same amt. of acid and with 6.6 grams $Fe_2(SO_4)_3$ per liter.

(*a*) Acid solution.

1	50 cc required	46.35 cc Na_2CO_3 for neutralization
2	50 cc required	46.40 cc Na_2CO_3 for neutralization
3	50 cc required	46.35 cc Na_2CO_3 for neutralization

(*b*) Acid solution with $Fe_2(SO_4)_3$ present. Solution freed of air and Fe^{+++} all reduced with cadmium amalgam.

1	50 cc required	46.4 cc Na_2CO_3
	50 cc required	46.3 cc Na_2CO_3
2	50 cc required	46.3 cc Na_2CO_3
	50 cc required	46.4 cc Na_2CO_3

(4) Analysis of mine water for H_2SO_4, ferrous and ferric iron.

Procedure.—1st. A portion of solution was titrated with $KMnO_4$ for ferrous iron. *2nd.* Solution was then freed from oxygen, the iron reduced with the amalgam and portions of this were titrated with Na_2CO_3 for acid content. *3rd.* Another portion of the same lot was titrated with the permanganate for total iron content. From the value gotten thus is subtracted the value for the ferrous iron, the balance being the amount of ferric iron in that volume of the original solution.

Made up a liter of mine water containing:

Fe^{++}	1.509 gram
Fe^{+++}	1.3217 gram
H_2SO_4	9.074 gram

Analysis of above:

1 50 cc required 14.2 cc $KMnO_4$ (or 1.493 gram Fe^{++} per liter) 1 percent low
50 cc required 14.2 cc $KMnO_4$ (or 1.493 gram Fe^{++} per liter)
2 50 cc reduced required 92.6 cc Na_2CO_3 (or 9.82 gram H_2SO_4 per liter) 1 percent high
50 cc reduced required 92.55 cc Na_2CO_3 (or 9.82 gram H_2SO_4 per liter)
3 50 cc reduced required 26.9 cc $KMnO_4$
50 cc reduced required 26.9 cc $KMnO_4$
26.9 − 14.2 = 12.7 cc $KMnO_4$ indicating (1.334 gram Fe^{+++} per liter) 1.0 percent high

By the same method and procedure another mine water was analyzed. Solution was made up nearly like natural mine water and contained per liter:

Fe^{++}	0.429 gram
Fe^{+++}	0.774 gram
H_2SO_4	3.85 gram

Also small amounts of Al, Ca, Mg (as sulphates), and Na as NaCl:

On analysis	Fe^{++}	0.427 gram (about 0.5 percent low)
	Fe^{+++}	0.769 gram (about 0.7 percent low)
	H_2SO_4	3.825 gram (about 0.6 percent low)

Another similar mine water, made up with

Fe^{++}	0.518 gram per liter
Fe^{+++}	0.868 gram per liter
H_2SO_4	3.85 gram per liter

showed on analysis:

Fe^{++}	0.513 gram per liter (about 1.0 percent low)
Fe^{+++}	0.866 gram per liter (about 0.4 percent low)
H_2SO_4	3.843 gram per liter (about 0.3 percent low)

The ease with which iron could be reduced in this way suggested a very simple procedure in the reduction of iron for permanganate titration.

Since it was not necessary to preserve acid concentration unchanged, the solution was not freed of oxygen before reduction. However, it was kept acid in order for the reduction to take place and also to prevent fine particles of the reducing amalgam from remaining in suspension after shaking.

The apparatus used was an ordinary separatory funnel of about 500 cc capacity with the delivery tube cut off short. The iron solution was introduced and made acidic and the liquid amalgam poured in. The air of the apparatus was displaced by carbon dioxide, the funnel corked, and the system shaken to complete reduction of the iron. When the KCNS test showed the absence of ferric iron, the amalgam was run out through the stopcock and the solution, still in the funnel, was titrated with permanganate. If so desired, the solution could then be again reduced, as before, for a second titration as a check on the first.

Zinc amalgam was first tried. It gave a very powerful and swift reduction of the iron (only one-half minute or less being required) but could not be relied on to give satisfactory results as when 4 or 5 titrations were made on the same sample, the value for the iron present showed a steady decrease (1 below) due probably to the displacement of some iron from solution. Also in other cases the value for the iron rose steadily.

(2, below.) In some blank tests it was found that the reduction products of the $KMnO_4$ were acted upon in such a way by the zinc amalgam as to be themselves oxidizable by the $KMnO_4$.

(1)	Cc $KMnO_4$ used	(2)	Cc $KMnO_4$ used
a	45.7	*a*	32.7
b	45.65	*b*	32.75
c	45.6	*c*	32.8
d	45.65	*d*	32.9
e	45.55		

Next cadmium amalgam was taken up as a less powerful reducer. Although the time required for complete reduction was eight or ten times as great as in the case of the zinc amalgam (generally about 4 to 5 minutes), there was no displacement of the metallic iron nor "super-reduction" of the products of the permanganate. As many as six titrations of the same solution could be made with very good agreement by this method. (3) and (4) below show the results of two such runs:

(3)	Cc $KMnO_4$ used
a	37.4
b	37.4
c	37.4

(4)	Cc $KMnO_4$ used
a	44.95
b	44.9
c	44.9
d	44.95

Since the nature of our problem made this primarily a series of cation reactions, it was foreseen that practically any salts of iron would give the same results with an amalgam of about the same potential. In view of the fact that at times it is advisable to use iron in hydrochloric acid solution and titrating with dichromate, some runs were made conforming to these conditions. The following are the results of titrations of two such solutions:

(5)	Cc $K_2Cr_2O_7$ used ($N/10$)
a	40.9
b	40.9
c	40.85

(6)	Cc $K_2Cr_2O_7$ used
a	56.5
b	56.55
c	56.5

NEW BOOKS

A Text-book of Chemistry. *By William A. Noyes. 15 × 20 cm; pp. iii + 602. New York: Henry Holt & Company, 1913. Price: $2.25.*—The book is intended to meet the problem which confronts all university teachers of introductory chemistry, to be elementary enough to be adapted for people who have had no chemistry and yet not to be so elementary as to be useless for those who have had chemistry in the High School.

"The author has always tried to remember that he was writing for students who have scarcely more than begun the subject and not for experienced chemists. For this purpose clear, direct statements are most useful, to furnish the starting point from which a large knowledge may be developed later. While positive error should always be avoided, it is often impossible to secure complete, rigorous accuracy without sacrificing that simplicity of statement which every successful teacher knows to be essential.

"The atomic theory has been made the fundamental basis for the work and has been treated throughout as essentially true and not merely as a convenient hypothesis likely to be some time displaced by something very different. It is believed that the development of our knowledge during the last few years fully justifies this course. The theory of ionization has also been freely used, as the only means we have by which a large class of phenomena can be clearly presented and understood."

Ions are introduced on p. 48, phases on p. 77, the theorem of Le Chatelier on p. 111, and ionization on p. 112, so that the general attitude is quite different from that to be found in most text-books not so many years ago. There are a lot of nice things in the book. The paragraph on luminous flames, p. 299, is exceptionally clear. Throughout the book the author tries to keep in touch with every-day life, as in his reference to the uses of borax and sodium perborate p. 367. It is stated clearly, p. 243, that the spontaneous inflammability of phosphine is due to the presence of some P_2H_4. There is an account of the respiration calorimeter, p. 313. There are paragraphs on carbohydrates, p. 333; on enzymes and toxins, p. 344; on dialysis, p. 357; on osmotic pressure, p. 359; and on colloids, p. 262. Altogether the book represents a very distinct attempt to meet modern conditions. On the other hand, it is distinctly not the last word. Old associations are very strong, as may be seen by reading the introduction, which really belongs at the end of the book and not at the beginning.

There is another question suggested by this book though not bearing directly upon it. What sort of chemistry should be taught to students in the high school or the university who are not going to take any more chemistry? What we actually do is simple enough. We give them the same chemistry that they would take if they were going to specialize in the subject; but we justify ourselves by throwing in references to every-day life. In the first flush of ignorance the reviewer believes that we ought to give such people an entirely different course; that we ought to start with real life and work a little chemistry—a very little chemistry—into it. The reviewer does not yet know what such a course should contain or whether his colleagues would be willing to call it chemistry; but he is certain that we are not meeting the problem as we should and that some day we must give a general education course for people who are not going to specialize in chemistry. Presumably the people to work out such a course are those who are now teaching introductory chemistry. *Wilder D. Bancroft*

A Text-book of Elementary Chemistry. *By Alexander Smith. 14 × 19 cm; pp. iii + 439. New York: The Century Co., 1914. Price: $1.25.*—"One aim has been to provide a text suited to the needs of those who do not later continue the study of the subject. In the minds of such readers, an interest in chemistry is best awakened by calling attention to materials and processes used in the household and in commerce. A purely descriptive treatment, however, is of temporary value only. When, on the other hand, the elements of the science are presented in a somewhat rationalized form, they afford a basis for interpreting new phenomena and understanding new applications as they are met with in ordinary life, and the interest in the subject is thus not only awakened, but becomes permanent and fertile. Incidental remarks showing the rôle of chemistry in the prevention of industrial waste serve to emphasize the practical value of a knowledge of the science.

"Although such a course must be strictly limited in scope on the scientific side, still, so long as the foundation work is rational in method, the same plan fulfills perfectly the needs of those who afterwards continue the study of the subject. A few principles, thoroughly mastered, are better for any purpose than many principles, none of which are fully grasped."

This is worded very ingeniously and cuts the ground from under the reviewer's feet. A course, which is adapted to the needs of those who are not going to pursue the subject further, is a suitable one for those who are going to specialize; but the converse is not necessarily true and the converse is the form in which the problem presents itself. The first four chapters are distinctly good from the view-point of the layman because the author treats of such things as the action of caustic soda on wool, the rusting of iron, and the formation of zinc sulphide without telling us what wool, caustic soda, iron, zinc and sulphur are, or what their molecular weights are. That is as it should be. All people are familiar with sugar and salt, for instance, even though they may not know the composition of either or the structure formula of sugar. It is perfectly legitimate, therefore, to speak of sugar and salt without necessarily defining them more closely. By the time the fifth chapter is reached, the strain has begun to tell and we get the quantitative gas law which is probably not necessary for a student who is not going to take another course in chemistry. From here on the book becomes quite frankly an introductory text-book, and as such it is very good, as are all the books which the author has written.

In one or two places, pp. 50, 196, it seems to the reviewer that accuracy has been sacrificed over much to effectiveness. "The amount of heat required to raise the temperature of a given mass of water one degree is greater than that required for an equal mass of any other common material. Hence the temperature of the sea changes more slowly, and within a smaller range, than that of the rocks which compose the land. For this reason the climate of islands surrounded by much water is less variable from season to season within the year than is that of the continents." Without having made any definite calculations, the reviewer believes that the heat of vaporization, the heat of fusion, and the mobility of water are more important factors than the specific heat.

"If dust were not present, we should soon notice its absence. There would be no clouds or rain. It appears that moisture will *not* condense to fog or rain in air which has been *filtered* by being drawn through a wide tube containing a long (20 inches or more) plug of cotton, and has so been freed from dust. The particles act as nuclei, round which the liquid grows at the expense of the vapor. In the absence of dust the condensation would occur directly upon the surfaces of plants, houses, and animals. Thus, in a dustless atmosphere, an open shed or shelter, or an umbrella, would afford no protection whatever against a wetting."

The reviewer was very much interested in the ingenious way in which the author simplifies the definition of oxidation, p. 238, by saying that "oxidation is removing electrons and reduction is adding electrons." It may be right; but we are not yet at the stage where we can use such a definition.

Wilder D. Bancroft

Die Katalyse in der organischen Chemie. *By Paul Sabatier. Translated by Hans Finkelstein. 24 × 17 cm; pp. v + 243. Leipzig: Akademische Verlagsgesellschaft, 1914. Price: paper, 10 marks.*—In this book Sabatier has given an account of his work on catalysis. The headings of the chapters are: catalyzers; oxidation; introduction of different atoms and groups into organic molecules; hydrogenization; inversions, polymerizations and condensations; various dissociations; splitting off of hydrogen; splitting-off of water; splitting-off of alkali halides and halide acids; catalytic decomposition of carboxyl acids; catalytic decomposition of carboxyl esters; mechanism of catalysis.

In the chapter on the mechanism of catalysis, the author distinguishes between catalysis in homogeneous systems and in heterogeneous systems, the second being the one in which he has been especially interested and of which he says, p. 229. "This includes the case that a solid catalyzer is in contact with a liquid or gaseous reacting system. The reaction takes place only at the surface of the catalyzer if it is compact and remains so throughout the reaction. The reaction takes place throughout the mass of the catalyzer if the latter is porous and consequently has a surface which is enormously large relatively to the mass. The effect of the enormous surface of a pulverulent mass is so great that one is tempted to refer all cases of catalysis to surface action."

Sabatier considers that all cases of catalysis are to be considered as due to formation of intermediate compounds with the catalyzer. The argument does not seem convincing to the reviewer. One must, however, admit the force of the final paragraph, p. 242. "The theory of intermediate reactions in catalysis has the admitted defect that it is based on the assumption of hypothetical compounds. It is impossible, however, to give any other general explanation of catalytic processes. So far as I personally am concerned this theory has been my guide in all my work in the field of catalysis. It is possible that its value will seem less if we get a new and unexpected point of view with reference to the carefully studied field of chemical knowledge. For the present it seems to me that, despite its incompleteness, the theory is valuable because it is useful and enables us to predict new reactions."

Sabatier has done wonderful work on catalysis in heterogeneous systems and the importance of it from the theoretical and applied sides is likely to increase with time rather than to diminish. The book is therefore a very valuable one, well worthy of careful study by all chemists. *Wilder D. Bancroft*

Die Materie. *By The Svedberg. 24 × 16 cm: pp. 162. Leipzig: Akademische Verlagsgesellschaft, 1914. Price: paper, 6.50 marks.*—In the preface the author says that he wishes to discuss three questions: The first is whether there really are several forms of matter and whether they are convertible. The second problem is how the different forms of matter react one with another and the third is what is the internal structure of matter. "The first question involves the problem of the alchemists of the transmutation of metals, and the modern theory of radio-activity in regard to the spontaneous decomposition of certain elements. At certain times and to certain investigators the second question has seemed to be a statement of the whole problem which chemical science has to solve. The study of the third question has given rise to the atomic, molecular, and electron theories and to the views resulting from these."

The subject is treated under the heads: the conceptions of matter held by the Greeks; alchemy; the study of matter becomes scientific; the first period of quantitative study; the science of matter at the end of the nineteenth century; the most recent discoveries.

In the last chapter the author refers in turn to Röntgen's discovery of the X-rays, Becquerel's work on uranium, the discovery of radium by the Curies, the work of Crookes on the removal of photographic activity from uranium, Becquerel's study of inactive uranium and uranium X, Rutherford's work on the emanation, Rutherford's identification of the X-rays as positively charged helium atoms, and Debierne's work on actinium. The author offers the definition, p. 156, that an element is a substance which we cannot decompose. Since we cannot vary the rate of change of the radio-active substances, they are elements by this ingenious definition. In the last few pages the author refers to the work of J. J. Thomson, Lenard, and others on cathode rays.

Wilder D. Bancroft

Anesthesia. *By J. T. Gwathmey and Charles Baskerville. 24 × 18 cm; pp. xiv + 945. New York: D. Appleton and Company, 1914.*—The headings of the chapters are: the history of anesthesia; general physiology of inhalation anesthesia; the use of rebreathing in the administration of anesthetics; nitrous oxid; ether; ethyl chlorid; chloroform; the selection of the anesthetic and technique for special operations; treatment before, during, and after anesthesia; anesthesia by intratracheal insufflation; anesthesia by colonic absorption of ether; oil-ether colonic anesthesia; sequestration method of anesthesia; local anesthesia; intravenous anesthesia; local anesthesia as applied in dentistry; spinal analgesia and spinal anesthesia; electric analgesia, sleep, and resuscitation; mental influence in anesthesia; hypnosis in anesthesia; therapeutic uses of inhalation anesthetics; the medico-legal status of the anesthetist; a list of anesthetics; statistics. There are also appendices on ethyl ether, chloroform, and oxygen.

This is a full and authoritative statement of our present knowledge in regard to anesthesia and is the more valuable because much of the recent progress is due to the authors. It is interesting to note that only recently have people begun to regulate carefully the temperature, oxygen content, and carbon dioxide content of the anesthetic and yet these prove to be very important factors in the successful use of anesthetics. Under a different head comes the use of oil of orange in connection with anesthetics, p. 96. We do not know at all why this substance acts as it does; but our knowledge of the theory of anesthesia is still very limited.

Of distinct interest to the layman are the chapters on mental influence and hypnosis in anesthesia, pp. 644-665, and also the chapter on statistics, pp. 841-857. Some of the important conclusions are that nitrous oxid with oxygen (with or without ether) is the safest inhalation anesthetic we know of at present. Chloroform alone should not be used except in emergencies or in cases in which it is specially indicated. The chloroform-ether sequence is relatively safe, ranking higher than the nitrous oxide-ether sequence, or ether alone. The combination of chloroform and oxygen is safer than ether alone. Though ether alone is used in nearly half of the 488,000 administrations reported, it is not as safe as is generally believed. Ether is materially safeguarded by oxygen. Sequences and combinations, when properly used, are safer than any known single anesthetic.

This book is really a monumental piece of work and the world owes a debt of gratitude to the authors. *Wilder D. Bancroft*

Das latente Lichtbild. *By M. Andresen. 15 × 22 cm; pp. v + 61. Halle: Wilhelm Knapp, 1913. Price: 2.40 marks.*—This book does not represent the scientific knowledge of the day. The author believes the inaccurate statement that sodium nitrite prevents solarization and he consequently postulates that solarization is due to the latent image taking up bromine again. Since an unexposed plate can be brought into a solarized state by suitable treatment with a reducing agent, it is quite impossible that solarization can be due to a regeneration of the original silver bromide. The section on the development of the photographic plate is equally unsatisfactory. It is interesting to note the author's view that metol is the best of all developers and that it will gradually supersede all others. *Wilder D. Bancroft*

A Popular Treatise on the Colloids in the Industrial Arts. *By Kurt Arndt. Translated by N. E. Katz. 20 × 14 cm; pp. iii + 73. Easton: The Chemical Publishing Co., 1914. Price: 75 cts.*—The subject is taken up under the headings: colloidal solutions; colloidal solutions of metals; flocculation of colloidal solutions; reversible and irreversible states of aggregation; general remarks on dispersed systems: suspension and emulsion colloids; ruby glass; milky-white opaque glass; colloids in the mineral kingdom; silver and gold mirrors; manufacture of tungsten lamps; colloids in the ceramic industry; colloids in the hydraulic cement industry; colloids as adhesives and glues; usefulness of the colloids in the absorption of liquids; dehydration of peat by electro-osmosis; colloids as diaphragms and filters; adsorption; varnish making; dyeing; tanning; soap manufacture; brewing industry; lubricating greases; sewage purification; colloids in agriculture.

The author skims over these interesting topics at the rate of about two pages per topic. On p. 2 honeycomb and sponge structures are considered identical and on p. 27 there is a misprint of volt for watt. The translation is a bit crude. *Wilder D. Bancroft*

MOLECULAR ASSOCIATION OF LIQUIDS

BY DANIEL TYRER

In a previous paper[1] a study was made of the various methods of determining the association factors of liquids which have at various times been proposed, and it was shown that there does not exist a reliable method by which the molecular weight of an associated liquid may be determined. Each method was shown to be founded on untenable assumptions. Also several conditions were established which any equation employed to determine the molecular weight of an associated liquid must follow.

In the present paper it is proposed to extend this study to several other methods that have recently been proposed, to investigate some new equations containing the molecular weight as one term, and to study generally the properties of associated liquids.

To the conditions laid down in the previous paper, that any exact equation employed to calculate the association factors of liquids must follow, must be added the condition that *the equation must conform to the law of mixtures.* For it must be remembered that in the case of an associated liquid we are really dealing with a mixture and not with a pure liquid in the chemical sense. I mean, for example, that in the case of ethyl alcohol we are dealing very probably with a mixture of $C_2H_5OH_2$, $(C_2H_5OH)_2$, $(C_2H_5OH)_3$, etc., and not with a liquid consisting of only one kind of molecule. This must follow from the progressive dissociation which an associated liquid appears to undergo as the temperature rises. If M_1 be the molecular weight of a molecule ROH, M_2 the molecular weight of $(ROH)_2$ and M_3 the molecular weight of $(ROH)_3$, etc., the mean molecular weight of the associated liquid $(ROH)_x$ is

$$xM_1 = \frac{n_1M_1 + n_2M_2 + n_3M_3 + \text{etc.}}{n_1 + n_2 + n_3 + \text{etc.}} \dots\dots\dots\dots (1)$$

where n_1, n_2, etc., are the numbers of the respective kinds of

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[1] Zeit. phys. Chem., 80, 50 (1912).

molecules present in the mixture. Suppose now we have an equation connecting the molecular weight M of a liquid with the various physical properties α, β, γ, etc.

$$M = F(\alpha, \beta, \gamma) \quad \ldots\ldots (2)$$

which we have found to be true for normal liquids. If, then, we have a mixture of liquids A, B, C, etc., whether they be associated molecules or not, we should have for the mean molecular weight M_m of the mixture if Equation 2 is valid for mixtures

$$M_m = F(\alpha_m, \beta_m, \gamma_m) \quad \ldots\ldots (3)$$

where α_m, β_m and γ_m represent the observed physical properties of the mixture. Therefore, we should have from Equations 1 and 3

$$F(\alpha_m, \beta_m, \gamma_m) = \frac{n_1M_1 + n_2M_2 + n_3M_3 + \text{etc.}}{n_1 + n_2 + n_3 + \text{etc.}} \quad \ldots\ldots (4)$$

This equation should be valid for all mixtures whether an associated liquid or a mixture of normal liquids and every true equation for the determination of the association factor of a polymerized liquid should satisfy this condition. Now, any particular equation may be tested in this respect by applying it to a mixture of two normal liquids of known composition and seeing whether Equation 4 above holds. It is useless to apply this condition to any of the methods proposed for they have all been shown to fail to satisfy other less exacting conditions.

A new method for the determination of the association factors of liquids has been proposed by Bingham and Harrison,[1] based upon viscosity measurements or rather upon the reciprocal of viscosity, *viz.*, the fluidity. Briefly, the method is as follows: For a large number of liquids that temperature is experimentally determined at which the fluidity is equal to 200 units, and it is shown that this temperature is a constitutive property of the substance, that is, it depends upon the number, kind, and arrangement of the atoms in the molecule. They calculate the fluidity value of each atom, of

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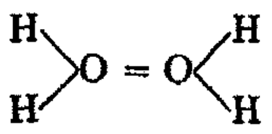
[1] Zeit. phys. Chem., 66, 1 (1909).

each double bond and triple bond, of each benzene ring formation, etc., and the sum of these values for the atoms of a given molecule is the temperature at which the liquid has a fluidity of 200 units. If $\Sigma(t)$ represents this sum for a simple molecule of an associated liquid, $x\Sigma(t)$ is its true value, x being the association factor. Hence, knowing the experimental value of the fluidity and the constitutional formula of the simple molecule, the value of x for an associated liquid can be determined. The method, however, contains this very grave error, that it is assumed that in an associated molecule there are no constitutional effects, *i. e.*, nothing must be added or subtracted from the value of $x\Sigma(t)$ which takes into account the manner in which the simple molecules are combined in the associated molecule. The inadmissibility of this assumption will be appreciated when it is mentioned that the constitutional influences are relatively enormous. For instance, whereas the value for a hydrogen atom is 59.2 and for an ether oxygen atom 24.2, the value for a ring formation is 141.8 and for a double bond 114.4. How do the authors of the method know that in an associated molecule of, say, water, there is not a double bond which would possess a value almost as much as that of two hydrogen atoms together? The molecule $(H_2O)_2$ might, for instance, have the constitutional formula



Exactly the same objections apply to the method of Bingham and Harrison as applied to Traube's co-volume method (see previous paper).

Furthermore, the results obtained by this method do not agree qualitatively with results obtained by other methods. For instance, Bingham and Harrison found that benzene and ethylene chloride are appreciably associated (for benzene $x = 1.17$ at 39° and for ethylene chloride $x = 1.21$ at 63.5°) while these liquids always show in their accordance with various equations that they are strictly normal.

Another method of determining the association factors of liquids has recently been proposed by Garver.[1] This method depends upon the following considerations concerning the latent heat of vaporization of a liquid.

If L is the latent heat, then

$$L = l + E + H$$

where l is work done against molecular attraction, E is external work done and H is the heat of dissociation of any associated molecules which split up as the liquid vaporizes. For normal liquids H is, of course, zero. E can be easily calculated by the equation

$$E = \frac{p}{J} \cdot (v_v - v_L)$$

where p is vapor pressure and v_v and v_L are volumes of vapor and liquid, respectively. If, then, we know l for an associated liquid we can calculate H and knowing H Garver has shown how, by aid of certain assumptions, the degree of association may be calculated. The trouble lies in determining l and in this Garver makes a fundamental error. The quantity l as already mentioned represents the work done against molecular attraction as the liquid expands to the vapor state and this force of attraction is equal to a balancing force tending to expand the liquid, set up by the motion and energy of the molecules. This is, of course, the usually accepted idea of liquid equilibrium. Now Garver assumes that this expanding force is equal to the Boyle pressure that a perfect gas would exert at the same molecular concentration. That is, if p be the expanding force or intrinsic pressure then

$$p = \frac{RT}{v_L}$$

and

$$-\frac{1}{J}\int_{v_L}^{v_v} \frac{RT}{v_L}\, dv = l.$$

This assumption is perfectly unjustifiable for several reasons. First, because the Boyle pressure of a perfect gas is caused by

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[1] Jour. Phys. Chem., 16, 454, 669 (1912).

the impact of particles of negligible size against the walls of the containing vessel while the intrinsic pressure in a liquid is caused by the impact of particles of comparatively appreciable size against each other. The two phenomena are radically different. The intrinsic pressure must be much greater and can, in fact, be shown to be much greater than $\frac{RT}{v_L}$. Secondly, assuming for a moment that the intrinsic pressure is really equal to $\frac{RT}{v_L}$, the expression

$$-\frac{1}{J}\int_{v_L}^{v_v}\frac{RT}{v_L}\,dv$$

is not equal to the internal latent heat as Garver supposes, for in no case does this agree with facts[1] but gives latent heats much too small. To take a case in point, the internal latent heat of pentane at 30° is approximately 77 calories, whereas the value calculated according to the above expression is only 20.2 calories. All liquids show a similar discrepancy. To explain this, Garver must assume that all liquids are strongly associated, an assumption which is quite untenable as it destroys the distinctiveness shown by hydroxyl compounds in their differences of behavior from other liquids. If all liquids were associated and to different degrees as they would naturally be, then none would follow such equations as the Ramsay, Shields-Eötvös equation or Trouton's equation.

Again, supposing that we could discover the correct expression for the intrinsic pressure of a liquid, let us call it $R\varphi(v,T)$, then we could not, even then, employ Garver's method, for the integral

$$-\frac{1}{J}\int_{v_L}^{v_v} R\varphi(v, T)\,dv$$

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[1] In the equation of Dieterici (Drude's Ann., 25, 569 (1908)) which is the integrated product of the expression $\left(CT \log \frac{d_L}{d_v}\right)$, the value of C is much greater than $\frac{R}{J}$.

is not equal to the internal latent heat for the simple reason that the force $R\varphi(v,T)$ is not equal to the attraction force when the volume lies in between v_i and v_L, for if it were so it would be possible for liquid to exist in this intermediate state at the same temperature.

There are many other objections to Garver's method, but those already mentioned are so fundamental that the method need not be further considered.

In the previous paper by the author a modification of the Ramsay-Shields method proposed by Batschinski was adversely criticized. In a reply[1] to my criticisms fresh evidence was brought forward by Batschinski which led me to make a further study of the method. And though the method obviates some of the objections to the Ramsay and Shields method I still consider that at the best it can only be considered as giving a rough idea of the degree of association. The principle of Batschinski's method is simply to substitute in the well-known Ramsay-Shields equation

$$\gamma(mxv)^{2/3} = K(T_c - T - d)$$

for the undeterminable critical temperature of an associated liquid (called by Batschinski the "metacritical" temperature) the value given by the following expression

$$T_c = \frac{16.31(\eta T^3)^{1/3}}{\rho_c^{1/3}}$$

where η is the viscosity at the absolute temperature T and ρ_c is the critical density. In the previous paper I pointed out that for an associated liquid ρ_c is not determinable and hence the equation is not really applicable. However, Batschinski pointed out that for ρ_c one can substitute the density at 0° C, and the resulting equation, with a fresh value for the constant, is approximately correct. However, attempting to calculate critical temperatures by aid of this equation I found, for normal substances, results which were in great disagreement with the observed values. This led me to examine the equation more carefully with the result that I found that the product ηT^3

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[1] Zeit. phys. Chem., 82, 86 (1913).

cannot by any means be regarded as constant as it ought to be according to Batschinski's equation. This is shown in the following three cases, using viscosity measurements by Thorpe and Rodgers:[1]

Liquid	t°	$\eta T^3 \times 10^{-2}$	Liquid	t°	$\eta T^3 \times 10^{-2}$
Carbon tetrachloride	0	2750	*n*-Hexane	0	816.3
	20	2453		20	819.6
	40	2287		40	830.3
	60	2189		60	844.5
	70	2156			
			Methyl butyrate	0	1552
				20	1458
				40	1406
				60	1381
				80	1371
				100	1373

For carbon tetrachloride over a range of 70° the "constant" varies by about 25 percent. However, I found that at a certain range of temperature for each normal substance the value of ηT^3 is really constant and it is this constant value that Batschinski has taken in his equation. But there is no use in determining the metacritical temperature of an associated liquid at 0°, for at this temperature (0°) it will have a very much different metacritical temperature from what it has at the temperature at which the function ηT^3 is constant. However, in calculating the metacritical temperature of associated substances Batschinski did not make this error but used the values of the viscosity at each point corresponding to which he wished to know the metacritical temperature. Since, however, it has just been demonstrated that the function ηT^3 is not constant under such circumstances it becomes necessary to test how far wrong the calculated critical temperatures will come.

In the following equation are given the values of the constant C of Batschinski's equation for some liquids at 0°.

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[1] Phil. Trans., 185A, 397 (1894); 189A, 71 (1897).

The values of η are mostly from Thorpe and Rodgers' measurements, and the other data are mostly according to Young.

Liquid	T_c	$\eta \times 10^{-6}$ at 0°	d_c	C	d_0	C_1
Ether	466.8	295	0.2622	16.63	0.7362	19.27
Carbon disulphide	546.0	437.7	0.377	18.26	1.293	21.82
Pentane	470.2	289.4	0.2323	16.55	0.6454	19.15
Octane	569.2	706.0	0.2327	15.53	0.7185	18.26
Carbon tetrachloride	556.1	1351	0.5576	14.29	1.6325	16.59
Ethyl acetate	523.1	943.5	0.3077	13.67	0.9244	16.00
Propyl acetate	549.2	773.4	0.2957	15.11	0.9102	17.74
Benzene	561.5	906.0	0.3045	14.83	0.9001	17.32
Ethylene bromide	582.8	2435	—	—	2.213	13.40
Methyl alcohol	513.0	816.6	0.2722	13.73	0.8101	16.05
Ethyl alcohol	516.1	1771.6	0.2755	11.10	0.8062	12.92
Water	643.0	1785	—	—	1.000	16.60

The last three liquids of the table are associated. The rest are usually considered to be normal. It will be seen that the values of C in Column 5 vary considerably, and what is more important is that the constant for methyl alcohol, a strongly associated liquid, lies within limits of variation of the constant for the normal liquids. And if for the critical density d_c we substitute the density at 0° (d_0), the results are worse, as the figures under C_1 in the last column of the above table indicate. Here the constant for water comes within the limits of variation of the constant for the normal liquids.

It cannot, therefore, be considered that Batschinski's equation is sufficiently accurate to be applied to the calculation of critical temperatures. The equation only appears to be true when for the function ηT^3 the constant value is taken which occurs for each liquid at a different and arbitrary temperature.

Even if the correct metacritical temperatures could be determined the method of determining the association factor would, as pointed out in the previous paper, only give results which referred to the condition of a liquid at its surface, and it is highly probable that the density of the surface layer is much different from that of the interior of the liquid.

Investigation of Some New Equations Containing the Molecular Weight

Below are given and studied some new relationships between the molecular weight and other properties which, though they do not allow of the exact determination of association factors, yet will furnish valuable evidence of the degree of association in fixing for this minimum value. Also some of the equations relate to other physical properties than surface tension and hence do not give results which merely refer to the surface condition.

The following equation has been shown by the author[1] to be approximately true for any given class of normal liquids

$$T_s = K\sqrt[3]{V_s}$$

where T_s is the temperature of the boiling point, V_s the molecular volume at this temperature and K is a general constant. The value of K varies somewhat for different classes of liquids. If, however, we modify the equation and write it

$$T_s = K_1\sqrt[3]{V_s}.\log. M$$

where M is the molecular weight, the variation of the constant for the different classes of liquids is considerably diminished and the value of K_1 may be regarded as approximately constant for all normal liquids, as the following table will show.

The constitutional effects on the value of the constant K_1 for normal liquids are quite marked but small enough to be neglected in comparison with the effects of association. Taking the mean value of K_1 to be 37, the deviation from this value for any normal substance seldom amounts to more than 6 or 7 percent. As will be seen from the liquids given in the latter part of the table the effect of association is considerably greater than this deviation.

For an associated liquid the equation should be written

$$T_s = K_1\sqrt[3]{xMv_s}.\log xM$$

where x is the association factor, M the molecular weight of the simple molecule and v_s the specific volume at the boiling point.

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[1] Phil. Mag., [6] 20, 522 (1910).

Liquid	V_s	T_s	K_1
Benzene	95·9	353·2	40.9
Toluene	117·9	382.2	39·7
Carbon tetrachloride	103·7	349·7	34
Ether	106.1	307.6	34·7
Hexane	139·8	341.9	34·1
Butyl ether	197·3	413·9	33·9
Ethyl benzoate	174.2	482	39·7
Phenyl propyl ether	172	463·5	39·1
Amyl chloride	136·3	374·5	35·9
Propyl bromide	97·2	344	35·8
Bromobenzene	119·8	429	39·4
Fluobenzene	101.9	358.2	38·7
Chloroform	84·5	334·1	36.6
Diallyl	125·7	332·2	34·7
Ethyl butyl ether	150.1	364·4	34·1
p-Xylene	140.2	411	39·1
Mesitylene	102.4	437·5	38.6
Methylene chloride	65.1	314·6	40·5
Allyl chloride	84·5	318·5	38·5
Amyl butyrate	222·3	457·8	34·4
Propyl acrylate	144·9	395·9	36.6
Associated Liquids			
Water	18.78	373	111.8
Methyl alcohol	42.6	337·9	64·3
Ethyl alcohol	62.2	351·3	53·3
Propyl alcohol	81.2	370.4	48.1
Formic acid	41.1	373	65
Acetic acid	63.6	391·5	55·2
Acetone	77·3	329.2	43·8
Phenol	103.6	467	50.4
Methyl cyanide	57·2	354·2	57

Putting $K_1 = 37$, we may write the equation

$$x^{1/3} \log xM = \frac{T_s}{37\, M^{1/3} v_s^{1/3}}.$$

If we knew T_s and v_s for an associated liquid we could, therefore, calculate the association factor x. But unfortunately we do not know these terms and have no means of determining them. For an associated liquid the observed boiling point is lower than the true boiling point T_s that should be taken in the equation and it is found that the value of $\frac{T}{V^{1/3}}$ increases with rise of temperature; hence, if in the above equation we calculate x, using the observed values of T_s and v_s, we shall obtain results that are too small. However, these results will be interesting as fixing approximate minimum values to the association factors at the observed boiling points. In the following table are given these minimum values for a few cases of associated liquids:

Liquid	M	V_s	T_s	x at T_s (minimum)
Water	18	18.78	373	6.3
Methyl alcohol	32	42.6	337.9	2.55
Ethyl alcohol	46	62.2	351.3	1.89
Acetic acid	60	63.6	391.5	2.05
Formic acid	46	41.1	373	2.71
Allyl alcohol	58	74.1	369.5	1.70
Phenol	94	103.6	467	1.77

The remarkable feature about the above results is the very high value for water in comparison with results obtained by methods based on the surface tension. This may possibly be explained by the fact that results obtained by surface-tension measurements can only refer to the surface condition and in the case of water the associated molecules in the surface layer may, owing to a smaller concentration, be much more dissociated than the molecules in the interior of the liquid. In the other cases there is no considerable difference from the values obtained by other methods. But it must be remembered that the true values are all bigger than those given in the above table. In the case of acetic acid, however, since the vapor is already considerably associated, the value of x given in above table will only be comparatively slightly less than the true value.

In contrast to the above method a new equation by which approximate values for the association factor may be determined, but which depends upon the surface tension, is given below.

I have shown[1] that the following equation is true:

$$\gamma = \frac{K_1 T_c d_L}{m d_s^2} (d_L^{2/3} - d_v^{1/3})^2$$

where γ is the surface tension, T_c the critical temperature, m the molecular weight, d_s the density at the boiling point and d_L and d_v the densities of liquid and saturated vapor, respectively. If this equation be equated with Walden's[2] equation

$$\gamma \frac{m}{d} = 8.89 (T_c - T - b)$$

so as to eliminate T_c we obtain the equation

$$m = \frac{K d_L (T + b)}{\gamma \left(\frac{d_s^2}{d_L^{1/3} - d_v^{2/3}} - \frac{K}{8.80} \right)}.$$

This equation gives the molecular weight in terms of temperature, surface tension and density. Now for an associated liquid we cannot take for d_v the observed value, since the liquid and vapor phases are not chemically the same. If, however, we restrict the application of the equation to temperatures well below the boiling point we can neglect d_v. Putting in observed constants the equation may now be written

$$m = \frac{3.75 (T + b) d_t}{\gamma \left[\left(\frac{d_s}{d_t} \right)^2 - 0.4264 \right]} \quad \ldots\ldots\ldots\ldots\ldots (A)$$

where d_t is the density of thie lquid at temperature T. The validity of the equation is tested in the following table for some normal liquids at a temperature of 0°.

The values of the surface tension γ_0 at 0° have been calculated for the most part from the results of Ramsay and Shields. The value of the small quantity b has been taken equal to 6.

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[1] Jour. Phys. Chem., 17, 717 (1913).

[2] Zeit. phys. Chem., 65, 129 (1909).

Liquid	γ_0	d_0	d_s	m (calc.)	m (obs.)
Carbon tetrachloride	28	1.6325	1.483	152.6	154
Carbon disulphide	36.61	1.2921	1.2224	78.4	76
Phosphorus trichloride	30.80	1.6127	1.4684	136.3	137.5
Phosphorus oxychloride	34.18	1.7116	1.5097	148.7	153.5
n-Octane	22.69	0.7185	0.6119	111	114
n-Hexane	19.11	0.6769	0.6160	92.2	86.1
Toluene	30.44	0.8850	0.7809	86.4	92.1
SO_2Cl_2	31.19	1.7081	1.5602	140.6	135
Ethyl iodide	32.58	1.975	1.806	155	155.5
Aniline	45	1.0379	0.8727	86.1	93
Benzene	30.3	0.9001	0.8135	79.5	78

There is quite a good agreement between the calculated and observed molecular weights as given in the last two columns of the above table. Most of the values of γ were obtained by extrapolation of results obtained by Ramsay and Shields at higher temperatures and are not, therefore, as accurate as otherwise might be. Also some accuracy is sacrificed in neglecting the term d_v in the original equation, particularly for the liquids with high vapor pressures.

In applying the equation to associated liquids we find that we cannot strictly take for d_s the observed value at the observed boiling point, since, if the liquid did not dissociate on vaporization the vapor pressure would be less and the boiling point consequently higher. Hence, the observed values of d_s are too high. Therefore, if we calculate the molecular weights of associated liquids using observed values for d_s we shall obtain results too small. However, since the density changes only comparatively slightly with the temperature, the results would not be very far from the true values. In any case they can only be regarded as minimum values. Also it must be remembered that as the equation contains the surface tension the results will refer only to the surface condition. In the following table are given a few of these minimum values for some associated liquids for a temperature of 0°:

Liquid	γ_0	d_0	d_s	Minimum values	
				m (calc.)	x
Water	73.21	1.000	0.9596	28.9	1.61
Methyl alcohol	25.17	0.8101	0.7518	77.5	2.42
Ethyl alcohol	23.86	0.8062	0.7405	84.7	1.84
n-Propyl alcohol	25.21	0.8193	0.7396	87.7	1.63
Acetone	25.43	0.8186	0.7537	80	1.38
Acetic acid	24.78	1.0697	0.9435	128.6	2.15

It will be seen from the above table that the values of the association factor x are, on the whole, much smaller than the results given by the previous method at the boiling point. This is particularly the case with water. At the boiling points the above results (except acetic acid) would, of course, be still smaller. It would appear then, as highly probable, that in the surface layer of an associated liquid the molecules are much less associated than in the interior of the liquid. In the case of acetic acid, since the vapor is already practically double molecules (and it will be shown later that acetic acid undergoes but little dissociation on vaporization), the degree of association at the surface will be but slightly different than in the interior of the liquid and hence the above result will not be far from the truth. It may be remarked, too, that the above association factor for acetic acid is in very good agreement with the result found by the previous method at the boiling point.

The Qualitative Detection of Association

The various equations which have already been studied in regard to the quantitative determination of the degree of association, although they have been found unsatisfactory for this purpose, may nevertheless be advantageously used for the detection of molecular association. Several of the methods, however, have so far disagreed with each other that in some cases it has become doubtful whether a liquid is associated or not. For instance, as already mentioned, Bingham and Harrison found some liquids to be associated which, according to the Ramsay-Shields method, appear to be quite normal, and according to Garver most of the so-called normal liquids are associated. Also, it is quite possible that, since methods which depend upon surface tension only really refer to the surface condition of a liquid, there are liquids which are really associated but which, according to such methods, appear to be quite normal. For example, the lower esters are, as will be shown in what follows, in all probability associated, though, according to Ramsay and Shields they are normal. It becomes, therefore, a matter of importance to study the effect of association on the various equations and to determine the best means by which one can find whether a given liquid is associated or not.

Trouton's Equation.—This well known equation is often used as a test for association. That it is not a reliable test, however, is proved by the fact that acetone, an associated liquid, gives a constant (22.0) which lies within limits of variation of the constant for normal liquids. Nor do all associated liquids affect the constant in the same way; for example, for water the value of the constant is 25.9, while for formic acid it is 14.9, the normal value being about 20. This varied influence is easily explained. The equation may be written

$$\frac{LM}{T_s} = K$$

where L is the latent heat at the boiling point T_s, M the molecular weight and K is a constant.

Now, for an associated liquid which dissociates on vaporization, the observed value of L is too great, since it includes the heat of dissociation. Also the observed boiling point is too low. Hence, the observed value of $\frac{L}{T_s}$ is too great while that of M is too small. Obviously, therefore, the effect of association on the constant K will depend upon the relative effects on $\frac{L}{T_s}$ and on M. In the case of water and the alcohols, whose associated molecules dissociate completely on vaporization, the effect on $\frac{L}{T_s}$ will preponderate and the value of the constant will appear larger than the normal. On the other hand, in the case of, say, formic acid, in which the amount of dissociation which occurs on vaporization is relatively small, the factor M will have the greater effect with the result that the constant falls below the normal value. If the two effects balance each other then we should have a case like acetone giving approximately a normal constant. It is clear, therefore, that Trouton's equation is not an infallible test for association.

Kistiakowski's Relation.—A similar relationship to Trouton's is that of Kistiakowski[1]

$$\frac{\alpha^2 M}{T_s} = K_1$$

where α^2 is the capillary rise in a tube of 1 mm radius at the boiling point T_s, and K_1 is a general constant equal to about 1.14. For an associated liquid the value of α^2 will sometimes be too large and sometimes too small according to the relative effects of too low a value for T_s and a partial dissociation of molecules in the surface layer. However, probably the observed value of $\frac{\alpha^2}{T_s}$ for an associated liquid is but little different from the true value, and hence the chief influence lies in the value of M, which being too small (*i. e.*, normal value of simple molecule), the constant for associated liquids will be always smaller than normal value. For methyl alcohol the value is 0.482, and for acetic acid 0.576. Kistiakowski's relation may therefore be considered a good test for association.

If Trouton's equation and Kistiakowski's equation be equated together so as to eliminate T_s we obtain a relationship independent of the molecular weight

$$\frac{\alpha^2}{L} = 0.0556$$

which is true at the boiling point only. This equation could be used to detect association, but the following equation dis-

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[1] Zeit. Elektrochemie, **12**, 513 (1906).

covered by the author[1] expresses the same relationship and is independent of the boiling point, and, therefore, is better to study.

$$\frac{\gamma d_s^{1/3}}{l(d_L - d_v)^{4/3}} = 0.295.$$

In this equation γ is the surface tension, d_s the density at the boiling point, l the internal latent heat and d_L and d_v the densities of liquid and saturated vapor, respectively. Restricting the application of the equation to temperatures below the boiling point we may neglect d_v and the equation becomes

$$\frac{\gamma d_s^{1/3}}{l d^{4/3}} = 0.295.$$

By the aid of this equation, which is independent of the molecular weight, we can calculate the approximate latent heat of vaporization of an associated liquid minus the heat of dissociation of the associated molecules. The observed value of d_s will, however, be slightly too great for liquids which dissociate on vaporization. Also probably the value of γ for such liquids will be too small on account of the partial dissociation in the surface layer. The two factors counteract so that the observed value of $\gamma d_s^{1/3}$ will not be far from the true value. In any case the variation can only be small compared with effect of association on the value of l.

In the following table are given for a few liquids, both normal and associated, the values of the internal latent heat l calculated according to the above equation. In the last column of the table under H are given the heats of dissociation of the associated molecules (*i. e.*, difference of calculated and observed latent heats). The surface-tension data are for most part calculated from Ramsay and Shields' results, while the observed values of l are mostly according to Mills.[2]

It will be seen from the table that for the normal liquids the calculated values of the internal latent heat agree well

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[1] Jour. Phys. Chem., 17, 717 (1913).

[2] Jour. Am. Chem. Soc., 31, 1099 (1909); Jour. Phys. Chem., 13, 512 (1909).

Liquid	t°	γ_t	d_t	d_s	l (calc.)	l (obs.)	H
Benzene	0°	30.30	0.9001	0.8135	99.9	99.1	− 0.9
Octane	0°	22.69	0.7185	0.6119	84.9	84.7	− 0.2
Hexane	0°	19.11	0.6769	0.6160	84.7	84.7	—
Chloroform	20°	25.88	1.481	1.409	56.4	58.1	+ 1.7
Chlorobenzene	0°	34.16	1.128	0.984	84.7	85	+ 0.3
Ether	0°	18.69	0.7362	0.6956	81.1	85.4	+ 4.3
Carbon disulphide	0°	32.2	1.292	1.222	79.7	82.8	+ 3.1
Carbon tetrachloride	0°	28	1.632	1.483	51.4	48.4	− 3
Water	0°	73.21	1.000	0.9596	24	565	+325
Methyl alcohol	0°	25.17	0.8101	0.7518	96.3	272.4	+176
Ethyl alcohol	0°	23.86	0.8062	0.7405	90.2	209.2	+119
Acetone	0°	23.43	0.8186	0.7537	87.6	131.8	+ 44.2
Methyl formate	0°	27.68	1.0032	0.957	89.5	113.2	+ 23.7
Ethyl acetate	0°	26.03	0.9244	0.8282	82.3	94.4	+ 12.1
Acetic acid	0°	24.78	1.0697	0.9435	65.9	76.4	+ 10.5

with the observed results, and the heats of dissociation H are practically zero. For the associated liquids, on the other hand, the values of H are very large. It is interesting to note that in the case of acetic acid the value of H is comparatively small, indicating that on vaporization of liquid acetic acid very few molecules dissociate. We may, therefore, in the case of acetic acid, employ several of the methods of determination of association factors which in other cases are rendered invalid on account of the dissociation of associated molecules which occurs on vaporization. It is also interesting to note, in the above table, that the two esters given are markedly associated. The above equation may be considered a good test of association.

A second, but less satisfactory, method of calculating the latent heat of vaporization of associated liquids minus the heat of dissociation of associated liquids is by aid of an equation by Lewis[1]

$$L = \frac{T\left(\frac{dv}{dt}\right)}{J\beta}$$

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[1] Phil. Mag., [6] 22, 268 (1911); Zeit. phys. Chem., 81, 626 (1913).

where L is the latent heat at the temperature T, v is the specific volume, β the compressibility and J the mechanical equivalent of heat. In the following table are given a few cases of the application of this equation. The data for β and dv/dt are by the author, and most of the observed values of L are according to Mills.[1]

Liquid	$t°$	dv/dt	$\beta \times 10^6$	L (calc.)	L (obs.)	H
Ether	0°	0.002051	152.97	88.6	92.5	+ 3.9
Benzene	0°	0.001316	81.95	106.1	106.1	—
Toluene	0°	0.001163	79.34	96.8	101	+ 4.2
Carbon tetrachloride	0°	0.000720	91.03	52.2	51.9	— 0.3
Chlorobenzene	0°	0.000841	67.02	82.9	89.9	+ 7
Bromobenzene	0°	0.0005778	56.32	67.7	67.4	— 0.3
Chloroform	0°	0.000794	85.90	61	64.8	+ 3.8
Hexane	30°	0.002120	178.3	87.1	86	— 1.1
Ethyl iodide	72.52°	0.0007242	149.6	40.4	46	+ 5.4
Ethyl bromide	38.40°	0.001052	155.4	46.1	59.9	+ 13.8
Carbon disulphide	0°	0.0008818	81.44	71.5	90	+ 18.5
Ethyl acetate	0°	0.001370	96.29	93.9	100.6	+ 6.7
Acetic acid	0°	0.001019	88.71	75.9	84	+ 8.1
Methyl alcohol	0°	0.001409	107.59	86.7	289.2	+202.5
Ethyl alcohol	0°	0.001288	99.95	85.1	220.9	+135.8
Water	50°	0.000455	44.4	80	56.5	+485

It will be seen from the table that for most of the normal liquids the value of H is very small, but, on the other hand, very large for the strongly associated liquids except in the case of acetic acid, for which, as was found also in the previous method, the heat of dissociation is comparatively small, indicating that very few molecules dissociate on vaporization. There are, however, some differences from the results found by the previous method. For instance, carbon disulphide would appear to be associated, and also slightly, ethyl bromide and iodide. Carbon disulphide shows in other respects some peculiarities which will be discussed later. In the cases of water and the two alcohols the values of H found are considerably greater than in the previous method, but it is prob-

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[1] Loc. cit.

able that in the previous method the values obtained were minimum values on account of the surface tension being included in the equation.

The effect of molecular association on the Ramsay-Shields equation is not necessarily always the same. Writing the equation

$$\frac{\gamma(mv)^{2/3}}{(T_c - T - b)} = K$$

we see that while the observed value of $(T_c - T - b)$ for an associated liquid is too small, the values of m and probably also of γ are also too small. The two effects react upon the value of the constant K in opposite ways, with the result that it is quite possible to have an associated liquid which gives a normal value for the constant or even a value greater than the normal. The lower esters, for example, are in all probability associated, yet they give normal values for the constant K. Carbon disulphide is possibly another case. On the other hand, if a liquid gives a value of the constant less than the normal value, it is undoubtedly an associated liquid. For substances of very high molecular weight it has been shown[1] that the equation is no longer valid, values of K being obtained much higher than the normal value even for liquids which are probably normal. In such cases it is probable that owing to the very great size of the molecules, comparatively speaking, the value of the molecular volume is no longer proportional to the other terms in the equation but is much too high.

As further tests of association the two equations

$$T_s = K\sqrt[3]{V_s}\log M$$

and

$$m = \frac{Kd_L(T + b)}{\gamma\left[\left(\frac{d_s}{d_L}\right)^2 - 0.4264\right]}$$

which have already been applied to the determination of

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[1] Walden: Zeit. phys. Chem., 75, 555 (1910); Dutoit and Friderich: Comptes rendus, 130, 327 (1900).

minimum values of the association factor, may be used but they are only applicable with certainty when the degree of association is comparatively large.

Some Special Cases

(*1*) *The Association of the Lower Esters.*—As already mentioned the lower esters behave in general towards the Ramsay-Shields equation like normal liquids. There is, however, considerable evidence that they are appreciably associated. In the following table are given a list of the constants for a number of esters of the various equations which have already been discussed. The normal values are given at the bottom of the columns.

Liquid	$\frac{D_c}{d_c}$	$\frac{d_s}{d_c}$	K = $\frac{T_s}{V^{1/3}\log M}$	x from Equation A[1]	H from Equation B[2]	$\frac{\alpha^2 M}{T_s}$
Methyl formate	0.255	2.74	43.7	1.38	23.7	0.957
Ethyl formate	0.257	2.71	39.9	—	—	1.02
Methyl acetate	0.254	2.72	40.4	—	—	1.02
Ethyl acetate	0.254	2.69	38.1	1.11	12.1	1.07
Normal values of constants	0.267	2.61	37	1.00	0	1.14

D_c = theoretical critical density; d_c = observed critical density. All other terms and equations have already been given.

The above table affords ample evidence of the association of the esters. The lowest ester methyl formate appears to be quite strongly associated. According to Equation A the value of its association factor x must be greater than 1.38. It may be mentioned also that Bingham and Harrison[3] also concluded that the lower esters are appreciably associated. Traube[4] also found them to be associated.

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[1] Equation A — $xM = \dfrac{3.75\, d_L(T + b)}{\gamma\left[\left(\dfrac{d_s}{d_L}\right)^2 - 0.4264\right]}$.

[2] Equation B — $H = l_{\text{obs.}} - \dfrac{\gamma d_s^{4/3}}{0.295\, d_L^{4/3}}$.

[3] Loc. cit.

[4] Ber. deutsch. chem. Ges., 30, 273 (1897).

(2) *The Association Factor of Acetic Acid.*—It has been shown by two different methods that when liquid acetic acid vaporizes comparatively little of it dissociates. We may, therefore, with a fair approximation determine its association factor by means of any of the foregoing equations which contain the molecular weight and for which the other terms are known. In the following table are collected the results obtained by various methods:

Values of x by Different Methods

Ramsay and Shields' equation with observed T_c	Traube's method
2.19 at 20°	2.1 at 0°

Equation $T_s = 37V^{1/3} \log M$	Equation $m = \frac{3.75 d_L (T + b)}{\left[\left(\frac{d_s}{d_L}\right)^2 - 0.4264\right]}$	Kistiakowski's equation	Equation[1] $\frac{M(C_p - C_v)}{V^{1/3}} = 2.12$
2.05 at 118°	2.15 at 0°	1.92 at 118°	2.02 at 0°

It will be seen from the table that in each case the value of the association factor x approximates closely to 2.0. That is to say, the molecules appear to be simply double molecules. It is interesting to compare these results with the values found by methods at present in use. Ramsay and Shields found for x between 16° and 46° the value 3.62 and Batschinski the value 3.47 at 20°. These results are widely different from the values found in the above table and the divergence serves to illustrate the inapplicability of the methods of Ramsay and Shields and of Batschinski. Traube, on the other hand, obtained the concordant result 2.1.

It would appear from these results that acetic acid does not undergo a gradual association of simple gas molecules depending upon the concentration, but that two simple gas

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[1] This equation is discussed later.

molecules unite to form a stable compound and a normal liquid which will undergo no further association.

(*3*) *The Case of Carbon Disulphide and Some Remarks on the Theory of Molecular Association.*—Carbon disulphide is usually considered to be a normal liquid and in its behavior in many respects it appears to be quite normal, but I have discovered that it shows certain peculiarities from which it would appear that it is really an associated liquid. In the Ramsay and Shields equation it gives an approximately normal constant; it follows Trouton's equation and Kistiakowski's equation; its heat of dissociation H as calculated according to the equation

$$\frac{\gamma d_s^{6/5}}{l d_L^{6/5}} = 0.295$$

(see page 97) is practically zero and it gives a normal molecular weight as calculated according to Equation A given on page 101. On the other hand, for the ratio of the theoretical critical density to the observed critical density it has a value 0.328, whereas the normal value is 0.267; the ratio of the critical temperature to the boiling-point temperature for normal liquids varies from about 1.45 to 1.58, but for carbon disulphide the value is 1.71; the value of the ratio of the density at the boiling point to the critical density is, for normal liquids, about 2.65, but for carbon disulphide the value is 3.24; the value of the function $T_s/\sqrt[3]{V}$ log M (page 90) for normal liquids is about 37, but for carbon disulphide the value is 42.8; and according to Lewis' equation (see page 98) it appears to be an associated liquid. Is, then, carbon disulphide a normal or an associated liquid? But these are not all the peculiarities shown by this substance. I have found that for a number of normal liquids the function $M(C_p - C_v)/V^{1/3}$ where M is the molecular weight, C_p and C_v the specific heats at constant pressure and constant value, respectively, and V is the molecular volume, is approximately constant at constant temperature. In the following table are given some values of the function for the temperature of 0°:

Liquid	$M(C_p - C_v)/V^{1/3}$	x
Benzene	2.22	
Ether	2.13	
m-Xylene	1.98	
Aniline	2.20	
Nitrobenzene	2.12	
Carbon tetrachloride	2.07	
Chloroform	2.07	
Ethylene chloride	2.12	
Toluene	1.95	
Anisol	2.18	
Hexane	2.23	
Bromobenzene	1.99	
Mesityl oxide	2.13	
Ethyl iodide	1.78	1.33
Ethyl bromide	1.80	1.29
Carbon disulphide	1.60	1.56
Acetic acid	1.34	2.02
Methyl alcohol	0.928	3.51
Ethyl alcohol	1.06	2.90
Propyl alcohol	1.22	2.25
Acetone	1.93	1.13
Water	0.00414	1170

It will be seen that for the majority of normal substances in the above table the value of $M(C_p - C_v)/V^{1/3}$ approximates to a constant. The associated liquids and a few liquids of high density, chief among which is carbon disulphide, form exceptions to this generalization. The question arises, therefore: Do carbon disulphide and ethyl bromide and iodide disagree with the above relation because the relation is inexact or because they are associated liquids? The constancy of the function in other cases excludes the explanation of the anomaly by inexactitude of the relationship. If we make use of the constancy of the function $M(C_p - C_v)/V^{1/3}$ to calculate association factors (x), we get the results given in Column 3 of the above table. It will be noticed the value of x for acetic acid agrees very well with values previously found. For water, owing to the very small value of $(C_p - C_v)$ the value of x appears to be extremely high. It is evident that for some reason the equation is not applicable in this case. Carbon disulphide too, it will be noticed, would appear to be strongly associated. The anomaly shown by water is connected with the peculiarity shown by water between 0° and 4° for the calculation of the function $C_p - C_v$ involves the value of *dv/dt*.

There are other equations in which carbon disulphide and also water show curious results. I have shown previously[1] that the following equation is approximately true

$$\frac{\beta\gamma^{4/3}}{T^{1/4}} = K$$

where β is the isothermal compressibility, γ the surface tension, T the absolute temperature and K is a constant independent of the nature of the liquid. In the following table are given in Column 4, values of K for a number of normal and associated liquids. The values of γ have been obtained for the most part from Ramsay and Shields' determinations and the values of β are from my own determinations. All the values are for temperature of 0° except otherwise stated.

Liquid	$\beta \times 10^6$	γ	K
Benzene	81.95	30.30	1.196
Ether	152.97	18.95	1.19
Chloroform	85.90	29.15	1.19
Carbon tetrachloride	91.03	28.17	1.20
Chlorobenzene	67.02	32.34	1.06
Toluene	79.34	29.75	1.13
Nitrobenzene	50.52	41.95	1.11
m-Xylene	75.39	30.17	1.09
n-Hexane at 30°	178.3	16.4	1.11
Ethyl acetate	96.29	26	1.15
Ethyl iodide	85.59	32.46	1.36
Ethyl bromide at 38.4°	155.4	21.9	1.40
Carbon disulphide	81.44	36.61	1.53
Acetone	106.3	25.5	1.23
Acetic acid at 20°	91.85	23.46	0.93
Ethyl alcohol	99.95	23.86	1.06
Methyl alcohol	107.6	25.17	1.22
Water	50.78	73.21	2.37

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[1] Zeit. phys. Chem., 87, 169 (1914).

Now it will be noticed that the preceding equation does not contain the molecular weight and it should, therefore, be valid for both normal and associated liquids. As, however, for associated liquids the chemical composition of the surface layer is probably different from that of the interior of the liquid owing to dissociation of associated molecules, the surface tension will probably be too small and hence for associated liquids we should find the value of K somewhat smaller than the normal. This is, however, only the case for acetic acid, and in this case the effect of the surface layer should only be slight, because acetic acid only dissociates a little on vaporization. In the other cases we find curious results. Ethyl alcohol gives a normal constant, methyl alcohol a constant rather too high and water, carbon disulphide, ethyl iodide and ethyl bromide, values of the constant much too high. We find again the same substances as before in disaccord with the general behavior of normal liquids. Also the associated liquids themselves do not show any similarity of behavior among themselves. It is possible that the value of the compressibility β for the associated liquids may be too high on account of the possible increase of association with a resulting diminution of volume, which occurs on compression. But this would not explain completely the high value of K given by water, for it would mean that more than half the decrease of volume which occurs when water is compressed would be due to an increase of the molecular association. And in the case of carbon disulphide it does not seem at all possible that it could be so much associated that the change of association on slight compression by one atmosphere pressure would be sufficiently great to account for the high value of K given by this substance. Nor can the anomalies be due to inexactitude of the relationship or to constitutional effects for, as seen from the preceding table, a large number of liquids of greatly differing constitutions give values of K, which, in the extreme case of carbon tetrachloride, only differ from the mean value (1.14) by about 5 percent, whereas the variation in the case of carbon disulphide is about 27 percent.

The existence of these anomalies renders necessary an examination of the theory of molecular association of liquids. Since the work of Ramsay and Shields in 1893 on the surface tension of liquids and the application of the equation of Eötvös to the determination of molecular weights, it has come to be regarded as chemical law that such liquids as the alcohols and water behave in their properties in general, and in particular in their disaccordance with various empirical relationships, such as the Ramsay, Shields-Eötvös equation, differently from the majority of other liquids because the simple gas molecules of these liquids are, in the liquid state, combined or associated together. This conception, however, rests upon no fundamental chemical principles, but is purely hypothetical. Only in the case of such liquids as acetic acid and nitrogen peroxide, which are associated in the gaseous state, can we be perfectly sure that there is molecular association in the liquid state. And the fact, as was seen above, that water and the alcohols along with carbon disulphide and several other liquids show differences of behavior to acetic acid, calls into question the truth of this theory. It may be mentioned here also, that Ramsay and Young[1] found that for the alcohols and the ordinary normal liquids the value of the function $(dp/dt)_v$ is independent of the temperature but that this is not the case for acetic acid and nitrogen peroxide, which seems to indicate some difference in the molecular condition between the alcohols and acetic acid.

To explain these anomalies I put forward the following hypothesis: In the cases of such liquids as water and carbon disulphide and also probably, though to a lesser degree, the alcohols, the molecules in the liquid state have not a translational kinetic energy strictly proportional to the absolute temperature as is the case with gases; but that, through the crowding together of molecules under the influence of strong attractive forces, the motion of the molecules is hindered somewhat so that the mean kinetic energy is constantly less

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[1] Phil. Mag., [5] 24, 196 (1887).

than the mean kinetic energy of external free molecules with which the liquid is in thermal equilibrium. The number of stationary molecules or molecules possessing little energy becomes greater than can be compensated for by molecules possessing extremely great kinetic energies. It is not difficult to understand that in a compact group or system of molecules there is a limit to the velocity or energy that a molecule may have while any number of molecules may for an instant be stationary. Or it may be regarded that such liquids are approaching the condition of the solid state when the molecules possess comparatively little kinetic energy.

It may be mentioned in support of this hypothesis that Amagat[1] has demonstrated from his experiments on compressibility under very high pressures that as the molecules come closer together at constant temperature the internal pressure (pressure of molecular attraction) at first increases, reaches a maximum and then begins to decrease rapidly with further diminution of the volume. If now, we imagine the same phenomena occurring when the volume is diminished by cooling at constant pressure instead of by pressure, it would necessarily mean that the molecules began either to associate or to be losing kinetic energy at a greater rate than gas molecules at the same temperature. But, as we have seen, association will not explain all the facts, and hence we are compelled to accept the alternative of an abnormally low kinetic energy.

It may be mentioned also that van der Waals[2] has found it necessary to introduce a very similar hypothesis in order to explain the disagreement between the observed results and those determined from the equation of state for liquids at high density. He prefers to consider, however, that the molecules (of normal substances even) tend to form loosely combined groups which for an instant behave as single molecules. This process he calls quasi-association. Unless, however, it be considered that each molecular complex has not the normal

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[1] Ann. chim. phys., [8] 28, 1 (1913).

[2] Proc. K. Akad. Wetensch. Amst., 13, Pt. I, 107 (1910).

molecular kinetic energy, then, so far as the effect on the physical properties of the substance is concerned, it will be just the same as ordinary association. If, however, it be granted that these molecular complexes possess less kinetic energy than the normal free molecule at the same temperature, then the hypothesis of quasi-association reduces to the same conception as I have put forward here, and the reason for the abnormally large compressibilities of water, carbon disulphide, etc., becomes comprehensible. The molecules bombarding each other with less energy than external gas molecules at the same temperature will offer less resistance to an external pressure, and hence the compressibility coefficient β is abnormally large and the value of the function $\beta\gamma^{4/3}/T^{4/3}$ in consequence greater than the normal value. A liquid composed of associated molecules possessing the normal kinetic energy would, of course, behave towards pressure like a normal liquid and give a normal value for the above function.

In most other respects the retardation of the motion of the molecules would have the same effect qualitatively, at least, as molecular association. For instance, the latent heat would be abnormally large (though the effect would not be so great as association), since it would include the extra energy required to raise the kinetic energy of the molecules to the normal value. The boiling point and vapor pressure would be similarly affected. On the other hand, for such a liquid the molecular weight as calculated by an equation such as the Ramsay-Shields equation would be normal or approximately so.

But this hypothesis is not sufficient in itself to account satisfactorily for the quantitative results. For instance, if we took an extreme case in supposing that for water all the molecules are at rest in the liquid state, then on vaporization at the boiling point 373 × 3 = 1119 calories would be absorbed per gram molecule to give the molecules their proper energy, and taking the value 325 calories per gram as calculated on page 98, as the latent heat absorbed other than work done against molecular attraction in vaporization, we find for 1 gram molecule 325 × 18 = 5850 calories. Hence, the theory of the retardation of the velocity of the molecules is not sufficient to account for the high value of the latent heat. We are, therefore, compelled to conclude that molecular association also exists in the case of water and probably also for hydroxyl compounds in general, and that the two factors, *i. e.*, the retardation of the velocity of the molecules and molecular association both play a part in affecting the physical properties of the liquids.

It must be concluded also that in the cases of carbon disulphide, ethyl iodide and bromide and perhaps also for many other liquids that there is no molecular association, but only the retardation of the molecular kinetic energy.

So long as these two factors cannot be separated the determination of association factors is futile.

It is hoped later, when more experimental data are available, to study this hypothesis and conclusions more closely.

Summary

Any equation used for the exact determination of association factors of liquids must be valid for mixtures as well as for pure liquids.

The method of Bingham and Harrison of determining association factors based upon measurements of fluidity is not reliable because it leaves out of account constitutional effects in the associated molecules.

The Batschinski modification of the Ramsay and Shields method rests on an unsound basis.

The method of Garver is based on untenable assumptions.

By means of the following equation

$$T_s = K\sqrt[3]{V_s}\log M$$

where T_s is the boiling-point temperature, V_s the molecular volume at the boiling point, M the molecular weight and K is a general constant equal to about 37, approximate minimum values of the association factors at the boiling points are determined. The minimum value for water thus determined is about 6.3.

Approximate values of the molecular weights of liquids are calculated by aid of the following equation

$$M = \frac{3.75(T + b)d}{\gamma\left[\left(\frac{d_s}{d}\right)^2 - 0.4264\right]}$$

where d is the density at absolute temperature T, d_s the density at the boiling point and γ is the surface tension. Applied to the calculation of association factors this equation gives values which are minima.

Several methods for the qualitative detection of association are examined. It is shown that an associated liquid does not necessarily disagree with Trouton's equation.

The relation of Kistiakowski

$$\frac{\alpha^2 M}{T_s} = K$$

where α^2 is capillary rise in a tube of 1 mm radius, M the molecular weight, T_s the boiling point and K a general constant may be considered a good test for association.

By means of the following equation

$$\frac{\gamma d_s^{2/3}}{l d_s^{5/3}} = 0.295$$

where l is the internal latent heat and the other terms are as before, the heats of dissociation of associated molecules on vaporization are calculated. It is shown by this means that acetic acid dissociates comparatively slightly on vaporization.

The following equation of Lewis

$$L = \frac{T\frac{dv}{dt}}{J\beta}$$

where L is the latent heat and β the compressibility, is applied to the same object as previously. According to this equation carbon disulphide and a few other "normal" liquids appear to be associated.

It is shown that an associated liquid does not necessarily give an abnormal constant in Ramsay-Shields' equation.

Evidence is adduced to show that the lower aliphatic esters are quite appreciably associated.

Taking advantage of the discovery that acetic acid dissociates only slightly on vaporization, fairly accurate values of the association factor are calculated in various ways and a good agreement is obtained in the results by the different methods. In the liquid state acetic acid appears to exist simply as double molecules.

The special case of carbon disulphide is discussed. This substance appears to behave sometimes as a normal liquid and sometimes as an associated liquid. By means of the equation

$$\frac{M(C_p - C_v)}{V^{1/3}} = K$$

where C_p and C_v are the specific heats at constant pressure and constant volume, respectively, molecular weights of liquids may be calculated and it is found that carbon disulphide and a few other liquids behave like associated liquids.

The following equation

$$\frac{\beta\gamma^{4/3}}{T^{1/3}} = K$$

not containing the molecular weight should be valid for associated liquids as well as for normal liquids, but it is found that water and alcohol and carbon disulphide give too high constants, while acetic acid gives a constant too low.

To explain these and other anomalies the theory is put forward that in the cases of carbon disulphide and water and some other liquids the mean kinetic energy of the molecules is, owing to dense crowding together under influence of attractive forces, less than the kinetic energy of free gas molecules at the same temperature. Evidence is adduced in support of this theory.

It is concluded that in the case of water and the alcohols both molecular association and the retardation of the kinetic energy of the molecules exist and affect the physical properties, while in case of carbon disulphide and a few other liquids only the retardation of the molecular kinetic energy comes into play.

Manchester University
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A STUDY OF LITHOPONE

BY W. J. O'BRIEN

Lithopone is an intimate mixture of barium sulphate and zinc sulphide precipitated from a solution of barium sulphide and zinc sulphate. It is put through a special process by which its physical properties are changed so that it is made suitable for use as a pigment.

Lithopone is known as Griffith's White, Jersey Lily White, Beckton White, Ponolith, Oleum White, etc. These whites are practically 30 percent zinc sulphide and 70 percent barium sulphate. Theoretically, equivalent solutions of barium sulphide and zinc sulphate produce 29.5 percent zinc sulphide and 70.5 percent barium sulphate. Some manufacturers in Germany reduce these mixtures with barytes and use seals which indicate the quality. As a general rule, green seal German or Dutch lithopone contains the maximum amount of zinc sulphide which is 29.5 percent. Next comes red seal, which varies from 24 to 26 percent; then blue seal, white seal, and yellow seal, which contain varying amounts of zinc sulphide according to the whim or custom of the manufacturer. There are, however, two grades of lithopone, one known as gold seal and another as bronze seal, which contain between 40 and 50 percent zinc sulphide, and naturally have much more hiding power and tinctorial strength than the so-called "green seal." These are made by adding an additional percentage of pure zinc sulphide to the pulp prior to the roasting operation, which is described later on. Sulphopone contains calcium sulphate instead of barium sulphate.

There has been a growing tendency during the past thirty years to replace white lead as a base for white pigments by zinc sulphide with other mixtures such as barium sulphate, magnesia, calcium sulphate, etc.

Ostwald[1] states that "there are certain difficulties with

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[1] Zeit. Elektrochemie, 2, 946 (1905).

the pale shades of color. The ground color of many pigments is white lead and white lead gradually becomes brown and dark. Further, colors, such as ultramarine, cadmium yellow, and vermilion, which contain sulphur, are acted upon by white lead and become dark. It is, therefore, desirable to substitute another white material for white lead. Lithopone can be used for this purpose."

Lithopone has many characteristics which make it a very valuable pigment. It is brilliant white, very fine in texture and according to Toch[1] has the same tinctorial strength but more hiding power than pure zinc oxide. It has also the advantage over white lead in that it can be mixed with pigments containing sulphur.

"Lithopone[2] is likewise very largely used in the cheaper grades of enamel paints, because it does not combine with rosin or semi-resin varnishes, and, therefore, remains unaltered in the package....

"As an inferior white, a first coat white, a ready mixed flat paint for surface, or as a pigment in the lighter shades for floor paints, lithopone cannot be excelled for its body, durability, hardness, fineness of grain, and ease of application. It does not oxidize progressively and this single feature has made it invaluable to the table oilcloth and floor oilcloth industry throughout the world....As a marine paint where other whites would be necessary, it is found to outlast both zinc oxide and lead carbonate."

It might be worth while to mention here the work of M. Ragg[3] on the effect of lithopone on linseed oil. This author finds that neither linoleic acid nor linseed oil has any marked effect at the temperature of the water bath upon the hydrated zinc sulphide, zinc sulphide, or lithopone. At a higher temperature the hydrated zinc sulphide is acted upon to some degree by the acids of linseed oil, stearic acid, and oleic acids;

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[1] Toch: "Chemistry and Technology of Mixed Paints," 26.

[2] Toch: Ibid., 30.

[3] Ragg: Farben Ztg., 15, No. 41 (1910).

linseed oil does not act upon the hydrated zinc sulphide or upon lithopone.

In an address on zinc, lithopone, and lead, before the Ohio Association of Master House Painters and Decorators, Mr. H. A. Gardner says: "Preliminary long time exposure tests have shown that lithopone may become a valuable component of colored paints, even for exterior wooden surfaces. Up to the present time, however, a satisfactory exterior white lithopone paint for wood has not, to the writer's knowledge, been prepared. Nevertheless the fact that this pigment is, however, finding considerable usage in the making of paints for cement, is well known.

"Lithopone is today finding a wider application than any other pigment in the decoration of interior wall surfaces. Nearly all of the modern flat wall paints contain a very large percentage of this opaque white pigment often in combination with zinc oxide. The varnish vehicles used with these pigments in flat wall paints are especially suited for inside wall work, the completed mixtures having proved much more satisfactory than the old-style paste pigments ground in oil and subsequently washed with turpentine. The ease of application and the great extent of surface covered by one or two coats of lithopone-zinc flat wall paints have created a wide demand for painted surfaces.... Actual tests made by the writer have shown that a properly prepared zinc-lithopone flat wall paint has a spreading power forty percent greater than the old-style washed pigment-oil pastes. These tests, moreover, demonstrated the superior hiding power of lithopone paints as well as their greater ease of working. The evident economies of their use are so overwhelming that it is safe to predict that for interior work they will be universally used within a comparatively short period of time, and, further, that the custom of painting the interior walls of all kinds of structures will grow to such an extent that the painter will be a more important factor in our building trades than ever before."

According to the Farben Zeitung,[1] lithopone has the following advantages:

1. It is free from poisonous properties and has greater covering properties than white lead.

2. It has great covering properties and high tinctorial strength.

3. It is unaffected by sulphur gases and mixes easily with oil and other colors.

"The following is a comparison of the covering properties of the following pigments:

22 parts Green Seal Lithopone are equivalent to
29 parts Zinc White
49 parts White Lead
50 parts Blanc Fixe

In addition, lithopone is cheaper than white lead."

According to a private communication from Mr. Maximilian Toch these comparative data are not accurate. He finds that twenty parts of green seal zinc lithopone are equivalent to twenty parts of white lead, thirty parts of chemically pure zinc oxide, and one hundred fifty parts of blanc fixe. This is for hiding power and not for covering capacity.

The earliest reference which has been found for the production of lithopone is in the English patent of John B. Orr, February 10, 1874. This patent according to Hurst[2] is as follows: "This process consists in first preparing barium sulphide by calcining barytes with charcoal for some hours at a white heat; the calcined mass is then lixiviated with water to dissolve out the barium sulphide which is formed. The solution so obtained is divided into two equal portions. To one of these is added a solution of zinc chloride, whereby a precipitate of zinc sulphide is obtained according to the equation

$$BaS + ZnCl_2 = BaCl_2 + ZnS.$$

"The precipitate is not separated, but to the mass is now added the rest of the barium sulphide and sufficient solution

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[1] Farben Ztg., 6, 275 (1901).

[2] Hurst: "Painters' Colors, Oils and Varnishes," 66.

of zinc sulphate, when a combined precipitate of zinc sulphide and barium sulphate will be obtained. This precipitate is washed with water, filter-pressed, dried, and then calcined at a red heat in a suitable furnace. While still hot the mass is thrown into cold water, which causes it to become rather denser than it otherwise would be, and thus have more body; the product is ground as fine as possible and dried, when it is ready for use."

Dr. S. Riderer[1] described the process also. He states that solutions of barium sulphide and zinc sulphate are mixed in molecular proportions, the resulting precipitate of zinc sulphide and barium sulphate is then dried, heated in a furnace, ground, washed and reduced.

"The barium sulphide is obtained by roasting ground barium sulphate with coal or other carbonaceous material in a reducing atmosphere. Two types of furnaces are used; *viz.*, flat-bed reverberatory and rotary kiln (Bruckner), either is equally good. Lixiviation of the product of the roasting gives a solution of sufficient purity for the next stage of the process."

"For the zinc sulphate solution, any zinc-bearing material may be used. Spelter and dross leave little or no zinc in the insoluble residue but zinc ashes usually leave so much mud in the solution tanks that the unit of zinc in the material is not so valuable. As regards impurities, the sulphide metals cause little trouble. Arsenic or antimony usually disappear as arsine or stibine where metallic zinc is used or are precipitated with copper and cadmium by adding some barium sulphide solution. Iron and manganese are usually removed by boiling with bleaching powder. A more powerful oxidizing agent and longer boiling are usually necessary when manganese is present."

There are a number of facts in the manufacture of lithopone which are of interest. Sowies[2] points out that the presence of natural barytes in lithopone has a harmful effect.

The barium sulphate can only be obtained in a suitable

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[1] Jour. Soc. Chem. Ind., 28, 403 (1909).

[2] Sowies: Farben Ztg., 18, 1117–9 (1913).

condition when it is precipitated with the zinc sulphide. In this way an intimate mixture is obtained, the barium sulphate adsorbing probably the zinc sulphide.

Heating the barium sulphate-zinc sulphide precipitate affects its physical condition in a number of ways. In the first place, the zinc sulphide as precipitated from solution is highly hydrated. The composition of the precipitated zinc sulphide according to A. Souchay[1] is as follows:

	When dried
at room temperature	$3ZnS.2H_2O$
at 100°	$2ZnS.H_2O$
at 150°	$4ZnS.H_2O$

Heating dehydrates the zinc sulphide. Hydrated zinc sulphide tends to work smeary on grinding. The effect of heat on the zinc sulphide is very similar to that obtained by Farnau[2] on chilling the zinc sulphide to a very low temperature. The zinc sulphide becomes brittle and capable of being crushed to a very fine powder. A denser substance is also obtained, thereby increasing the body of the pigment.

The great danger in heating the zinc sulphide is that the zinc sulphide is easily oxidized to zinc oxide. A slight oxidation cannot be avoided even in a most favorable atmosphere. This oxidation not only decreases the yield of the pigment but hurts the body of the pigment as well. According to a recent paragraph, Zerr[3] says:

"Lithopone manufacturers decided that by technically pure lithopone is understood one that contains besides the barium sulphate and zinc sulphide not more than one percent zinc oxide." A higher content of zinc oxide is to be objected to since it is shown by experiment that the higher the zinc oxide content the less stable is the lithopone to weather conditions.

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[1] Zeit anal. Chem., 7, 78 (1868).

[2] Jour. Phys. Chem., 17, 639 (1903).

[3] Farben Ztg., 17, 1381 (1912).

W. Hurschell[1] says that "the ground material barium sulphate cannot be substituted for the precipitated barium sulphate since it has other properties. On the other hand, the addition of zinc oxide helps to prevent the yellowing of the oil in dark moist rooms."

It is doubtless true that zinc oxide hurts the body of the pigments somewhat, but of all additions to prevent darkening it is the least harmful and adds other good qualities to the lithopone. In a communication to us Mr. H. A. Gardner states that the addition of zinc oxide and whiting improves the weathering qualities of lithopone. Mr. Gardner's experiments were made on two-foot boards and have never been tried out on a large scale. We have been told by others that up to now lithopone is not suitable for exterior paint purposes, even when admixed with other materials.

There is also a tendency for an overheated pigment to have a yellowish tinge. This yellow color is due to the zinc oxide film as was shown by Farnau.[2]

"These observations shed light on another set of phenomena, the change of color of oxides when hot and cold. When zinc oxide is heated in a matrass in the Bunsen flame, it becomes yellow; but returns to its original color when cold. Bismuth oxide and stannic oxide similarly treated, become darker when hot and lighter in color when brought back to room temperature, but do not become white again. Cooling the heated oxides causes disintegration of the coalesced particles and in their original state of fine subdivision, the masses show more or less their original color. This disintegration is not complete in the case of bismuth and stannic oxide.

"An experiment was made by heating the surface of zinc oxide contained in a crucible with the point of an oxyhydrogen flame. A good deal of volatilization occurred. On cooling, the mass of material regained its original color, but that which

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[1] Farben Ztg., 17, 1592 (1912).

[2] Farnau: Jour. Phys. Chem., 17, 639 (1913).

sintered together by immediate contact with the flame remained yellow. It was still yellow after several months."

The only apparent reason for quenching in water is to prevent too much oxidation. Red-hot zinc sulphide exposed to the air oxidizes very readily. It was found by us that hot zinc sulphide does not oxidize in an atmosphere of carbon dioxide.

Lithopone has one peculiar property, that of turning gray in the sunlight and becoming white again in the dark. Toch says:[1] "Under normal circumstances if lithopone be mixed with any vehicle containing linseed oil or varnish and exposed to the sunlight, it turns gray very readily, and if again placed in the dark it returns to its normal white color."

There is frequent mention in the literature of this strange phenomenon and although the darkening of lithopone was observed at least thirty years ago, no satisfactory explanation of it has been offered up to the present. As Ostwald says: "It is still a riddle."

The earliest work done on the darkening of lithopone is that of Dr. Phipson.[2] Phipson made a number of observations but could advance no satisfactory explanation for the facts observed. Dr. Phipson observed that a gate post painted white with lithopone turned black in the sunlight and became white again in the dark.

"I found that when this white powder [lithopone] was spread upon a piece of paper and exposed to the direct rays of the sun, it became fawn colored, brown, and finally a dark slate color in the course of about twenty minutes. When in this state it was placed in darkness, it became white again in two and a half to three hours time."

He first thought the color was due to barium sulphide. "The phenomenon was doubtless due to the use of sulphide of barium in the preparation of the pigment; for specimens made by another process in which no sulphide of barium was

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[1] Toch: "Chemistry and Technology of Mixed Paints," 28.

[2] Phipson: Chem. News, 43, 283; 44, 83 (1881).

used, did not show it at all." It then occurred to him that it might be silver.

"Of course these phenomena could not be due to any compounds of silver; nevertheless specimens were tested for silver, and with great care, but without the slightest result."

Finally he suggested the existence of a new element which he called actinium.

"It was hinted that I was dealing with a new element (to be called actinium) but continuation of my experiments led me to believe that the phenomenon described above may be probably due to the presence of sulphide of barium and protoxide of iron in the specimens rather than to some unknown metal.

"I observed that the dark slate-colored product was immediately soluble in cold acetic acid (as sulphide of iron is); and if the dark color be due to the production of sulphides of iron, the return of the pigment to its original white tint when placed in darkness for some hours, may be owing to the gradual oxidation of this sulphide of iron and consequent disappearance of the dark color.

"I found also that a strong calcination with free access of air, destroys, or considerably hinders the production of the actinic phenomena. I have also observed that although this pigment will retain this property of darkening in the sunlight for more than a year, some specimens have lost this property in a few months; and the gate post painted white after darkening, in the manner above mentioned, for the space of several days, will at last remain white."

In another article Phipson[1] draws the following conclusions:

1. The phenomenon the [blackening] is due to a reduction which when the substance is removed to the dark becomes an oxidation and the pigment is restored to its original whiteness.
2. Pyrogallic acid facilitates the reduction.
3. The dark product is soluble in acetic acid, which allows it to be separated from the zinc sulphide.

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[1] Phipson: Chem. News, 44, 73 (1881).

4. The original white pigment allowed to remain for two nights and days in a large excess of acetic acid does not, previous to the action of light, dissolve the substance which is affected by this action (and this points to sulphide of zinc itself as being the substance affected).

"The constant minute quantities of iron in the numerous samples of these white pigments which I have examined led me to believe that the dark slate-colored product obtained by exposure to sunlight was owing to the production of the sulphide of iron, or to some compound sulphide of iron, zinc, and barium as mentioned in my first note. In order to decide this point, if possible, I took a specimen of the pigment which contained very little iron, and by exposing it over and over again to the alternate action of sunlight (reduction) and the darkness (oxidation)—renewing the surface after each experiment—I hoped to oxidize the iron completely, so that a moment would arrive when the pigment would no longer darken on exposure to the light. But, although the experiment was continued on a very thin layer, the newly exposed surface continued to darken as at first. It appears probable that the minute quantities of iron present are not the cause of the phenomenon."

Mr. Cawley also made many observations on the darkening of lithopone which appear in three papers,[1] two in 1881 and the third,[2] ten years later. The writer did not discover this paper, hidden under the title, "The Curious Behavior of Certain Zinc Compounds," until after we had duplicated many of Mr. Cawley's results independently. These results will not be given with Mr. Cawley's since they will be discussed more in detail later.

While Mr. Cawley made many observations, he could advance no satisfactory explanation for the facts observed. Mr. Cawley studied the darkening of lithopone and has the following to say about it:

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[1] Chem. News, 44, 51, 167 (1881).

[2] Ibid., 63, 88 (1891).

"In general, however, it [lithopone] is subject to the grave defect of darkening when exposed to the sunlight, the darkening apparently being due not only to light but also dependent on the conditions of the atmosphere in respect to moisture content, etc. I have prepared pigments so sensitive as to be turned almost black when exposed to the sunlight for one or two minutes. A curious thing to be noted in this connection is that the darkened pigment will completely regain its whiteness when placed in the dark for a few hours, and when so bleached it appears to be somewhat less sensitive than it was originally. It would be a long story to go into all the details of experiments made by me in connection with this matter. I will, therefore, content myself by giving a brief account of the more important observations, interpolating here and there remarks of an explanatory character.

"1. The dried hydrated zinc sulphide before ignition is not altered by exposure to light, after ignition it darkens readily.

"2. The white stand purest zinc blend obtainable was levigated and exposed to the light. No darkening was observed but the same blend, calcined so as to be slightly oxidized, was readily darkened.

"3. Zinc sulphide was prepared in a very finely ground condition and free from hydration by burning zinc in an atmosphere of sulphur vapor and collecting the product in a chamber, the temperature of which was high enough to prevent the condensation of the sulphur. The sulphide was unchanged by light but like the blend darkened readily after slight calcination. In connection with the observations above named, I may say, I had been struck by the resemblance which the color developed in the pigment by light bore to that of finely divided metal deposited from certain metallic solutions. I found, too, as might have been expected, that in the heating of hydrated zinc compounds, when air is excluded, oxidized zinc compounds are always formed, and in this way the idea was suggested to me that light might be able, under certain conditions, to effect the reactions which it is well known heat does. These reactions may be expressed by the equations

$$ZnS + 2ZnO = 3Zn + SO_2$$
$$ZnS + ZnSO_4 = 2Zn + 2SO_2.$$

According to this hypothesis the darkening is due to the formation of a film of metallic zinc, which, owing to its finely divided condition would readily oxidize in the absence of light; the bleached pigment would therefore be less sensitive than it was originally, as it would be protected somewhat by a film of non-sensitive zinc oxide. This theory explained easily all the observed facts for a time but was afterwards found to be untenable.

"4. Noting that the pigment moistened with water was more sensitive than when in a dry condition, a sample was dried at 120° C and while warm was placed in a glass tube which was sealed before the blow pipe. Result—no discolorization after one year's exposure.

"An attempt was made to apply this observation by thoroughly drying the pigment immediately before grinding in linseed oil, the latter being as free from water as possible, the idea being that the oil would exercise a protective effect similar to that of a sealed tube. Result—not satisfactory.

"5. Taking a sample of pigment not very sensitive, *per se*, it was noted that its sensitiveness was greatly increased by moistening it with a weak solution of zinc sulphate, from which it was inferred that the sensitiveness might be due to imperfect washing. The most thorough washing, however, would not remove the basic sulphate formed in the process of ignition. Attempts were made to decompose this basic sulphate into zinc oxide and an inert sulphate by treating the pigment with solutions of the hydrates of potassium, barium, sodium, and calcium; the first three were rejected as they appeared to act on the zinc sulphide itself. Lime water exercised for a short time a decidedly protective effect. Afterward it seemed to lose its power of making the pigment permanent to light.

"The best results were obtained by mixing with the zinc sulphide about one percent of freshly precipitated magnesium hydroxide. The resulting pigment was fairly resistant to light but the presence of magnesium somewhat impaired its general qualities."

This is the extent of the research done on this problem that can be found in the literature. There are a good many patents published; the principal ones will be discussed later in the paper. The following is the experimental part done by us.

Experimental Part

The conditions most satisfactory for the blackening of the lithopone were first studied.

It was known that certain salts such as sodium chloride, zinc sulphate, etc., accelerated the blackening. Accordingly mixtures were made of a sample of lithopone that would darken with varying amounts of the different salts, ground with the same quantity of water. These were exposed on microscopic slides first to the action of the sun rays.

Lithopone plus

	Percent					
NaCl	1	10	20	30	40	50
$ZnSO_4$	1	10	20	30	40	50
$ZnCl_2$	1	10	20	30	40	50
$CdSO_4$	1	10	20	30	40	50

All the above salts accelerated the blackening. While the final intensity of darkening was the same in each case, the rate of darkening was different and there was an optimum percent of salt for the rate of darkening in each case. For example, it was found, keeping all the conditions the same, that a mixture of thirty percent zinc sulphate with seventy percent lithopone darkened more quickly than ten percent zinc sulphate with ninety percent lithopone.

The effect of acid and alkali on the rate of darkening was next observed. A mixture of thirty percent of zinc sulphate and seventy percent of lithopone was made into a thin paste as before and a little sulphuric acid added drop-wise to a very faint acidity. In the same way sodium hydroxide was added drop-wise to a portion of the same mixture till faintly alkaline. Portions of the two samples thus prepared were then rubbed on the glass slides and exposed. It was found that acid or alkali rather hindered the darkening, and that the darkening took place best in a neutral medium. Finally it was found that all salts which formed soluble zinc salts accelerated the darkening, while salts which formed insoluble zinc salts, such as the alkali phosphates, ferrocyanides, borates, cyanides, or bicarbonates stopped or retarded greatly the darkening. A discussion of these results will be taken up later.

The effect of moisture on the darkening of the lithopone was next studied. The results obtained agreed with Mr. Cawley's results already given. A piece of paper, covered with a moist suspension of lithopone was put into a quartz glass flask, which was then evacuated, sealed, and exposed to the rays of a large Macbeth printing lamp. The blackening took place more quickly than in air. This is probably due to the fact that moisture does not escape when the flask is sealed while it tends to evaporate in the air, the presence of moisture greatly aiding the darkening. On the other hand, a piece of paper prepared as above but dried in an air bath was exposed in a dry, evacuated quartz flask. No change was observed. This proves that moisture is necessary for the darkening.

It was also found that the lithopone darkened more readily in a moist hydrogen atmosphere or any atmosphere free from oxygen. The blackened lithopone did not become white again on being put into a flask which was then evacuated.

The reason for this is that the change from the black to the white color is evidently an oxidation and not a reversible reaction. Blackened samples of lithopone on paper were treated with a dilute solution of hydrogen peroxide. The blackened surface whitened immediately. The same effect was obtained when strips of paper, covered with lithopone and darkened, were held in an atmosphere of ozone.

The ideal conditions found for making the lithopone most sensitive were an addition of thirty percent zinc sulphate to the lithopone which was then made up to a thin paste and exposed in an atmosphere of moist hydrogen. The atmosphere of moist hydrogen was secured by using a large test tube of Uviol glass and closing it with a two-hole rubber stopper through which the moist hydrogen gas was passed by means of a glass tube reaching up into the inverted tube. The thin paste of lithopone and zinc sulphate was applied to the glass slide by means of a spatula and rubbed to form a thin film. The glass slide was then put into the Uviol tube and partly exposed. The nature of the surface had also an effect on the reaction. It was found that the reaction went faster on roughened glass than on paper, wood, or smooth glass.

The source of light in all these experiments was a Macbeth printing lamp. This lamp is run on a 110-volt circuit and requires about 25 amperes. The carbon rods are cored and filled with a special composition which gives, on burning, a very powerful light rich in the shorter wave lengths. The light is quite steady, the current being automatically controlled by means of a coil and plunger which regulates the distance between the burning ends of the carbon rods. A reflector of aluminum throws the light forward in one direction. This light is more satisfactory for most purposes than sunshine.

Our first thought was that the black product was iron sulphide. Hydrogen sulphide, formed by the decomposition of the zinc sulphide by light and moisture according to the reaction

$$ZnS + H_2O + \text{light} = ZnO + H_2S,$$

might react with iron salts in the lithopone forming the black ferrous sulphide. The ferrous sulphide in a very thin film would be oxidized to the light yellow ferric salt, accounting for the disappearance of the black color.

Lithopone made from chemically pure reagents was analyzed for iron by the colorimetric sulphocyanate method. Result—only a slight trace was found, that is, less than 0.001 percent. This lithopone darkened when exposed to light.

The black film could be removed by dipping the blackened lithopone carefully into water; the black film would float usually on top of the water, leaving a new surface beneath, which darkened as before. This could be repeated as often as desired. We concluded that it was unreasonable to believe that a mere trace of iron could cause all this darkening. This confirms Dr. Phipson's and Mr. Cawley's work.

Phipson[1] says that "the darkening was not due to iron as he first supposed or to other impurities such as one would most likely find in zinc salts such as cadmium, lead, arsenic, silver, bismuth, etc." John B. Orr[2] states that if the pigment is properly made it does not contain iron, lead, arsenic, or manganese, and yet insolation produces this bluish coloration unless means be taken to prevent it. Having excluded the possibility of ferrous sulphide, the next step in the experimental work was to find out what the black product was. We could form no theory to fit in with the facts observed until we had definitely decided on what the black product was.

This problem offered many difficulties. One trouble in testing the black film was due to its extreme sensibility to reagents. It oxidized very readily in the air when isolated in any quantity. It also disappeared very quickly in water. It was very soluble in acetic acid and soluble in most salt solutions such as sodium chloride, sodium sulphate. It was quite stable in carbon bisulphide. This behavior could be explained by the fact that we were dealing with metallic zinc in a very fine state of division.

Microscopic tests were first tried. The fact that other zinc salts were present besides the metallic zinc eliminated the ordinary microscopic tests. Attempts were first made to spread a film of gelatine over the blackened surface and to allow a dilute solution of hydrochloric acid to diffuse in. The acid would act slowly on the zinc sulphide as well as the

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[1] Phipson: Chem. News, 44, 73 (1881).

[2] Orr: Ibid., 44, 12 (1881).

metallic zinc if present, causing a slow evolution of hydrogen sulphide and hydrogen gas. Hydrogen sulphide is to a great extent soluble in gelatine whereas hydrogen is not and could be observed, if present, as minute bubbles of gas under the microscope.

Glass slides were, therefore, covered with a sensitive sample of lithopone and blackened quickly in a moist atmosphere of hydrogen, in this way avoiding as much as possible an oxide film on the blackened product. The slide with the blackened product and one unblackened were then covered with a film of gelatine. A large drop of dilute acid was placed on each slide and allowed to diffuse in. The test was not satisfactory, the gelatine did not adsorb entirely the hydrogen sulphide evolved and there were always observed on the blank some bubbles of gas, probably due to carbonates. On the other hand, there was a greater evolution of gas from the blackened product.

Electrolytic methods were then tried in the hope that if metallic zinc were present, metallic lead or copper would be thrown out of the solutions of these salts. It is well known that when metallic lead is thrown out of solution, it tends to form characteristic lead trees. Solutions of lead and copper of varying concentrations were, therefore, tried, and while the black product immediately dissolved in the solution of these salts, no trace of lead trees or metallic copper could be identified under the microscope. This could be accounted for by the fact that the black film is very thin and contains but a small amount of zinc, not sufficient in quantity to throw out the copper or lead.

There are a large number of reactions that show a color change in the presence of a reducing agent. A dilute solution of iodine colored blue with starch was found to be unsatisfactory as also was alkaline permanganate. Potassium ferricyanide was then tried. As is well known, potassium ferricyanide in the presence of a ferrous salt gives Prussian blue. This reaction is very sensitive.

The solutions used were about a 10 percent solution of ferricyanide, 10 percent solution of ammonium acetate and about 0.1 percent solution of ferric alum.

The method of testing for the zinc was as follows: A drop of the ferric alum solution and a drop of the potassium ferricyanide solution were placed side by side near the object to be tested for and then caused to run together. Where the ferric alum, the reducing substance, and the potassium ferricyanide solutions meet, a reduction of the ferric alum takes place and a blue color results.

Trials were first made on mere traces of zinc, such as light lines of zinc made by rubbing a piece of metallic zinc over some barium sulphate paper. With traces of zinc as small as these, the test worked beautifully. On trying it out on the blackened lithopone, however, the zinc sulphide present interfered, the hydrogen sulphide caused by the action on the zinc sulphide of the free acid present in the ferric alum, due to hydrolysis, also reduced the ferric alum. This was overcome to a great extent by adding ammonium acetate to the ferric alum, a large part of the free acid of the ferric alum being neutralized.

By adjusting carefully the amount of ammonium acetate added to the ferric alum, comparable results could be obtained.

In conducting the tests, one glass slide was covered with a sample of lithopone which was very sensitive to light. It was blackened by exposure to light. Another slide was covered with an undarkened sample of the same lithopone and then covered with a thin film of zinc dust, made by buffing a piece of metallic zinc on a carborundum wheel and catching the fine zinc dust on the slide covered with moist lithopone. In this way a very sensitive zinc dust could be obtained and one less liable to be covered with an oxide film. Another slide was taken and covered with the lithopone alone. The three slides, side by side, were tested as described above. The slide, covered with fine metallic zinc, acted instantly, as did the black product, giving the blue color, while the blue color appeared on the lithopone slide only after several minutes. While these tests do not prove that we have metallic zinc, since an unknown subsulphide of zinc may be present, all the facts point clearly to the formation of a film of very finely divided metallic zinc. The substance oxidizes readily, is extremely soluble in acetic acid, dissolves in solutions of sodium chloride, or sodium sulphate, is extremely soluble in alkalies, and is not soluble in carbon bisulphide.

That it is a direct product of the action of light on the zinc sulphide is shown by the fact that if the lithopone is shaken in acetic acid for some time and then washed and exposed, the blackening takes place as before, the black product, however, is quickly dissolved in acetic acid, showing that the action of light gave rise to a product soluble in acetic acid.

The reaction was studied under the microscope. A slide was covered with lithopone and exposed while under the microscope to the light of the arc lamp by directing a beam of light from the arc through a small opening in an asbestos board onto the slide. It was observed that the darkening took place in spots. A bubble of gas formed and then on the side of the bubble a black spot would appear, growing larger.

Cadmium sulphate acted in two ways when mixed with lithopone. In the air it accelerated the blackening; in a hydrogen atmosphere the blackening was also accelerated but some cadmium sulphide was also formed, the black showing a yellow tinge. Cadmium sulphide oxidizes very readily in the air and is probably oxidized as quickly as it is formed. In hydrogen this is not the case.

It was thought that perhaps cadmium sulphate hydrolyzed slightly, the free acid acting on the zinc sulphide setting free hydrogen sulphide. This was found not to be the case, a paper saturated with a solution of cadmium sulphate, placed near the exposed slide covered with lithopone, but not in direct contact with it, turned yellow, showing that the zinc sulphide in the presence of moisture in a hydrogen atmosphere is decomposed, one of the products being hydrogen sulphide. This is analogous to the action of magnesium sulphide on water.

$$MgS + 2H_2O = Mg(OH)_2 + H_2S.$$

The finer the lithopone is, the more easily should it be reduced, as there would be a greater surface exposed. That this is so was shown to be the case. Three samples of lithopone, one that was quite sensitive to light, one only slightly so, and one not at all, were found to show, under the microscope, appreciable difference in the size of the particles. The one most sensitive to light was found to be the finest grained. Measurements of the size of the particles under the microscope could only be approximate since the average size was found to be less than 0.01 of a micron in diameter, a value too small for the ordinary microscope to handle accurately.

The sensitiveness of the zinc sulphide to light was thought to be due to the fact that it was carried down in a very fine condition by barium sulphate. Barium sulphate and zinc sulphide were precipitated in molecular proportions according to the equation

$$BaS + ZnSO_4 = BaSO_4 + ZnS.$$

The barium sulphate-zinc sulphide precipitate was filtered, washed, and dried at about 100° C. This was then subjected to the following treatment: the barium sulphate-zinc sulphide precipitate was ground with zinc sulphate to a very fine powder, moistened, and exposed on glass slides to the light of the arc lamp. After three hours' exposure, no darkening was observed.

It was then thought that barium sulphate did not adsorb the zinc sulphide as efficiently as other substances, for example, aluminum hydroxide. Aluminum sulphate and zinc sulphate were mixed together and ammonium sulphide was added. A precipitate of zinc sulphide and aluminum hydroxide was obtained. This precipitate was washed, dried, and tested as the barium sulphate-zinc sulphide was, with no darkening taking place.

A colloidal solution of zinc sulphide was then prepared in the following manner: a zinc sulphate solution was poured into a solution of sodium hydroxide until the zinc hydroxide just barely dissolved. This was then diluted to about ten times its volume with water and a rapid stream of hydrogen sulphide passed through till the precipitate just dissolved. The colloidal zinc sulphide was then precipitated by adding aluminum chloride. In this way a very amorphous precipitate of zinc sulphide was obtained. On exposing this precipitate to the light with reducing agents and other sensitizing substances no darkening was obtained.

Chemically pure zinc sulphide was ground with barium sulphate in an agate mortar crusher. As we were unable to grind the zinc sulphide at ordinary temperatures, pieces of solid carbon dioxide were thrown into the agate mortar crusher, chilling the zinc sulphide and making it brittle. We were able to grind the zinc sulphide as fine as the sensitive lithopone. This zinc sulphide did not darken on exposure to light in presence of reducing agents.

Since we were unable to get zinc sulphide to darken by precipitating it in a finely divided condition, or by having it adsorbed, or by grinding it to a very fine condition, it was concluded that heat must be necessary for some unknown reason.

The following possible theories could be advanced as to the effect of heat on the barium sulphate-zinc sulphide. Since it is known that zinc sulphide melts at about 1440° C and in the presence of sodium chloride at a much lower temperature, it was thought probable that in the reducing atmosphere metallic zinc was formed which went into colloidal solution in the solid solution of zinc sulphide. The light acted as a pectonizing agent as did also the salts which accelerated the darkening, such as sodium chloride, zinc sulphate, etc. Another possible explanation offered itself in the possibility of a metastable compound being formed on heating which broke down under the action of light, depositing metallic zinc. There was still also the chance that some powerful reducing agent might be formed on heating the zinc sulphide-barium sulphate precipitate since it is known that reducing agents greatly aid the darkening of the lithopone. The presence of a powerful reducing agent in the lithopone seemed hardly probable since this reducing agent would be oxidized on standing in the air and moisture.

The barium sulphate-zinc sulphide precipitate prepared as described in the previous work was heated in an electric tube furnace. An electric tube furnace was used because it was thought that atmospheric conditions could be better controlled and the temperature measured if desired. An objection to the tube furnace, however, was that only a small quantity could be heated at one time so relatively high percentage oxidation, as we found out afterwards, could not be prevented. This was due to the fact that the small quantity of hot zinc sulphide came in intimate contact with the air on pouring it from the tube into the water.

The tube furnace was evacuated and the barium sulphate-zinc sulphide precipitate was heated for about half an hour at about 700° C. It was then quenched in cold water, washed, dried, ground, and tested under the most favorable conditions for darkening. This product would not darken. This substance on analysis showed

$BaSO_4$	ZnO	ZnS
71.21	10.00	18.60

It was then thought that a certain temperature was most favorable for the production of a lithopone that would darken. The barium sulphate-zinc sulphide precipitate was then heated in the electric tube furnace which was kept well evacuated in order to prevent the oxidation of the zinc sulphide at a temperature of 500° C. This product on testing showed no darkening. Another run was made at 800° C and a product was obtained which would not darken. Runs were made up to 1400° C under otherwise the same conditions with the idea that temperature played an important part in producing a lithopone that would darken. In no case was a lithopone obtained that would darken. Analyses of the substances obtained showed a high zinc oxide content.

Preventing excessive oxidation of the zinc sulphide on heating, is rather difficult. Zinc sulphide precipitated from an aqueous solution is always hydrated. A. Souchay's work on this has already been mentioned. This water is held in more or less intimate union with the zinc sulphide and it is possible that on heating it goes over to $ZnS.xZnO$ as for example:

$$2Zn(OH)(SH) + 3O + \text{heat} = ZnS.ZnO + 2H_2O + SO_2$$

Oxidation of the zinc sulphide was prevented by mixing intimately in a mortar the barium sulphate-zinc sulphide with about five percent of common salt and about one percent of ammonium chloride and heating this mixture in a graphite crucible, covered tightly with a graphite cover. This mixture was heated in a muffle furnace at about 1000° C for about ten minutes. In this way a substance was obtained which was very sensitive to light.

The use of the ammonium chloride and the sodium chloride is to prevent oxidation. The ammonium chloride volatilizes at a low temperature and displaces most of the oxygen. The fused sodium chloride dissolves off the zinc oxide film that is formed about the zinc sulphide particles, giving a very white, fine sample of lithopone which, however, is very sensitive to light.

It was thought advisable to see if under the same conditions lithopone made as pure as possible would darken as much as lithopone made from commercial zinc sulphate and barium sulphide. Barium sulphide as pure as possible was obtained which contained only traces of impurities. It was dissolved in boiling hot water; the solution was allowed to stand until clear and then was poured into a solution of zinc sulphate which was also very pure. The precipitate was well washed, dried, and heated as described above. A product was obtained which darkened just as readily as the lithopone obtained from the impure barium sulphide and zinc sulphate.

Having found that chemically pure lithopone would darken it was next sought to find out whether barium sulphate was necessary for the darkening. Chemically pure zinc sulphide was made by precipitating zinc sulphide from a chemically pure solution of zinc sulphate. This precipitate was washed, dried, and ground to a fine powder. It was then ground with sodium chloride and heated as described above. The zinc sulphide so obtained darkened on exposure.

Having found an easy way of darkening the zinc sulphide alone, it was now sought to find out whether, on sudden cooling, a metastable compound was obtained as in the case of glass, which under the action of light broke down into metallic zinc.

By slow cooling it was thought that the formation of the metastable phase could be prevented and so a product that would not darken be obtained. Some zinc sulphide-barium sulphate precipitate was taken and heated to about 1000° C and then allowed to cool slowly. This product did not darken but analysis gave the following results

$BaSO_4$	ZnO	ZnS
74.06	17.93	8.64

To prevent excessive oxidation, another sample was run as before, but instead of allowing it to cool in air, it was cooled in an atmosphere of carbon dioxide. This product gave on analysis

$BaSO_4$	ZnO	ZnS
69.49	2.76	27.74

and did darken.

The rate of cooling was now decreased with the idea that perhaps the cooling in the air was quick enough to carry the substance over to the metastable condition. Some more of the unheated barium sulphate-zinc sulphide precipitate was then heated in a quartz tube which was kept continually filled with carbon dioxide by means of a Kipp generator. The product was brought to a temperature of about 1000° C and then allowed to cool slowly for three hours. The product on analysis showed a low oxide content and darkened.

The presence of some slightly soluble, though powerful reducing agent in the heated zinc sulphide-barium sulphate precipitate now occurred to us. On the face of it, this seemed improbable, as it is hard to see how a reducing agent could exist in lithopone without undergoing oxidation. On the other hand, it was shown that reducing agents greatly accelerate the darkening.

Tests were made for the presence of the reducing agent in the lithopone as follows: A very dilute solution of iodine was colored blue with starch. Zinc sulphide and barium sulphate were ground together in the proportions found in the lithopone that would darken. Uniform suspensions were then made by shaking equal weights of the barium sulphate-zinc sulphide and the lithopone in the same quantity of water and adding to each the same quantity of solution of iodine. Decolorization took place immediately with both samples.

A very dilute solution of alkaline permanganate was then tried; the lithopone seemed to act even more slowly on this solution than the barium sulphate-zinc sulphide, proving that there was no strong reducing agent formed by heating the lithopone.

Up to now we could obtain no satisfactory theory that would explain all the facts observed. Repeated analyses of many samples of lithopone which would darken and which would not, show a marked difference in their zinc oxide content. Below are some of the analyses of samples that would and would not darken.

Would darken			Would not darken		
$BaSO_4$	ZnO	ZnS	$BaSO_4$	ZnO	ZnS
69.50	2.49	27.34	——	4.03	21.15
69.61	1.86	28.15	67.57	3.74	28.61
69.74	0.98	29.66	71.06	5.82	22.72
71.41	1.51	26.45	74.06	7.24	19.62
			74.06	8.64	17.93

In no case did we get a sample that would darken, as made by us, whose oxide content ran much above 3 percent zinc oxide. The analyses were conducted as directed by Holley.[1]

It seemed evident then that we were dealing with a protective film of zinc oxide over the zinc sulphide, preventing its decomposition by light and moisture. If this were so, we should be able to remove the zinc oxide film from the zinc sulphide by boiling in an aqueous solution of zinc chloride, as it is known that zinc chloride dissolves zinc oxide. The zinc sulphide should then darken in the light even though it had not been heated.

Concentrated solutions of zinc chloride and sodium chloride were added to separate portions of chemically pure zinc sulphide in Erlenmeyer flasks, provided with return condensers and were boiled for some time. The zinc sulphide was originally slightly yellow but a beautiful white zinc sulphide resulted on boiling, showing that most of the zinc oxide film had dissolved. This zinc sulphide, well washed, was then mixed with a little sodium hydrosulphite and exposed in a moist hydrogen atmosphere to the light. It darkened readily.

We were unable to get zinc sulphide to darken without the use of a reducing agent. The reduction of the zinc sulphide in lithopone is probably helped greatly by the presence of barium sulphate which adsorbs zinc sulphide and the metallic zinc, since barium sulphate is known to adsorb gold. This was shown by Antony and Lucchesi,[2] "Further, if barium sulphate and mercurous chloride are suspended in water, and excess of auric chloride then added, the barium sulphate takes up the gold and becomes the color of purple of Cassius."

Barium sulphate and zinc sulphide were precipitated together in the usual way, washed, dried, and ground. Exposure of the barium sulphate-zinc sulphide had no effect even with reducing agents. The barium sulphate-zinc sulphide was then boiled for a considerable time in concentrated zinc chloride solution. It was then washed a number of times by

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[1] Holley: "Analyses of Paint and Varnish Products," 123.

[2] Antony and Lucchesi: Jour. Chem. Soc., 72 II, 43 (1897).

decantation and dried in air. The precipitate was then ground very fine and exposed. After some exposure, darkening occurred as we had expected, without the use of a reducing material. A solution of sodium chloride was found to work the same way as zinc chloride in dissolving off the zinc oxide film but not so energetically.

The presence of a zinc oxide film over the zinc sulphide explains the behavior of zinc sulphate, zinc chloride, sodium chloride, and reducing agents in accelerating the darkening of the lithopone. They dissolve the oxide film away from the zinc sulphide as fast as it is formed, leaving always a sensitive zinc sulphide. The use of sodium chloride in heating the zinc sulphide in order to get a substance that will darken is also explained. Fused sodium chloride is a good solvent for zinc oxide.

This explanation is borne out by the many patents that have appeared in the literature on this subject. Rudolf Alberti,[1] in a patent for making lithopone more stable, uses barium peroxide, hydrogen peroxide, and sodium peroxide. "$BaO_2.H_2O_2$, Na_2O_2 are used to oxidize the black material which blackens in the light. This material is converted to a higher oxide and is permanent to light."

The black material that Alberti has in mind does not exist. He is simply oxidizing the zinc sulphide, forming a protective layer over the zinc sulphide and so making it stable to light.

R. Steinau,[2] in making a light and weatherproof lithopone, has the following to say: "The darkening of lithopone is due to the presence of zinc and cadmium chlorides. A lightproof lithopone can, therefore, be obtained if one uses a chlorine and oxygen adsorbing salt." He uses zinc carbonate or magnesium carbonate with alkali nitrite.

Mr. Steinau probably mixed some cadmium and zinc chloride with lithopone and found that they accelerated the

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[1] Alberti: Centralblatt, 1906, II, 651.

[2] Steinau: Ibid., 1908, I, 1593.

darkening, as we found. He, therefore, concludes that they are the cause of the darkening of lithopone. Just what he means by a chlorine or oxygen adsorbing salt is not quite clear. He probably means a reducing salt. One would hardly see the need of that as there is no free chlorine present. His patent is probably somewhat efficient because he gets an insoluble film of zinc carbonate formed. There is doubtless a small quantity of soluble zinc salts always held by the zinc sulphide-barium sulphate precipitate which in the presence of some soluble carbonate would form a film over the zinc sulphide.

Cawley[1] makes lithopone fairly resistant to light by mixing one-half to one percent of freshly precipitated magnesium hydroxide. Mr. Cawley found that the presence of the magnesia somewhat impaired the qualities of the lithopone. The magnesium hydroxide forms a film over the zinc sulphide as before.

W. Ostwald[2] claims that lithopone can be made stable to light if one washes the product with non-acid water solution of such salts as soda, potash, or alkali phosphates, borates, cyanides, bicarbonates, ferrocyanides, sulphides, sulphydrides, and hydroxides.

It is evident that Ostwald has picked out nearly all the soluble salts that form insoluble zinc salts. The significance of this is that an insoluble zinc salt is formed around the zinc sulphide which protects the zinc sulphide from the action of light. For example, he found alkali phosphates to work well. The slight traces of soluble zinc salts combined with the phosphate, forming zinc phosphate which, as we all know, is insoluble.

Allendorf[3] does the same thing when he mixes with the lithopone, after heating, soap solutions of the earth metals or aluminum. In the United States patent 883,142, P. Lihme oxidizes the zinc sulphide with some soluble nitrate.

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[1] Cawley: Chem. News, 63, 88 (1891).
[2] Ostwald: Centralblatt, 1908 II, 1707.
[3] Allendorf: Ibid., 1909 I, 116.

"A soluble nitrate is added to the product heated in a muffle furnace, corresponding to the reacting or darkening products."

How he knows what the darkening products are and how much soluble nitrate to add is beyond the most lively imagination.

Bayer and Company,[1] make lithopone stable to light by subjecting the finely divided lithopone, in suspension in the anode chamber in water containing sufficient electrolyte, to the electric current.

W. Brase[2] makes light-proof lithopone by adding to the moist or dry lithopone 0.5 percent potassium nitrate.

W. Ostwald[3] claims to make lithopone stable to light by burning and cooling in absence of oxygen. The air is completely removed and an indifferent gas passed in.

Ostwald probably burns the hydrated zinc sulphide so that it oxidizes according to this equation

$$2Zn(SH)(OH) + \text{heat} = ZnS + ZnO + H_2O,$$

the zinc oxide forming around the zinc sulphide.

There are a number of other patents which embody the same idea, an insoluble film over the zinc sulphide.

The objection to all these applications, for preventing the darkening of lithopone, is that they hurt the good qualities of the lithopone. The presence of an alkali salt is bound to cause trouble sooner or later with the oil. Alkalies also cause the lithopone to turn yellow when mixed with the oil.

To prevent the darkening of lithopone a coating over the zinc sulphide is necessary. This hurts the strength and covering properties of the lithopone, however, and a choice should be made of an additive substance that affects the quality of the lithopone the least and which adds some good qualities. In this laboratory we were able to obtain a lithopone of good quality, that would not darken by controlling the zinc oxide

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[1] Bayer and Company: German Patent, 259,953 (1911).

[2] Brase: German Patent, 254,291 (Sept. 29, 1909).

[3] Ostwald: German Patent, 202,709 (1905).

content, that is, by keeping it down below five percent and above three percent.

The advantage of zinc oxide is that it helps to prevent the yellowing of lithopone.

W. Hurschel[1] says, "On the other hand, the addition of zinc oxide helps to prevent the yellowing of the oil in a dark, moist room."

It was found by us that the zinc oxide could be replaced by aluminum oxide. It is well known that a soluble aluminum salt in the presence of hydrogen sulphide forms aluminum hydroxide, a gelatinous precipitate. This precipitate is adsorbed by the zinc sulphide. On dehydration, a very inert film of aluminum oxide is obtained.

Grinding lithopone with five percent flowers of sulphur gives a mixture which is a little less sensitive to light. It is probable that a more efficient protection could be obtained by precipitating sulphur in a finely divided state on the surface of the lithopone.

The results of this paper can be summed up as follows:

1. Quenching in water prevents further oxidation of the red hot zinc sulphide. It also disintegrates the semifused mass and dissolves out most of the soluble salts.

2. Heating the barium sulphate-zinc sulphide precipitate is necessary to dehydrate the zinc sulphide and to change its physical condition, so that it forms a dense mass with good body which can be ground more readily.

3. The yellow color produced on over-heating is due to an oxide film as was shown by Farnau.

4. The darkening of lithopone is not due to impurities such as iron, lead, cadmium, etc.

5. The presence of salts which form soluble zinc salts such as sodium chloride, sodium sulphate, etc., accelerates the darkening of the lithopone. These salts dissolve away the zinc oxide film. This is similar to the behavior of magnesium in water. Magnesium does not decompose water very readily

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[1] Hurschel: Farben Ztg., 17, 1592-3 (1912).

at ordinary temperatures. In the presence of magnesium chloride, however, the action takes place vigorously.

6. The presence of salts which form insoluble zinc salts such as the alkali phosphates, bicarbonates, ferrocyanides and borates, retards or prevents the darkening of lithopone.

7. The action of light on the zinc sulphide is a reducing one, hydrogen sulphide and metallic zinc being formed.

8. The reaction is not a reversible one, the metallic zinc formed is oxidized to the white zinc oxide.

9. Barium sulphate is not necessary for the darkening of the zinc sulphide.

10. Heating the zinc sulphide is not necessary to get it to darken, although heating makes the zinc sulphide more sensitive to light, probably because the reducing atmosphere and the sodium chloride used removes the zinc oxide film more efficiently.

11. The zinc oxide film can be removed by boiling in a concentrated solution of zinc chloride. The zinc sulphide so treated will darken in the presence of a reducing agent.

12. When barium sulphate is precipitated with the zinc sulphide, it aids the darkening due to the fact that it adsorbs the zinc sulphide, thereby giving increased surface exposure of the zinc sulphide. It probably also adsorbs the metallic zinc.

13. The zinc sulphide will darken without the presence of a reducing agent if it is precipitated with barium sulphate and boiled in a concentrated solution of zinc chloride. The barium sulphate probably adsorbs metallic zinc as well as zinc sulphide, thus making the latter sensitive to light.

14. The patented processes for the prevention of the darkening of lithopone depend upon the fact that they form an insoluble film around the zinc sulphide.

15. It is impossible to make a lithopone that will not darken unless there is a film protection of some kind over the zinc sulphide.

16. We made a lithopone of good quality that would not darken by producing an oxide film on the zinc sulphide and

keeping the oxide content above 3 percent and below 5 percent. Aluminum oxide can be substituted for zinc oxide. A film of sulphur protects to some extent; no experiments were made to determine the maximum efficiency possible.

In conclusion, the author wishes to acknowledge the kind help of the chemical faculty, especially Dr. Bennett. This research was suggested by Prof. Bancroft and carried out largely under his direction; I wish to express my great appreciation for his kindly advice and criticisms.

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THE THEORY OF DYEING. V

BY WILDER D. BANCROFT

In the preceding papers I have discussed some of the characteristics of acid dyes, basic dyes, and mordants. In this paper I propose to take up the question of fastness. There is very little satisfaction to be obtained on this point from any book with which I am acquainted. Knecht, Rawson and Loewenthal[1] say: "With certain classes of dyed and printed materials, fastness to washing is of prime importance, whereas with others it is not of much moment. Thus printed calicoes which have to be frequently washed (often with soap and soda), and the colours in figured woolen goods which are milled with soap during the process of manufacture, must necessarily be fast to washing. On the other hand, in such goods as carpets, furniture coverings, and fine silks this fastness is not of great importance.

"The behaviour of colours in washing varies enormously. Some, like the ordinary azo-scarlets and oranges fixed on cotton, are stripped by water alone. The direct cotton colours dyed on cotton mostly give up a certain amount of colour to boiling water, but only up to a certain point, and no more can be removed unless fresh water is used. Many colours are little affected by boiling water, but are easily affected by such as contain free alkali. Some colours, lastly, like aniline black, indigo, and other vat dyes, and most of the alizarin colours fixed on chromium mordant are fast enough to withstand the action of boiling soap. Since the production of shades fast to washing generally involves a larger number of operations, the use of more costly dye-stuffs, and, consequently, greater expense to the dyer, he will, as a rule, employ those dye-stuffs and methods which will bring about the desired result in the least time and at the smallest cost, and will only produce fast shades where they are a requirement of the trade, or when specially asked for.

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[1] A Manual of Dyeing, 2, 747 (1910).

"The loss of colour in washing is not the only drawback which the dyer has to guard against, especially in dyed yarns, which are used in figured fabrics. Many colours have the disagreeable property, when immersed in water or soap, of colouring other yarns in the piece, especially the whites. Such colours are said to 'bleed' or 'run' and their use in any fabrics which have to stand washing, other than plain ones, must be carefully avoided."

Beech[1] is more explicit but unfortunately not accurate. "The affinity of the basic dyes for wool increases with increase of temperature. This is a property that has an important bearing on the method of dyeing, and to any person who pays some attention to theory in its practical applications it indicates the most rational method of working, which is to enter the goods into the bath cold, or, at the most, at a hand heat, then, after working a short time to get the goods thoroughly impregnated with the dye-stuff, to gradually raise the temperature to the boil and work for from half an hour to an hour longer, even if before this time the dye-bath be exhausted. The reason for giving a fair length of time in the bath is to get the colour properly fixed on the fibre. The combination of the dye-stuff and the fibre is a chemical one, and, as stated above, the dye-stuff has to be decomposed so that the base may combine with the essential constituent of the wool fibre, while it is obvious that this decomposition and then the union of the colour base with the wool must take time, and as it is effected more easily and completely at the boiling point, it is advisable to work the goods in the bath so as to fully insure that they are given the necessary time for the chemical change to take place."

If the bath is completely exhausted by the fiber, washing cannot extract enough dye to color the water perceptibly and consequently the dyed fabric will be fast to washing with water. This is often the case with basic dyes and wool;[2] but it is more

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[1] "The Principles and Practice of Wool Dyeing," 65 (1902).

[2] Beech: "The Principles and Practice of Dyeing," 65 (1902).

difficult to obtain level dyeing if the bath is to be exhausted completely. If the bath is not to be exhausted completely, the goods must be removed before dyeing is completed and when the shade is that which would be in equilibrium with an exhausted bath; or the bath must be so arranged that it has a high stripping power and consequently will dye only to the shade which is in equilibrium with boiling water. Ganswindt[1] points out that the color is fast to washing when wool is dyed in an acid bath from which the color is exhausted slowly but very completely, whereas the color is less fast, other things being equal, the less completely the bath is exhausted With the direct colors on cotton, for instance, the bath is rarely completely exhausted.[2] The same thing is true for many acid colors dyed on cotton.[3] "The acid colours, with very few exceptions, cannot be fixed on cotton or linen so as to resist washing. If precipitated in these fibres as metallic lakes with the aid of salts of aluminum, tin, etc. (similarly to the mordant colours), the lakes are decomposed by water and the colour is extracted. The soluble blues or cotton blues resist water slightly better. Of the other acid colours the Crocein scarlets and allied colours only—*i. e.*, the azo-compounds prepared by combination of amidoazobenzene or amidoazotoluene with betanaphthol sulphonic acid (B.), or the so-called gamma acid, or alphanaphthol disulphonic acid (Sch.)—are of some importance in cotton dyeing, since they resist light better than the benzidine colours and are not sensitive to acids. For this reason they are still employed in cotton dyeing in spite of their inferior fastness to washing. The acid colours have never been used to any large extent in the dyeing of linen, but they find application on jute." In the dyeing of cotton with acid colors "the dye-bath is used as concentrated as possible to produce full shades; it is never exhausted by the cotton. Both the mordant and dye liquors are used continuously and freshened up regularly. The shades which are

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[1] Theorie und Praxis der modernen Färberei, 2, 3 (1913).

[2] Knecht, Rawson and Loewenthal: A Manual of Dyeing, 1, 6 (1910).

[3] Ibid., 2, 510, 511 (1910).

produced by any one of the methods are not fast even to a light soaping, but they resist light moderately." There is another factor which is more important in determining the fastness and that is the temperature. The natural thing is to assume as Beech did that the fiber has a greater affinity for the dye at high temperatures. As a matter of fact this is not always so. This follows indirectly from a passage by Ganswindt.[1]

"With dyes which are taken up rapidly, it is not unusual to get uneven dyeing especially if the wool gets into the hotter portions of the bath or comes in contact with the hot walls of the drum, while other dyes do not show this unpleasant characteristic. This leads one to assume that the affinity of wool for the dyes, which dye unevenly, increases very rapidly with the temperature whereas with the other dyes we must assume that the affinity at high temperatures is not appreciably greater than at ordinary temperatures." Fortunately we do not have to rely on this indirect evidence. Mills and Rennie[2] have shown that the amount of rosaniline acetate taken up by wool reaches a maximum at 31° and drops off to a low figure at 81°. Dreaper[3] gives some data for the adsorption of certain dyes by wool. The figures in Table I are the percentages of the dye left in solution.

TABLE I

Dye	20°	40°	60°	80°	100°
Acid magenta	79	14	4	4.3	5.6
Tartrazine	46	3	1	1	0.97
Indigo carmine	46	3	3.4	3.5	6.2
Acid green	79	18	4	3.6	5.2
Acid violet 4 BW	44	26	20.8	20.8	28.7

This table disposes of the generalization that the adsorption is greater at higher temperatures. On the other hand, it

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[1] Theorie und Praxis der modernen Färberei, 2, 65 (1903).

[2] Jour. Soc. Chem. Ind., 3, 215 (1884).

[3] "Chemistry and Physics of Dyeing," 101 (1906).

is a general rule to heat the bath after the fabric has been entered. The real object of this is to coagulate or agglomerate the dye, thus making the dye much less soluble. This is a general phenomenon. If soot, intended for lamp-black, is heated too hot or too long, it becomes sandy. After short ignition silica dissolves in a boiling solution of sodium or potassium carbonate; but after long ignition it does not.[1] When lime has been heated above 1100°, it takes up carbon dioxide much more slowly than lime which has only been heated to a dull red heat.[2] Freshly precipitated arsenic sulphide gives off a good deal of hydrogen sulphide when boiled with water. If previously heated to 125°, this is not the case.[3] Hydroxides and sulphides on standing or on heating change so that they are less readily dissolved or peptonized. Luppo-Cramer[4] points out that "the state of the silver bromide is of fundamental importance for the emulsification in gelatine by means of bromine ions and the same thing is true for the emulsification of ammonia. The silver bromide gel loses its peptonizable properties completely just by standing. Samples which had stood for one, three, six, ten, and twelve hours in the dark at ordinary temperature showed a gradual decrease in the tendency to form an emulsion. After twelve hours' standing, no emulsion could be formed at all."

Kutschera and Utz[5] have done some work on the influence of steaming on the fastness of color lakes after dyeing. "Having frequently made the observation that when dyed patterns are dried and steamed, they are faster to soaping than those which are not steamed; an explanation of the cause was sought for. The observation was made with aniline colours dyed on antimony tannate or on catechu grounds, further with alizarin and other colours dyed on aluminum, iron, or chromium mordants. The greatest improvement is always noticed when

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[1] Rammelsberg: Ber. deutsch. chem. Ges., 5, 1006 (1872).

[2] Raoult: Comptes rendus, 92, 189 (1881).

[3] De Clermont and Frommel: Comptes rendus, 87, 330 (1878).

[4] Phot. Correspondenz, 44, 578 (1907); Jour. Phys. Chem., 14, 22 (1910).

[5] Jour. Soc. Chem. Ind., 5, 532 (1886).

the dye-baths are exhausted at a *low* temperature. Two suppositions for such a change may be offered. First, that the mordant itself, or the colour-lake already fully formed in the dye-bath, is simply better fixed upon the fibre; or, secondly, that during the dyeing operation the colour-lake is incompletely formed, and only completed during the subsequent steaming. If the first supposition is correct, then the amount, both of mordant and colouring matter present in the fibre, would be larger after steaming than before;[1] if the second supposition is correct, then the amount of mordant on the fibre would be the same both before and after steaming, and the deeper colour would be due simply to a larger quantity of colouring matter having been taken up. A trial was made by mordanting cloth with three different amounts of chromium mordant and dyeing with alizarin. The cloth was then divided into two parts, one was dried and steamed, the other not. Finally both were soaped, and the chromium estimated in equal portions of the two patterns. In two cases the steamed patterns contained an increase of chromium; but the shades of the patterns were proportionately much deeper than could be ascribed simply to the increase of chromium, and in a third case where the steamed pattern contained less chromium the tone of the dyed colour was nevertheless deeper, hence the authors concluded that the second supposition is the most likely one—*viz.*, that the steaming renders the colour faster to soaping by completing the formation of the colour-lake initiated in the dye-bath."

It is a little unsatisfactory to criticize an abstract of a paper, especially when that abstract is not written by the authors. Since the original is not accessible, one must do the best one can with the abstract. One cannot be absolutely certain whether the difference in tint is due entirely to less

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[1] [What the authors mean is that soaping would remove more mordant and dye from the sample which had not been steamed than from the one which had been. As worded they imply that steaming increases the amount of the dye present in the fiber instead of saying that it increases the amount which is not removed by soaping.—W. D. B.]

dye being removed from the fiber or whether there is, as the authors assume, a difference due to the coagulation of the dye. This latter is quite possible because we know, for instance, that very finely ground cadmium yellow is paler than a somewhat coarser pigment. The time to have determined this, however, was before the soaping and not after it. In spite of these difficulties the experiments of Kutschera and Utz show that the high temperature has made the dye faster to washing. Similar results have been obtained by Dreaper and Wilson.[1] When Night Blue is adsorbed by silk above 40° C, "a second and more resistant dyeing effect is produced with part of the dye absorbed; this effect increases with the temperature up to 100° C, a greater proportion of the dye being fixed in this way. When dyed at 15° C, a subsequent soaping at the boil or treatment with alcohol of ordinary strength will practically remove all the dye from the fibre, but as the temperature of the dye-bath is increased, a certain proportion of the dye is fixed against the action of the solvents. In all cases the total amount of dye on the fibre was kept constant. This effect has been noticed with other basic dyes, but the dyes vary in their resistance against re-solution in some way yet to be determined, especially with different solvents.

"These experiments have been extended to the so-called acid class of dyes, with interesting results: similar differences have been observed when working with the same fibre, so that this action is not confined to basic dyes, the temperature effect being of a similar order when expressed in terms of the resistance of the dye to the action of solvents. It has not yet been proved, however, that the dye is fixed in two ways, as in the case of Night Blue, when dyeing at a high temperature, which result may be due to the dissociation of the dye into more basic compounds, which are known to be more insoluble. This point is being investigated. The effect of drying the dyed fibre between the drying and re-solution treatments

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[1] Jour. Soc. Chem. Ind., 26, 667 (1907).

has no appreciable effect on the proportion of colour removed. At any rate an increased temperature of the dye solution gives an increased resistance against the solvent action of soap solution or alcohol in the case of acid dyes."

While we do not need to believe that the Night Blue is taken up in two different ways, these and other experiments by Dreaper are convincing evidence that a rise in temperature makes most dyes more resistant to solvent action—a result which is absolutely in line with what we have known for years in regard to hydroxides, sulphides, etc.

The effect of liquids and solutions in removing color from the fabric seems to be fairly simple theoretically. If the mordant or the dye is readily soluble in a given liquid or solution or is readily peptonized by it, the mordant or the color will be extracted more completely than by a liquid or solution having less solvent or peptonizing action. Many dyes are more soluble in alcohol, for instance, than in water and more color is taken out in these cases by alcohol than by water. Spring has shown that soap[1] will peptonize soot or rouge. If it will peptonize rouge there is no apparent reason why it should not peptonize iron, alumina, and chrome mordants as well as the dye itself. That is why soap strips more than plain water. Further, if wash goods are given a more vigorous soaping after drying than they will ever receive under ordinary conditions, they will be practically fast afterwards in the laundry, always supposing that the heavy soaping left any color.

If a mordant is precipitated too rapidly, so that it is chiefly on the outside of the fiber, it and the color will tend to rub off readily and will also be removed easily by soap.[2] There is another possibility to which I have found no reference in the literature, of the color lake becoming friable and less readily adsorbed. We know that an emulsion will often crack on standing and the emulsifying agent will settle as

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[1] Zeit. Kolloidchemie, 4, 161 (1909); 6, 11, 109, 164 (1910).

[2] Knecht, Rawson and Loewenthal: A Manual of Dyeing, 2, 743 (1910).

a curdy mass. It is conceivable that certain dyes, or still more, certain dyes in certain mordants, may change with time so that either the dyes or the mordants are not adsorbed so strongly by the fibers as before. Under these hypothetical conditions the dye would rub off readily. This should show itself by the freshly dyed fabric being more resistant to rubbing than a fabric which had been dyed quite a while before. This point may be familiar to practical dyers; but it seems not to be discussed in the books on dyeing.

The whole question of fastness to light is in a very bad way because so little systematic work has been done. About all that I can hope to do at present is to point out how much we do not know in the hope that some enthusiastic person will fill in some of the gaps in our knowledge some day.

Only light which is absorbed can produce chemical action and all light which is absorbed tends to produce chemical action.[1] Whether a given substance is changed appreciably by light depends upon the readiness with which the substance reacts or upon the presence of suitable depolarizers. With some silver salts or with Eder's solution of mercuric oxalate, we get visible decomposition by light. With chromium salts we get no measurable change. With some substances the action of light causes fluorescence of phosphorescence, thus indicating the occurrence of chemical changes even though these may be no measurable decomposition. While a copper sulphate solution is apparently not sensitive to light, that is because we usually do not have a sufficiently powerful depolarizer present. What change takes place in any given dye when exposed to light will depend on the chemical characteristics of the dye and on the chemical conditions prevailing when the dye is exposed to light.[2] Methylene blue, for instance, may fade as a result of reduction[3] or of oxidation. The bleaching of methylene blue is usually an oxidation be-

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[1] Bancroft: Jour. Phys. Chem., 17, 596 (1913).

[2] Bancroft: Ibid., 16, 529 (1912).

[3] Cf. Wender: Jour. Chem. Soc., 66 II, 122 (1894).

cause of the oxygen in the air. In presence of gelatine[1] or of stronger reducing agents the bleaching of methylene blue by light is due to a reduction. On standing in the dark the leuco base is oxidized and the color comes back.

The presence of a reducing agent should, therefore, make oxidizable dyes more stable, at any rate until the reducing agent itself is oxidized. It is claimed by von Grabowski[2] that a preparation of zinc, alkali and sugar will make benzopurpurine, benzo-blue, thiazol yellow, and geranin more stable to light. Editorial comment on this is to the effect that the protection does not last long enough to be worth the extra cost. The alleged beneficial action of sodium hyposulphite with some colors[3] is probably due to its being a reducing agent.

A more interesting case of protection was discovered by Stobbe[4] who found that many colors were made more stable to light by the addition of copper sulphate, which was taken up by the fiber to form copper mordant. Stobbe attributed this effect to the fact that the copper mordant cut off some of the rays which did the most damage.[5] This is in line with what apparently happens with vermilion and madder. Toch[6] states that vermilion is remarkably permanent when glazed over with madder after it is thoroughly dry. It is hard to see how the madder can act in any way except as a light-filter. That the copper salt acts as a screen is made more probable by the experiments of Krais[7] who increased the fastness to light for diamine blues, benzo-blues, benzo-green, diamine green, benzo-violet, diamine-violet, benzo-azurine, rosazurine, direct black, and direct orange on cotton by adding copper sulphate or a practically colorless mixture of cobalt and nickel sulphates. No protection was obtained with any

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[1] Gebhard: Zeit. phys. Chem., 79, 639 (1912).
[2] Zeit. Farbenindustrie, 2, 399 (1903).
[3] Krais: Ibid., 1, 22 (1902).
[4] Eder's Handbuch der Photographie, 3rd ed., 1, II, 389 (1906).
[5] Cf. Justin-Müller: Zeit. Farbenindustrie, 3, 300 (1904).
[6] "Materials for Permanent Paintings," 108 (1911).
[7] Zeit. Farbenindustrie, 1, 22 (1902).

yellow. There are only two weak points about this. One is that Krais found no protecting action in the case of colors on wool. Of course, it may be that copper on cotton cuts out certain rays which are not cut out by copper on wool; but there is no evidence as yet that that is the case. The other weak point is that copper salts often act as oxygen carriers[1] and it is hard to see why they should not sometimes act in this way with dyes. Of course, a negative catalytic agent would be an ideal thing if one knew where to find one.[2] It is also possible that a careful study would show the presence of positive catalytic agents and that removal of these would decrease the light-sensitiveness.

In most cases the lakes are less sensitive to light than the free colors.[3] Purpurine bleaches less readily in presence of lime salts or of alum. Colors on iron, chrome, and copper mordants are less sensitive than on alumina or tin mordants. Eosine with lead mordant is less sensitive than with tin mordant. The data are not sufficient to let us say that dyes on colored mordants are generally faster to light than those on colorless mordants; but it looks a little like this. Stobbe[4] found that the alizarine dyes fade more quickly on zinc mordant than on chrome mordant. A number of dyes bleach more rapidly on starch paper than on gelatine or albumenized paper. I have no idea why this is so. Basic dyes are faster to light when mordanted with tannin and fixed with antimony, the antimony apparently being the important factor. It is even claimed that under these conditions methylene blue on cotton becomes quite fast to light.[5]

The facts in regard to the effect of the fiber itself are very confused. Indigo is faster on wool than on cotton[6] and the

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[1] Lothar Meyer: Ber. deutsch. chem. Ges., **20**, 3058 (1887).

[2] Bigelow: Zeit. phys. Chem., **26**, 493 (1898); Titoff: Ibid., **45**, 641 (1903).

[3] Cf. Eder: Handbuch der Photographie, 3rd ed., **1**, II, 384, 389, 390 (1910).

[4] Zeit. Elektrochemie, **14**, 480 (1908).

[5] Knecht, Rawson and Loewenthal: A Manual of Dyeing, **2**, 485 (1910).

[6] Stobbe: Zeit. Elektrochemie, **14**, 480 (1908).

same is true for the direct colors[1] and most of the basic colors.[2] On the other hand, safranine and methylene blue[3] are said to be more stable on cotton than on wool. It is probable that this discrepancy is due to an unstated difference in the method of dyeing. The experiments would not be comparable, if, for instance, the methylene blue were fixed on cotton with tannin, and antimony and were not so fixed on wool. There are a good many contradictions to be found in the literature. Thus, it is stated in one place that the lakes made from synthetic alizarine are less sensitive to light than those from the madder root.[4] On the other hand, Cajar[5] says that the madder root gives a faster color than synthetic alizarine, purpurine carboxylic acid being the stable substance.

Mumford[6] voices a popular but unfounded prejudice in regard to synthetic dyes and mordants. "Color is the Orient's secret and its glory. These dark-skinned peoples, lagging so far backward along the pathway of civilization, mastered long ago the chromatic mysteries lurking in the shrubs of their deserts, the vines, leaves and blossoms which make these lands radiant, and they have guarded this subtle knowledge from foreign participation with greater care and jealousy than they seem to have exercised for their bodily welfare, or their place among races. The royal purple of Tyre, which the Phoenicians by some magic won from the molluscs of their seas, is virtually obsolete now.[7] Science has found, in the refuse of factories, gaudy hues to serve the purpose; but the old dyes of the East still boast a splendor and lastingness which chemistry cannot counterfeit—a permanence emblematic of the countries where alone the marvel of their compounding has been understood....

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[1] Eder: Handbuch der Photographie, 3rd ed., 1, II, 384 (1910).

[2] Knecht, Rawson and Loewenthal: A Manual of Dyeing, 2, 463 (1910).

[3] Ibid., 2, 458 (1910).

[4] Eder: Handbuch der Photographie, 3rd ed., 1, II, 391 (1910).

[5] Zeit. angew. Chem., 24, 793 (1911).

[6] "Oriental Rugs," 42, 47 (1901).

[7] [Not through lack of knowledge. Cf. Bancroft: Philosophy of Permanent Colours, 1, 157 (1813)].

"The distinctive feature of the old Eastern dyeing system was that nearly every tingent was of vegetable or animal origin, and that similar ingredients were employed for mordants or fixations. The treatment of the yarn with borax, saltpeter, tartar, copperas and the like had not been known. The native dyers held to the merits of the old-fashioned mordants—valonia, pomegranate-rind, sumac, divi-divi, and the barks of different trees, from which they had for so long obtained renowned results."

Mumford evidently believes that natural products are faster to light than are synthetic products. This is rather remarkable in view of the way in which leaves and most flowers change color. It would be more accurate to say that most vegetable colors are not fast at all to light. What the old dyers have done is to pick out the most permanent of the natural coloring matters. Even then, the situation is not at all what Mumford pictures it. The chief dyes used by the Oriental dyers are madder, indigo, cochineal, orchil, turmeric or saffron, and Persian berries. Of these madder and indigo are colors which are made commercially from coal tar; the coloring matters in Persian berries are flavonol derivatives and could be made on a large scale if it were worth while; the coloring matter of cochineal is apparently a naphthaquinone derivative though the structure formula is not yet known definitely, while orchil and saffron are admittedly not fast to light. Of these six dyes, three have been made from coal tar and two are not permanent. The mordants used by the Oriental dyers were chiefly impure tannins. Though Mumford rejoices in the fact that the eastern dyers do not use tartar emetic, yet we know that colors mordanted with tannin and fixed with tartar emetic are faster to light than those which are not so fixed. Where the Oriental dyers may have an advantage is in the use of impure mordants. It is quite possible that a suitable mixture of mordants may work better than any single one.[1] It seems probable that work along this line might be very well worth while.

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[1] Cf. Koechlin: Chem. News, 46, 179 (1882).

It is quite true that many of the so-called aniline colors are not fast to light but there are also others which are quite permanent. It is merely a question of people insisting on getting permanent colors and of being willing to pay the cost. I know of Japanese grass-cloth papers which have stood twenty years of bright sunshine without any marked fading. The making of modern Oriental rugs to rival the old ones is a question of time, skill, artistic taste, and cost; but it is not a question of secrets of dyeing. It is quite probable that it would help matters if the use of fugitive dyes were discouraged. A list might be made showing what dyes were permanent in fabrics and paper, and if people would insist on having those, we should hear less about the rapid fading of synthetic dyes.

The general results of this paper are as follows:

1. If a fabric exhaust the dye completely in a given bath, the dyed fabric will not bleed in an exhausted bath or in any solution having a lesser solvent action for the dye in question.

2. The object of heating a dye-bath is to agglomerate the dye in the fabric and to make it faster to washing.

3. Many dyes are faster to light in iron, chromium and copper mordants, than in aluminum or tin mordants. It is probable, though not proved, that this is due to certain wave-lengths being absorbed more or less completely by the colored mordants.

4. The contradictory statements in regard to fastness of dyes on different fibers are probably due to unspecified differences in making the experiments. It is not legitimate, for instance, to ascribe to the fiber differences in fastness to light between a basic dye on wool and the same dye mordanted on cotton with tannin and antimony.

5. People can get synthetic dyes which are very fast to light if they will insist upon having them and are willing to pay for them.

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OXYCELLULOSE

BY WILDER D. BANCROFT

The literature in regard to oxycellulose is a bit confusing, there being apparently not less than three oxycelluloses; and an ambitious person would probably increase the number so as to have at least one for every oxidizing agent. I am going to give an outline of what is in Schwalbe's book[1] and will then describe some experiments by Mr. R. H. Currie, Jr., which simplify the problem somewhat.

Ozone oxidizes cotton cellulose while oxygen acts only in presence of light. A three percent hydrogen peroxide solution reacts very slowly at ordinary temperatures; but reacts readily at higher temperatures, especially in presence of small amounts of alumina, ferric oxide or chromic oxide. More concentrated solutions react energetically without being heated and without the presence of oxides as catalytic agents. Thirty-two percent nitric acid has no effect cold, but oxidizes cellulose at about 80°. According to Cross there is an intermediate formation of hydrocellulose, but this is disputed. Chromic acid oxidizes cellulose to oxycellulose. It is undoubtedly true that moist chlorine oxidizes cellulose, but it is very probable that the oxidizing agent is really hypochlorous acid and not chlorine itself. Concentrated chlorine water dissolves or peptonizes cellulose. A mixture of bromine and water oxidizes cellulose but not readily, and iodine appears to have no oxidizing action. Chloric acid is a powerful oxidizing agent in presence of vanadium salts. Hypochlorous acid is a very powerful oxidizing agent and it is consequently necessary to keep the concentration of bleaching powder low if one is to bleach a fabric without weakening the fibers. Alkaline permanganate solution has a greater effect on cellulose than a neutral solution. Potassium ferricyanide has practically no oxidizing action. Ammoniacal copper oxide

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[1] Schwalbe: "Die Chemie der Cellulose," 129–144, 221–256 (1911).

solution oxidizes cellulose in presence of air, and ammonium persulphate is said to oxidize cellulose both to oxycellulose and to cellulose peroxide.

The oxycellulose, obtained by oxidizing with nitric acid, is a white, flocculent substance which becomes gelatinous when the acid is washed out. After precipitation with alcohol it dissolves readily in dilute, hot alkali, the solution becoming golden yellow. With more concentrated alkali the mass becomes gelatinous, liquefying again with still higher concentrations of alkali. When alcohol is added to an apparent solution of cellulose in dilute alkali, the oxycellulose is precipitated and carries down no appreciable amount of alkali. The oxycellulose obtained with nitric acid does not take up metallic mordants. If oxycellulose is precipitated from alkaline solution by means of acids and then dialyzed to remove the acid, it dissolves in water. Boiling with soda solution has the same effect. Concentrated sulphuric acid gives rise to a pink color. If the cellulose is not heated too long with nitric acid, the product has a reducing action on Fehling's solution. The yield of oxycellulose may vary between 30% and 90%, depending on the concentration of the nitric acid. The yield is higher with a moderately dilute acid because the stronger acid oxidizes a good deal of the cellulose to oxalic acid.

When oxycellulose is obtained by oxidizing cellulose with chloric acid, the product turns yellow when heated to 100° in the air. It is only partly soluble in alkali, the solution being yellow and having a reducing power which disappears if the solution is heated. Only part of the alkali-soluble product is reprecipitated by acids. As in the preparation with nitric acid, the yield is greater the more dilute the chloric acid solution.

When oxycellulose is prepared by oxidation with permanganate, the product is soluble in dilute alkali. When boiled with alcoholic caustic soda, 50% remains insoluble and has no reducing power. The insoluble portion takes up metallic mordants. If the permanganate oxycellulose is heated with sulphuric acid and afterwards with soda, the product dissolves in boiling water after the removal of the soda. The water-soluble cellulose becomes insoluble in presence of acids but can be made soluble again by another treatment with soda.

The oxycellulose prepared with bleaching powder is permanent *in vacuo* at 100°, but becomes colored in moist air. It is then partly soluble in alkali, the residue being colored, however. This oxycellulose does not become colored when boiled with water, but does when boiled with caustic alkali or with a soda solution. If the freshly prepared oxycellulose is treated with dilute alkali, part of it dissolves and the residue does not turn yellow when treated with soda solution. The freshly prepared oxycellulose reduces Fehling's solution, but prolonged boiling with caustic alkali destroys the reducing substance. It is claimed that the oxycellulose from bleaching powder takes up metallic mordants.

One would expect an oxycellulose prepared by the action of bromine in presence of calcium carbonate to be practically the same as one prepared with bleaching powder, but this seems not to be the case.[1] When prepared in this way it is entirely insoluble in dilute alkalies, though it yields a golden yellow liquid when heated with dilute alkali; it reduces Fehling's solution.

When cotton cellulose is treated for sixty days with a concentrated hydrogen peroxide solution, a product is obtained which Bumcke and Wolffenstein[2] call "hydral cellulose," but which Schwalbe considers to be an oxycellulose. It is a white pulverulent mass which reduces Fehling's solution and also ammoniacal silver solution. It is partly soluble in dilute caustic soda solution, from which sulphuric acid precipitates the peptonized portion. If this oxycellulose is heated with 10 percent caustic soda, two-thirds of it remain undissolved and seem to be unchanged cellulose; the portion which has dissolved has lost all reducing power and no longer

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[1] von Faber and Tollens: Ber. deutsch. chem. Ges., 32, 2592 (1899).

[2] Ber. deutsch. chem. Ges., 32, 2493 (1899).

reacts to form a hydrazone. This product is called acid cellulose by Bumcke and Wolffenstein. Acid cellulose dissolves in concentrated hydrochloric acid from which it can be precipitated unchanged on addition of water or alkali. If the hydrochloric acid solution of acid cellulose be allowed to stand for a long time or if it be heated, addition of water causes no precipitate and the solution reduces Fehling's solution which it did not do before. When acid cellulose has been dried, it does not dissolve in caustic soda and is not readily decomposed by concentrated hydrochloric acid solution. Acid cellulose can also be prepared by boiling cellulose with 30 percent NaOH or by precipitation from an ammoniacal copper solution of cellulose. It is said to have been obtained by the action of ammonium persulphate on cellulose.

Even if one omits the so-called acid cellulose, the other oxycelluloses are not at all alike except in the fact that they reduce Fehling's solution if they have not been heated too much. Some are soluble and some nearly insoluble in dilute alkali. There is nothing to show whether all become soluble in water after treatment with soda or not. Nastukoff[1] considers that one gets varying mixtures of three oxycelluloses: α-oxycellulose which is insoluble in alkali (from bleaching powder or bromine and calcium carbonate); β-oxycellulose which is soluble in alkali (from nitric acid); γ-oxycellulose which is soluble in water after boiling with soda. It is not very safe to base the existence of definite compounds on differences in solubility or peptonization of colloids. Carefully dried β-oxycellulose is not readily soluble in alkali and would, therefore, be classed as α-oxycellulose. Haber and Oordt[2] found that one equivalent of freshly precipitated beryllium hydroxide is peptonized by about eight equivalents of alkali whereas over ninety are necessary if the beryllium hydroxide has been heated or allowed to stand. Haber knew better than to postulate different modifications, but other people are not so cautious.

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[1] Schwalbe: "Die Chemie der Cellulose," 248 (1911).

[2] Zeit. anorg. Chem., 38, 377 (1904).

It seemed desirable to find out to what extent the properties of oxycellulose or the oxycelluloses differed when prepared by means of different oxidizing agents. Mr. R. H. Currie, Jr., made a preliminary study of the action of nitric acid, permanganate, chloric acid, and bleaching powder on cellulose as his senior research work, and his results are distinctly interesting.

The cotton used was surgeon's absorbent cotton which was boiled for a number of hours with dilute caustic soda and then washed. This is an improvement on Parker's method[1] and was devised by Mr. Leighton in this laboratory. It is not certain that this gives an absolutely pure cellulose, but, at least, it gives a material which can be duplicated by anybody at any time. The oxidation with nitric acid was done as follows: Thirty-five grams of purified cotton and 350 cc 60 percent HNO_3 were placed in a flask with a return condenser and heated on a water-bath for twenty hours. The gelatinous mass was filtered through calico hardened with nitric acid. It was washed twice with 60 percent HNO_3 by decantation, pumped dry, and then washed successively with water, 60 percent ethyl alcohol, 90 percent ethyl alcohol, and with ether. To wash the material it was removed from the filter and rubbed with the liquid until all lumps were broken up. When thoroughly dry, the product was ground to a fine light powder, clear white in color.

In the preparation of oxycellulose by means of permanganate, 32 g cotton were heated with three liters of 15 percent H_2SO_4 to which had been added 32 g $KMnO_4$. The flask containing the solution was fitted with a return condenser and was heated on a water-bath until the solution was decolorized. The solution was poured off and the cotton was heated again with the same amounts of acid and permanganate until this second solution was decolorized. The decolorized solution was poured off and the gelatinous mass was freed from the precipitated manganese dioxide by heating

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[1] Jour. Phys. Chem., 17, 219 (1913).

with 15 percent H_2SO_4. The product was washed free from acid with water, and 90 per cent ethyl alcohol, followed by ether. This oxycellulose was of a light creamy color.

By means of chloric acid another oxycellulose was prepared which differed in its physical appearance from the others. To 30 g cotton were added three liters of water containing 150 g $KClO_3$. This was heated to boiling and 125 cc conc. HCl were added slowly, the solution being kept stirred. The solution was kept at 100° for an hour, after which the liquid was poured off and the oxycellulose was washed with water, and 90 percent alcohol, followed by ether. The dry product was light and flocculent; it was made up of short fibers.

To prepare oxycellulose with bleaching powder, 30 g cotton were digested for twenty-four hours with one liter of a filtered solution of bleaching powder (4° Bé). The solution was then poured off and the operation repeated. The product was washed with water, 90 percent alcohol, and ether; it forms a fine white flocculent powder. In order to duplicate Witz's work, thirty grams of cotton were hung on glass rods in the air and were kept moistened with a bleaching-powder solution (4° Bé) for five days during which time about 700 cc of bleaching powder solution were added. The product was then washed as in the other experiments; it was similar in properties to that obtained by a bleaching powder solution without evaporation, though a little more fibrous.

All five preparations behave very much alike. When heated to 100° they turn brown. When the temperature is raised, they turn a deeper brown and then black, owing to charring. This was rather a surprise for it had been anticipated that the first change would be from white to yellow.

When heated with water to 50°, the liquid tends to gelatinize and, on cooling, the oxycelluloses settle as a gelatinous mass. The supernatant water contains no oxycellulose as is shown by the fact that no precipitate is left when the clear liquid is evaporated to dryness and that addition of alcohol, hydrochloric acid, sulphuric acid, or sodium hydroxide caused no precipitation. All the oxycelluloses are partly soluble in dilute solutions of sodium or potassium hydroxide, the solutions turning golden yellow when heated. These solutions become gelatinous on addition of a more concentrated alkali. When alcohol is added to a solution of oxycellulose, a precipitate is obtained which is peptonized readily by water. When boiled with a dilute soda solution the oxycelluloses dissolve and the solutions become yellow. Addition of alcohol precipitates oxycellulose in a form soluble in water.

When treated with concentrated sulphuric acid, the oxycellulose first turns brown and then black owing to charring. Nothing was seen of the pink color noted by other observers. All the oxycelluloses reduce Fehling's solution if they are not heated too long.

In order to determine whether the oxycelluloses adsorbed metallic mordants, samples were treated with solutions of ferric sulphate, aluminum sulphate, and copper chloride. After the cotton had been washed and dried, it was ignited and the ash tested microscopically for these metals. They were found. The experiments were repeated, giving the cotton a much more thorough washing. The copper was washed out completely and the microscopic test showed no copper in the ash. It was harder to wash out the aluminum salt and the iron was not removed completely. Whether one says that the cotton takes up these mordants or not depends on how carefully one washes. It seems like stretching a point to speak of the cotton taking up these mordants under these conditions, but the discrepancy in the different statements is probably due to a difference in definition.

However prepared, the oxycelluloses are soluble to a greater or lesser extent in caustic potash or soda solutions. The color is yellower in the KOH than in the NaOH solutions. The oxycellulose prepared with chloric acid turns yellower than any of the others. It seemed possible that the cellulose was not converted entirely into oxycellulose and that the varying solubility in alkali might be due in part to the presence of unchanged cellulose. To test this hypothesis, one-gram samples of the five oxycelluloses were heated with a potassium hydroxide solution in a water-bath for twenty-four hours, the flask being equipped with a return condenser. The solution was then poured off and the residues washed with water until free from alkali. They were then dried at 100° and weighed, the loss of weight giving the amount of oxycellulose which had gone into solution.

The data are given in Table I.

TABLE I

Oxycellulose prepared with	Solvent 10 percent KOH	Time of heating	Percent soluble
Nitric acid	200 cc	24 hours	43.3
Permanganate	200 "	24 "	41.1
Chloric acid	200 "	24 "	45.3
Bleaching powder	200 "	24 "	24.9
Bleach in air	200 "	24 "	29.4

The insoluble portions of the oxycelluloses were combined and the whole treated with chloric acid, washed, and dried with alcohol and ether. A one-gram portion was then heated on a water-bath with 200 cc 10 percent KOH for twenty-four hours. The residue was treated as before and the amount dissolved was found to be 36.1 per cent. It is thus clear that the so-called insoluble oxycellulose is really unoxidized cellulose and that the present methods do not give complete oxidation to oxycellulose. Some of the discrepancies, that have been noted in the past, have been due to the fact that people have not always been careful to distinguish between the properties of the alkali-soluble substance and those of the total product obtained on oxidation.

Whether prepared with nitric acid, permanganate, chloric acid, bleaching powder, or bleaching powder and air, the product always has the following characteristics:

1. Does not change color on heating to 100° in air.
2. Forms a gelatinous mass when warmed with water.
3. Partially soluble in KOH or NaOH with yellow color.
4. Dissolves readily in water after precipitation from alkali solution with alcohol and dialysis.

5. Dissolves in water after precipitation from alkali solution with acid and dialysis.

6. Dissolves partially when boiled with soda. Can be precipitated with alcohol and is then soluble in water.

7. When heated with sulphuric acid and then with sodium carbonate solution, a part dissolves. Can be precipitated with alcohol and is then soluble in water. This is really a repetition of No. 6, but it is inserted because others have done the experiment in this way.

8. Reduces Fehling's solution if not heated too long.

9. No intense adsorption of copper, aluminum or iron mordants. The iron is adsorbed the most strongly of the three and the copper the least.

10. Concentrated sulphuric acid gives rise to a brown color and then to a black one. This is the result of charring.

11. Contains unchanged cellulose in considerable amounts.

This is sufficient to show that essentially the same product is obtained with the different oxidizing agents. Nastukoff's α-oxycellulose is evidently unchanged cellulose. Whether the oxycellulose is peptonized by water or only by alkali is apparently merely a matter of agglomeration and there is absolutely no evidence for the existence of two modifications. Schwalbe considers that the ability to reduce Fehling's solution is an essential characteristic of oxycellulose. This property disappears readily on heating, without producing any essential change so far as we know in the other characteristics. It seems simpler for the present to consider the reducing action on Fehling's solution as due to the presence of some other substance than oxycellulose. The data are not sufficient to enable one to tell whether this substance is a product intermediate between cellulose and oxycellulose or whether it is a decomposition product of cellulose though the behavior of so-called acid cellulose implies the latter.

Owing to the limited time at Mr. Currie's disposal, no study was made of the oxycellulose obtained with hydrogen peroxide. No analyses of oxycellulose were made because we do not know that anybody has ever had pure oxycellulose. The product obtained by the direct oxidation is unquestionably a mixture and the alkali-soluble portion may be. The most promising line of attack would probably be to do fractional precipitation of the water-soluble oxycellulose, though even here there is no certainty that the product may not adsorb cellulose or some of the decomposition products.

The general results of this paper are:

1. There is no evidence for the existence of three different oxycelluloses: α-oxycellulose insoluble in dilute alkali; β-oxycellulose soluble in dilute alkali; and γ-oxycellulose soluble in water.

2. The α-oxycellulose is apparently unchanged cellulose, very likely more or less contaminated with some of the decomposition products.

3. The β-oxycellulose and the γ-oxycellulose are the same substance in different degrees of agglomeration. They do not differ anything like so markedly as do freshly precipitated and aged beryllium hydroxide.

4. The same products are obtained when cellulose is oxidized by nitric acid, permanganate, chloric acid or bleaching powder. No experiments have been made with hydrogen peroxide.

5. With no one of these oxidizing agents is all the cellulose oxidized under the experimental conditions described.

6. It is probable that the reducing action on Fehling's solution is not a characteristic of oxycellulose. It is probably due to other decomposition products.

7. There is no certainty that anybody has ever prepared pure oxycellulose though the water-soluble oxycellulose may be a homogeneous product.

8. Oxycellulose does not adsorb metallic mordants intensely.

Cornell University

NEW BOOKS

The Electrical Conductivity and Ionization Constants of Organic Compounds. *By Heyward Scudder. 17 × 24 cm; pp. v + 566. New York: D. Van Nostrand Co., 1914. Price: $3.00.*—The author has prepared "a bibliography of all the measurements of the ionization constants and the electrical conductivity of organic compounds that have appeared in the periodical literature between the years 1889 and 1910 inclusive, together with the values of the ionization constants, and certain values of the electrical conductivity."...

"In order to aid identification or to show the purity of a compound for which any numerical data are given, the melting-point or boiling-point is given in the tables when it is stated in an article. This melting-point or boiling-point refers to the sample measured, and not necessarily to the most highly purified sample described in the article. In some cases the melting-point or boiling-point of a derivative (as a salt) may be given, when the article does not furnish such data for the pure compound. The position of these identifying data is directly after the ionization constant, or after the measurement of the conductivity. In many cases, where the original supplies no such data, I have looked up the mode of preparation, in order to make sure what the compound is. There is a good deal of reasonable doubt as to the position of substituted groups in a number of compounds, for instance in the toluidine sulphonic acids.

"Immediately after the name are given (in parenthesis) the synonyms. These are inserted in some cases only for convenience in referring to the original articles, since the names used there have been abandoned. After the synonyms comes the empirical formula, and when convenient the extended formula. Cyclic formulae are given only in the grouping of the pages directly in front of the tables. The extended formulae are intended to be of assistance, but not to represent the definitive structure, nor to exclude the possibility of tautomeric forms, floating double bonds, etc.

"The bibliographical references for each compound are arranged under definite readings which are not specifically named in the text. These headings are: (1) the specific conductivity of the pure compounds; (2) the ionization constant; (3) the conductivity in aqueous solution; (4) the conductivity in solvents other than water; (5) miscellaneous measurements, as the conductivity of mixtures with other compounds, conductivity under varying pressure, etc.; (6) the conductivity of the salts....

"When there is an advantage in one article, either from its greater accuracy, or from its more extended measurements, that reference number is placed first. In other cases the reference numbers are given in numerical order, though of course the number of an article from which any data are taken is placed directly after such data, followed by the numbers of the other articles. If the ionization constants or conductivity measurements in two articles are widely different, both are usually given, placing first the more reliable, and stating any possible explanation of such difference. But if the data in one article are evidently inaccurate, they are not given, though the reference number of that article is given. When there may be some doubt from the name alone, what compound is referred to, greater weight is usually given to articles containing some means of determining what compound was really measured, and how pure it was. In the case of isomers, when no identifying statements, such as melting-point, mode of preparation, etc., are made in an article, I have assumed that the most easily prepared or procured isomer was used."

The author has done his bibliographic work in a masterly manner. The book appeals to a limited circle; but it should prove of great value to those specializing in this particular line. If it were not for the high cost of publication and the limited sale, we could turn out as good monographs and bibliographies in this country as are published abroad. *Wilder D. Bancroft*

Alloys and their Industrial Applications. *By Edward F. Law. Second Edition. 22 × 14 cm; pp. vii + 332. London: Charles Griffin and Company, Limited, 1914.*—The subject is treated under the following headings: introduction; properties of alloys; methods of investigation; constitution; influence of temperature on properties; corrosion of alloys; bronzes; brass; special bronzes and brasses; German silver and miscellaneous copper alloys; white metal alloys; lead, tin, and antimony; antifriction alloys; aluminum alloys; silver and gold alloys; iron alloys; miscellaneous alloys.

In some respects the book is very good. Special stress is laid, pp. 112, 114, 227, on the effect due to the form in which a second phase appears, whether laminar or globular. The discussion of antifriction alloys is good and the remarks on the proper temperature for casting such alloys, p. 245, are also interesting. The attitude in regard to corrosion, p. 130, is also good.

"In some cases the process of corrosion stops itself automatically by the production of compounds which hinder further corrosion. Cases of this description are not uncommon, and an example of the greatest importance occurs in the employment of lead pipes for carrying water. It is well known that lead is appreciably soluble in water, and to such an extent as to render the water unfit for drinking purposes. Moreover, nearly all waters contain considerable quantities of sulphuric acid in the form of sulphates, which also have a corroding action on lead; but the product of the corrosion in this case is a practically insoluble compound, lead sulphate, which forms a coating on the surface of the metal and effectually prevents further corrosion, either by sulphates or by the water itself.

"Similar incorrodible coatings are formed on certain alloys, and an interesting example may be cited to illustrate this and also another protective influence exerted by one metal upon another. This is found in the case of an alloy of gold and silver containing 50 percent of each metal, which is practically insoluble in the ordinary acids. In hydrochloric acid or aqua regia a coating of silver chloride is immediately formed, and all action ceases. In nitric acid the silver on the surface is dissolved, and the alloy is then protected by a coating of gold which prevents further action taking place. This fact is well known to all assayers and refiners, and in the operation of 'parting' bullion (*i. e.*, dissolving out the silver with acid) it is necessary that the amount of silver should be considerably in excess of the gold, or the parting is incomplete. Certain copper alloys behave in a similar manner, the alloying metal being dissolved out until a surface deposit remains, which is only slightly acted upon by the corroding liquid. These facts are of the greatest importance and should always be borne in mind when considering the results of experimental tests, as they will frequently explain the startling differences between the results of actual practice and those obtained in experimental tests. Nearly all the results of experimental tests have been obtained by simple immersion of the alloy in water, dilute acid, or other corroding liquid; but in actual practice corrosion is usually accompanied by erosion to a greater or lesser extent, and the effect of this erosion in removing protective coatings and exposing fresh surfaces to the action of corrosion can readily be imagined, although it is often overlooked."

The book would be better if there were any evidence that the author had read any articles or books other than those published in England. While the reviewer does not believe that Tammann's method of thermal analysis will do all that is claimed for it, a reference to it should certainly be made in a book of this character. *Wilder D. Bancroft*

Physikalische Chemie der Zelle und der Gewebe. *By Rudolf Höber. Fourth Edition. 24 × 18 cm; pp. vii + 808. Leipzig: Wilhelm Engelmann, 1914. Price: 20 marks.*—The third edition was reviewed (15, 881) in 1911. This new edition is nearly one-fifth larger and the arrangement has been changed considerably, the chapter on colloids now preceding those on cell permeability and on the theory of narcosis. The book is still a remarkably good one; but one cannot go on indefinitely increasing the size of a book without changing its character. The difference between this edition and the previous one is an increase in the number of facts. By the time the fifth edition is called for, the author will have to make the book chiefly a compendium of data, or he will have to develop the theoretical side much more strongly, so that the experimental data can be presented briefly as illustrations of the general theory. It is to be hoped that the latter plan will be the one adopted by the author.

A great deal of work must be done before this is possible. The admirable chapter on the permeability of cells shows how far we still are from a satisfactory theory of this phenomenon. The reviewer feels confident, however, that part of this difficulty is due to attempts to carry through in its entirety some one theory in the form originally proposed. It is probable that there is something sound in nearly every one of the explanations offered and that the final theory will be a composite. We have been through much the same thing in colloid chemistry. When Müller published his book, in 1907, he distinguished solution theory, suspension theory, adsorption theory, distribution theory, theory of chemical complexes, and other theories. Under each head he had several subdivisions, all more or less mutually exclusive. The difficulty was that each man was interested especially in certain phenomena and worked out the particular form of the general theory which was best applicable to his particular problem and did not bother himself much about the other portions of the field. Thus, the electrical phenomena are the important ones with so-called colloidal suspensions in aqueous solutions and the theory of Hardy and Bredig took that into account without bothering itself very much in regard to adsorption, and without taking any account of the behavior of gelatine by itself or as a protective colloid. It is only by taking the good portions of each theory and combining them into one general theory that one can hope to reach a satisfactory result.

Höber classifies the views in regard to permeability of cells under the general headings: plasma film as molecular sieve; plasma film as lipoid membrane; plasma film as albumin membrane. The view that we are dealing with a lipoid membrane is the one that has been worked out in most detail and which accounts for the most facts. On the other hand, it seems certain that this theory cannot account satisfactorily for all the facts and that it must be modified to some extent.

The reviewer was glad to see special stress laid, p. 170, upon the fact that Congo red is a colloid and that its use as an indicator is, therefore, affected by the presence of substances which may be adsorbed. Attention is also called by the author, p. 189, to Henderson's work on the importance of sodium phosphate in keeping the hydrogen concentration of the blood constant. On the other hand the reviewer is sorry to see so much stress laid on Schulze's law, which is only a first approximation. As such it is valuable, but it becomes positively harmful when promoted to the dignity of a law. The author also fails to appreciate fully that one is dealing throughout with selective adsorption, and that the order of the anions and cations is not necessarily the same with different substances.

Wilder D. Bancroft

Introduction to Physical Chemistry. *By James Walker. Seventh Edition. 15 × 22 cm; pp. xii + 420. New York: The Macmillan Company, 1913. Price, cloth, $2.60.*—The first edition of this book was reviewed in the Journal of Physical Chemistry (4, 41). The new edition is very similar to the last edition, not having been changed in form, but a number of minor changes have been made. More accurate values for constants, made possible by more accurate work, are given with some few minor changes. This book still holds the high standard which it deserves as a descriptive treatise of physical chemistry. The plan here, as before, is to select certain parts of the field and elaborate these, rather than to give a comprehensive view of the whole field. The book, however, is elementary in nature as before, and is still well suited as a basis for a lecture course in general and physical chemistry.

C. W. Bennett

Complex Ions in Aqueous Solutions. *By Arthur Jaques. 22 × 15 cm; pp. v + 151. New York: Longmans, Green and Co., 1914. Price: $1.35.*—The author gives a summary of our knowledge of complex ions and of the methods for determining the composition of a complex ion. The chapters are entitled: introductory; the chemical method; the ionic migration method; the distribution method; the solubility method; the electric potential method; some examples; ammoniacal salt solutions, etc.; some cobalt and copper solutions; some special cases of equilibrium; the hydrate theory. Such a compilation is likely to be distinctly serviceable. The author has overlooked or ignored the work of Parsons on the non-existence of KI_3 and he does not consider the possibility of colloidal solutions in the case of alkaline copper tartrate solutions for instance.

Wilder D. Bancroft

STUDIES ON THE SILVER VOLTAMETER

BY G. A. HULETT AND G. W. VINAL

I. Introduction

At the suggestion of Prof. E. B. Rosa, of the Bureau of Standards, a comparison has been made of the silver voltameters and methods employed at the Bureau of Standards with the voltameters and methods used at Princeton University by Prof. Hulett and his co-workers. Accordingly, in January, 1914, one of the authors (G. W. V.), came to Princeton with part of the Bureau of Standards equipment of voltameters.

This work was intended to include a comparison of the methods of preparing the electrolyte, of the porous cups and their manipulation, of the methods of washing and weighing the deposit and of other details of operation in order to find an explanation for certain differences in conclusions reached and to see whether when the electrolyte was pure and the manipulation the same, the voltameters, which were of different sizes and shapes would give identical results. In addition it was planned to study the question of inclusions in the deposit if time permitted.

This program was in the main carried out except for the matter of the inclusions for which, owing to unexpected developments in some of the other work, there was not sufficient time. It seems worth while to call attention to these new developments at the present time.

Throughout the following discussion the apparatus and methods which have heretofore been used and described by Prof. Hulett and his students are designated as the Princeton apparatus or method. Similarly also we shall refer to the Bureau apparatus and methods as previously described in the recent publications of the Bureau of Standards on this subject.

II. Comparison of the Voltameters

a. Preliminary Work

A preliminary comparison of the voltameters was made in four experiments (of which the first is designated as a trial experiment) to determine the relation of the Princeton volt-

TABLE I

Preliminary Comparison of Voltameters

(No. 27 and No. 28 are B. S. voltameters; I and II are Princeton voltameters)

Date	Cup	Deposit	Mean	Difference B.S.-Princ.	Method of drying
		Mg	Mg		
Feb. 18	27	4103.34	4103.34	$+\frac{5.4}{100{,}000}$	Heated to 160°
	28	(4102.94)			
	I	. . .	4103.12		Vacuum dried
	II	4103.12			
Feb. 26	27	4090.84	4090.87	$+\frac{10.7}{100{,}000}$	Heated to 160°
	28	4090.90			Heated to 160°
	I	4090.39	4090.43		Heated to 160°
	II	4090.47			Heated to 160°
Mar. 7	27	4118.32	4118.34	$+\frac{17.7}{100{,}000}$	Heated to 160°
	28	4118.36			Heated to 160°
	I	4117.54	4117.61		Heated to 160°
	II	4117.68			Heated to 160°
Mar. 20	27	4094.55	4094.55	$+\frac{7.7}{100{,}000}$	Heated to 160°
	28	4094.55			Heated to 160°
	I	4094.23	4094.23_5		Heated to 160°
	II	4094.24			Heated to 160°
			Mean,	$+\frac{10.4}{100{,}000}$	

ameters with those of the Bureau of Standards. In each case the voltameters were assembled and treated in accordance with the customary procedure. But the electrolyte used in all the voltameters of any experiment was always the same[1] so that we have a comparison of the voltameters themselves not involving any differences due to the preparation of the silver nitrate. The voltameters were all of the porous cup variety.[2]

The values are given in Table I. On the average the deposits in the Bureau voltameters exceeded those in the Princeton voltameters by about ten parts in one hundred thousand.

A systematic search was now begun for the cause of this difference. In Table II we give the physical aspects of the voltameters employed.

Differences in the method of washing the deposits proved to be important and without doubt influenced the results given in Table I. We shall describe under the heading "Washing the Deposits" the experiments which we made in this connection. The essential fact here is that according to the Princeton method the voltameters always stood over night filled with distilled water, while the Bureau procedure has been to complete the washings of the deposit at once, unless the lateness of the hour made it convenient to allow the cups to remain filled with water over night. This was a most unexpected result and on examining the matter carefully we have discovered that when water is allowed to stand on silver which has been deposited on platinum a slow and progressive loss of silver takes place. During the interval between closing work for one day and beginning the next the loss is appreciable in amount.

Comparative determinations of the acidity of the elec-

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[1] This electrolyte was prepared according to the methods of the Bureau of Standards. Bulletin Bureau of Standards, 9, 524 (1913).

[2] Details of construction of these voltameters are given in Trans. Am. Electrochem. Soc., 12, p. 257; 22, p. 367; and Bulletin Bureau of Standards, 9, p. 151.

Table II—Comparison of the Physical Aspects of the Voltameters
(No. 27 and No. 28 are Bureau Voltameters; I and II are Princeton Voltameters)

No.	Cathodes					Anodes	Porous cups			
	Material	Depth	Diam.	Capac.	Surface		Manufacture	Diam.	Depth	Treatment
		Cm	Cm	Cc				Cm	Cm	
27	Platinum	7	6	125	Bright	Electrolytic	German	3.8	5.8	Kept in $AgNO_3$
28	Platinum	7	6	125	Bright	Electrolytic	German	3.8	5.8	Kept in $AgNO_3$
I	Platinum	10	5	165	Matte	Cast	American	2.5	12.0	Kept in H_2O rinsed with $AgNO_3$ before use
II	Platinum	10	5	165	Matte	Cast	American	2.5	12.0	

trolyte for the various voltameters before and after the electrolysis showed the following results. These tests were made according to the method described by Rosa, Vinal and McDaniel,[1] except that methyl red was employed as an indicator instead of iodeosin because it is much more convenient to use and seems to be equally reliable.

The acidity measurements are given in Table III.

TABLE III

Changes in Acidity of Electrolyte for the Preliminary Experiments

Date	Cup	Initial acidity	Final cathode acidity	Increase B. S. cups	Increase Princeton cups
Feb. 18	27	0.5×10^{-6}	1.2×10^{-6}	0.7×10^{-6}	—
	28	0.5×10^{-6}	2.1×10^{-6}	1.6×10^{-6}	—
	I	0.5×10^{-6}	—	—	—
	II	0.5×10^{-6}	—	—	—
Feb. 26	27	0.9×10^{-6}	1.9×10^{-6}	1.0×10^{-6}	—
	28	0.9×10^{-6}	2.1×10^{-6}	1.2×10^{-6}	—
	I	0.9×10^{-6}	—	—	—
	II	0.9×10^{-6}	—	—	—
Mar. 7	27	0.9×10^{-6}	2.3×10^{-6}	1.4×10^{-6}	—
	28	0.9×10^{-6}	2.7×10^{-6}	1.8×10^{-6}	—
	I	0.9×10^{-6}	15.7×10^{-6}	—	14.8×10^{-6}
	II	0.9×10^{-6}	7.3×10^{-6}	—	6.4×10^{-6}
Mar. 20	27	0.6×10^{-6}	0.6×10^{-6}	0.0×10^{-6}	—
	28	0.6×10^{-6}	1.6×10^{-6}	1.0×10^{-6}	—
	I	0.6×10^{-6}	4.6×10^{-6}	—	4.0×10^{-6}
	II	0.6×10^{-6}	7.0×10^{-6}	—	6.4×10^{-6}
			Average,	1.1×10^{-6}	7.9×10^{-6}

It thus appears that the change in acidity of the electrolyte is appreciably greater in the case of the Princeton voltameters than in the Bureau of Standards voltameters. The reason for this appears to involve the question of the equilibrium of the porous cup and the silver nitrate solution which we shall discuss more at length farther on. It will be noted in Table II that the method of treating the porous cups was

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[1] Bulletin Bureau of Standards, 9, p. 526.

different in the two cases. Our results showed that when the same procedure for preparing the two kinds of porous cups was employed they yielded the same results. The difference between the Princeton and the Bureau's results is not, therefore, to be attributed to the fact that the porous cups were made by different makers[1] and from different materials.

b. Final Comparison of the Voltameters

Working on the assumption that the difference between the Princeton voltameters and the Bureau's voltameters was due partly to the differences in the length of time that the deposits were washed and partly to the difference in the method of preparing the porous cups, two experiments were made in which these differences were eliminated. The washings for all were done as expeditiously as possible and the porous cups for the Princeton voltameters were put into silver nitrate solution the day before each experiment. This solution was changed several times so that the equilibrium between the

Table IV

Final Comparison of Voltameters

(No. 27, 28 are Bureau of Standards Voltameters; I and II are Princeton Voltameters)

Date	Cup	Deposit	Mean	Difference B. S.-Princ.	Method of drying
1914		Mg	Mg		
June 19	28	4113.29	4113.29	—0.5	Heated to 160°
				100,000	
	II	4113.31	4113.31		Heated to 160°
June 23	27	4133.56	4133.54_5		Heated to 160°
	28	4133.53	—	+0.3	Heated to 160°
				100,000	
	I	4133.60	4133.53_5		
	II	4133.47	—		Heated to 160°
				0	
			Mean,	100,000	

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[1] The Princeton voltameters contained porous cups made by John Maddock & Son of Trenton, N. J. The Bureau voltameters contained porous cups made by the Königliche Porzellan Manufaktur of Berlin.

porous cup and the neutral solution might be as complete as possible and similar to the method of keeping the porous cups in silver nitrate as has been done at the Bureau.

Table IV gives the results of these two experiments in which some gold cathodes were also used, but we give here only the results of the platinum cathodes for comparison with Table I. It can be seen from Table X that the results with the gold cathodes were equally concordant.

The values obtained in these last comparisons show very perfect agreement. The changes in acidities of the electrolytes also were about the same for the two forms of voltameter. The results of the acidity measurements made as before are given in Table V.

TABLE V

Date	Cup	Initial acidity	Final cathode acidity	Increase B. S. cups	Increase Princ. cups
1914 June 19	28	0.8×10^{-6}	3.1×10^{-6}	2.3×10^{-6}	—
	II	0.8×10^{-6}	2.9×10^{-6}	—	2.1×10^{-6}
June 23	27	0.8×10^{-6}	3.1×10^{-6}	2.3×10^{-6}	—
	28	0.8×10^{-6}	4.1×10^{-6}	3.3×10^{-6}	—
	I	0.8×10^{-6}	3.5×10^{-6}	—	2.7×10^{-6}
	II	0.8×10^{-6}	2.5×10^{-6}	—	1.7×10^{-6}
			Mean,	2.6×10^{-6}	2.2×10^{-6}

III. Washing the Deposits

The practice of nearly all observers has been to continue the washing of the deposit until the presence of silver nitrate can no longer be detected in the wash waters by chemical tests, but many have taken the further precaution of allowing distilled water to stand on the deposit for a considerable period of time. In considering this matter we found the fact that chemical tests for the presence of silver were not particularly satisfactory when we were concerned with very small amounts of silver nitrate in the wash waters. In our final washings we were using "conductivity" water, and soon found that the change of conductivity of this water was a most admirable method for determining the completeness of the washing. The increase in conductivity due to dissolved silver nitrate was entirely reliable when we used a blank, that is a clean platinum cup similarly filled with conductivity water and standing beside these containing the deposit. We could rapidly make tests of the water standing on the deposit and also that standing in the clean platinum cup. These observations showed a most unexpected state of affairs which led to a special investigation.

It was found in the beginning that, when conductivity water was put into the cups containing the deposits and allowed to stand only a short time, the increase in conductivity of the water was very small provided of course that the silver deposits had been washed in the usual manner. This is illustrated by measurements on the final wash water for No. 27 and No. 28 in the experiment of March 8th. This last water was allowed to stand on the deposits for five minutes.

Conductivity of water originally	0.98×10^{-6} at 20° C
Conductivity of water taken from No. 27	1.00×10^{-6} at 20° C
Conductivity of water taken from No. 28	1.05×10^{-6} at 20° C

It was found, however, that in the case of Cups I and II of the same experiment which had been washed as thoroughly as No. 27 and No. 28 that the last water which stood in them over night showed a distinct increase in conductivity. After standing about 10 hours we found:

Conductivity of water originally	1.44×10^{-6} at 20°
Conductivity of water taken from I	2.85×10^{-6} at 20°
Conductivity of water taken from II	3.00×10^{-6} at 20°

This increase in conductivity suggested that some silver nitrate was actually soaking out of the crevices, but repetitions of this soaking process showed only small differences. That is, instead, of the silver nitrate all coming out on continued washing so that the water could finally stand on the deposit without sensible change, as it does in a clean platinum cup, we found that the effect would repeat itself after a number of washings.

This effect is best illustrated by the measurements made on Cups I and II of the experiment of April 4th. These cups had been thoroughly washed five times and also soaked over night before the measurements recorded below were begun. The following table shows the increases in conductivity observed in this case.

TABLE VI

Date	Cup	No. of wash water	Duration of washing	Increase in conductivity	$\frac{\text{Increase}}{\text{Time}}$
1914			Hours		$\times 10^{-6}$
Apr. 5	I	7	10	1.03×10^{-6}	0.103
	II	7	10	1.02×10^{-6}	0.102
Apr. 6	I	8	12	1.23×10^{-6}	0.102_5
	II	8	12	1.02×10^{-6}	0.085
	I	9	12	1.25×10^{-6}	0.104
	II	9	12	1.08×10^{-6}	0.090
Apr. 7	I	10	11½	1.09×10^{-6}	0.095
	II	10	11½	1.05×10^{-6}	0.091
				Mean I,	0.101
				Mean II,	0.092

In the case of each wash water that stood on the deposit over night we could detect the presence of silver chemically by concentrating the solution in a platinum dish to about 10 cc and testing it with potassium iodide. These tests were always conclusive and left no room for doubt that silver was actually in solution in the water.

In searching for an explanation of this phenomenon we tried letting a sheet of pure silver stand in conductivity water in a glass beaker that had been thoroughly steamed and otherwise cleaned. The glass did not cause a significant increase in the conductivity of the water as we had ascertained by previous experiment. When the silver was immersed in the conductivity water contained in this glass no change in conductivity was observed other than a very small, gradual increase due to contact of the air. The experiment was continued for one hundred and sixty-six hours and to confirm it we repeated it with another beaker and another piece of silver. The numerical results of these two experiment are given in Table VII and plotted together as Curve I in Fig. 1.

TABLE VII
(Conductivities Corrected to 20° C)

Date	Sample	Time	Increase in conductivity	Remarks
1914		Hours		
May 13	A	13	0.14×10^{-6}	First water
15	B	23	0.12×10^{-6}	First water
14	A	24	-0.05×10^{-6}(?)	Second water
16	B	34	0.06×10^{-6}	Second water
15	A	48	0.05×10^{-6}	Second water
18	B	70	0.04×10^{-6}	Second water
16	A	82	0.34×10^{-6}	Second water
18	A	118	0.13×10^{-6}	Second water
20	B	118	0.21×10^{-6}	Second water
20	A	166	0.35×10^{-6}	Second water

Taking the final values, 0.35×10^{-6} at 166 hours for A and 0.21×10^{-6} at 118 hours for B we find that the rates of increase for A and B are as follows:

A 0.0021×10^{-6} per hour
B 0.0018×10^{-6} per hour

Comparing this with the results of Table VI where the silver was deposited on the platinum we find

I 0.101×10^{-6} per hour
II 0.092×10^{-6} per hour

That is when the silver is deposited on platinum it affects the conductivity of the water at least fifty times as fast as when the platinum is absent. Probably the effect is very much greater than this since one may reasonably say that the increase in conductivity of the water standing on silver in the beakers is due largely, if not entirely, to dissolved substances from the glass and the contamination by the air. In any case the observed differences are large enough to be unmistakable.

Curve II of Fig. 1 shows the increases in conductivity of the water plotted against time. The various points are results for various deposits in various experiments and made under widely varying conditions. In some cases the deposits had been dried and weighed before the deposits were put to soak in water; in other cases they were not. In some cases the results are for the third wash water and in others for even the twelfth. Consequently it is not surprising that the points do not lie more closely to the curve. We do not wish to lay emphasis on the position or form of the curve as we have drawn

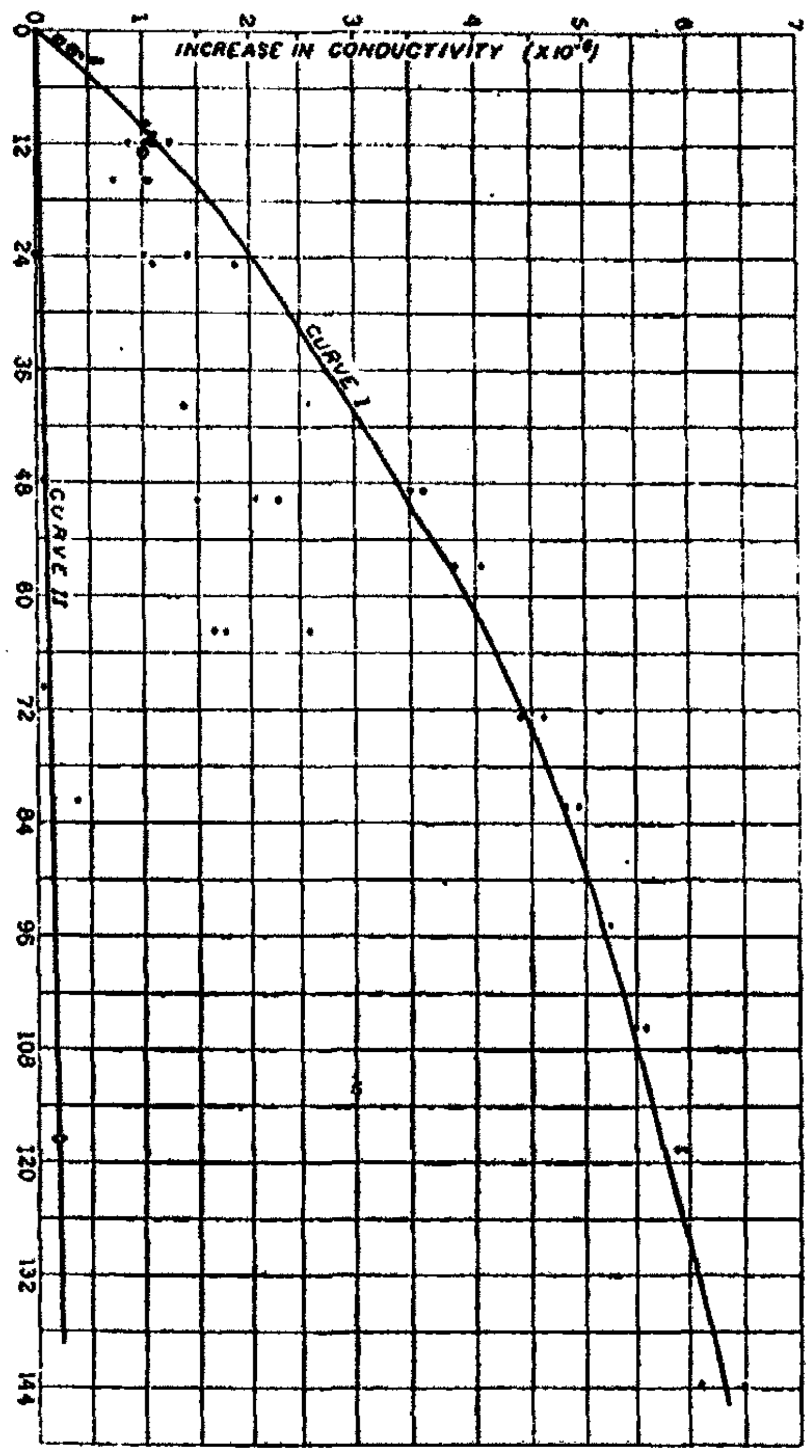

Fig. 1

TABLE VIII
Conductivities of Wash Waters

Date	Cup	No. of wash water	Duration of washing	Observed conductivity	Conductivity of water initially	Increase in conductivity	Deposit previously dried?
1914			Hours	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$	
Mar. 8	27	6	1/6	1.05	0.98	0.07	No
	28	6	1/6	1.00	0.98	0.02	No
Mar. 21	27	6	13	2.00	1.00	1.00	No
	28	6	13	2.00	1.00	1.00	No
Apr. 4	27	5	1/6	1.07	0.93	0.14	No
	28	5	1/6	1.08	0.93	0.15	No
Apr. 5	27	6	12	2.01	0.93	1.08	No
	28	6	12	2.04	0.93	1.11	No
Apr. 5	I	7	10	2.09	1.06	1.03	No
	II	7	10	2.08	1.06	1.02	No
Apr. 6	I	8	12	—	—	1.23	No
	II	8	12	—	—	1.02	No
	I	9	12	—	—	1.25	No
	II	9	12	—	—	1.08	No
Apr. 7	I	10	11 1/2	—	—	1.09	No
	II	10	11 1/2	—	—	1.05	No
Apr. 30	27	7	1/12	1.10	0.96	0.14	Yes
	27	8	1/12	1.09	0.96	0.13	Yes
	27	9	1/6	1.06	0.96	0.10	Yes
May 1	27	9	16	2.04	0.96	1.08	Yes
May 2	27	10	16	1.97	0.96	1.01	Yes
	27	10	24	2.36	0.96	1.40	Yes
May 4	27	10	64	2.69	0.96	1.73	Yes
May 5	27	11	12	1.80	0.95	0.81	Yes
May 6	27	12	16	1.66	0.95	0.71	Yes
	27	12	24	1.95	0.95	1.00	Yes
May 7	27	12	40	2.31	0.95	1.36	Yes
May 21	27	3	1/2	1.02	0.96	0.06	No
	28	3	1/2	1.02	0.96	0.06	No
	125	3	1/2	1.00	0.96	0.04	No
	27	3	1 1/4	1.21	0.96	0.25	No
	28	3	1 1/4	1.15	0.96	0.19	No
May 21	125	3	1 1/4	1.15	0.96	0.19	No
	27	3	2 1/4	1.30	0.96	0.34	No
	28	3	2 1/4	1.33	0.96	0.37	No
	125	3	2 1/4	1.30	0.96	0.34	No
	27	4	2 1/4	1.32	0.96	0.36	No
	28	4	2 1/2	1.30	0.96	0.34	No
	125	4	2 3/4	1.39	0.96	0.43	No
	27	4	3 1/4	1.57	0.96	0.61	No
	28	4	3 1/4	1.48	0.96	0.52	No
	125	4	3 1/4	1.52	0.96	0.56	No

TABLE VIII (*Continued*)

Conductivities of Wash Waters

Date	Cup	No. of wash water	Duration of washing	Observed conductivity	Conductivity of water initially	Increase in conductivity	Deposit previously dried?
1914			Hours	$\times 10^{-6}$	$\times 10^{-6}$	$\times 10^{-6}$	
May 22	I	4	25	2.77	0.93	1.84	No
	II	4	25	2.00	0.93	1.07	No
May 23	I	4	50	3.20	0.93	2.27	No
	II	4	50	2.40	0.93	1.47	No
May 24	I	4	64	3.50	0.93	2.57	No
	II	4	64	2.60	0.93	1.67	No
May 25	27	5	49	4.55	0.96	3.59	Yes
	125	5	49	4.45	0.96	3.49	Yes
	27	5	57	5.00	0.96	4.04	Yes
	125	5	57	4.78	0.96	3.82	Yes
May 26	27	5	73	5.55	0.96	4.59	Yes
	125	5	73	5.34	0.96	4.38	Yes
	27	5	$82^{1}/_{2}$	5.88	0.96	4.92	Yes
	125	5	$82^{1}/_{2}$	5.75	0.96	4.79	Yes
May 27	27	5	95	6.19	0.96	5.23	Yes
	125	5	95	6.09	0.96	5.14	Yes
	27	5	106	6.54	0.96	5.58	Yes
	125	5	106	6.44	0.96	5.48	Yes
May 28	27	5	119	6.91	0.96	5.95	Yes
	125	5	119	6.84	0.96	5.88	Yes
May 29	27	5	144	7.05	0.96	6.09	Yes
	125	5	144	7.44	0.96	6.48	Yes

it, for this may be open to question, but the one fact that deserves attention is that all the results unite in showing that the conductivity of water standing on silver deposited on platinum increases at a much greater rate than when the water is standing on silver in a glass vessel.

We give in Table VIII complete data from which the curves in Fig. 1 are plotted. All the conductivities were measured at room temperature which averaged about 23° and ranged from 21° to 25°. Since we were primarily interested in the increases of conductivity rather than the absolute conductivities the corrections for temperature are negligible.

One might readily assume that this increase in conductivity of the water is due to entrapped silver nitrate soaking gradually out in spite of the evidence in Table VI that the effect repeats itself. We, therefore, took one of the sheets of silver used for the results recorded in Table VII and put it to soak in conductivity water in a platinum cup. The silver rested on the bottom of the cup. The results were as follows:

TABLE IX

Date	Elapsed time	Increases in conductivity	Remarks
1914			
May 26	$2^1/_2$	None	Water in Pt cup. *No silver*
26	$3^1/_4$	0.06×10^{-6}	Silver in the cup
26	$6^1/_4$	0.14×10^{-6}	
27	19	0.38×10^{-6}	
27	30	0.58×10^{-6}	
28	43	0.86×10^{-6}	
29	68	1.40×10^{-6}	

These results are shown in the Curve I of Fig. 2. For comparison we have also plotted the results when the sheets of silver stood similarly in a glass beaker. This is the same curve as I in Fig. 1. The difference is smaller than is shown in the curves of Fig. 1 but shows the effect quite certainly. To complete this test we boiled down the water that had stood on the sheet silver in a platinum cup and tested it chemically for silver. We found this solution to contain silver just as we had found in the case of the silver deposits. In this case there was no possibility of silver nitrate producing

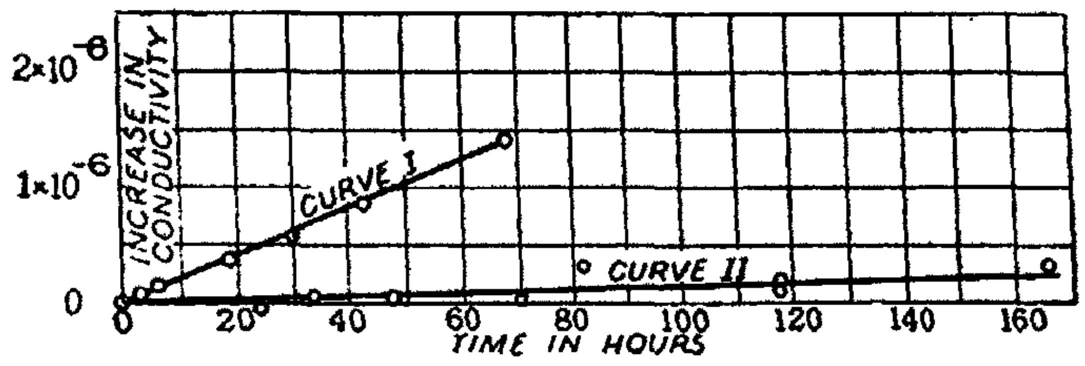

Fig. 2

this effect. These results indicated an electrochemical action by which the silver passed into the solution.

Accordingly, we made the following experiment to see whether evidence of an electric current passing from the platinum to the silver and into the water could be found: A platinum bowl filled with the best conductivity water was connected to the + terminal of a high resistance potentiometer. In this and resting on the bottom was placed a sheet of silver (used in the experiments recorded above). This was connected to the negative terminal of the potentiometer. At a convenient time the silver was raised slightly and held in position in the water but not in contact with the platinum cup. We then took the readings which are plotted in Curve I of Fig. 3. Curve II shows a similar curve for a gold cup instead of the platinum. These results confirmed the idea that an electrolytic phenomenon was taking place. In a few cases we measured the loss of silver from the platinum bowl at the conclusion of the soaking process, either by estimating the silver in the water by the silver chloride produced by KCl after acidifying the solution or by reweighing the cup. We also tried estimating the silver by ammonium sulphocyanate but without satisfactory results because of the extremely small quantities involved. The results recorded below are not very

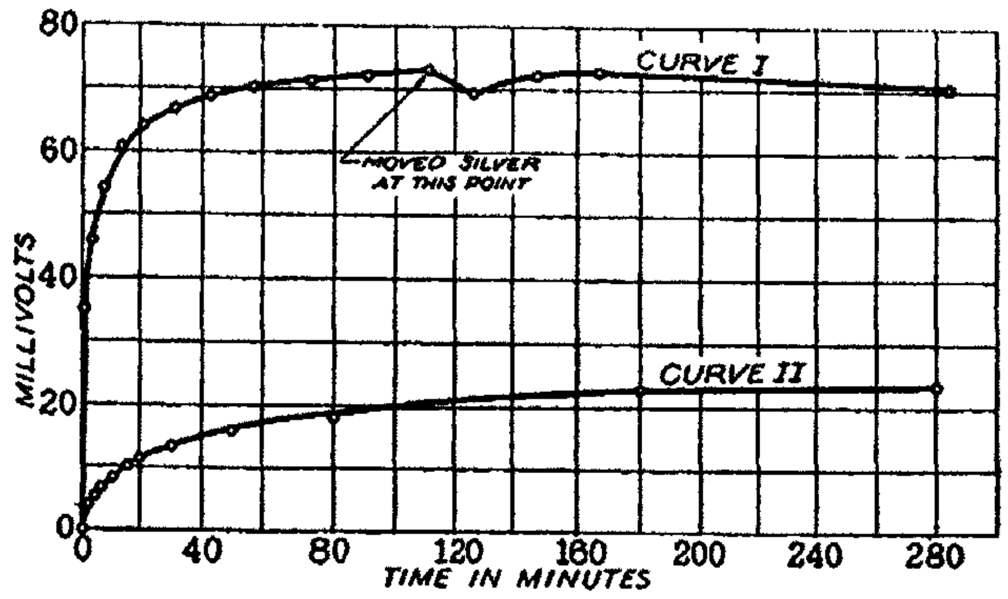

Fig. 3

concordant but show that the losses of silver from the cathode bowl are about the same order of magnitude as the amounts of silver found in the water. If we take 0.006 mg as the average amount lost to the cathode deposit per hour from 4 g of silver deposited on platinum we see that soaking the deposit for one day of twenty-four hours means a loss of from 3 to 4 parts in 100,000 of a four-gram deposit, and that soaking the deposits over night (about 16 hours) quite certainly means a loss of 2 in 100,000 of the deposit. In many cases the rate may be much greater than this, since probably a slightly higher conductivity in the water initially would increase the rate. Perhaps the reason that the effect seems greater at the start than after a long time is due to a gradual polarization.

TABLE IX

Date	Cup	Hours	Increase in conductivity	(1) Loss of silver by weighings	(2) Loss of silver by determ. of AgCl	Ratio: $\frac{(1)}{\text{Hours}}$	Ratio: $\frac{(2)}{\text{Hours}}$
1914			$\times 10^{-6}$	Mg	Mg		
May 1	27	16	1.08	0.21	—	0.013	—
May 4	27	64	1.73	0.34	0.49	0.005	0.008
May 7	27	40	1.36	—	0.20	—	0.005
May 29	27	144	6.09	0.67	0.52	0.005	0.004
May 29	125	144	6.48	0.64	0.53	0.005	0.004
					Mean,	0.007	0.005

Mean of all 0.006 mg per hour from 4 g of silver on platinum.

This loss of silver during the washing of the deposits, of course, shows that the deposits should be washed and dried immediately.

One further point in this connection remained to be investigated. While it seemed fairly certain from the above experiments that an electrochemical action was taking place, there still remained the possibility that a little silver nitrate entrapped behind the crystals might be slowly soaking out and adding to the observed effects. Accordingly, we tried the following experiment: Two cups, No. 25 and No. 125, of the run of May 21st were filled with water for 144 hours while an exactly similar cup, No. 28, remained dry. We scraped down half the silver deposit in No. 27 and No. 28 with a clean platinum spatula and then put 50 cc of conductivity water in each for five minutes to dissolve whatever $AgNO_3$ might have been trapped between the crystals and the platinum. If the soaking process appreciably lessened the amount of $AgNO_3$ entrapped, we should expect the conductivity of the water put in No. 28 to be increased more than that put in No. 27. The results given below show that this is not the case. To find what increase in conductivity of the water would take place, due to mere contact with the deposit not scraped down, we put 50 cc. in No. 125 for 5 minutes also. This affords a blank experiment and the results are to be subtracted from those found for No. 27 and No. 28. The results are as follows:

Conductivity of water initially	0.98×10^{-6} at 22.5°
Blank experiment (water from No. 125)	1.35×10^{-6} at 22.5°
Increase to be subtracted from others	0.37×10^{-6} at 22.5°
Water from No. 27 which was soaked for 144 hours	1.56×10^{-6} at 22.5°
Net increase for No. 27 after subtracting blank	0.21×10^{-6} at 22.5°
Water from No. 28 which was not soaked	1.49×10^{-6} at 22.5°
Net increase for No. 28 after subtracting blank	0.14×10^{-6} at 22.5°

If we may assume that these small net increases for No. 27 and No. 28 represent silver nitrate trapped between the silver and the platinum we may estimate the whole amount of such silver nitrate for each cup and find for

No. 27	0.03 mg
No. 28	0.02 mg

The conclusion of the whole matter is, that prolonged washing of the silver deposits produces a measurable diminution in deposit and it is, therefore, advisable that the deposits should be washed as speedily as possible.

IV. Comparison of Deposits on Gold and Platinum Cathodes

The Princeton gold cups are quite different in appearance from those of the Bureau of Standards. The former are more yellow than the latter which have a greenish yellow appearance. It is believed that the Princeton cups are of the purer gold. These gold cups were compared in only the last two experiments although one of the Bureau of Standards cups was used in several previous experiments for other purposes. The results are given in Table X and show the substantial agreement of the deposits on gold and platinum cathodes of both the Princeton voltameters and the Bureau of Standards voltameters.

Table X

Comparison of Gold and Platinum Cathodes

(Nos. 27, 28, 125, 126 are Bureau of Standards Cups; I, II, III, IV are Princeton Cups)

Date	Cup	Material	Deposit	Mean	Remarks
1914			Mg		
June 19	28	platinum	4113.29		gold-platinum = $\frac{+0.5}{100,000}$
	125	gold	4113.27	4113.31	
	II	platinum	4113.31		
	III	gold	4113.37		
June 23	27	platinum	4133.56		gold-platinum = $\frac{+1.5}{100,000}$
	28	platinum	4133.53		
	125	gold	4133.62		
	126	gold	4133.58	4133.57	
	I	platinum	4133.60		
	II	platinum	4133.47		
	III	gold	4133.69		
	IV	gold	4133.52		

Mean excess of deposits on gold over those on platinum is:

$$\frac{1.1}{100,000}$$

which we consider excellent agreement.

These experiments do not explain the results of Dr. Buckner using the Princeton platinum and gold voltameters where he found an excess of $\frac{12}{100,000}$ in the deposits on gold over those on platinum. We are at a loss to assign a reason for the differences which he found since no such differences developed in our work, but we incline to the belief that the cause must have been in the electrolyte. We think that the fact that such a case may arise emphasizes the necessity of making the proposed international specifications rigid in requiring platinum cathodes since that is the most generally used.

V. Comparison of Porous Cups from Different Sources

The porous cups used in the Princeton voltameters were made by John Maddock and Son of Trenton, N. J., while those used by the Bureau of Standards in its previous work and for the most part in the present work also were made by the Königliche Porzellan Manufaktur of Berlin, Germany. The American made porous cups have a great advantage in having vitreous tops, but in their original condition they are too thick to be easily prepared for the voltameter. This difficulty was overcome by grinding down the sides and bottom

TABLE XI—COMPARISON OF VOLTAMETERS USING DIFFERENT MAKES OF POROUS CUPS

Date	Porous pots	B. A. voltameters	Δ	Princeton voltameters	Δ	Mean of all	Observer
1914		Mg	Mg	Mg	Mg	Mg	
June 17	Trenton	3667.92	−0.05			3667.97	Vinal
	Berlin	3668.02	+0.05				Vinal
June 19	Berlin	4113.29	−0.02				Vinal
	Berlin	4113.27	−0.04				Vinal
	Trenton			4113.31	0.00	4113.31	Vinal Hulett
	Trenton			4113.37	+0.06		Vinal Hulett
June 23	Berlin	4133.56	−0.01				Vinal
	Trenton	4133.53	−0.04				Vinal
	Berlin	4133.62	+0.05				Vinal
	Berlin	4133.58	+0.01			4133.57	Vinal
	Trenton			4133.60	+0.03		Hulett
	Trenton			4133.47	−0.10		Hulett
	Trenton			4133.69	+0.12		Hulett
	Trenton			4133.52	−0.05		Hulett

Average deviation of Berlin pots from mean +0.007 mg
Average deviation of Trenton pots from mean −0.002 mg

with carborundum paper until the walls were about 1 mm thick. Tests were made of the solubility of the porous material of both kinds of cups and these showed that, after an initial washing to remove the free alkali, the cups could stand for hours in double distilled water without producing any significant increase in its conductivity.

In Table XI we give a comparison of results using these two kinds of porous cups. This table contains all the comparative results in which the porous cups were prepared as described in the Bureau of Standards Bulletin IX, p. 185. The agreement of results with these two makes of porous cups is very satisfactory.

VI. Summary

We have made a comparison of porous cup voltameters that differ considerably in size and shape and particularly in the manufacture of the porous cups. We find that when the porous cups are brought into equilibrium with the electrolyte as shown by acidity tests that all the voltameters are in excellent agreement.

We have found that when the voltameter cups containing deposits are allowed to stand filled with water (even conductivity water) that a progressive solution of the silver takes place. That this is a galvanic action we have shown in several ways. The discovery of this effect makes it seem desirable to wash the deposits quickly.

Throughout the present work we have used methyl red as an indicator in the acidity measurements and have found it to be preferred to iodeosin because it is much simpler to use and at the same time gives sufficient accuracy.

Laboratory of Physical Chemistry
Princeton University
July 1, 1914

[CONTRIBUTIONS FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY, NO. 244]

IONIZATION EQUILIBRIUM[1]

BY JAMES KENDALL

The well-known dilution law for weak electrolytes:

$$\gamma^2/(1 - \gamma)v = k; \text{ or } c_i^2/c_u = k \ldots\ldots\ldots\ldots\ldots (1)$$

(where γ = fraction ionized, v = dilution, c_i = ionic concentration, c_u = concentration of the undissociated part, k = dissociation constant) formulated by Ostwald in 1888 from the law of mass action, was one of the earliest and strongest confirmations of the dissociation theory of Arrhenius. The ionization equilibrium of all normal members of the class of weakly-ionized acids was shown by Ostwald to be represented by the above law; a similar proof for the weak bases was given by Bredig in 1894. The remaining electrolytes, however (strongly-ionized acids and bases, and all salts) have not yet been brought into line with the law of mass action; the various formulas that have been proposed to express their ionization equilibrium, such as the van't Hoff equation, $\gamma^3/(1 - \gamma)^2v = c$, are merely empirical.

Later investigations have shown that *exact agreement* with the dilution law is to be obtained only within certain limits even in the case of weak electrolytes. No definite line of demarcation can be drawn between weak and strong acids; one class merges into the other through the intermediate "transition" electrolytes. These deviate more and more appreciably from the dilution law as their acidic strength increases; the weaker approximate very closely to the Ostwald equation; the stronger approach more nearly the formula of van't Hoff. The dilution law is, therefore, to be regarded as a limiting case, divergences from which increase rapidly with the strength of the electrolyte.

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[1] A paper presented before Section of Astronomy, Physics and Chemistry of the New York Academy of Sciences, November 16, 1914.

Furthermore, although any deviations from the dilution law in dilute solutions of *weak electrolytes* lie wholly within the limits of experimental error, exact agreement being obtained in the most accurate work, yet, in more concentrated solutions, the divergences become appreciable. The law is consequently found, on examination, to break down *in two directions.*

In the first place, it is followed *exactly* only if the *ionic concentration* is small. When a certain limiting ionic concentration (approximately 0.01 N) is exceeded, the dissociation constant begins to *increase*, and increases steadily with c_i. Divergences from the dilution law in this direction are, therefore, found in all strong electrolytes, and in many of the transition electrolytes at the higher concentrations. This is known as the "anomaly of strong electrolytes."

In the second place, the law is followed *exactly* only if the *total concentration* of the electrolyte is small. The limit of exact applicability is found to lie between $v = 32$ and $v = 16$ for typical weak electrolytes. In more concentrated solutions the dissociation constant shows a *decrease*, which becomes more and more rapid with increase of concentration. This constitutes the "anomaly of concentrated solutions."

It must be understood that the limits stated above are only approximate, since it is evident that the deviations will be capable of observation at a greater dilution, the greater the accuracy of the experimental work. In certain cases also where both disturbing factors are present in the same solution, the influence of each upon the dissociation constant will be obscured, since one effect tends to counterbalance the other. The anomaly of strong electrolytes and the anomaly of concentrated solutions are therefore studied separately in the following pages, which contain a critical examination of the divergences from the dilution law as exhibited by acids of widely-varying strengths in aqueous solution.

It is necessary first of all to give a brief explanation of the experimental method for the *exact* determination of the dissociation constant of an electrolyte.

Determination of the Dissociation Constant

In the form $\gamma^2/(1 - \gamma)v = k$ the dilution law of Ostwald is not accessible to direct test; in order to evaluate k we must know the degree of ionization, γ, at any dilution, v. For this we have at our service the fundamental relation of Arrhenius, $\gamma = \Lambda/\Lambda_0$ (Λ is the equivalent conductivity at dilution v, Λ_0 the equivalent conductivity at infinite dilution, where the electrolyte is wholly ionized). For any given solution, we are able to determine Λ by direct conductivity measurements, but to obtain γ we must also determine Λ_0. This may be done either by extrapolation from the results obtained for Λ through a series of high dilutions, or by the measurements of migration ratios. The former method gives Λ_0 directly, but the accuracy of the value obtained is affected by errors of extrapolation. The latter method shows the ration between the mobilities of the two ions of the electrolyte; if we know this ratio and the mobility of one ion we can evaluate Λ_0, which is the sum of the ionic mobilities.

In the case of acids, two main difficulties have been encountered in the exact determination of Λ and Λ_0 by the methods indicated above. The first has lain in the fact that the mobility of the hydrogen ion was not accurately known, the suggested values ranging from 338 (Rothmund and Drucker) to 365 (Noyes and Sammet) at 25° C. The second has been that the impurities contained in the water used in conductivity measurements have prevented the accurate determination of the equivalent conductivities of acids at very high dilutions, and no trustworthy correction for the influence of these impurities has yet been applied.

In a recent paper,[1] I have determined by an indirect method the mobility of the hydrogen ion, the value obtained being 347.2 at 25° C, with a maximum divergence of 0.4. In the course of the same investigation it was found that the disturbing influence of the impurities in the water employed could, in the case of acids stronger than acetic acid, be neg-

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[1] Jour. Chem. Soc., 101, 1275 (1912).

lected entirely if the specific conductivity of the water were less than 1.2×10^{-6}. The values obtained for Λ up to very high dilutions may, therefore, be employed in the calculation of *k* without the application of any correction. This paper has been subjected to a searching examination by Derick,[1] who has tested the results by means of a "sensitive precision criterion for conductance data" and found them to be completely substantiated.

The exact value for Λ_0 being established for any electrolyte, we can, by substituting for γ in Equation 1 bring the dilution law into the form:

$$\Lambda^2/\Lambda_0(\Lambda_0 - \Lambda)v = K \qquad (2)$$

to which experimental data can be directly applied. As an example, the results obtained for a typical weak electrolyte, acetic acid, are given in the following table:

ACETIC ACID.[2] 25° C

v	Λ	100 k
13.57	6.086	0.001845
27.14	8.591	0.001851
54.28	12.09	0.001849
108.56	16.98	0.001849
217.1	23.81	0.001851
434.2	33.22	0.001849
868.4	46.13	0.001850
1737.0	63.60	0.001854
3474.0	86.71	0.001855
	387.7	—

The constancy of the values obtained for *k* illustrates the high degree of accuracy with which the dilution law is found to hold for weak electrolytes at the highest dilutions. The dissociation constant is a *true* constant throughout the entire series of concentrations examined.

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[1] Jour. Am. Chem. Soc., 36, 2268 (1914).

[2] Jour. Chem. Soc., 101, 1283 (1912).

The Anomaly of Strong Electrolytes

In a weak electrolyte such as acetic acid the ionic concentration is always small, since the degree of ionization in concentrated solutions is extremely slight. The results obtained from the examination of a more highly ionized electrolyte, however, through the range of concentration indicated above, are entirely different in character. Here the anomaly of strong electrolytes becomes evident. As examples, the figures for cyanoacetic acid (with a dissociation constant 200 times that of acetic acid) and dichloroacetic acid (with a dissociation constant nearly 3000 times that of acetic acid) are given below:

Cyanoacetic Acid.[1] 25° C

v	Λ	$100k$ (expt.)	$100[k + c(1 - \gamma)/\gamma]$
16.82	88.0	0.400	0.402
33.64	117.0	0.392	0.391
67.28	152.5	0.383	0.383
134.6	193.9	0.378	0.378
269.1	238.7	0.372	0.374
538.2	282.6	0.371	0.372
1076.4	320.0	0.371	0.370
2153.0	347.1	0.371	0.369
	386.1	—	—

$k = 0.00368;\ c = 0.00010$

Dichloroacetic Acid.[1] 25° C

v	Λ	$100k$ (expt.)	$100[k + c(1 - \gamma)/\gamma]$
16	231.6	5.64	5.65
32	273.1	5.38	5.34
64	309.7	5.12	5.14
128	338.7	4.96	5.02
256	359.2	4.94	4.94
512	371.5	4.96	4.90
	385.6	—	—

$k = 0.0485;\ c = 0.0120$

For these acids, the dissociation constant is a true constant only at very high dilutions; in the more concentrated solutions,

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[1] Meddelanden från K. Vetenskapsakademiens Nobelinstitut, 2, 38 (1913).

it shows an *increasing* value. This increase is more rapid, the stronger the acid, as will be seen on comparison of the third columns of the above tables.

The two acids here examined belong to the class of "transition" electrolytes, and the divergences exhibited by k at the higher concentrations are characteristic of this class. A strong electrolyte, such as hydrochloric acid (with a dissociation constant 60,000 times that of acetic acid at 0.1 N concentration) would be expected to show a still more marked increase in k when the ionic concentration exceeds its limiting value, and this is indeed found to be the case. With strong electrolytes, however, a difficulty arises in the determination of k at the higher dilutions. The ionization is here so nearly complete that the expression $\Lambda_0 - \Lambda$ in Equation 2 becomes extremely small, consequently experimental errors in the determination of either Λ or Λ_0 are sufficient to vitiate the results, even of very accurate measurements.[1] From the most recent work,[2] however, it appears probable that ultimately, when the ionic concentration is very small, strong electrolytes also follow the dilution law.

At higher concentrations, the ionization equilibrium of strong electrolytes may be represented by the empirical equation of van't Hoff, $\gamma^3/(1 - \gamma)^2 v = c$. Since the transition acids are intermediate in strength between typical strong acids (such as hydrochloric acid) and typical weak acids (such as acetic acid) it is to be expected that their ionization equilibrium may be represented by some equation intermediate between those of van't Hoff and Ostwald. In fact, the following formula has been found to apply exactly:

$$\gamma^2/(1 - \gamma)v = k + c(1 - \gamma)/\gamma \ldots\ldots\ldots\ldots (3)$$

This is illustrated in the last columns of the tables for cyano-

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[1] At any given concentration, $\Lambda_0 - \Lambda$ decreases more and more rapidly as the strength of the electrolyte increases. Thus, for the three acids considered above, $\Lambda_0 - \Lambda$ at $v = 500$ has the (approximate) values 350, 110 and 14, respectively.

[2] Arrhenius: Meddelanden från K. Vetenskapsakademiens Nobelinstitut, 2, 42 (1913).

acetic acid and dichloroacetic acid above. The agreement between the calculated and experimental values for the dissociation constant is seen to be satisfactory throughout the entire concentration range.

For the transition acids in general, the constant c in Equation 3 is found to increase with the acidic strength, but much more rapidly. In the case of strong electrolytes, c becomes so large that k is negligible in comparison; the equation thus reduces to van't Hoff's formula. Similarly, for the weak electrolytes, c becomes so small that it approximates to zero; we are left with the dilution law of Ostwald. The relation expressed in Equation 3 above is, therefore, found to be perfectly general, representing the ionization equilibrium of acids of *all strengths* in dilute aqueous solution. Van't Hoff's formula for strong acids and Ostwald's equation for weak acids correspond to two particular limiting cases.

Similar equations have recently been brought forward by Kraus and Bray[1] and by MacDougall.[2] While it is certainly convenient to be able to represent the ionization equilibrium of all types of electrolytes in one general equation, the fact must always be remembered that such equations as have been proposed remain, at present, purely empirical. The cause of the increase in the dissociation constant of an electrolyte with increasing ionic concentration has still to be discovered. Correlation with other abnormalities observed in solutions of strong electrolytes, *e. g.*, the catalytic activity of the undissociated molecule, will no doubt ultimately lead to the solution of the problem.

The Anomaly of Concentrated Solutions

Since the expression $(1 - \gamma)/\gamma$ increases as the dilution v is decreased, we should expect to find the dissociation constant of a transition electrolyte increasing more and more rapidly, the more concentrated the solution. This, however, is not the case beyond a certain limit, as the following figures will show:

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[1] Jour. Am. Chem. Soc., 35, 1315 (1913).

[2] Ibid., 34, 855 (1912).

CYANOACETIC ACID.[1] 25° C.

v	Λ	100 k
2.102	33.61	0.395
4.205	47.30	0.407
8.41	65.2	0.408
16.82	88.0	0.400

DICHLOROACETIC ACID.[1] 25° C.

v	Λ	100 k
1	81.5	5.67
2	114.9	6.33
4	151.7	6.38
8	190.2	6.00
16	231.6	5.64

It will be seen that in both cases the dissociation constant, with increase of concentration, reaches a maximum and then *decreases*. We have here the "anomaly of concentrated solutions" coming into play; this effect is sufficient, at the highest concentrations given, not only to counterbalance the increase in k due to the high ionic concentration, but actually to cause k to decrease.

It is simpler to study the decrease of k at high concentrations in solutions where the ionic concentration effect is entirely absent. This may be done by considering concentrated solutions of a weak electrolyte; the figures for acetic acid are given below.

ACETIC ACID.[1] 25° C.

v	Λ	100 k	100 k (corrected)
0.989	1.443	0.00140	0.00184
1.977	2.211	0.00165	0.00188
3.954	3.221	0.00176	0.00188
7.908	4.618	0.00181	0.00188
15.816	6.561	0.00184	0.00187
31.63	9.260	0.00185	0.00186
63.26	13.03	0.00185	0.00186

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[1] Meddelanden från K. Vetenskapsakademiens Nobelinstitut, **2**, 38 (1913).

From the third column of this table, it will be evident that the dissociation constant is a true constant only for solutions less concentrated than $v = 16$; for higher concentrations the value obtained decreases, first slowly and afterwards more rapidly. There is a correction for the viscosity of the more concentrated solutions to be applied to these results,[1] which reduces the divergences to some extent, but a steady decrease in the dissociation constant at the highest concentrations is still evident. Further examination into the cause of these divergences is, therefore, necessary.

In the following section, the dilution law itself is critically examined and its exact theoretical basis tested. A modified form of the dilution law is tentatively proposed, which is subsequently applied to the above experimental data and found to account for the divergences up to very high concentrations.

A Modification of the Dilution Law.—The exact significance of the Ostwald dilution law will first be studied from the simple kinetic standpoint.

We have, for a uni-univalent electrolyte of the type RX, the dissociation equation,

$$RX \rightleftarrows R^+ + X^-$$

from which, by the application of the law of mass action, the dilution law is immediately obtained in the form

$$c_i^2/c_u = k \dots\dots\dots\dots\dots\dots\dots (1)$$

The reaction on the right-hand side of the dissociation equation presents no difficulty from the kinetic standpoint. The concentration of each ion is c_i, and by the impact of two ions of opposite charge the undissociated salt is formed, with the mutual neutralization of the charges. The mechanism of the equilibrium reaction on the other side of the equation, however, is by no means so clear. *A definite conception of the nature of the reaction on the left-hand side of the equation has not yet been obtained, and, in spite of the importance of the*

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[1] This correction will be found discussed in a previous paper, Jour. Am. Chem. Soc., 36, 1072 (1914).

question, it does not seem to have attracted any great attention, or to have been answered in any but the vaguest manner.

The above statement may be further emphasized by an extract from a recent communication by Walden:[1] "The greater the dielectric constant of the interposed solvent, the less is the electrostatic force (between ions of unlike charge), and with the greater difficulty does the recombination to electrically neutral molecules take place. Nevertheless, the neutral molecules will be formed in the solution. Why then do they again break up into ions? *For what reason does the neutral salt molecule break up into ions at all, as soon as it enters into solution?* This fundamental question has, up to the present, not been answered. Strangely enough, we do not even make a serious attempt at its solution."

In the dilution law, as it stands, it is tacitly assumed that the undissociated molecules RX break up *quite spontaneously* into the separate ions R^+ and X^-. The whole equilibrium is taken to be exactly analogous to that existing in gaseous dissociation, and the analogy is indeed sufficiently striking. Nevertheless, there are fundamental differences between the two phenomena of gaseous and ionic dissociation, and one is the influence of the solvent medium upon the equilibrium in the latter case. *The nature of the solvent plays an important part in determining the degree of dissociation of the dissolved electrolyte.*

The rôle of the solvent in the dissociation equilibrium (except from the point of view of the dielectric constant) has been strangely neglected by the followers of the dissociation theory of Arrhenius. The tendency has been to treat the solvent simply as so much "dead space." The upholders of the solvate theory, on the other hand, have referred all dissociation phenomena to interaction between solvent and solute.

A general, but indefinite, feeling of dissatisfaction with the present position (as is indicated above by Walden) has cer-

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[1] Jour. Am. Chem. Soc., 35, 1649 (1913).

tainly existed among the followers of the dissociation theory, and this feeling has occasionally found its way into print in well-known text-books, where definitions of electrolytic dissociation may be found which undoubtedly do not agree with the hypothesis of spontaneous dissociation of the undissociated molecule tacitly assumed above. For example, Stieglitz[1] states: "When an ionogen is dissolved in water, its molecules are immediately, more or less completely, *dissociated by the water* into smaller fragments or molecules of unlike composition." Similarly, Alexander Smith[2] writes: "The conducting power of the solution is indissolubly connected with the fact that the original molecules of the solute have been broken up by the solvent into smaller molecules containing one or more atoms." Nernst[3] states: "Der Umstand, dass gerade das Wasser die ganz besondere Fähigkeit besitzt, gelöste Stoffe electrolytisch zu spalten, legt die Vermutung nahe, dass bei der Ionenspaltung chemische Verbindungen mit dem Wasser eine Rolle spielen." Here there is not only the statement that *the solvent* splits up the dissociated molecules into the separate ions, but the possibility also is noted that, in so doing, the solvent actually combines with the solute to form hydrates and hydrated ions. Ostwald[4] himself goes so far as to say: "Das Wasser nimmt, in Bezug auf seine Fähigkeit elektrolytische Lösungen zu bilden, oder Stoffe in Ionen zu spalten, eine ausgezeichnete Stellung ein." Arrhenius[5] also speaks of "die Fähigkeit der Lösungsmittel, Elektrolyte in Ionen zu verlegen."

Now if the molecules of the undissociated salt in the solution are indeed broken up *by the molecules of the solvent* into the separate ions, then the concentration of the solvent

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[1] "Qualitative Chemical Analysis," Part I, page 41. The italics are in the original.

[2] "Introduction to Inorganic Chemistry," page 317.

[3] "Theoretische Chemie, Sechste Auflage," page 534 (1909).

[4] "Lehrbuch der allgemeinen Chemie," Vol. 2, Part I, page 705 (1893).

[5] "Lehrbuch der Elektrochemie," page 55 (1901). Also "Theories of Chemistry," page 83 (1907).

in the solution should appear in the equation of equilibrium and the simple dilution law is not valid. The equation is modified into the form:

$$c_i^2/c_u . c_s = k \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

(c_s = concentration of solvent in the solution). At moderately high dilutions c_s becomes practically constant, and the equation reduces to the simple dilution law. At higher concentrations c_s begins to diminish, since molecules of solvent are being replaced in the solution by molecules of solute.

We may write Equation 4 in the form:

$$c_i^2/c_u = kc_s$$

from which it is at once evident that the equation is *qualitatively* in accordance with the fact, shown by the results of experiment, that c_i^2/c_u is not constant at high concentration of solute, but exhibits a *decreasing* value. The validity of the equation at high concentrations may be tested *quantitatively* with the help of the density data.

This is done for acetic acid in the last column of the table given above (page 200). The values under 100 *k* are corrected by means of the ratio:

weight of solvent in one liter of pure solvent/weight of solvent in one liter of solution.

It will be seen that the values for the dissociation constant are now *really constant*, up to normal concentration of solute. Equation 4 is, therefore, found to be valid for the expression of the dissociation constant of acetic acid *in concentrated solutions*. The tables given below show that the equation is similarly applicable to other weak electrolytes.

PROPIONIC ACID.[1] 25° C.

v	Λ	100 *k*	100 *k* (corrected)
2	1.700	0.00116	0.00145
8	3.704	0.00138	0.00147
32	7.436	0.00141	0.00143

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[1] White and Jones: Am. Chem. Jour., 44, 1591 (1910).

n-Butyric Acid.[1] 25° C.

v	Λ	100 k	100 k (corrected)
2	1.730	0.00120	0.00161
8	3.891	0.00153	0.00164
32	7.902	0.00159	0.00162

The constancy of the corrected values of k for both acids is satisfactory throughout. Hence the modified dilution law may be held to apply, for these acids, up to solutions of at least half-normal concentration.

In one respect it may, at first sight, appear that the dilution law of Ostwald claims preference over the modified law advanced above, namely in its simplicity. In Equation 4 a variable factor, c_s, has been brought into the equation for the dissociation equilibrium, and this factor varies with the concentration in the desired direction for improving the constancy of k at high concentrations. Hence it may seem that the introduction of the variable factor c_s into the equation is simply a mathematical trick, which improves the agreement with the experimental results only by destroying the original simplicity of the dilution law. If this were indeed so, then the generally accepted theoretical basis lying behind the dilution law of Ostwald (the assumption of spontaneous dissociation of the undissociated molecule) could not legitimately be called into question here.

An exact thermodynamic examination shows, however, that the original simplicity of the dilution law is not sacrificed by the modified view taken of the nature of the ionization equilibrium, but that the dilution law has, on the other hand, *actually become less complicated,* inasmuch as certain simplifying assumptions, necessary for the development of the equation in its original form, may now be dispensed with.

This examination[2] cannot be given in full here, but the general results may be summarized as follows:

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[1] White and Jones: Am. Chem. Jour., 44, 1591 (1910).

[2] Jour. Am. Chem. Soc., 36, 1076 (1914).

(I) The Ostwald dilution law in its original form leads to the equation $\Lambda^2/\Lambda_0(\Lambda_0 - \Lambda)v = k$; but this equation can, in any case, represent the ionization equilibrium accurately only in solutions of such dilution that the regions of solvent influenced by each molecule of solute are independent.

(II) The thermodynamic derivation of the dilution law in its modified form leads to the equation $\Lambda^2/\Lambda_0(\Lambda_0 - \Lambda)v' = k$ (v' is the dilution of the solution, expressed in *weight* units of concentration). This equation will represent the ionization equilibrium accurately *at all concentrations*.

The modified form of the dilution law possesses therefor, at high concentrations, the two advantages of *simplicity* and of *agreement with the experimental data*. As regards the change from volume concentrations (equivalent weights of the solute per fixed *volume of solution*) to weight concentrations (equivalent weights of the solute per fixed *weight of solvent*) it may be stated that the latter method of expression is preferable from a theoretical viewpoint, and that its general adoption in several branches of physical chemistry, closely related to equivalent conductivity, has already furnished important results.

In the concluding section of this paper, the mechanism of the ionization process and the role of the solvent in the ionization equilibrium will be more closely examined.

The Role of the Solvent in Ionization

In correspondence with the view that the dissociation of the undissociated molecule RX into its component ions R^+ and X^- is brought about by impact with molecules of the solvent, the equation representing the process of ionization may be written:

$$RX + (H_2O) \rightleftharpoons R^+ + X^-$$

It will appear at this point that the above equation is incorrectly stated, inasmuch as it does not balance. (As a matter of fact, the corresponding equation for the original dilution law also does not balance, since the ionic charges appear only on one side.) A simple explanation can be given: the solvent is not considered as acting *chemically* in the ionization equation written above. The part played by the solvent in the process of dissociation is to be regarded as entirely physical in its nature, the action of the solvent molecules being ascribed to their *unsaturated character*.

The ionizing power of a solvent is intimately connected with its power of association into large molecules. All highly-ionizing solvents are known to be unsaturated; for example, water contains an unsaturated oxygen atom with two free valences, and the simple molecule may be written $H_2O^{\pm}$, a valence consisting of a unit charge, positive or negative, on the atom. Hence, by the loss of two free valences (the positive charge on one oxygen atom being neutralized by the negative charge on another) two simple molecules can combine to form a complex molecule $+OH_2.H_2O-$. Such association can evidently continue further, each step being accompanied by the loss of two free valences. The association equilibrium may be represented, therefore, by a series of equations of the type:

$$(H_2O)_n^{\pm} \rightleftharpoons (H_2O)_{n-1}^{\pm} + (H_2O)^{\pm}$$

Stieglitz[1] has remarked in this connection: "One can readily see that such (associated) molecules would be *electrically polarized*, and their charges might easily have the *power to cause electrolytic dissociation or ionization.* The larger the associated molecule, the further apart might be the positive and negative charges upon it: the further apart the charges, the smaller would be their mutual attraction: and the smaller the mutual attraction, the stronger, presumably, would be the dissociating power of such a molecule."

This view of ionization is clearly in accordance with that developed in the preceding pages. The molecules of the solvent induce ionization on impact with molecules of the undissociated solute by virtue of their *free valences*, and act simply as *a means of supply of the electric charges.* To the two free valences attached to each molecule of the solvent, Walden[2] has given

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[1] "Qualitative Chemical Analysis," Part I, page 65.

[2] Jour. Am. Chem. Soc., 35, 1661 (1913).

the convenient name "neutron" and the notation ⊕ ⊖. The equation representing ionization may now be expressed in the form:

$$RX + \oplus\ominus \rightleftharpoons R^+ + X^-$$

This equation balances exactly. Since, however, the ionic charges are supplied to the undissociated molecules directly by the molecules of the *solvent*, the concentration of the latter is the factor that must appear in the equation of equilibrium: $c_i^2/c_u.c_s = k$. This equation will hold so long as the concentration of "neutrons" in the solution is proportional to the concentration of the solvent, *i. e.*, until the degree of association of the solvent is appreciably changed by excessive addition of solute.

We have now a simple means of expressing the mechanism of electrolytic dissociation. By impact of an undissociated molecule of the solute, RX, with a molecule of the solvent, a "neutron" is transferred from the latter to the former, and the undissociated salt breaks up into its separate ions R^+ and X^-. Similarly, by impact between ions of unlike charge, R^+ and X^-, a molecule of the undissociated salt RX is formed, with the liberation of a "neutron," which is transferred to a molecule of the solvent. The solvent molecules thus lose and gain "neutrons" alternately, just as in their own association equilibrium.

Non-associated solvents, which possess no free valences, do not dissociate salts dissolved in them. All ionizing solvents have the two characteristic properties of *unsaturation* (presence of "neutrons") and *association*. The above view of the mechanism of the dissociation process is evidently perfectly in accordance with these facts, and may even be considered as, in some measure, furnishing an explanation of their general validity.

Summary

The divergences from the dilution law exhibited by acids in aqueous solution have been critically investigated.

The *increase* in the dissociation constant when the *ionic* *concentration* is large is found to be represented quantitatively by the equation: $\gamma^2/(1 - \gamma).v = k + c(1 - \gamma)/\gamma$. This empirical formula is applicable to acids of all strengths.

The *decrease* in the dissociation constant when the *total concentration* is large is found to disappear under the assumption that ionization is not spontaneous, but induced by the solvent. The legitimacy of this assumption has been discussed, and the experimental data shown to be in its support. The dissociating power of the solvent is ascribed to its unsaturated character, *i. e.*, to the presence of free valences.

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EXPERIMENTS ON EMULSIONS: ADSORPTION OF SOAP IN THE BENZENE-WATER INTERFACE

BY T. R. BRIGGS

Introduction

The Gibbs equation, $u = -c/RT.d\sigma/dc$, expresses the relationship between the surface tension of a solution and the distribution of the solute between the body of the solution and the interfacial film. If the surface tension, σ, of the pure liquid is *lowered* by the addition of a given solute, since $d\sigma/dc$ is then a negative expression, u (the excess of solute in the surface film) becomes positive and the surface layer becomes richer, with respect to the dissolved substance, than the body of the solution. On the contrary, when the surface tension is *raised* by a solute, the latter is more or less squeezed out of the interfacial film and its concentration in the interior of the liquid is correspondingly increased. Both of these effects are in accordance with the principle of Le Chatelier.

Corollaries to the above are at once suggested. Consider the case where the surface tension is raised by the solute. The latter is forced out of the interface to a certain extent, but since the concentration of the disturbing factor in the surface film is thereby reduced, the increase in the surface tension is somewhat lessened. The final equilibrium is a balance between the two opposing tendencies—the increase of the surface tension by the solute and the expulsion of the latter from the surface film. One should expect a *gradual* increase in the surface tension as the amount of dissolved substance becomes larger: experiment has demonstrated the correctness of this deduction.

As the great majority of the organic solutes and especially the emulsion colloids tend to lower the surface tension of the pure solvent, this case is of most interest to us. Here the surface effects lead to a concentration in the interface and equilibrium results from the sum of the two actions—lowering of the tension and increase of solute in the surface—which are no longer opposed as they were in the previous case. By reason of the enormous bulk of the liquid in comparison to the surface layer, we should expect to find mere traces of organic impurities exerting a marked effect upon the surface tension of a liquid, the latter decreasing rapidly at first with a small increase in the concentration of the dissolved substance and thereafter remaining more or less independent of the solute present. Experiment has amply confirmed this deduction as well.

Ordinary adsorption is believed usually to be the result of condensation of a solute or disperse phase upon the surface separating a solid from a liquid. It may take place, according to the above theory, when the tension of the interface between liquid and solid is lowered; if the opposite occurs the solute will be squeezed out of the surface and we shall have a case of *negative adsorption*.

Condensation of a dissolved substance in the interface of two immiscible phases—liquid-vapor or liquid-liquid—is to be considered as adsorption in the general sense. Since the aggregate result produced by adsorption is directly proportional to the specific surface,[1] where the latter is great adsorption plays an important rôle. To study adsorption by a liquid-vapor interface, one should employ *foams*, or *emulsions* of two non-miscible liquids for the case of liquid-liquid. A brief summary of the work done along these paths will be given.

As regards foam, attention will be called to the numerous papers of G. Quincke and especially of Lord Rayleigh, whereby the subject has been developed very completely. Foams owe their existence as more or less stable structures to the formation of viscous, often semi-solid, films on the air-liquid interface, and these films are produced by surface condensation of dissolved impurities, the actual amount of which is often vanishingly small. Indeed "a pure liquid does not foam" and a liquid does so only when it contains a third substance which

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[1] Cf. Wo. Ostwald: "Grundriss der Kolloidchemie," 1909.

lowers its surface tension against air and so forms a viscous film by adsorption in the interface.

Metcalf[1] has described the production of semi-solid films on solutions of peptone and Rohde[2] has found that certain dyes in solution behave similarly. Ramsden[3] was able to coagulate a number of colloidal solutions (especially of albumens) by shaking them up with air so as to produce a very great development of foam. Under these circumstances, the dissolved substances become highly concentrated in the air-water interfaces and irreversible changes leading to permanent coagulation at once ensued, analogous, in the case of albumen, to the irreversible coagulation caused by heat.

Hall[4] observed that the foam from a sodium oleate solution is richer in dissolved substance than the body of the liquid, and Miss Benson[5] found that a like behavior was shown by foaming aqueous amyl alcohol solutions. Zawidzki[6] has measured the concentration of saponine in the foam from its solution, following the course of events by refractometrical measurements.

Quantitative verification of the Gibbs equation applied to condensation in an air-liquid interface has been attempted by Milner,[7] who bubbled air through sodium oleate solutions and measured the change in concentration by the conductivity, finding about 0.4 mg adsorbed per square meter of surface. This result differed widely from that calculated from the Gibbs equation. A recent research by Donnan and Barker[8] with nonylic acid and saponine solutions was more encouraging but still left much to be desired.

The case of the interface between two immiscible liquids

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[1] Zeit. phys. Chem., **52**, 1 (1905).

[2] Drude's Ann., **19**, 935 (1906).

[3] Du Bois Reymond's Archiv., 1894, 517; Zeit. phys. Chem., **47**, 336 (1904).

[4] Proc. Roy. Soc. Dublin, **9**, 56 (1899).

[5] Jour. Phys. Chem., **7**, 532 (1903).

[6] Zeit. phys. Chem., **35**, 77 (1900); **42**, 612 (1903).

[7] Phil. Mag., (6) **13**, 96 (1907).

[8] Proc. Roy. Soc., **85A**, 557 (1911).

is similar to the preceding. If a substance dissolved in liquid A is insoluble in liquid B, and also *lowers* the surface tension of A against B, Gibbs' law requires that the solute should concentrate in the A-B interface. Examples of such surface condensation are known.

W. C. McC. Lewis[1] has measured the interfacial condensation of sodium glycocholate (bile salt), congo red and methyl orange, using emulsions of oil in aqueous solutions of the above substances. The adsorption observed was about 60 times that calculated from the Gibbs equation, the colloidal nature of the solutions mentioned no doubt being one reason for this discrepancy. Better results were obtained with caffeine and with aniline adsorbed from aqueous alcohol solution by liquid mercury,[2] except that in these cases the amount actually adsorbed was rather small.[3]

Winkelblech[4] has described experiments analogous to those of Ramsden wherein he was able to coagulate and precipitate colloidal solutions by shaking these up with nonmiscible oils, such as benzine, benzole, chloroform, carbon bisulphide, etc. Gelatine solutions were especially sensitive to such treatment; 10 cc of a gelatine solution containing only 0.06 mg of solid became visibly turbid and opalescent when shaken with pure benzine. The accepted explanation is surface condensation and formation of solid films about the drops of oil, with concomitant irreversible changes of state.

Since colloidal solutions are usually regarded as heterogeneous systems, the substance in solution may be considered as a third liquid or solid phase, in the experiments of Winkelblech. The behavior of a third liquid phase between two others (all being mutually immiscible) has been discussed by Freundlich[5] and the case of particles of a solid phase existing in contact with two immiscible liquids has been treated by Reinders[6]

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[1] Phil. Mag., (6) 15, 499; 16, 466 (1908).

[2] Lewis: Zeit. phys. Chem., 73, 129 (1910).

[3] Cf. Donnan and Barker: Proc. Roy. Soc., 85A, 557 (1911).

[4] Zeit. angew. Chem., 19, 1953 (1906).

[5] Kapillarchemie, 136 (1909).

[6] Zeit. Kolloidchemie, 13, 235 (1913).

the theory in both cases being based upon the equilibrium between the three different surface tensions existing. Reinders' experiments have an interesting bearing upon the oil-flotation methods employed in concentrating sulphide ores, as well as upon Winkelblech's work, and upon emulsions in general.[1]

Freundlich[2] has pointed out the relationship between Gibbs' law and the "adsorption isotherm" $x/m = \alpha c^{1/n}$. He shows that, in the case of Rohde's experiments with dye solutions against air, the concentration of the dye in the surface varies with the amount of dye in solution according to the equation

$$\phi = \alpha c^{1/p}$$

where ϕ is the solidity of the surface film (considered proportional to the concentration of dye in the surface). Adsorption by a liquid-vapor interface is thus analogous to that by a solid in liquid or vapor and is apparently governed by the equation of the isotherm in its usual form.

Adsorption by a liquid interface has been studied by Patrick[3] in Freundlich's laboratory. The author measured the surface tension of mercury against solutions of mercurous sulphate, salicylic acid, picric acid, neufuchsin, morphine hydrochloride and caffeine of varying concentration. He also determined the adsorption of the same by mercury. In the above series, the surface tension of mercury was lowered most by mercurous sulphate and least by caffeine; likewise the sulphate was adsorbed to the greatest extent and the caffeine least. No quantitative relation between surface tension and adsorption was found, however, but the adsorption by the liquid mercury was found to follow the ordinary course, the isotherm having the usual somewhat parabolic form. Other cases where the isotherm has been worked out for a liquid-liquid interface are unknown to me.

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[1] See also Bancroft: Jour. Phys. Chem., 16, 177 (1912) et seq.; Hillyer: Jour. Am. Chem. Soc., 25, 513 (1903); Donnan: Zeit. phys. Chem., 31, 42 (1899).

[2] Kapillarchemie, 1909, and Zeit. Kolloidchemie, 3, 212 (1908).

[3] Zeit. phys. Chem., 86, 545 (1914).

The purpose of the following experiments was to determine the concentration changes occurring in the aqueous phase of soap-water-benzene emulsions. Since it is now universally accepted that the stability and existence of an emulsion of the above type lies in the production of a viscous, semi-solid film of soap about the globules of benzene, it ought to be possible to measure the quantity of soap required by this process and to discover what dependence this value may have upon the amount of soap in the body of the solution. Furthermore, since the behavior of a solute with regard to a liquid-liquid interface seems to follow the Gibbs-Freundlich adsorption rule, one ought to be able to work out the "adsorption isotherm" between the amount of soap adsorbed by unit quantity of benzene, and the concentration of the soap in solution.

The gist of these introductory remarks may be stated as follows: The Gibbs law affords a valuable qualitative rule regarding surface tension and adsorption, and the latter phenomenon is known to occur at liquid-vapor and liquid-liquid interfaces, as well as at those of solid-vapor and solid-liquid. Film formation plays a leading role in the process of emulsifying an oil in soapy water and the object of these experiments is to ascertain the amount of soap required in the production of such protective films.

Experimental

Briefly summarized, the following procedure was employed in the experiments to be described: sodium oleate solutions of widely varying composition were prepared and equal volumes of each solution were shaken with a fixed amount of distilled benzene in glass-stoppered bottles until emulsification was complete, after which the emulsions were allowed to stand until the benzene globules floated to the top in a well-defined layer. With the aid of a pipette, a sample of the *lower* aqueous layer of each emulsion was withdrawn for analysis and a comparison made between the alkali content of this sample and that of an equal volume of the corresponding original soap solution, this comparison being made by titration with approximately $N/20$ hydrochloric acid and methyl orange as indicator. In every case it was found that the soap content (as measured by the alkali number) of the original oleate solutions was greater than that of the excess aqueous layer of the emulsion, volume for volume, so that, granting that the decrease in concentration was due to adsorption of sodium oleate in the benzene-water interface, this decrease was a measure of the amount of soap adsorbed. While *absolute* measurements were not obtained, for reasons to be discussed later, nevertheless comparative data were found possible and very interesting.

Reagents, Solutions, etc.—The sodium oleate employed was of good quality and contained no free alkali, according to tests made by Mr. H. G. Carter in this laboratory. The distilled water used in preparing the oleate solutions was carefully saturated with benzene; likewise the benzene used in the emulsions was saturated with water previous to employment. The benzene was recovered from previous emulsification experiments by decomposing the creamy emulsions with dilute sulphuric acid, distilling the benzene over, drying the distillate over calcium chloride and again rectifying. Fifty cubic centimeters of the benzene so recovered were shaken with an equal volume of water and the latter tested for acidity or alkalinity; a neutral test confirmed the suitability of the benzene for the required purpose.

In preparing the different solutions of sodium oleate, a stock solution was first made up by heating 50 g of the dry oleate with about 500 cc of distilled water on a steam bath, until a rather viscous, brownish solution resulted, whereupon the solution was filtered by suction. A known volume of the cold stock solution was then made up to 500 cc in a measuring flask, stoppered and set aside—in this way solutions of the desired approximate composition were quickly obtained. These solutions kept well for periods of several days, but, on longer standing, appreciable decomposition by hydrolysis occurred and flocks of the difficultly soluble acid oleate settled to the bottom of the flask.

Approximately $N/20$ solutions of NaOH and HCl were prepared. The former was compared with a standard $N/10$ HCl reagent, 1 cc containing 0.00207 g NaOH. By comparison of this reagent with the $N/20$ HCl, 1 cc of the latter was found equivalent to 0.00207 g NaOH, or to 0.01576 g sodium oleate.

Procedure.—Having prepared the stock solution of sodium oleate described above, the following test solutions were made up in 500 cc flasks:

Number of solution	Stock oleate in 500 cc solution cc
1	5
2	10
3	25
4	50
5	100
6	150
7	180

Seven 250-cc glass-stoppered bottles were carefully cleaned, dried and marked 1, 2, 3, etc., to correspond with the above soap solutions. Into each bottle 60 cc of the proper soap solution were poured, after which 90 cc of benzene were added gradually and with constant shaking until the emulsification was complete; thereupon each bottle was given five minutes' extra shaking, all of the latter being done by hand. The bottles were then set aside for a day, until the emulsified contents had separated into the usual two layers[1]—an upper "cream" of emulsified benzene and a fairly clear, lower layer containing no measurable amount of the latter substance. The separation complete or nearly so, a sample of the lower layer was removed for comparison with the original soap solution to which it corresponded, in order to determine the change in composition brought about by adsorption of the solute

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[1] Cf. F. R. Newman: Jour. Phys. Chem., **18**, 34 (1914).

(sodium oleate) in the benzene-water interface. This removal was done without disturbing the upper creamy layer, by fixing a long and fine drawn-out capillary, proboscis-like, to the end of a 10 cc pipette, and carefully extracting a sample in this fashion. The capillary and pipette were first rinsed with a little of the original soap solution in the measuring flask and allowed to drain; by this means drying the pipette was avoided with the introduction of only an infinitesimal error.

The accurate determination of the soap content of each solution was a very troublesome problem. It was proposed to follow the usual methods and to decompose the sodium oleate with standard acid (in this case $N/20$ HCl) using methyl orange as indicator. Although this mode of analyzing soap solutions gave results which were satisfactory enough when measured by the standards of ordinary analysis, yet the method was not sufficiently sensitive to detect the small changes in composition met with in these experiments. In the first place, methyl orange is not the easiest indicator to work with even under normal conditions and in the second place, especially when dealing with the stronger oleate solutions (Nos. 3 to 7 inclusive), the oleic acid set free by the interaction of soap and mineral acid remained in suspension in the form of a persistent emulsion, the milky turbidity of which masked the color change at the end point entirely. As a result, duplicate analyses failed to agree with a closeness sufficient to warrant any serious deductions being drawn from them. Nor did other indicators give results better than those afforded by methyl orange and it became evident that a special procedure had to be devised.

Accordingly, determination of the absolute quantity of soap in unit volume was abandoned and comparative results alone were sought. To this effect, 10 cc of a given soap solution and an equal volume obtained from the lower layer of the corresponding emulsion were decomposed with standard acid, under identical conditions, and a comparison made of the number of cubic centimeters of acid required to bring each solution to *exactly the same shade of color*, using methyl orange as indicator. The data obtained by this method proved to be entirely satisfactory. The procedure follows:

Into a 250 cc Erlenmeyer flask, 10 cc of a given original soap solution (say No. 1) were pipetted (the same pipette being used throughout the work), 50 cc of distilled water were added and 1 cc of a solution of methyl orange. Standard hydrochloric acid was then run in slowly from a scrupulously clean burette until, as nearly as could be judged, the end point was reached. One or two drops more of acid were then added, usually imparting a suggestion of pink to the milky liquid in the flask. The reading of the burette was done with great care, by estimating volumes to 0.01 cc and allowing carefully for drainage. The temperature was likewise noted and all end-point observations were made against a background of white.

The flask, after completion of the titration, was carefully set aside to serve as a standard for comparison and a second and similar flask taken. Following the procedure noted above, a 10 cc sample was extracted from the lower layer of the corresponding emulsion (in this case supposed to be No. 1), and 50 cc of water were added together with 1 cc of indicator solution. Acid was run in very slowly until the appearance and color of the liquid in the second flask corresponded *exactly* with that of the solution in the first flask which served as the standard end point for color comparison. The color comparison could be made with great accuracy —certainly to within one drop (0.04 cc) of $N/20$ hydrochloric acid. This done, the burette was read.

A second burette was filled with standard $N/20$ sodium hydroxide reagent, previously compared with the acid as described. The reading taken, an unknown volume of alkali was added to the solution in the flask until the latter was strongly alkaline. Following the procedure of the last paragraph, the comparison was again made with the standard end point and acid added until the color difference disappeared.

Reading of both acid and alkali burette was carried out. The readings are as follows:

(*a*) *Comparison of standard acid and alkali:*

1 cc NaOH = 0.998 cc HCl

(*b*) *First titration of emulsion with standard acid:*

	cc
Sample of aqueous layer taken for analysis	10
Reading of HCl burette after titration	28.14
Reading of HCl burette before titration	14.81
Acid required (*a*)	13.33

(*c*) *Back titration:*

	cc
Reading of burette after adding alkali	7.81
Reading of burette before adding alkali	6.70
Alkali added	1.11
HCl equivalent to NaOH added	1.11
Reading of acid burette after second titration	29.26
Reading of acid burette before first titration	14.81
Total acid required	14.45
Less HCl equivalent to NaOH added	1.11
Acid required (*b*)	13.34
Acid required (*a*)	13.33
Average	13.34

Ten cc of the original solution, used as the standard of comparison in the above titration, required 13.83 cc of standard acid. A second sample, analyzed exactly like the emulsion above, required 13.79 cc HCl. The average thus becomes 13.81 cc HCl. The change in composition of the outside phase by removal of sodium oleate is accordingly proportional to the difference 13.81 — 13.34, 0.47 cc HCl.

Experiments with Hand-shaken Emulsions.—The following set of emulsions was prepared, using the solutions and volumes stated below:

Bottle marked	No. of solution	Vol. oleate cc	Vol. benzene cc
2	2	60	90
3	3	60	90
4	4	60	90
5	5	60	90
6	6	60	90
7	7	60	90

The emulsions were prepared according to the method already described and were allowed to stand over night. After about 24 hours the lower aqueous layer had become sharply defined in every case and was more or less clear. It is interesting to note in this connection that the line of demarcation between the lower aqueous layer and the superimposed creamy emulsion was sharpest in the case of the strongest soap solution (No. 7) and least sharp in the case of the dilute solution (No. 3). Likewise the lower layer was perfectly clear in the case of (No. 7), while the dilute oleate gave an emulsion whose aqueous layer showed a persistent and distinct turbidity. The data follow:

TABLE: HAND-SHAKEN EMULSIONS

Volume of Soap Solution, 60 cc; Volume of Benzene, 90 cc; 10 cc of Soap Solution Required:—

Emulsion No.	Originally cc HCl	After emulsification cc HCl	Difference cc HCl
2*a*	1.01	0.85	0.16
2*b*	1.02	0.95	0.07
3	2.38	2.29	0.09
4	4.46	4.32	0.14
5	9.31	9.08	0.23
6	13.78	13.55	0.23
7	16.87	16.60	0.27

Examination of the above data convinces one at once that the act of shaking a solution of sodium oleate with benzene and the consequent formation of an emulsion of the latter, results in extracting a certain amount of the soap from the solution (now become the outside phase of the emulsion) and increasing the dilution of the latter. Although the data are rather irregular, it is apparent that there is a gradual increase in the quantity of soap removed as the concentration of the latter is increased through a wide range—yet the removal is not proportional to the strength of the oleate solutions, but tends to approach a maximum as the concentration rises. This behavior is shown by the dotted curve in Fig. 2, where the ordinates are the numbers given under "difference" in the above table and the abscissae are the values of the equilibrium concentration of soap in the aqueous phase of the emulsions, measured in cc of standard HCl.

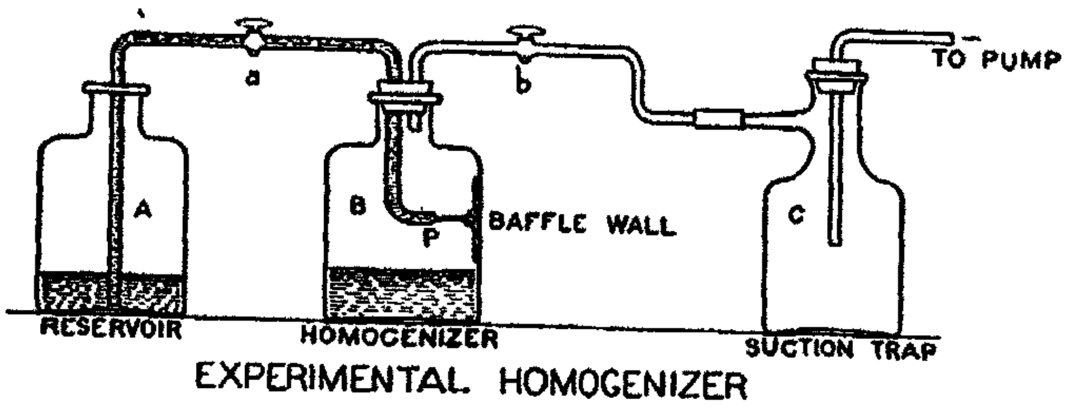
Returning to the table of data, one observes a great difference between emulsions 2*a* and 2*b*, with respect to the amount of soap adsorbed. The discrepancy is decidedly greater than the error of experiment, which is extremely small when the concentration of oleate is low, because the distinctness of the end point under these circumstances enables one to make very accurate titrations. The two emulsions, however, were not produced under the same conditions. The first one (2*a*) was prepared with difficulty, owing to the benzene being added too rapidly during the shaking, and required very much longer agitation than did any other of the series. Other things being equal, since adsorption is a surface phenomenon, the smaller the globules of benzene in a given emulsion, the greater will be the removal of soap from the outside phase. Therefore, that a comparison of emulsions may be of value, it is required that they contain the disperse phase in globules of uniform size; if this condition is not satisfied, discordant results must be expected.

Microscopic examination was then resorted to, and it was found that in every case the globules of benzene were irregular in size and comparatively large, except that the globules of

2*a* were much smaller and rather more uniform. No doubt this observation accounts for the discordantly high value for the soap removed from solution in the case of this emulsion.

Such observations led to two obvious conclusions—first, some means had to be devised to increase the uniformity of a series of emulsions as regards the size of the globules; and secondly, the globules themselves had to be made as small as possible, so that, by increasing the oil-water interface, the soap adsorbed by unit volume of benzene might be made larger. The emulsions were accordingly put through a process of "homogenization."[1]

The apparatus employed in homogenizing the crude benzene emulsions is shown in Fig. 1. A and B are clean and dry liter bottles; C is a filter-flask serving as a safety-trap between the apparatus and a large suction-pump while the rest of the apparatus consists of glass tubing arranged according to the diagram. The usual emulsion, prepared by hand shaking, is poured into reservoir A, stopcock *a* is turned off, and, by opening the cock at *b*, the stoppered chamber B is connected with the pump and evacuated as much as possible.



EXPERIMENTAL HOMOGENIZER

Fig. 1

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[1] This term has long been applied to the process of disintegrating the globules of emulsified fat in milk, by subjecting the latter to mechanical treatment. The milk is pumped at high pressure through narrow orifices and against revolving baffle plates, so that the tiny fat globules are shattered. This process results in increasing the degree of dispersion of the fat throughout the menstrum, to such an extent that the cream will no longer rise in milk that has been so treated. For particulars regarding "mulsers" and "homogenizers" see Pharm. Journal, (4) 36, 734 (1913).

Cock *a* is then opened and the emulsion is sucked through the connecting siphon, whence it emerges from the orifice P, approximately 0.5 mm in diameter, in a horizontal stream. The latter impinges violently upon the inner wall of the bottle and this, serving as a baffle plate, brings about the gradual disruption of the globules in the emulsion. Finally, when reservoir A is emptied, cock *b* is closed and A and B are interchanged, whereupon the process is repeated until the desired result is obtained. In my experiments, each emulsion was forced through the apparatus at least eight times and then examined under a microscope with attached micrometer eyepiece, whereby the diameter of the globules was estimated by direct measurement.

A number of preliminary experiments were carried out with the help of this homogenizing apparatus. An emulsion, prepared from equal volumes of dilute sodium oleate and of benzene, was divided into two portions, one of which was homogenized. A striking diminution in size of the particles occurred. Of the benzene globules, the great majority were under 5μ in diameter and, indeed, there were plenty smaller than 1μ, and showing the Brownian movement most strikingly. Few globules exceeding 10μ in width; the general effect was one of marked uniformity. On the other hand, the original, hand-shaken emulsion contained particles of widely varying size; most of these were 25μ in diameter or over, though there were present some extremely small globules as well. It was difficult to measure the real size of the large globules, owing to their being squeezed flat under the cover glass; and besides, these hand-shaken emulsions decomposed very quickly while under observation. On the homogenization being carried still further, the size of the globules was reduced until the average diameter fell to about 2–3μ, or even less.

The homogenized emulsion was compared with samples of three different fresh milks and a striking similarity in appearance was observed, the globules of the artificial emulsion being, if anything, smaller than those of the natural ones and very much more abundant. To compare the benzene emulsion with milk under the microscope, the former had first to be diluted strongly with distilled water.

Homogenization produces an interesting effect upon the appearance of benzene emulsions to macroscopic observation. In the case under discussion, as the homogenization was continued, the milky opacity of the emulsion increased, rapidly at first, then slowly. This change in external appearance is an indication of the increased dispersion of the benzene phase. Likewise, the emulsion became more and more viscous, though no measurements of this property were made.

As one might expect, the stability of an emulsion is tremendously enhanced by homogenization. Whereas in my experiments with hand-shaken emulsions two hours' standing was sufficient to complete the separation into the characteristic two layers—aqueous layer and cream—it was found that this separation, in the case of the homogenized emulsions, was far from complete even after 24 hours. In some cases the aqueous lower layer was strongly turbid even though no globules of benzene could be detected under powerful magnification. In short, homogenization actively retards the *creaming* of an emulsion, which is exactly the effect that the process has upon ordinary milk. It would be interesting to study the effect produced upon artificial emulsions by a powerful commercial "homogenizer."

A set of seven emulsions was then prepared and given careful treatment with the homogenizer. Examination of the emulsions while the latter were still fresh showed that the particles were very nearly uniform in size and fairly small (5-10μ diam.). On standing twenty-four hours the size of the globules increased somewhat and their uniformity became less. Another interesting circumstance was observed at this time. In preparing the slides, a very small amount of the emulsion under consideration was stirred into a drop of distilled water and the whole covered with a cover-glass. In the case of the emulsions containing dilute sodium oleate, the benzene globules were to be seen distributed fairly uniformly throughout the drop of water, whereas, when the concentrated solution formed the external phase, the globules tended to agglomerate—to form distinct clusters, very much like bunches of grapes, with clear liquid between. This may explain the fact, several times observed in my experience, that separation of the two layers (cream-formation) seemed to occur more rapidly with those emulsions in which the soap concentration was high.

These homogenized emulsions were set aside for 22 hours. At the end of this time Nos. 5, 6 and 7 showed perfectly clear lower layers; the others were slightly turbid, especially No. 3. Exactly the same phenomenon, only to a less extent, had already been observed while studying the hand-shaken emulsions. By employing the capillary pipette already described, 10 cc samples of the aqueous layers were removed for analysis, as in the previous experiments. The data follow:—

Table: Homogenized Emulsions

Soap Solution, 60 cc; Benzene, 90 cc; 10 cc of Soap Solution Required:—

Emulsion	Originally cc HCl	After emulsification cc HCl	Difference cc HCl
1	0.54	0.38	0.16
2	1.02	0.75	0.27
3*a*	2.40	1.98	0.42
3*b*	2.39	2.05	0.34
4*a*	4.47	4.10	0.37
4*b*	4.43	3.97	0.46
5	9.25	8.79	0.46
6	13.81	13.34	0.47
7	17.01	16.50	0.51

As in the case of hand-shaken emulsions, a curve was drawn using the numbers under "difference" in the above table as ordinates and those in the third column from the left as abscissae. It will be noticed that this curve (the heavy line in Fig. 2) lies entirely above the one corresponding to the hand-shaken emulsions. Homogenization acted as a great stimulus to adsorption.

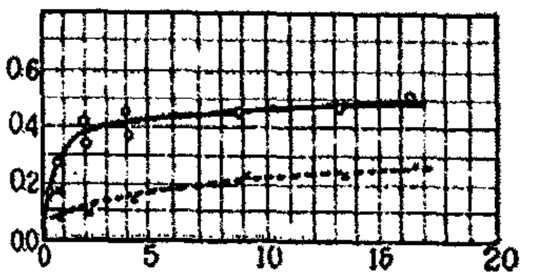

Fig. 2

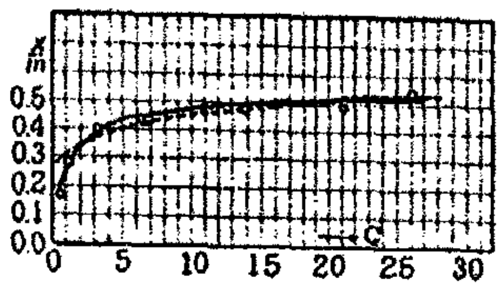

Fig. 3

Discussion of Results

The data, though not very complete and a bit wobbly in places, show that sodium oleate solutions decrease in alkali content by being shaken up with benzene. It is assumed that the decrease in alkali content is a measure of the sodium oleate extracted.[1]

What is the cause of this extraction? Suppose one considers the possibilities.

(*a*) *The Soap Solution Becomes Diluted with Dissolved Benzene.*—This theory may be dismissed at once. Not only is the benzene practically insoluble (immiscible) in sodium

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[1] There is the possibility that this assumption is inaccurate, but this would be without effect upon the general results of this paper. For it is quite probable that the hydrolytic production of the difficultly soluble *acid* sodium oleate is an important factor in emulsification. (S. U. Pickering: Jour. Chem. Soc., 91, 2013 (1907).) Pickering writes: "With soap, the particles requisite for emulsification are also provided in another way; for when soft soap is dissolved in much water..........a considerable amount of a very fine deposit is obtained and this is often in such a minute state of division that it remains suspended in the liquid for weeks."

It may be that the peculiar stability of soap emulsions is due to surface films of the insoluble acid oleate, the minute particles of which are more or less cemented together with neutral salt, the whole forming an unusually strong membrane, not unlike the rubbery "haptogen membrane" of the fat globules in milk. If this be the case, the mass of soap adsorbed would be greater than that calculated on the basis of *neutral* sodium oleate.

Furthermore, another factor must be taken into consideration. In calculating the amount of soap adsorbed by unit volume of benzene the assumption is made that this is extracted as *anhydrous* sodium oleate. This is very probably not the case. The soap in the benzene-water interface is almost certainly in a hydrous condition, so that the amount of sodium oleate removed from the aqueous dispersion-medium is not a true measure of the adsorptive power of the disperse phase. The total adsorption in the interphase is probably greater than these experiments indicate.

oleate solution but the water used in preparation of the latter was previously saturated with benzene, as described.

(*b*) *Sodium Oleate Dissolves in Benzene.*—Under these circumstances one should observe a distribution of the solute between the two solvents according to Henry's law, so that, assuming that the soap exists in both solvents in the same molecular condition, the amount removed by a fixed volume of benzene should be proportional to the equilibrium concentration in a fixed volume of soap solution. Experiment shows that this is not the case.

Moreover, the distribution of the soap between the two solvents should be dependent, among other things, only upon the *total volume* of the benzene globules and not upon the *average size* of these globules, equilibrium being reached. According to the solution theory then, homogenization and the accompanying increase in the surface separating the phases, should have little or no effect upon the distribution of sodium oleate between the two solvents, except to hasten the production of equilibrium; whereas experiment shows that a greatly increased removal of soap by benzene accompanies homogenization. It should be observed at this point that loss of both benzene and water probably occurred during the process of homogenization, owing to evaporation at reduced pressure, but this process can only tend to make the aqueous medium of the emulsion richer in sodium oleate and so to act in a sense opposed to the surface forces.

Furthermore, some experiments by Mr. Carter, in this laboratory, throw light upon the question. Certain emulsions upon analysis were set aside and, after a considerable period, were found to have "cracked" and very nearly de-emulsified. The lower aqueous portion of the "cracked" product was analyzed and found to be identical in composition with the original solution, the soap required by the benzene globules having been returned to the solution on the collapse of the emulsion. Other emulsions were destroyed by freezing and similar results obtained. The removal of soap from solution is contingent upon the production of an emulsion, and not upon the presence of a layer of benzene as solvent.

Direct tests of the solubility of sodium oleate in benzene showed that it is small enough to be negligible.

(*c*) *Sodium Oleate is Adsorbed by the Benzene-water Interface.*—Most of the experimental observations are in accord with this theory and, qualitatively at least, the results of this paper establish the rôle of adsorption in the production and existence of emulsions. Moreover, the quantity of soap removed by the benzene is a function of the area of the benzene-water interface, as the homogenized emulsions clearly indicate. By homogenization, the size of the benzene globules was decreased and the specific surface of the latter augmented sufficiently to double or even treble the quantity of soap extracted by unit volume. The quantitative determination of the relation existing between the specific surface and the amount adsorbed was not carried out.

In the case of the homogenized emulsions, the curve between soap extracted and its concentration in the solution bears a striking resemblance in form to the graph of the adsorption isotherm.[1] Viewed quantitatively, however, the results are less satisfactory, chiefly because unavoidable circumstances prevented the more complete mapping out of the curve, especially at low concentrations of soap. It is proposed to carry out a further study of dilute solutions, possibly using the drop method of detecting changes of composition.[2]

The general equation of the isotherm is

$$x/m = \alpha c^{1/n} \qquad (1)$$

where x/m is the amount of adsorbed substance for unit mass of adsorbent; c is the final or equilibrium concentration of the substance in solution and α and $1/n$ are constants depending upon the substances present. If one takes the logarithms of both members of the above equation,

$$\log x/m = \log \alpha + 1/n \log c.$$

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[1] Cf. Freundlich: Zeit. Kolloidchemie, 3, 212 (1908).

[2] Cf. W. C. McC. Lewis: Phil. Mag., [6] 15, 499; 16, 466 (1908).

This being the equation of a straight line, by drawing a curve between log x/m as ordinates and log c as abscissae, the slope of such a curve gives $1/n$ directly and the y-intercept equals log α, whereby the constants are readily computed from the experimental data.

TABLE: ADSORPTION DATA

c Grams	x/m (observed) Gram	log c	log x/m	x/m (calculated) Gram
0.60	0.17	—1.778	—1.226	0.29
1.18	0.28	0.072	—1.453	0.32
3.18	0.40	0.502	—1.601	0.38
6.36	0.44	0.804	—1.645	0.42
13.85	0.48	1.142	—1.684	0.48
21.03	0.49	1.323	—1.694	0.51
26.01	0.54	1.415	—1.729	0.53

The numbers in the above table were computed from the experiments with the homogenized emulsions, as follows: c represents the equilibrium concentration expressed in grams of sodium oleate per liter; x/m, the grams of oleate adsorbed by liter volume of benzene; and x/m (*calculated*) is the value calculated from the logarithmic equation. If the first two pairs of values of log c and log x/m be excluded, the logarithmic curve is approximately a straight line, whence the constants are calculated as follows:

$\alpha = 0.316$ approximately, and
$1/n = 0.156$ approximately

The calculated values of x/m show that the amount of soap adsorbed agrees fairly well with that required by the theory of Freundlich, except when the concentration of soap is small. In such cases, the actual adsorption is much less than that calculated. One may explain this discrepancy by postulating hydrolysis of the sodium oleate—a behavior common to soaps in dilute solution, as Kahlenberg[1] has shown. If a given oleate solution were partially hydrolyzed and the NaOH set free were adsorbed only slightly, then the acid

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[1] Cf. Kahlenberg and Schreiner: Zeit. phys. Chem., 27, 552 (1898).

number of the solution would cease to be a measure of the quantity of sodium oleate present—the concentration of the soap in solution would be *less* than that calculated from analysis.

The curves shown in Fig. 3 give the relationship between x/m and c according to the data above. The dotted curve is plotted by using the *calculated* values for x/m, for comparison.

Summary

Condensation of solute in the surface separating liquid and vapor or liquid and liquid, is to be considered as a special case of adsorption although very few attempts have been made hitherto to show that such is the case.

Sodium oleate is removed from solutions of different strength during the process of emulsifying benzene and the amount of this removal depends upon the strength of the soap solution and the specific surface of the benzene phase.

The amount of soap removed increases rapidly at first with small increases in the concentration of the solution and then remains very nearly constant while the composition of the solution undergoes great change; in this respect a strong similarity to ordinary adsorption is shown.

The quantitative application of Freundlich's equation gives partially satisfactory results.

A simple method of "homogenizing" emulsions has been devised.

This paper is only a preliminary study and further work is contemplated.

Worcester Polytechnic Institute
June, 1914

HYDROUS FERRIC OXIDE

BY WILDER D. BANCROFT

In a previous paper[1] I have pointed out that, since any substance may be converted into a colloidal suspension by being subdivided sufficiently, it follows that we may have any number of different colloidal solutions of the same thing if we start, for instance, with ferric oxide or aluminum oxide having different amounts of water in the particles. In this paper I shall show that this point of view helps us to understand some of the experimental data in regard to ferric oxide. Two different samples of ferric oxide may differ in water content and in the size of the particles; and both factors will affect the properties of the substance.

If the colloidal ferric oxide is prepared by hydrolysis of a ferric salt, the general conditions for obtaining a ferric oxide with a low water content will be high temperature and long heating. The highly hydrous salt is gelatinous, becoming sandy as the oxide becomes more nearly anhydrous. Other things being equal there will be more adsorption, the more hydrous the salt is. It seems not unreasonable to assume also that the decrease in adsorption with decreasing water content will be greater for ions which are adsorbed strongly than for ions which are adsorbed but slightly. This has an important bearing on the case of coagulation because these sols precipitate when they are electrically neutral and they remain suspended only when one ion is adsorbed more than the other. Since ferric oxide moves normally to the cathode, it owes its stability to the adsorption of the cation. If the cation is readily adsorbed and the anion only slightly, a high concentration of the electrolyte will be necessary before the degree of adsorption of the anion becomes equal to that of the cation and before coagulation takes place. This state of things is realized with hydrochloric acid and nitric acid which

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[1] Bancroft: Jour. Phys. Chem., 18, 555 (1914).

have to be present in fairly high concentration in order to coagulate certain ferric oxides. If we cut down the adsorption of the cation relatively by making the suspended ferric oxide more nearly anhydrous it will take a much lower concentration of hydrochloric acid to coagulate the ferric oxide provided the size of the particles remains the same. This has been found experimentally. The converse is also true, that we shall get precipitation at relatively low concentrations if we add an electrolyte with a readily adsorbed anion instead of cutting down the adsorption of the cation. This can be done by adding sulphuric acid, the bivalent anion being adsorbed more strongly than chloride or nitrate ion. If the precipitate is distinctly gelatinous, the precipitated particles will coalesce readily and consequently will not peptonize readily when the excess of precipitating agent is washed out. If the precipitate be sandy, however, there will be a lesser tendency for the particles to agglomerate firmly into large groups; and consequently peptonization ought to take place more readily.

Graham[1] obtained a highly hydrous ferric oxide by allowing a cold solution of ferric acetate to hydrolyze, and removing the acetic acid by dialysis. The same product was also obtained by dissolving gelatinous ferric oxide in a ferric chloride solution and then removing the chloride as far as possible by dialysis. Krecke[2] obtained Graham's soluble ferric oxide by hydrolysis of 0.10 and 0.125 percent ferric chloride solutions at 20° or by heating solutions containing up to 1.0 percent ferric chloride for a short time to 87°. More concentrated solutions gave the same product when heated to still higher temperatures; but the hydrolysis was forced back when the temperature was lowered. When water contains one percent of Graham's ferric oxide[3] (gelatinous) the solution has the dark red color of venous blood. "The red solution is coagulated in the cold by traces of sulphuric acid, alkalies, alkaline carbonates, sulphates, and neutral salts in general, but not by

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[1] Jour. Chem. Soc., **15**, 249 (1862).
[2] Jour. prakt. Chem., (2) **3**, 286 (1871).
[3] Graham: Jour. Chem. Soc., **15**, 250 (1862).

hydrochloric, nitric, and acetic acids, nor by alcohol or sugar. The coagulum is a deep red-coloured jelly, resembling the clot of blood, but more transparent. . . . The coagulum formed by a precipitant, or in the course of time without any addition having been made to the solution of peroxide of iron, is no longer soluble in water, hot or cold, but it yields readily to dilute acids. It is, in short, the ordinary hydrated peroxide of iron."

What is usually considered another modification of colloidal ferric oxide was obtained by Péan de St. Gilles[1] by boiling a dilute solution of ferric acetate, thus driving off the acetic acid. Krecke has obtained it by heating a half percent solution of ferric chloride to 100°–130°. Graham says in regard to the Péan de St. Gilles ferric oxide: "The characteristic properties of this substance, which indicate its allotropic nature, are the orange-red colour and the opalescent appearance of its solution. The metaperoxide of iron is entirely precipitated of a brown ochreous appearance by a trace of sulphuric acid, or of an alkaline salt, and is insoluble in all cold acids, even when the latter are concentrated." If a suspension of this ferric oxide is poured into hydrochloric acid or nitric acid solution, a precipitate is obtained which dissolves in water when the acid is washed out. The precipitate obtained from Graham's ferric oxide does not dissolve in water when the excess of acid is washed out.

Graham, of course, made no quantitative measurements on the amount of electrolyte necessary to precipitate a ferric oxide suspension. Duclaux[2] has made some experiments on a suspension containing 203×10^{-6} gram atoms Fe and 16.6×10^{-6} gram atoms Cl per 10 cc. It took $13\text{–}19 \times 10^{-6}$ gram equivalents of sodium sulphate, citrate, chromate, carbonate, phosphate, hydroxide, or ferrocyanide to precipitate the iron oxide while 1880×10^{-6} gram equivalents $NaNO_3$ were necessary and over 2000×10^{-6} gram equivalents NaCl. In all

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[1] Comptes rendus, 40, 568, 1243 (1855).

[2] Jour. chim. phys., 5, 29 (1907).

cases except those of chloride and nitrate, the amount of the salts which has to be added is apparently equivalent to the amount of chloride in the hydrosol. With chlorides and nitrates the amount to be added decreases very much more rapidly than the decrease in the amount of chloride originally present in the ferric oxide. Of this chloride originally present probably only a small part is actually adsorbed by the ferric oxide. The balance is a measure of the cation adsorbed—presumably hydrogen—which gives the hydrosol its stability. If we add an anion which is adsorbed as much or nearly as much as the hydrogen ion, we shall get coagulation when the new anion is added in approximately equivalent quantities. This would account for Duclaux's results. It seems to me, however, very improbable that these six anions are all adsorbed to practically the same extent and I think it extremely probable that a repetition of the experiments will show a greater variation than from 13 to 19. In fact, Duclaux's experiments do not agree with those of Pappadà.[1] The order of anions according to Duclaux is chromate, hydroxide, citrate, and sulphate, the chromate being adsorbed the most. From Pappadà's experiments on coagulation, I deduce the order: citrate, chromate, sulphate, hydroxide. Duclaux's results do not agree either qualitatively or quantitatively with those of Hardy.[2]

Giolitti[3] has made quite an extended study of colloidal ferric oxide. He finds that considerable quantities of hydrochloric, hydrobromic, hydriodic, nitric, perchloric, and bromic acids must be added to a suspension of the Péan de St. Gilles ferric oxide in order to cause precipitation. The oxide comes down as a brick-red powder which is peptonized by water as soon as the excess of acid is washed out. For a suspension containing 0.116 percent Fe the limiting concentration of the acid necessary to produce complete precipitation was found to be 0.730–0.773 percent HNO_3. Less nitric acid was necessary with more dilute suspensions of ferric oxide, but the acid

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[1] Zeit. Kolloidchemie, 9, 233 (1911).

[2] Höber: "Physikalische Chemie der Zelle und Gewebe," 333 (1911).

[3] Gazz. chim. ital., 35 II, 181 (1905); 36 II, 157, 433 (1906).

concentration falls off much less rapidly than the iron concentration.

Traces of sulphuric, sulphurous, iodic, periodic, boric, and phosphoric acids, and of salts precipitate the Péan de St. Gilles ferric oxide; but they precipitate it in a gelatinous form which does not redissolve when the precipitate is washed. Owing to the marked adsorption it is not easy to wash out these acids and salts, and the insolubility may be due in part to that. It seems to me more probable that the insolubility in water is due chiefly to the precipitate being gelatinous and, therefore, coalescing into a continuous mass which is not peptonized readily by water.

This precipitation of ferric oxide as a sandy mass by hydrochloric acid and as a gelatinous one by sulphuric acid is an important matter about which we appear to know very little theoretically. The formation of the gelatinous precipitates cannot be a matter involving the hydrogen ion because we get the effect with sodium sulphate and do not get it with hydrochloric acid. Since it occurs with a number of different acids and salts, the effect cannot be due to a specific anion. The one common characteristic is that the anions precipitate in low concentration and are, therefore, adsorbed strongly; but this does not enable us to distinguish between the possible hypotheses of the effect being due to the strongly adsorbed anion or to the solvent action of the adsorbed salt. It has been shown by von Weimarn[1] that cellulose can be converted into a gelatinous mass by heating with concentrated salt solutions, preferably under pressure. In the particular case of ferric oxide, the salt concentrations are low, which makes it a little more probable that we may be dealing with an effect of the anion rather than of the salt; but on the other hand it is open to anybody to postulate a high salt concentration in or at the surface of the ferric oxide.

There are no data as to whether it is a general phenomenon that certain coagulants precipitate suspended particles in a

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[1] Zeit. Kolloidchemie, 11, 41 (1912).

distinctly gelatinous form; but isolated cases are known. Odén states[1] that different salts cause colloidal sulphur to coagulate in different ways. "When precipitated with hydrochloric acid, the coagulum is liquid; when precipitated with barium salts, a plastic mass is obtained; with copper sulphate the precipitate is very fine-grained; while certain other salts cause a slimy precipitate."

It is quite probable, though not proved in any way, that the differences in the degree of reversibility when albumin is precipitated by different salts may be due in part to the physical characteristics of the deposit. Lime and sodium nitrate both flocculate a suspended clay under certain conditions; but lime is added to soils to keep them in good physical state, while sodium nitrate is said to be detrimental in this respect. Since the gelatinization of ferric oxide is due to the taking up of water, it is quite possible that the action of acids and salts in causing the swelling of gelatine may be another instance of the same sort. We know also that certain salts will stabilize the blue hydrous copper oxide;[2] but no experiments have been made to see whether the hydrous form is obtained when black copper oxide is ground up with a suitable quantity of one of these salts. We know, however, that caustic soda tends to change sandy silica to gelatinous silica and we know also that when silica is ground very fine, it goes into solution when heated with water, and then separates in a gelatinous form.[3]

The sandy suspension, obtained by the method of Péan de St. Gilles, seems to be fairly uniform. It all precipitates at once when a certain concentration of nitric acid is reached. This is not the case with the ferric oxide prepared by the method of Graham. Addition of a suitable amount of nitric acid to the Graham ferric oxide causes a fractional precipitation. This is because the more hydrous form changes gradually on standing to the less hydrous form which latter precipitates first when nitric acid is added. The first precipi-

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[1] Odén: "Der kolloide Schwefel," 157 (1912).

[2] Blucher and Farnau: Jour. Phys. Chem., 18, 629 (1914).

[3] Desch: "The Chemistry and Testing of Cements," 58 (1911).

tate shows the general properties of the Péan de St. Gilles oxide and is readily peptonized by water.

Giolitti estimates the diameter of the particles which are peptonized by water at about 7 μ, while the gelatinous precipitate is made up of particles so fine that their size could not be determined. These very small particles react readily with cold acids while the coarser particles, obtained by the method of Péan de St. Gilles, do not.

The color changes of hydrous ferric oxide are distinctly interesting. Goodwin[1] pointed out that a dilute colorless solution of ferric chloride changes spontaneously to a yellow color and then to a reddish yellow color, the conductance increasing all the while owing to the setting free of hydrochloric acid. Malfitano[2] obtained a yellow solution by a gentle warming of a dilute ferric chloride solution or by adding ferric chloride to the reddish brown precipitate of the Graham ferric oxide. Fischer[3] prepared the yellow colloid by heating the Graham ferric oxide with hydrochloric acid. Under these conditions, he always obtained, in addition, varying amounts of a red to black precipitate. The yellow substance is apparently a limonite and the red a haematite. The fact that a mixture of these two substances is formed, one with a water content of 10–50 percent and the other with a water content of less than 5 percent, is due undoubtedly to the fact that the Graham ferric oxide is not uniform. The haematite is the result of aging the Péan de St. Gilles ferric oxide, while the limonite comes from the Graham oxide. Fischer did not try the experiment; but it is quite certain that the relative amounts of the yellow and the dark red oxides would vary if one changed the lengths of time between precipitation and heating.

Ruff[4] considers that the yellow modification consists of a definite chemical compound, $(Fe_2O_3)_2.3H_2O$, plus adsorbed

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[1] Zeit. phys. Chem., 21, 4 (1896).
[2] Ibid., 68, 232 (1909).
[3] Zeit. anorg. Chem., 66, 37 (1910).
[4] Ber. deutsch. chem. Ges., 34, 3417 (1901).

water, and that it is a hydrous hydrated ferric oxide instead of a hydrous ferric oxide. While this may be true, the evidence in favor of this hypothesis is distinctly not conclusive.[1] What we do know definitely is that the yellow form is denser than the other and that it contains more water under the same conditions. It is possible that the yellow form owes its color to the presence of an adsorbed ferric salt. That would account for the yellow modification being obtained by addition of ferric chloride (Malfitano), by heating with hydrochloric acid (Fischer) or by oxidation of ferrous oxide (Phillips). We might bring Goodwin's results into line by postulating that the acid concentration was so low in his solutions that the positive charge was due to adsorbed iron and not to adsorbed hydrogen. This is a more plausible hypothesis than Ruff's; but it is as yet nothing more than a hypothesis.

By adding glycerine, Fischer[2] has obtained a hydrous ferric oxide which is not coagulated by dilute alkali. Since this adsorbs hydroxyl in excess, it moves to the anode under electrical stress. The conditions of precipitation have not been studied sufficiently to make it worth while to discuss this case further.

The general results of this paper are:

1. Any number of hydrous ferric oxide solutions can be prepared, each differing somewhat from the next.
2. The ferric oxide, prepared by the method of Péan de St. Gilles, is sandy and contains relatively little water.
3. The ferric oxide, prepared by the method of Graham, is gelatinous and contains more water than the Péan de St. Gilles oxide.
4. The ferric oxide, prepared by the method of Graham, is not as homogeneous as the other because it is always changing slowly into the less hydrous form.
5. Though the particles of the Péan de St. Gilles oxide are coarser (about 7μ) than those of the Graham oxide, their

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[1] Cf. van Bemmelen: "Die Absorption," 76 (1910).

[2] Biochem. Zeit., 27, 223 (1910); Cf. Grimaux: Comptes rendus, 98, 1485 (1884).

sandy character makes them coalesce less readily and consequently they are peptonized more readily after precipitation by hydrochloric or nitric acid.

6. The salts and acids which precipitate the Péan de St. Gilles oxide readily, precipitate it in a gelatinous form approximately that of the Graham oxide. The irreversibility of the precipitation seems to be due more to the coalescing of the somewhat gelatinous particles than to the difficulty of washing out the excess of the precipitating agent.

7. It is probable, though not proved, that a difference in the physical properties of the precipitated mass may play a part in the irreversibility of precipitation of albumin, etc.

8. The coarse particles of the Péan de St. Gilles oxide are less readily attacked by cold acids than are the very fine particles of the Graham oxide.

9. There is no satisfactory theory as yet for the yellow color of hydrous limonites. It is not probable that we are dealing with a hydrous hydrated oxide and it is not proved that the color is due to the adsorption of an iron salt, though this is a possible hypothesis.

10. The fact that Fischer obtained both limonite and haematite by heating the Graham ferric oxide with hydrochloric acid is undoubtedly due to the inhomogeneity of the Graham oxide.

Cornell University

A UNIQUE GEOPHYSICAL PHENOMENON, TRINIDAD ASPHALT, INTERESTING FROM THE POINT OF VIEW OF DISPERSOID CHEMISTRY

BY CLIFFORD RICHARDSON

The asphalt, found in a deposit of many millions of tons in the crater of an old mud spring or geyser in the Island of Trinidad, B. W. I., is a unique geophysical phenomenon and one which must be interpreted by the principles of dispersoid or colloidal chemistry. Over an area of more than a hundred acres and to a depth of more than 135 feet the asphalt exists in this crater as an astonishingly uniform material. It is in process of formation at the present time. It consists of a complex system of several phases, gaseous, liquid and solid, organic and inorganic, more or less in equilibrium, displaying colloidal properties of industrial as well as scientific interest. The asphalt owes its origin to certain geological conditions existing side by side in that locality. Oil sands occur at different depths, which contain vast quantities of petroleum as has been demonstrated by the many wells which have been successfully sunk, a petroleum of unique character, differing from any previously known, and of a highly asphaltic nature. Rising toward the surface along some line of least resistance the petroleum meets the paste of fine silica and clay which forms the mud of the spring. With this the oil becomes emulsified, probably by the action of the natural gas which accompanies it at very high pressure. In the lapse of time the entire crater of the spring has been filled with the resulting material and it has overflowed the rim, running down the slopes to the sea. Fresh material is in process of formation today and issues at several points on the surface of the deposit of a consistency so soft that it can be readily moulded into balls with the hands, without adhering to them, owing to the free water. with which it is associated. This so-called "soft pitch" is also accompanied with natural gas of unusual composition, containing in addition to the hydrocarbons usually found in such gas, carbon dioxide and hydrogen sulphide, in some localities in the neighborhood of the deposit, as much as 33 percent of the former and 3.5 percent of the latter. At the same time the soft pitch itself is evolving gas, either the result of the release of pressure or of a reaction going on between the bitumen and the mineral matter it contains, this gas consisting largely of hydrogen sulphide and carbon dioxide, probably the latter cause, as it continues for years after the material has been exposed to the air, while if the soft asphalt is sealed up in a tin can the latter will explode in the course of time from the gas pressure developed.

The main mass or older form of the asphalt in the crater is sufficiently hard to make it possible to flake it out in large pieces of from 50 to 100 pounds in weight. In this form it resembles an exaggerated Swiss cheese owing to the gas cavities it contains. While brittle enough for this, an excavation of some depth at any point is filled up and obliterated in twenty-four hours by the flow of asphalt from the adjoining material. Large masses of the asphalt taken from the deposit and kept in storage, without lateral support, present all the features of the glacial flow of ice.

The asphalt, therefore, originating in a soft condition, as demonstrated by the fresh material, which is constantly being formed and which emerges near the center of the deposit, becomes hard in the course of a year or two. The cause of this and of the evolution of the gas which is observed may be attributed to the presence of a catalyzer. As will be shown, the asphalt contains clay in a highly dispersed condition, carrying adsorbed ferrous sulphate, which may play such a rôle.

As long ago as 1891 and again in 1895, the writer made a personal inspection of the deposit and collected specimens of the asphalt at various points on the surface and to a depth of 135 feet, the latter with the aid of a wash drill. In connection with this operation it was found that the mass of asphalt was in a constant state of motion owing to the evolution of gas, as evidence of which the drill was tilted to such an angle that the boring could not be continued beyond the depth reached. The same fact was also demonstrated by driving a line of wooden plugs in the surface of the deposit and noticing their displacement in the course of time.

It was found from an examination of the specimens representing the material as it exists in different parts of the deposits, that it contains everywhere 29 percent of water, which proves to be of thermal origin and of remarkable character, in that there was found to be present in solution, on evaporation of some of it obtained in the early methods of drying and refining the material, about 20 grams of different salts per liter, and that these were of a somewhat surprising character. Although the principal salts are chlorides and sulphates of soda, there is also present ferrous sulphate in sufficient amount to give the water a strong acid reaction, together with sulphate of ammonia and small percentages of iodides and borates. Attempts to separate this water from the crude asphalt, by the use of solvents for the bitumen, were not successful, as it was found to be closely held by the clay and mineral matter of the material. It does not rise to the surface of the solvent. The sample examined was, therefore, obtained from refining stills in which the material was heated and melted and is, in consequence, somewhat altered and concentrated by the conditions to which it has been subjected. It is a notable fact, however, that on pulverizing the crude asphalt and exposing it to the air for some hours, all the water is lost which does not exist as water of hydration of the clay.

The specimens thus dried at their source were examined in the United States, with results, averages of which are given in the accompanying table.

The method of examination consisted in extracting the bitumen with carbon disulphide and ignition of the residue for the determination of mineral matter. By this method of analysis it was found that over 9 percent of material remained undetermined. For some years this was looked upon as being organic matter not soluble in carbon disulphide, but further

Average Composition of Trinidad Lake Pitch in Circles

	Bitumen by CS_2 percent	Mineral matter percent	Undetermined percent
Circle 2, 200 ft. from center	55.02	35.41	9.57
Circle 4, 400 ft. from center	54.99	35.40	9.61
Circle 6, 600 ft. from center	54.84	35.49	9.67
Circle 8, 800 ft. from center	54.66	35.56	9.78
Circle 10, 1000 ft. from center	54.78	35.44	9.78
Circle 12, 1100 ft. from center	54.62	35.45	9.93
General average	54.92	35.46	9.72
Circle 14, 1400 ft. from center	53.86	36.38	9.76

researches showed that it is, in fact, water of hydration of the clay, a small percentage of bitumen absorbed by the latter and not removed by carbon disulphide, and of volatile salts lost on ignition. This has been discussed in a paper entitled "The Proximate Composition and Physical Structure of Trinidad Asphalt," presented before the American Society for Testing Materials and appearing in the proceedings of the Society, Vol. 6, 509 (1908).

The results of the preceding analyses show plainly the fact that the enormous mass, many millions of tons, of the crude asphalt found in the deposit, is of astonishingly uniform composition, and that the conditions under which it was and is being formed involve a certain equilibrium between the components which the writer will not attempt, as yet, to explain.

The proximate composition of the crude material is as follows:

	Crude Trinidad asphalt
Water and gas	29.0
Bitumen soluble in cold carbon disulphide	39.0
Bitumen adsorbed and retained by the disperse mineral matter	0.3
Mineral matter on ignition with tricalcium phosphate	27.2
Water of hydration of clay	4.2

The character of the gas and the water in the crude asphalt has already been mentioned. The mineral matter obtained on ignition consists of impalpably fine silica, clay, and the residue of the salts contained in the water which are not volatile. The silica exists as sharp transparent flakes having all the appearance, under the microscope, of having existed in solution in water under pressure, on releasing which it has separated in its present form, as suggested by Dr. Carl Barus. The particles of silica are much larger, naturally, than those of the clay, but the largest are no greater than 0.26 mm in diameter. By treatment of the mineral matter obtained on ignition with strong hydrochloric acid, it can be obtained in a perfectly white condition, the iron readily going into solution, probably, being largely derived from the ferrous sulphate existing in the water. The insoluble portion amounts to 85 percent.

In the study of the asphalt efforts were made for many years to prepare from it, by means of solvents, a bitumen free from mineral matter. None of these was successful, a certain amount of it remaining in a solution made with any solvent which completely dissolved the bitumen. At the same time this was not to be detected under the ordinary microscope. An explanation was not discovered until recently, when it was found, on examining a solution of the crude asphalt or of the dried material in pure carbon disulphide, which had been allowed to settle for some weeks or months, and even when it had been centrifugaled for some hours, that it contained mineral matter to the extent of 2 percent or more, which, with the aid of the ultra-microscope, was revealed as particles in the high state of motion, characteristic of highly dispersed solids. This accounts for the fact that they could not be removed by ordinary filtration or by centrifugal force, nor could they be entirely removed by passing once through a Chamberland filter. By repeated use of such a filter, the colloidal material becomes agglomerated and clogs the pores to such an extent that it forms an ultra filter and can be collected. It has been found to consist largely of bitumen adsorbed by clay and other mineral matter existing in the highly dispersed condition in which it occurs. On ignition of this material the residue amounted to 20.5 percent, which, of course, owing to the loss of water of hydration of the clay and the volatile inorganic matter, is much smaller than the actual amount of hydrated mineral matter present. This figure is evidence of the peculiarly high adsorptive power of the disperse solid colloids and, probably, also of a selective adsorption, as will appear later.

If the disperse material immediately after filtration is treated with carbon disulphide it is again dispersed as a sol, which may, therefore, be denominated a bitusol.

If while still adhering to the Chamberland filter it is further washed with disulphide removing some of the bitumen, it no longer becomes a sol on taking up with the disulphide, showing that the bitumen has acted as a protective colloid.

If light naphtha is used as a solvent all the bitumen of the asphalt is not dissolved, that is to say, this is not a universal solvent for all classes of bitumen. With a naphtha of 88° B. density, only 57 percent of the entire bitumen in the air-dried crude asphalt goes into solution, and the solution differs from one made with carbon disulphide in that it carries no disperse solids, showing that the bitumen soluble in naphtha is not adsorbed by the disperse solids in the same manner as that soluble in carbon disulphide alone.

The crude asphalt appears from the preceding observations to consist of a suspension of relatively large size mineral particles in an extremely viscous medium, together with highly dispersed mineral matter in colloid form, intimately mixed with an emulsion of a thermal water with the bitumen present.

If the dried or refined material is treated with a solvent and attempts made to remove the mineral matter, as in the case of the asphalt from the deposit still containing water, the same results are obtained as far as the presence of disperse solids is concerned, showing that its colloidal character is not essentially changed by the heat treatment.

It is of interest to observe that, as an indication of the amount of colloidal material present in the asphalt, the mineral matter obtained on ignition of the bitumen present in the carbon disulphide solution amounted in the case of the crude materlai to 8.02 percent after one week's subsidence. After further sedimentation, probably by agglomeration, it fell to 3.4 percent in three months. This shows that a large amount of disperse colloid material is present in the original undried asphalt. In the refined or dried material the original percentage was 4.5 percent after one month's sedimentation, and the changes which were found to go on in the course of time were as follows:

1 month	4.5 percent
2 months	3.0 "
3 "	2.57 "
4 "	2.67 "
5 "	2.74 "
6 "	2.75 "

It appeared to be of interest to determine whether a system such as that found in nature in the case of Trinidad asphalt, could be prepared synthetically with the purer forms of bitumen. For this purpose a crude Bermudez asphalt, which is practically free from mineral matter, was softened at a temperature below that of boiling water and a paste of colloidal clay and water intimately emulsified with it, something which can be done with great readiness.

When this emulsion was treated with carbon disulphide and allowed to settle, treating it in the same way as the crude Trinidad asphalt, it presented under the ultra-microscope the same appearance, the bitumen carrying disperse solid colloids which it had taken from the water, probably due to the greater capacity of the colloidal clay for adsorption of bitumen than of water. When a similar emulsion was made with a very dense asphaltic oil of 0.994 specific gravity, liquid enough to flow at ordinary temperatures, much less of the colloid matter was taken from the water by the bitumen, showing the selective adsorption exercised by the disperse clay.

When the water was removed from the Bermudez emulsion, which has been described, in the same manner as is practiced in refining the crude Trinidad asphalt, a material was obtained containing clay and corresponding to refined Trinidad asphalt. On dissolving in carbon disulphide and centrifugaling for one hour, the presence of disperse solid colloids were evident under the ultra-microscope and, on ignition, a residue of clay, 0.67 percent of the bitumen, was recovered, as compared to 2.08 percent in the case of the refined Trinidad asphalt. The difference may be attributed either to the fact that the clay in use in making the synthetical Bermudez product was not as highly colloidal as that associated with the Trinidad bitumen, or to the fact that the bitumen of the Trinidad asphalt is one which is adsorbed more readily and acts as a better protective colloid than that of the Bermudez material or the oils. With the liquid asphaltic bitumen the amount of colloidal clay which was taken up was only sufficient to give a residue of 0.17 percent on representing the clay present as a bitusol.

In addition to the scientific interest in the presence of solid disperse matter to such an extent in the Trinidad Lake asphalt, it is of great importance from an industrial point of view, since the presence of such a large amount of material in a suspensoid and dispersoid state adds enormously to the surface energy developed by the material, and this has been shown to be of great importance in the construction of asphalt surfaces. At the same time the great powers of adsorption of the disperse solid colloids present contribute an additional feature of value. Such an asphalt presents greater viscosity, smaller ductility and susceptibility to temperature changes than bitumens in which disperse solids are not naturally present, and the lack of which is made up in practice by the addition of an ordinary mineral dust which cannot present the same surface area as that provided by the highly dispersed colloids which are contained in Trinidad asphalt.

From the data presented it appears that in Trinidad asphalt we have a unique geophysical phenomenon and one which it will be of interest to study further for the purpose of explaining its origin and constitution.

In conclusion the writer desires to thank Dr. Philip Schneeberger, who has aided him efficiently in the more recent laboratory work, which has supplied the data contained in this paper.

January 15, 1915

NEW BOOKS

Zur Lehre von den Zuständen der Materie. *By P. P. von Weimarn. Vols. I and II. 22 × 15 cm; pp. v + 190. Dresden: Theodor Steinkopff, 1914. Price: 7 marks, paper.*—The author has put into book form the articles which he has published in the last half a dozen years. The first volume contains the text while the second volume is an atlas containing microphotographs of precipitates in different stages of crystallization.

The author distinguishes five stages of supersaturation of sparingly soluble substances. In the first stage, precipitation is very slow and large crystals are obtained in the course of years. In the second stage good crystals are formed in a relatively short time. With increasing supersaturation we reach the third stage in which skeleton crystals precipitate. In the fourth stage we get a plastic or jelly-like precipitate, while the fifth stage gives a precipitate which cannot at first be differentiated either by the microscope or the ultra-microscope. For barium sulphate produced by the interaction of manganese sulphate and barium sulphocyanate, the limiting concentrations for the five stages are approximately $N/20000$–$N/7000$, $N/7000$–$N/600$, $N/600$–$0.75N$, $0.75N$–$3N$, $3N$–$7N$. The author states that he has studied over a thousand cases and has never found an exception. It must be remembered, however, that most people would consider the dilute solutions as colloidal suspensions, and that there is also a question to what extent the precipitates from the concentrated solutions are or are not hydrous.

In addition to a theory of precipitation the author has also a theory of peptonization. He considers that the precipitate first dissolves in the peptonizing agent and then precipitates again. On this basis, peptonization would apparently always mean the conversion of a fine-grained precipitate into a coarser one. In fact, von Weimarn says, p. 67, that the necessary and sufficient conditions for peptonization are:

1. The solid crystalline substance must be of so small crystals that the physical and chemical properties vary with the size of the crystals.

2. The peptonizing substance must have the power at sufficiently high concentrations to form a stable, soluble, chemical compound with the substance which is peptonized. When the concentration of the peptonizing agent is sufficiently low, no such compound must be formed.

3. The medium in which peptonization takes place must have practically no solvent action on the substance to be peptonized when no peptonizing agent is present.

This formulation has the great advantage of being definite. One knows exactly where the author stands and he is not juggling with words. So far as the reviewer knows the author is the only person who has ever dared to commit himself to a theory of peptonization. For this we owe him many thanks quite regardless whether his theory proves to be right in all details or not. It seems to the reviewer that the author has not laid sufficient stress on the conditions of stability of a sol and that he, therefore, does not take sufficiently into account the importance of the adsorption of a specific ion in causing peptonization. The reviewer is also somewhat doubtful whether the particles in a sol are always coarser than those in a precipitate which can be peptonized. The fact that a soap solution will carry rouge through filter paper indicates pretty strongly that a disintegration has taken place. *Wilder D. Bancroft*

Tables annuelles internationales de constantes et données numériques. *Edited by Ch. Marie. Vol. III, 1912. 23 × 28 cm; pp. v + 593. Chicago: University of Chicago Press, 1914. Price: $6.80.* The indefatigable editor has succeeded in getting out a third volume of this valuable reference book. Though the field to be covered grows larger each year the editor has shortened the volume by one hundred and thirty pages. In the sections on chemical equilibria, reaction velocities and electrical conductivity, it has been found possible not to give all the data in full. This is a distinct improvement. The section on colloids has been cut down by eliminating data in regard to substances which are in themselves ill-defined or which have been obtained under conditions which are ill-defined.

Owing to special financial assistance it has been found possible to issue the sections on spectroscopy, radioactivity, electricity, magnetism and electrochemistry, metallurgy and engineering, mineralogy, and biology as separate pamphlets. The volume was completed before the European war broke out, so it is not known what effect this will have on the International Tables; but it seems probable that the financial support will be decreased to some extent and that the difficulties of compiling the tables will necessarily be increased enormously.

Wilder D. Bancroft

A Laboratory Guide to the Study of Qualitative Analysis. *By E. H. S. Bailey and Hamilton P. Cady. Seventh Edition. 15 × 21 cm; pp. v + 280. Philadelphia: P. Blakiston's Son & Co., 1914. Price: $1.25 net.* The fifth edition has been reviewed (10, 223). The present one differs from it only in a few places, some changes having been made in the separation and identification of iron, aluminum, chromium, manganese, zinc, nickel, and cobalt. Since every other page is blank in the body of the text, there are not so many pages of reading matter as one might expect from the size of the book.

The reviewer was distinctly interested in a broader statement of Berthollet's Law, p. 9. "The conditions which favor reactions are that two or more of the ions shall unite to form either a compound which passes out of solution, or that they shall unite to form a compound which is only slightly dissociated." The first condition is the one usually given of the formation of an insoluble or volatile substance. The second covers such cases as the addition of hydrochloric acid to a sodium acetate solution or the addition of potassium cyanide solution to silver cyanide. One valuable feature about the manual is that stress is laid on the reversibility of reactions. *Wilder D. Bancroft*

Von Nostrand's Chemical Annual. *By John C. Olsen. Third edition. 13 × 19 cm; pp. 669. New York: D. Van Nostrand Co., 1913. Price: $2.50.* The third edition of this chemical handbook presents a much neater appearance than the old edition. It is printed on a good quality of thin paper and contains an unusually large number of useful constants, chemical formulae, and properties. It contains, respectively, the following tables: Atomic Weights, the Periodic System, Specific Gravity of Gases, Physical Constants of the Elements, Factors and Logarithms for Direct and Indirect Gravimetric Work, Various Factors for Volumetric Analysis, Various Constants for Oils, Fats and Waxes, Gas Analytical Determinations, Physical Constants of Chemical Compounds, Specific Gravity Tables, Vapor Pressure and Boiling Point Tables, Equivalent Weights and Measures, and a number of tables giving the thermochemical changes for chemical reactions.

A classified bibliography of books published since 1909 with price of the books and the place of publication is given at the end of the volume.

Tables are arranged in a clear-cut manner, and the index serves as a ready guide to these tables. The actual values given are, in general, probably more accurate than those of handbooks published heretofore, and while not containing as many facts as the "Chemiker Kalendar," it contains the facts better arranged and with an index. The mass of *useful* facts in this volume is probably as great as in that of the "Chemiker Kalendar." *Charles W. Bennett*

The Spectroscopy of the Extreme Ultra-Violet. *By Theodore Lyman. 23 × 16 cm; pp. v + 135. New York: Longmans, Green & Co., 1914. Price: $1.50.*—This book is one of a series of monographs on physics edited by J. J. Thomson. The author is the best person to speak authoritatively on the subject because he took up the work where Schumann was forced to drop it and has carried it on in an admirable manner. The book is divided into two parts, the first dealing with the ultra-violet and the second with the extreme ultra-violet. In the first part the chapters are entitled: photometry in the ultra-violet; absorption of solids and gases. In the second and more important part, the subject is treated under the headings: apparatus and methods of investigation in the extreme ultra-violet; absorption of solids and gases; emission spectra of gases; emission spectra of solids; photo-electric and photo-abiotic phenomena; the limit of the spectrum.

It seems to be fairly well established, p. 17, that the limit of the solar spectrum is independent of the altitude between sea-level and 9000 meters. It is evident, therefore, that the absorbing agent must either possess an extremely steep absorption curve or reside in the very uppermost layers of the earth's atmosphere. The author inclines to the view, p. 22, that the absorbing agent is ozone, though he considers that this is not yet established definitely.

There is an interesting paragraph on p. 91. "After the work with the [aluminum] spark in hydrogen was completed, an investigation by Lenard on volume ionisation renewed the interest in the nature of the aluminum spark in air. It has been shown that the ability to produce volume ionisation by light increases in the Schumann region with decrease in wave-length; in fact, some investigators go so far as to assert that the phenomenon only occurs when light on the more refrangible side of λ1400 is employed. Now Lenard obtained very strong ionisation when he used a very powerful spark between aluminum terminals, and his results indicated that the effective light lay in the extreme Schumann region. On consulting the data for the aluminum spark in hydrogen, it was obvious that no strong lines existed in the extreme ultra-violet. Unless, therefore, lines are to be found in the spectrum of the aluminum spark in air which were not present with the spark in hydrogen, Lenard's results could not easily be explained New experiments were accordingly undertaken with the grating spectroscope; they yielded more interesting results than any of the previous attempts of this character. . . . Near λ1300, with the spark in air, there is a group of strong lines not observed with the aluminum spark in hydrogen. It is to this group that the ionisation effects observed by Lenard are largely to be attributed." The author does not give any reason for the appearance of these lines in air; but it seems to the reviewer that they should be attributed to some reaction taking place in air and not in hydrogen.

Another interesting paragraph is to be found on p. 107. "The statement that indirect experiments on the extension of the spectrum are not conclusive has obviously no reference to the extremely important work of Lane, Friedrich, Knipping, and the Braggs. They have established the fact that the X-rays are a form of ether vibrations whose wave length is of the order of one Ångström unit, or about one nine-hundredth that of the shortest wave length obtained by the direct method. There is thus a gap of about nine hundred units between the shortest known wave lengths which have been directly measured and the region of the X-rays. In this gap the behavior of light towards solid and gaseous substances suffers a profound change. In the Schumann region the general opacity of matter to light is the most important characteristic; in the region of the X-rays, its transparency is a most striking phenomenon. The alteration in the behavior of matter toward light is intimately connected with the vast increase in frequency. It will probably necessitate a considerable change in the methods of investigation if the gap in question is to be successfully bridged.

"An example of the direction in which this change of methods is likely to take place is furnished by the recent work of Dember. He has produced X-rays by the bombardment of photo-electrons whose speed was acquired in falling through a difference of potential of the order of twenty volts. He has estimated the wave-length of the rays by means of the Planck-Einstein formula, $eV = hn$. The value he obtained is 745 Ångström units, a figure strikingly near to the present limit of the spectrum from the concave grating. The result is very interesting and important, but the estimated wave-length cannot be accepted without reservation until the Planck-Einstein formula has been more fully established for a wider range of frequencies." *Wilder D. Bancroft*

Lehrbuch der physikalischen Chemie. *By Karl Jellinek. Vol. I. 16 × 25 cm; pp. vii + 732. Stuttgart: Ferdinand Enke, 1914. Price: paper, 24 marks.* It is the author's plan to write an exhaustive treatise on physical chemistry from the viewpoint of the physicist rather than of the chemist. The first volume deals with the properties of gases and includes also a long section on the properties of liquids. The manuscript for the second volume is finished; it includes: the rest of the work on liquids; properties of solids; properties of dilute solutions and colloidal solutions of non-electrolytes. The third volume is to be devoted to a discussion of ether, electrons, ions, atoms, molecules. The fourth volume will probably be the largest of the four because it is to include chemical statics and dynamics, mechanochemistry(?), thermochemistry magnetochemistry, electrochemistry, and photochemistry. It is an overwhelming task that the author has set himself and it is to be hoped that he will emerge from the struggle a victor.

In the present volume one hundred and forty-five pages are devoted to a discussion of some of the fundamental principles of physical chemistry. The next section, of two hundred and seventy pages, deals with the gaseous state, after which comes a chapter on the condensation of gases. A third section of nearly two hundred and fifty pages deals with the density, compressibility, thermal expansion, specific heat, viscosity, heat conduction, surface tension, and vaporization of liquids. There is also a very elaborate bibliography and a rather inadequate index. The book contains portraits of Helmholtz, Clausius, Kelvin, and Boltzmann.

The volume is dedicated to Chwolson and is evidently intended to come half-way between Chwolson's Physics and Ostwald's General Chemistry. The first volume does not really enable one to tell how successful the author is to be. To the reviewer it seems as though the book were more purely a text-book of physics than Chwolson's, but the difference will probably come out more clearly in the later volumes.

In many places the author discusses matters in great detail; in others he is concise to the point of obscurity. The unfortunate student, who wonders why the nature of the tube has no effect on the capillary rise, will get very little comfort or enlightenment out of the paragraphs on pages 610 and 618. Throughout the book the author seems to be more interested in the things we think we understand than in the ones that we know we don't.

The author classifies the Nernst heat theorem as the third law of thermodynamics, p. 158, and gives as a formulation of it that "there is no process taking place on a finite scale, by means of which a system can be cooled to the absolute zero." On this basis the first law of thermodynamics postulates the impossibility of a perpetual motion machine of the first class, the second law postulates the impossibility of a perpetual motion machine of the second class, while the third law, so-called, postulates the impossibility of reaching the absolute zero.

The author defines physical chemistry, p. 10, as the science which attempts to explain the more complex chemical phenomena by means of the simpler physical phenomena. He considers that physical chemistry tries to apply the experimental and theoretical methods of physics to chemical phenomena. On p. 11 he says: "While research in physical chemistry from 1890 to 1905 was concerned chiefly in developing the field opened up by the great theories [of Guldberg and Waage, Gibbs, van't Hoff, Arrhenius, and Nernst], a new period dates from the discovery by Nernst in 1906 of the third law of thermodynamics, which is very closely related to Planck's quantum theory (1900). This new period of physical chemistry is also characterized by the putting of the atomic theory on a firmer basis and by the development of the theories of radiation and of electrons."

Wilder D. Bancroft

Evolution of Sex in Plants. *By John Merle Coulter. 19 × 14 cm; pp vii + 137. Chicago: The University of Chicago Press, 1914. Price: $1.00 net.* The headings of the chapters are: asexual reproduction; the origin of sex; the differentiation of sex; the evolution of sex organs; alternation of generations; differentiation of sexual individuals; parthenogenesis; a theory of sex. In the first chapter the author says: "In any discussion of the evolution of sex it is necessary to consider asexual reproduction. The extent to which asexual reproduction occurs among plants is probably not fully appreciated. In many of the lower thallophytes sexual reproduction is unknown, and in all plants exhibiting it there are also asexual methods of reproduction. It is probably true, taking the plant kingdom as a whole, that the multiplication of individuals is greater by asexual than by sexual methods. It is obvious, therefore, that sex is not an essential feature of reproduction. Historically it was the last method of reproduction attained among plants, and when it appeared it did not replace the older methods, but was added to them.

"The significance of sex, therefore, is not to secure reproduction, but to secure something in connection with reproduction that the other methods do not. It is necessary to keep this fact in mind in considering the origin and real function of sex. Our conceptions of sex have largely been determined by its place in the life histories of the higher animals, in which it has become the only method of reproduction. It is difficult, therefore, to think of it as having any function apart from reproduction. Even among the flowering plants, which represent the culmination of the plant kingdom, and which would have eliminated asexual reproduction if it was eliminated at all among plants, reproduction by tubers, bulbs, and cuttings, as well as the universal occurrence of microspores (pollen grains) and megaspores, testify to the fact that asexual reproduction is not even a declining method."

The primitive gametes are only swimming spores greatly reduced in size. Though they are small, motile, pairing cells which give rise to nuclear fusion, these things are not peculiar to gametes (p. 135). "If pairing and nuclear fusion are not peculiar to gametes, although universally displayed by them, what is the essential feature? The only answer that can be made is that gametes are pairing cells whose nuclear fusion results in the production of a new individual. This means that in addition to possessing mutually attractive substances formed in connection with low metabolism, gametes possess nuclei so constructed that when the two fuse a new individual is initiated. This does not mean that neither gamete can produce a new individual alone, for parthenogenesis would contradict this. It means that a new individual can only be produced after the nuclei have fused. In other words, the essential feature of sexuality must lie in the peculiar structure of the nuclei of the sexual cells. Whether this peculiar structure is chemical or physical or both, must be a matter of opinion based on no direct evidence. It is reasonable to suppose that it is a problem belonging to the overlapping regions of physics and chemistry. . . .

"In conclusion, the impression one obtains of sexuality as a method of reproduction is that it represents photoplasts engaged in reproduction under peculiar difficulties that do not obtain in reproduction by spores or by vegetative multiplication, and that its significance lies in the fact that it makes organic evolution more rapid and far more varied." *Wilder D. Bancroft*

Examination of Lubricating Oils. *By Thos. B. Stillman. 23 × 16 cm; pp. 120. Easton: The Chemical Publishing Co., 1914. Price: $1.25.*—This book gives a very clear account of the tests to be made in examining lubricating oils. Many of these tests are essentially physical chemical in nature, such as the flash and fire test, and the determinations of viscosity and specific gravity. The author has not confined himself solely to questions of manipulation. The discussion of the flash test takes up the principles involved. Under the subject of lubricating oils containing blown rape-seed and blown cotton-seed oils, p. 94, the author says: "It is a peculiar fact, however, that a mineral oil alone does not give as satisfactory results in lubrication (especially cylinder lubrication) as does a mixture of mineral and vegetable or mineral and animal oils, one of the primary causes being that the viscosity of mineral oils diminishes rapidly at high temperatures whereas the reduction of viscosity of vegetable and animal oils is very much less. If it were not for this peculiarity between these two classes of oils, mineral lubricating oils could easily supplant (on the score of cheapness) all other oils used in lubrication." *Wilder D. Bancroft*

Handbuch der Mineralchemie. *By C. Doelter. Vol. II. Part VI. 18 × 25 cm; pp. 160. Dresden: Theodor Steinkopff, 1914. Price: 6.50 marks.*—This number deals with the aluminum and iron silicates. The evidence seems to be conclusive that no definite aluminum silicate is formed directly in the wet way. We get merely mixtures of colloidal alumina and colloidal silica. At high temperatures definite compounds are formed and of course the colloidal precipitate may change in time under conditions to a definite compound, though nobody knows whether this actually occurs or what the conditions are. The experiments of Mellor and Holdcroft are cited, p. 83, to show that kaolin breaks up above 500° into free alumina, silica, and water. While this change seems very probable, the proof of it is not as satisfactory as one could like.

There is an interesting chapter on the chemistry of porcelain, the subject being discussed under the headings: kinds of porcelain; manufacture of porcelain; physical and chemical changes during the firing of porcelain; the properties of porcelain and the way they change with changing composition.

There is a very pretty problem for somebody to work out, the reason for the color changes in topaz, p. 26, when exposed to radium rays, etc. Röntgen rays turn colorless topazes yellow and intensify the tint of colored topazes. Radium rays color white topazes orange and change yellow or pink topazes to a dark orange. The dark orange color is changed to lilac by the action of ultraviolet light or by heating in air. When heated in sulphur vapor the dark orange topazes become green. Nothing seems to be known as to the chemical changes involved. *Wilder D. Bancroft*

Taschenbuch für Gerbereichemiker und Lederfabrikanten. *By H. R. Procter. Translated by Josef Jettmar. 12 × 15 cm; pp. v + 248. Dresden: Theodor Steinkopff, 1914.*—This little book deals chiefly with the analytical details in the leather industry as is shown by the headings: introduction; alkalimetry; testing water; unhairing, deliming and bating; qualitative testing of vegetable tannins; sampling and grinding of tanning materials; quantitative determination of tannin; testing the substances used in mineral tanning; analysis of formaldehyde and of salt; testing of soaps; oils and fats; testing for and determining grape sugar; analysis of leather; use of microscope; bacteriology and mycology. *Wilder D. Bancroft*

MOLECULAR ATTRACTION. XI. NEW RELATIONS REVEALED BY DIAGRAMING INTERNAL PRESSURE AS A NEGATIVE PRESSURE

BY J. E. MILLS

Symbols.—Subscripts to symbols designate special or particular values. Pressures are expressed in millimeters of mercury, temperatures in degrees Centigrade, volumes in cubic centimeters, and energy in small calories.

A, a, α, β, b, C, c are constants.

d denotes density of a liquid.

D denotes density of saturated vapor.

E denotes energy.

E_E denotes energy spent in overcoming external pressure.

f denotes force.

L denotes total latent heat of vaporization.

λ denotes internal heat of vaporization $= L - E_E$.

M denotes total mass taken.

m denotes molecular weight, m' the mass of a molecule.

μ' is the constant of molecular attraction given by the expression $\frac{L - E_E}{\sqrt[3]{d} - \sqrt[3]{D}}$.

$\mu = c\mu'\sqrt[3]{m}$.

n is the number of molecules in the mass taken.

P denotes the external pressure.

p denotes the internal pressure caused by the molecular attractive forces.

R is the gas constant $= \frac{62392}{m}$.

s denotes the distance apart of the molecules.

T denotes absolute temperature.

t denotes temperature in degrees Centigrade.

v denotes the volume of a gram of liquid.

V denotes the volume of a gram of vapor.

Although the significance of our thermodynamical formulae, and their mechanical explanation in terms of our usual molecular-kinetic conceptions, leave much to be desired, yet these formulae stand today apparently entirely deserving of the universal trust which they receive. For this reason I choose to begin the proof of the conception to be presented by using a thermodynamical equation, although as a matter of fact the conception arose from a consideration of very different equations and ideas.

The Thermodynamical Equation, $\lambda = \frac{1}{J}\left(\frac{dP}{dT}T - P\right)(V - v)$.

The Clausius-Clapeyron thermodynamical equation for the heat of vaporization of a liquid,

1. $$L = \frac{dP}{dT}\frac{T}{J}(V - v) = 0.0_{4}31833\frac{dP}{dT}T(V - v) \text{ calories},$$

can be combined with the thermodynamical equation for the energy spent in overcoming the external pressure during the change of volume,

2. $$E_E = \frac{P}{J}(V - v) = 0.0_{4}31833\,P(V - v) \text{ calories},$$

and we have,

3. $$L - E_E = \lambda = 0.0_{4}31833\frac{dP}{dT}T(V - v) - 0.0_{4}31833\,P(V - v),$$

or,

4. $$P(V - v) = \frac{dP}{dT}T(V - v) - 31414\,\lambda.$$

The measurements desired have been accurately made for isopentane[1] by Dr. Sydney Young and that liquid is, therefore, chosen for study. The data used are shown in Table I.

The $\frac{dP}{dT}$ were obtained from the Biot equation,

5. $$\log P = a + b\alpha^{t} + c\beta^{t},$$

used by Young for smoothing the vapor pressures. On differentiating and changing to Naperian logarithms we obtain

6. $$\frac{dP}{dT} = 5.3019\,P(b\log\alpha.\alpha^{t} + c\log\beta.\beta^{t}).$$

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[1] Sci. Proc. Roy. Dublin Soc., 12, 374 (1910); Proc. Phys. Soc. London, Session 1894–95, p. 602.

The constants are given in the references cited. The values of the $\frac{dP}{dT}$ so obtained are given in Table I.

Drawing the usual pressure-volume curve, Fig. 1, for isopentane at 120° C, we represent $P(V - v)$ of Equation 4 by the rectangle ABFE, and this area represents the work done

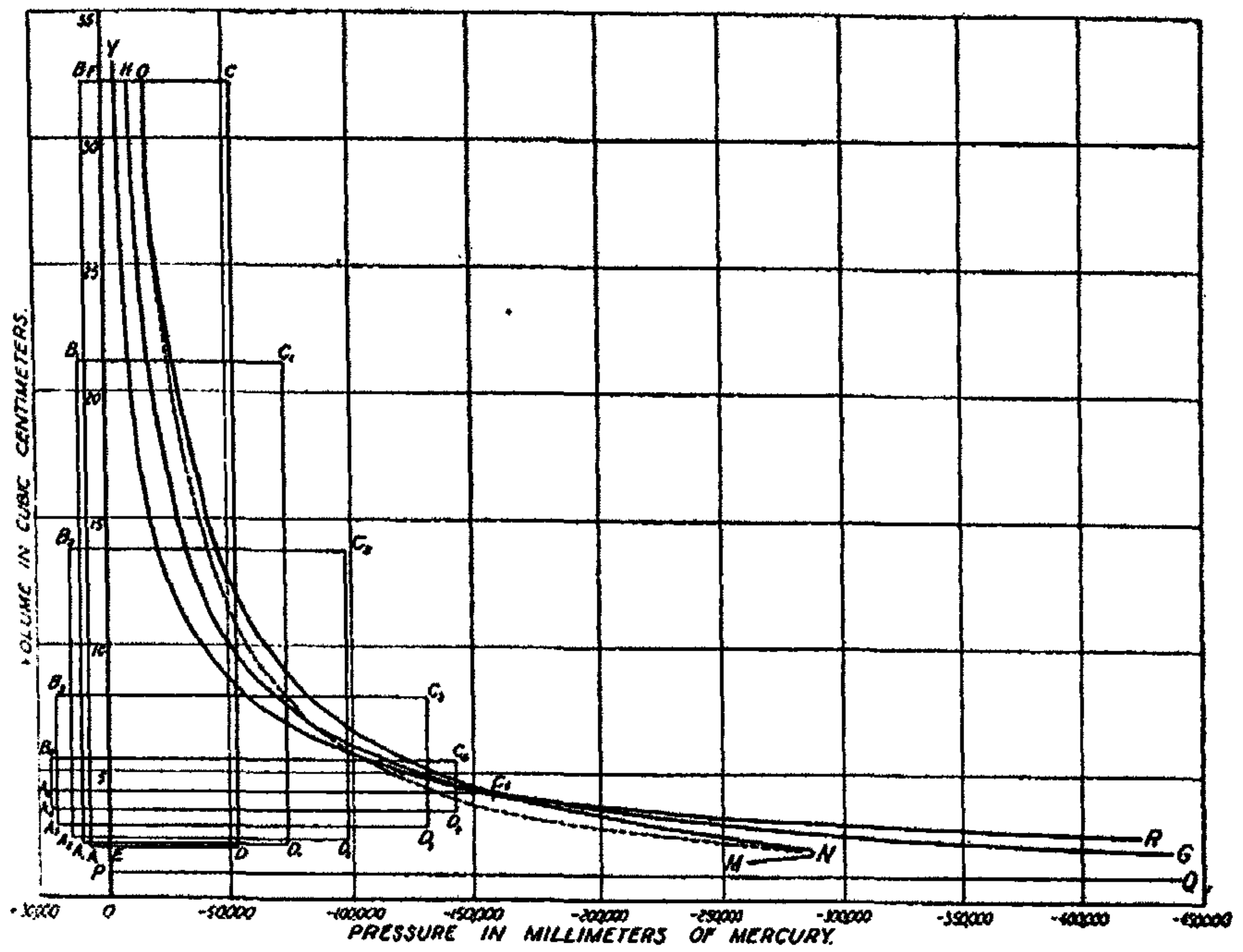

Fig. 1

The rectangles ABCD, $A_1B_1C_1D_1$, etc., represent the heats of vaporization given by the thermodynamical Equation 4, each rectangle being upon a different temperature plane, and the internal heat of vaporization being represented by that portion of the rectangle below the line of zero pressure. A_6C_6 represents the critical volume line. The line G-H represents equation 10 of Mills. The line MNO is the projection of the end points of the lines represented by Equation 17 from Dieterici's Equation 15, a complete curve for 120° C being given by the dotted line NO. The curve R-Y is the locus of the points a of Equation 22 of Ramsay and Young. The lines A_6C_6, G-H, R-Y, and MNO, intersect at C_6. The diagram shows the possibility of plotting and studying the region of negative internal pressure.

during expansion from volume v to volume V against the external pressure P. If now we undertake similarly to represent the term $\frac{dP}{dT}T(V - v)$ by an area, it clearly has the same base as before, *but the pressure ordinate is enormously greater than P and must, therefore, be extended into the region of negative pressure or must be extended as a positive pressure far beyond P (that is beyond A in the diagram).*

If extended from E in a positive direction, the line $\frac{P}{dT}T$ passing beyond A will clearly represent no pressure of which we have any direct evidence. While if $\frac{dP}{dT}T$ be regarded as representing a total pressure, made up of the external pressure, and an internal pressure, it may be extended from A so as to pass into a region of negative pressure and *this negative pressure may prove to represent the pressure arising from the molecular attraction.* One knows certainly after a most elementary acquaintance with mechanical conceptions that the internal pressure arising from the molecular attraction does act in a direction opposite to the usual pressure due to the kinetic motion of the molecules, and can be regarded, in a sense at least, as a negative pressure.

Extending $\frac{dP}{dT}T$, therefore, from A in the negative direction it becomes represented in the diagram by the line AD. The area ABCD, therefore, represents $\frac{dP}{dT}T(V - v)$, which is from Equation 4 the total heat of vaporization. Since ABFE represents the external work done in pushing back the external pressure during the vaporization, the area EFCD will represent the internal heat of vaporization, denoted in Equation 4 by the term 31414 λ. Therefore, according to our method of representation the internal heat of vaporization will appear always as a pressure-volume area below the line of zero pressure. Similar diagrams are drawn for isopentane at 140°, 160°, 180° 187° and at the critical temperature 187.8°.

It is important to note that at the critical temperature no area results because the factor $V - v$ becomes zero, the factor $\frac{dP}{dT}T$ still retaining a significant value.

I have here introduced and discussed the thermodynamical Equation 6 to show that it suggests very naturally the idea that the internal heat of vaporization should be represented as an area lying wholly below the line of zero pressure in an isothermal plane. If this idea is correct it should lead to conclusions not hitherto recognized. No further conclusions of value are at once apparent from Figure 1 and this probably accounts for the failure of other investigators to study the facts from the point of view here adopted. Moreover the method of representation adopted would lead one to suppose that *the negative internal pressure remained a constant during a change in volume.* This certainly cannot be true. The true situation can be stated as follows:

The negative pressures found are the average internal pressures during the given change in volume except at one point, the critical temperature. At the critical temperature there is no change in volume and the "average" negative pressure above found should represent the true internal pressure at this volume. This we find below to be the case when a correct value for the $\frac{dP}{dT}$ at the critical temperature is used. (We have before clearly proved[1] that Equation 5 at and very near the critical temperature does not correctly represent the observed vapor-pressure curve, and that Equation 6 in this region will in consequence give values for the $\frac{dP}{dT}$ much too low. By directly smoothing the observations of vapor pressure and their rate of change, a more nearly correct value of the $\frac{dP}{dT}$ at the critical temperature, 379, is obtained. This value is also somewhat too low owing to the fact that the percentage errors of observation are multiplied more than 60 times in obtaining the $\frac{dP}{dT}$ directly from the observations.)

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[1] Jour. Phys. Chem., 9, 402 (1905).

The Equation of Mills, $\lambda = \mu'(\sqrt[3]{d} - \sqrt[3]{D})$.

In work upon molecular attraction and closely related phenomena I have shown,[1] I think conclusively, that the equation,

$$7.\quad \frac{L - E_E}{\sqrt[3]{d} - \sqrt[3]{D}} = \text{constant} = \mu' \text{ or } \lambda = \mu'(\sqrt[3]{d} - \sqrt[3]{D}),$$

is true, and that this equation can be derived easily and follows naturally, if the law governing the molecular force, *f*, is

$$8.\quad f = \frac{\text{constant}}{s^2} = \frac{\mu' M}{s^2}, \text{or more fully, } f = -\frac{c\mu'^3\sqrt{mm'}}{s^2} = -\frac{\mu m'}{s^2}.$$

The truth of Equation 7 has been admitted finally by nearly all of those who have examined the work critically and who have published the results of their investigations, but a good many of these investigators have never been convinced that Equation 7 is really caused by the law of molecular force given in Equation 8. The objections advanced to Equation 8 for the law of force have been from time to time answered in the papers cited, and all of this work is now undergoing revision in order that it may be published in a convenient form for critical inspection.

We will proceed next upon the assumption that the internal molecular pressure does arise from an attraction obeying the law given in Equation 8 and proceeding from the individual molecules. To determine the effect of this attraction per square centimeter of surface we note that the attraction of a molecule varies inversely as the square of the distance apart of the molecules. Now the number of molecules in any square centimeter of surface also varies inversely as the square of their distance apart. Consequently the internal molecular pressure per square centimeter varies as the fourth power of the distance apart of the molecules, and as a matter of fact

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[1] Jour. Phys. Chem., 6, 209 (1902); 8, 383, 593 (1904); 9, 402 (1905); 10, 1 (1906); 11, 132, 594 (1907); 13, 512 (1909); 15, 417 (1911); 18, 101 (1914); Jour. Am. Chem. Soc., 31, 1099 (1909); Phil. Mag., Oct. (1910); July (1911); Oct. (1912); Trans. Am. Electrochem. Soc., 14, 35 (1908); Chem. News, 102, 77 (1910); and related papers, Mills and MacRae: Jour. Am. Chem. Soc., 32, 1162 (1910); Jour. Phys. Chem., 14, 797 (1910); 15, 54 (1911).

is given in millimeters of mercury, using the symbols and constants adopted, by the expression,

$$10. \qquad p = -\frac{31414\mu'}{3V^{4/3}}.$$

For isopentane $p = -\frac{1,104,300}{V^{4/3}}$, since $\mu' = 105.46$.

To those readers who are not familiar with the conception of molecular attractive forces advanced in previous papers, I would explain that the *essential difference* between my conception of the behavior of the attractive forces and the conception usually held, lies in the fact that I consider a molecule to have a certain total power of attraction which remains a constant at a given average distance apart of the molecules, independently of how that attraction may be distributed to the surrounding molecules and independently of the number of molecules. (I have never found any method of determining certainly how this total attraction is distributed, but it is quite possible, and in my opinion it is very likely, that its distribution in a sense follows Newton's law of gravitation.)

Consequently in calculating the effect of the attraction upon the pressure per square centimeter I have only to take the attraction of one molecule at the given distance and multiply this attraction by the number of molecules in the square centimeter of surface. In other words, the attraction of the molecules is a constant property of the molecule precisely as is its molecular weight (only the attraction varies with the distance apart of the molecules).

The above idea has been shown in the papers cited to be in accord with the facts and it is important that it be clearly understood. I will illustrate, therefore, by a concrete example. Since the direction and distribution of the total attraction is mathematically a matter of no importance for most purposes, I can consider the total attraction of a molecule A to be exerted upon a molecule B at distance s. If I then place beside B another similar molecule C the total attraction of A for B and C remains the same as it formerly was for B alone. According to the usual conception the attraction of A for B and C, two similar molecules, at distance s, is twice what it is for B alone at distance s. According to my conception, while the total attraction of A may be shared by both B and C it remains the same for B and C together at distance s as it was for B alone at distance s. The fact that the total attraction is now divided between the two molecules B and C has not increased its amount in the least.

However, I am not here trying to prove that my conception of the attractive force is the correct one. The conception has in the past proved to be in accord with the facts considered and if I can here deduce from this conception new relations in accord with the facts its use will be sufficiently justified.

That Equation 10 is correctly deduced from the premises, and that it is in accord with the fundamental law stated in Equation 7, will be clear upon considering that

$$11. \qquad E = \int P dV,$$

and substituting for P its value from Equation 10, we have, calling the internal energy given out λ,

$$12. \qquad \lambda = \int_{v}^{V} -\frac{31414\mu'}{3V^{4/3}}\,dV = \Big|_{v}^{V} -\frac{31414\mu' v^{-1/3}}{3 \times -1/3} = 31414\mu'(\sqrt[3]{d} - \sqrt[3]{D}),$$

an expression which can be reduced to calories by dividing by 31414 and is then in accord with the law given in Equation 7, and already proved in the numerous papers cited.

It is really a source of much gratification to be able to deduce Equation 7 in this way, because Equation 7 was originally (after correction of an earlier error) deduced[1] from a consideration of the individual action of the attractive forces upon the individual molecules. And yet it is clear if Equation 7 really resulted from the law of molecular force given in Equation 8, and if the effect of this force upon the total

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[1] Jour. Phys. Chem., 11, 143, 147 (1907). Note the two derivations of the law.

internal pressure is correctly given in Equation 10, that one should be able to arrive at the same result either by considering the individual forces between the molecules or by considering their resultant. Consequently the demonstration above given really completes a cycle of operations, and to arrive exactly at the starting point is gratifying evidence that no errors were made in the individual operations and arguments.

Moreover my idea as to the independence of the kinetic and attractive energies and of the connected external and internal pressures *under the conditions studied* were, to put it mildly, "viewed with suspicion," by some investigators. Yet this same independence is here again in evidence.

I have plotted in Fig. 1, line GH, the internal pressures calculated by Equation 10 against the volumes, the data being given in Table I. The ordinates of this curve represent the internal pressure in millimeters of mercury per square centimeter and it will be noted that *at the critical temperature this internal pressure does equal the internal pressure obtained from the thermodynamical equation within the limit of experimental error.* (149,635 = 159,500, attention has already been

TABLE I—ISOPENTANE

Temperature t °C	Pressure P	Volume of		Density of		$\sqrt[3]{d}$
		Liquid v	Vapor V	Liquid d	Vapor D	
0	257.74	1.5644	917.4	0.6392	0.001090	0.8614
20	572.59	1.6141	426.6	0.6196	0.002344	0.8525
40	1131.1	1.6700	224.4	0.5988	0.004456	0.8429
60	2035.6	1.7329	127.6	0.5769	0.007837	0.8325
80	3400.8	1.8055	77.7	0.5540	0.01287	0.8213
100	5354.5	1.8940	49.5	0.5278	0.02020	0.8081
120	8039.9	2.0037	32.20	0.4991	0.03106	0.7932
140	11620	2.153	21.15	0.4642	0.04728	0.7743
160	16285	2.378	13.72	0.4206	0.07289	0.7493
180	22262	2.858	7.95	0.3498	0.1258	0.7046
185	23992	3.183	6.355	0.3142	0.1574	0.6799
187	24713	3.500	5.455	0.2857	0.1833	0.6586
187.8	25005	4.268	4.268	0.2343	0.2343	0.6165

$m = 72.10$, $\mu' = 105.46$, $C = 1.688$

TABLE I (*Continued*)

Temperature t °C	$\sqrt[3]{D}$	$\frac{1}{v^{1/3}}$	$\frac{1}{V^{1/3}}$	$\frac{dP}{dT}$	$\frac{dP}{dT}T$	$\frac{dP}{dT}T-P$
0	0.1029	0.5506	0.0001121	11.16	3047	2789
20	0.1328	0.5282	0.0003112	21.04	6165	5592
40	0.1646	0.5048	0.0007339	35.66	11162	10031
60	0.1986	0.4803	0.001555	55.73	18558	16522
80	0.2344	0.4550	0.003018	81.85	28893	25492
100	0.2724	0.4264	0.005506	114.7	42783	37429
120	0.3144	0.3959	0.009771	155.2	60986	52946
140	0.3616	0.3594	0.01709	204.4	84425	72805
160	0.4177	0.3152	0.03045	264.0	114312	98027
180	0.5011	0.2465	0.06305	335.9	152163	129900
185	0.5400	0.2137	0.08503	356.1	163100	139100
187	0.5681	0.1882	0.1041	364.4	167600	142890
187.8	0.6165	0.1445	0.1445	367.8	169480	144475
187.8	—	—	Ob.	379.0	174640	149635

TABLE I (*Continued*)

Temperature t °C	$\frac{31414\mu'}{3v^{1/3}}$	$\frac{31414\mu'}{3V^{1/3}}$	λ		
			Ther. Equation 3	Mills Equation 7	Dieterici Equation 15
0	608000	124	81.35	79.98	80.96
20	583200	344	75.67	75.90	76.02
40	557400	810	71.10	71.53	71.37
60	530300	1718	66.20	66.85	66.59
80	502400	3330	61.59	61.89	61.80
100	470800	6080	56.72	56.49	56.63
120	437200	10790	50.89	50.49	50.77
140	396800	18880	44.04	43.52	43.89
160	348000	33620	35.39	34.97	35.31
180	272200	69620	21.04	21.45	21.55
185	236100	93900	14.05	14.75	14.74
187	207800	114900	8.89	9.55	9.49
187.8	159500	159500	0	0	0

called to the fact that the error in obtaining the value 149,635 is very large. That the poor agreement shown is only due to errors of observation will appear more clearly later.)

Moreover the internal pressures given by the thermodynamical equation at other temperatures are the "mean" or "average" values of the integral, $\int_v^V f(v)dv$, that is, they are the mean values of the ordinates between the proper limits, V and v of the curve GH. This follows because,

$$\int_v^V -\frac{31414\mu'}{3V^{4/3}}\,dv = 31414\mu'(\sqrt[3]{d}-\sqrt[3]{D}) = \left(\frac{dP}{dT}T-P\right)(V-v).$$

The first equality was shown above. The second equality was experimentally proved for numerous substances in former papers. After reduction to calories the values for isopentane are given in Table I under the headings λ-Ther., Mills, for convenient comparison here. In other words, *the mean values of the ordinates to the curve GH between the limits V and v are mathematically equal to* $\frac{31414\mu'(\sqrt[3]{d}-\sqrt[3]{D})}{V-v}$ *and this value we have proved experimentally is equal to* $\frac{dP}{dT}T-P$ *obtained for the corresponding temperature, pressure, volume, conditions.*

It should be constantly remembered that we really have to deal with a tri-dimensional pressure, volume, temperature, diagram, and that the curves ABCD, $A_1B_1C_1D_1$, etc., shown on Fig. 1 are really on different temperature planes, and that Fig. 1 is really made by the projection of points and lines that exist on different temperature planes. The fact that no temperature function enters into Equation 12, and the fact that it is true at all temperatures studied, cause the projection of all of the points and curves considered to fall into one line GH. However much we may be inclined to an opinion on the subject, we have as yet no experimental evidence to show that limits on the curve GH can be taken arbitrarily at any temperature.

Before leaving Equation 12 it is important to note that its definite integral can be obtained as follows on the supposition that it is true for all values of V.

$$13.\quad E = \int -\frac{31414\mu'}{3V^{4/3}}\,dV = 31414\mu'\sqrt[3]{d} + C = 31414\mu'\sqrt[3]{d}.$$

For when the volume is infinite, E is zero and d is zero. Consequently C is also zero. We can write

$$14.\quad \lambda_\infty = \mu'\sqrt[3]{d} \text{ calories, or } \lambda_\infty s = \mu'\sqrt[3]{m},$$

where λ_∞ indicates the heat given out when the molecules come from an infinite distance apart to a distance apart represented by s, that is to a density d.

This result I have previously derived in the papers cited from Equation 7, but this new deduction is worth while because *it shows that the internal attractive energy given out by a substance on contraction from an infinite volume to volume v, or density d, can be represented graphically by the area between the V axis, the curve GH, and the ordinate at the volume v.*

The Equation of Dieterici, $\lambda = CRT\ln\frac{d}{D}$.

Dieterici found an empirical equation for the internal heat of vaporization,

$$15.\quad \lambda = CRT\ln\frac{d}{D} = 4.573\,C\,\frac{T}{m}\log\frac{d}{D} \text{ calories} = CRT\ln V - CRT\ln v.$$

This equation has been carefully studied[1] by the author, by Dieterici himself, by Steinhaus, and by others. It is a remarkably accurate equation with a tendency to give slightly too high results at very low vapor pressures. The constant varies slightly for various substances but is usually around 1.7. For isopentane C has the value 1.688. The values of λ calculated from Equation 15 are given in Table I for comparison with the values of λ obtained from Equations 1 and 6 (see under the heading λ-Ther., Mills, Dieterici).

Equation 15 can be expressed,

$$16.\quad \lambda = \int_v^V \frac{CRT}{V}\,dV = \Big|_v^V CRT\ln V + C_1.$$

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[1] Mills: Jour. Am. Chem. Soc., 31, 1099 (1909); Dieterici: Drude's Ann., 25, 569 (1908); 35, 220 (1911); Richter: Dissertation Rostock, 1908; Steinhaus: Dissertation, Kiel, 1910.

When $v = 1$, $\ln v = 0$ and $\lambda = C_1$. The value of the constant of integration can, therefore, be found if the value of λ can be found when 1 gram of liquid occupies a volume of 1 cubic centimeter. The indefinite integration gives the area bounded by the ordinates $v = 1$ and $v = v$, plus a constant.

It is clear that we here deal with a curve in every respect similar to the usual PV curve for a perfect gas except that $\frac{PV}{T}$ equals CR instead of R. The curve is a parabola referred to its asymptotes as axes. The internal pressure is given by the expression,

$$17. \quad p = \frac{CRT}{V} = \frac{1.688 \times 62392}{72.10} \frac{T}{V} = 1460.7 \frac{T}{V} \text{ for isopentane.}$$

Values of $\frac{CRT}{V}$ for liquid and saturated vapor are given in Table II. The curves represented by Equation 17 are plotted in Fig. 1, the end points of the curves alone being shown on the line MNO except for 120° when the dotted line NO indicates the complete curve. These curves are, of course, projections from the corresponding temperature planes. The area bounded by these curves, the pressure ordinates, and the volume axis represents the internal heat of vaporization. These areas are equal to the areas between similar limits of volume as obtained from Equations 3 and 12 as is proven by the equality of the values of the internal heat of vaporization λ given in Table I, under the headings, Ther., Mills, Dieterici.

At the critical temperature we have

$$T\frac{dP}{dT} - P = \frac{31414\mu'}{3V_c^{4/3}} = \frac{CRT}{V_c},$$

and we get 149,635 = 159,500 = 157,700, the values agreeing to within the limit of experimental error.

Combining Equations 7 and 15 we have

$$18. \qquad \lambda = \mu'(\sqrt[3]{d} - \sqrt[3]{D}) = CRT \ln V - CRT \ln v,$$

or,

$$19. \qquad \mu'\sqrt[3]{d} + CRT \ln v = \mu'\sqrt[3]{D} + CRT \ln V.$$

Steinhaus (*loc. cit.*) first examined the equations in this form but seems to have been unable to understand the result. The values of the various terms for isopentane are given in Table II. Plotting the values of the various terms of Equation 19 against the temperature we have the curves shown in Fig. 2. Now these curves become identical if the diagram is rotated around the axis AB 180°. In other words the curves are the same curves but with a different origin and direction (sign). We find experimentally for isopentane (see Table II) that Equation 19 takes the form,

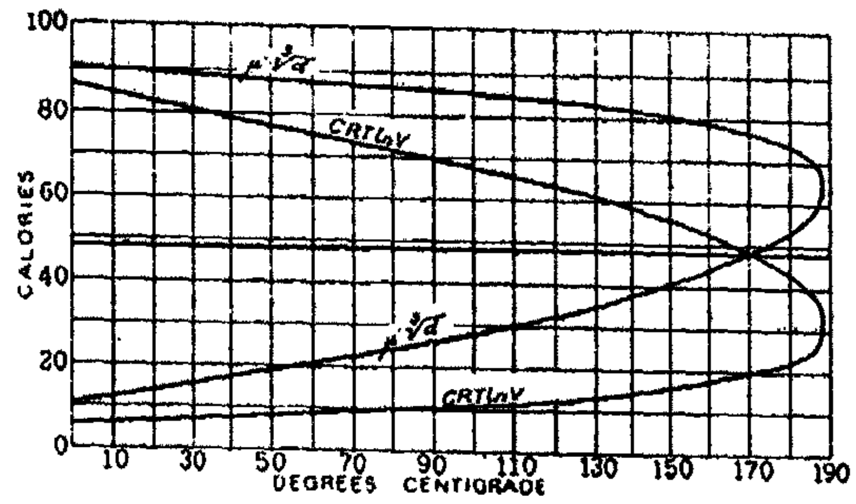

Fig. 2

The curves show the energy changes indicated by Equation 1 of Mills and 15 of Dieterici. The curves are clearly the same curves but with a different origin and direction. One curve becomes practically identical with the other if rotated around the axis AB 180°.

20. $\mu'\sqrt[3]{d} + \mathrm{CRT}\, ln\, v = 96.38 = \mu'\sqrt[3]{\mathrm{D}} + \mathrm{CRT}\, ln\, \mathrm{V},$

or,

21. $\dfrac{\mu'}{v^{1/3}} = 96.38 - \mathrm{CRT}\, ln\, v;$ or $\mathrm{CRT}\, ln\, v = 96.38 - \mu'\sqrt[3]{d},$

where *v* is the volume and *d* is the density either of the liquid or of the saturated vapor at any temperature. This equation for isopentane is remarkably accurate.

Considering isopentane at 120°, Figure 1, it now becomes clear that $\mu'\sqrt[3]{d}$ represents the area EGH-V when V represents an infinite volume, CRT*ln v* represents the area PQNOF, the latter area extending from the line PQ drawn at volume $v = 1$, in the direction indicated by the arrow.

If one is called upon to deal with liquids whose density is

TABLE II—ISOPENTANE

Temperature $t°$ C	CRT	$\frac{\text{CRT}}{v}$	$\frac{\text{CRT}}{\text{V}}$	$\mu'\sqrt[3]{d}$	$\mu'\sqrt[3]{\text{D}}$	CRT $ln\ v$	CRT ln V	$\mu'\sqrt[3]{d}$ + CRT $ln\ v$	$\mu'\sqrt[3]{\bar{\text{D}}}$ + CRT ln V	a Equation 22	
										Liquid	Vapor
0	398800	254900	434.7	90.83	10.85	5.69	86.64	96.52	97.49	—	—
20	428000	265200	1003	89.90	14.00	6.52	82.54	96.42	96.54	1,544,000	34
40	457200	273800	2037	88.89	17.35	7.47	78.83	96.36	96.18	1,438,000	114
60	486400	280600	3812	87.79	20.94	8.52	75.13	96.31	96.07	1,310,000	344
80	515600	285600	6635	86.61	24.71	9.70	71.49	96.31	96.20	1,177,000	867
100	544800	287500	11000	85.22	28.72	11.09	67.72	96.31	96.44	1,031,000	1,960
120	574000	286500	17830	83.64	33.15	12.71	63.49	96.35	96.64	884,400	4,780
140	603300	280000	28520	81.65	38.13	14.74	58.64	96.39	96.77	718,100	10,170
160	632500	266000	46100	79.01	44.03	17.45	52.76	96.46	96.79	538,300	22,030
180	661700	231500	83230	74.30	52.84	22.14	43.70	96.44	96.54	335,800	58,560
185	669000	210200	105300	71.70	56.95	24.67	39.40	96.37	96.35	265,500	85,230
187	671900	192000	123200	69.45	59.91	26.81	36.31	96.26	96.22	220,000	109,400
187.8	673100	157700	157700	65.01	65.01	31.11	31.11	96.12	96.12	159,900	159,900

$\mu' = 105.46$, $C = 1.688$, $m = 72.10$

great so that v becomes less than 1 then CRT$ln\ v$ will give negative values. This is true with stannic chloride.

Also when v is 1 and $ln\ v = 0$, $d = 1$, and Equation 21 becomes $\mu' = 96.38$. As a matter of fact μ' for isopentane is 105.46. This discrepancy indicates nothing except that either Equation 7, or Equation 15, or both, break down if extrapolated to points outside of the saturated vapor-liquid equilibrium for which they were proven. That this view of the question is correct follows from a consideration of stannic chloride. The data for this liquid are not detailed here, but $v = 1$ lies in the saturated vapor-liquid region attainable at about 310° C, and at this point $\mu'\sqrt[3]{d} + \text{CRT}ln\ v$ does equal μ'. It may be remarked in passing that for stannic chloride $\mu'\sqrt[3]{d} + \text{CRT}ln\ v$ does not always equal a constant, but varies slightly, and apparently linearly, with the temperature, passing through the value μ' at about the temperature indicated.

The peculiar form of the curve MNO for isopentane shown on Figure 1 should be noted, particularly in connection with the fact that Dieterici's Equation 15 gives too high results at low temperatures, and with the fact just shown that Equation 21 cannot be extrapolated for isopentane to volume $v = 1$.

As yet too little is known regarding this region of negative internal pressure that I am attempting to explore to indulge in speculation regarding the meaning of the relations found. But it must not be supposed that we are here studying merely mathematical relationships. The equations here under investigation have been extensively studied for many substances (see papers cited), and they certainly do closely represent physical relationships. Any study which will throw additional light upon these relationships is well worth while.

The Equation of Ramsay and Young, $P = bT - a$.

Sir Wm. Ramsay and Dr. Young so long ago as 1887 called attention to the fact that van der Waals' equation,

$$21a. \qquad \left(P + \frac{a}{V^2}\right)(v - b) = RT$$

at *constant volume* reduced to

$$P = bT - a = \frac{dP}{dT}T - a, \qquad (22)$$

where at constant volume $b = \frac{dP}{dT}$ = constant, and a was a constant. This equation was tested in a careful experimental study[1] for a good many substances both in the condition of liquid and gas and was found to be very nearly true. $\frac{dP}{dT}$ at constant volume does not remain exactly and absolutely a constant at all temperatures. Dr. Young found for isopentane[2] that at volumes lower than 4.6 cubic centimeters per gram, the values of b increase with rise in temperature, while at greater volumes up to about 400 cc they diminish. At still larger volumes they appear to be constant.

Values of a obtained by interpolation from Young's results are shown in Table II for the corresponding volumes. The values found for a for isopentane by Young are plotted on Fig. 1 forming the line R-Y. (Young obtained the values of a by two methods. I use his values from drawn isochors throughout.) It will be noted that this line intersects the other lines, A_6C_5, GH, MNO, at the negative pressure corresponding to the critical volume.

I have now obtained the value of the internal negative pressure at the critical temperature by four methods getting

$$\frac{dP}{dT}T - P = \frac{31414\mu'}{3V_c^{4/3}} = \frac{CRT}{V_c} = a. \qquad (23)$$

$$149{,}635 = 159{,}500 = 157{,}700 = 159{,}924.$$

I may add here that the first value, 149,635, is too low, due solely to the fact that no *accurate* $\frac{dP}{dT}$ can be obtained at the critical temperature either directly from the observations or

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[1] Ramsay and Young: Phil. Mag., (5) **23**, 195, 435 (1887); Phil. Trans., **180A**, 137 (1889); **183A**, 107 (1892); Young: Proc. Phys. Soc. London, **13**, 602 (1895); "Stoichiometry", pp. 203-213; Rose-Innes and Young: Phil. Mag., (5) **48**, 213 (1899); **43**, 126 (1897); **47**, 354 (1899); (6) **2**, 208 (1901); Amagat: Comptes rendus, **94**, 847 (1882); Ann. chim. phys., (6) **29**, (1893); Barus: Phil. Mag., (5)·**30**, 358 (1890).

[2] Proc. Phys. Soc., **13**, 648 (1895).

indirectly through the Biot formula, due to the great multiplication of the errors of the observations in obtaining the $\frac{dP}{dT}$. The correct value of the $\frac{dP}{dT}$ at the critical temperature is nearly always given by the expression

$$\frac{dP}{dT} = \frac{2R}{V_c} = \frac{124784}{V_c m}, \tag{24}$$

first discovered as an empirical equation by Dieterici and later independently derived by the author from an equation given by Crompton.[1] Using the value 405.4 of the $\frac{dP}{dT}$ so derived we would obtain for $\frac{dP}{dT}T - P$ the value 161,800.

The importance of the relations given in Equation 23 and their graphical representation as negative pressure is, I believe, great. One would expect further study of these relations to throw additional light upon the equation of state, thermodynamical formulae, and entropy relations.

Summary

It is pointed out that negative internal pressure can be diagramed and studied, and that this method of representation leads to relations not hitherto recognized.

University of South Carolina
November 23, 1914

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[1] Jour. Phys. Chem., 9, 402 (1905), and other papers cited.

THE THEORY OF EMULSIFICATION. VI

BY WILDER D. BANCROFT

In the preceding paper[1] of this series I showed that the liquid A will be the dispersing phase and liquid B the disperse phase in an emulsion in case the surface tension between liquid A and the emulsifying agent C is lower than the surface tension between liquid B and the emulsifying agent. It was also shown that a corollary of this is that an aqueous colloid will tend to make water the external phase while a non-aqueous colloid[2] will tend to make water the internal phase. I did not take up specifically the conditions under which a substance acts as an emulsifying agent; but this is important both in its bearing on the formation of emulsions and in its bearing on the allied problem of ore flotation. For a substance to be an emulsifying agent, it must tend to pass into the surface separating the two liquids and form a coherent film there. If the emulsifying agent does not form a coherent film the emulsion will crack; if it does not pass into the liquid interface, it will not form a film round one of the liquids. Since the adsorption of air plays an important part in ore flotation and since it may be of importance in the formation of emulsions, I propose to consider the general problem of the concentrating of a dissolved or suspended substance at an interface between liquid and liquid or between liquid and vapor. To avoid circumlocution the surface separating two liquid phases will be called a dineric interface[3]

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[1] Bancroft: Jour. Phys. Chem., 17, 501 (1913).

[2] In the preceding paper I used the term hydrophobe colloid to denote a substance forming a colloidal solution readily in some non-aqueous solvent and not doing so in water. This is not the usual sense of the term; but the usual distinction between hydrophile and hydrophobe colloids becomes meaningless if we no longer distinguish between emulsion colloids and suspension colloids. It seems foolish to invent new words when we have two perfectly good ones with no meanings attached to them. I suggest, therefore, that hydrophile be used for colloidal solutions in water and hydrophobe for colloidal solutions in non-aqueous solutions.

[3] Bell: Jour. Phys. Chem., 9, 531 (1905).

and the surface separating liquid and vapor a foam interface. We will begin with the concentrating of a dissolved substance at a dineric interface. An interesting case of this sort has been studied by Wilson,[1] whose paper seems generally to have been overlooked.[2]

"When chloroform is placed in a test-tube, or other vessel of glass, standing on a horizontal surface, it exhibits, like other substances which wet that solid, a curved surface with the concavity upwards. If water or an aqueous solution of nitric, sulphuric, or muriatic acid, be poured upon the stratum of chloroform, the surface of the latter immediately changes the direction of its curve, and becomes convex upwards, the convexity induced being much greater however than the previous concavity. If, on the other hand, an aqueous solution of potash, soda, or ammonia be placed above the chloroform, the latter ceases at its upper limit to present a sensible curvature upwards or downwards, and shows a surface which, to the unassisted eye, appears to be flat. It is to this property of an acid to round, and of an alkali to flatten the surface of various liquids, of which chloroform is one, that I seek specially to direct attention.

"The phenomena referred to, cannot seem remarkable when merely described; but they have appeared striking and, I may say, startling to most who have witnessed them. They are best observed by dropping into a perfectly clean, flat-bottomed glass vessel containing pure water, a quantity of chloroform too small in amount to touch the walls of the vessel on every side. The heavier liquid then shows itself as a brilliant, highly mobile globule. If alkali be now added the globule in a moment collapses, sinks as if exposed to a crushing force, and flattens out on the bottom of the glass. On slightly supersaturating the alkali with an acid, the flattened chloroform starts into its previous globular shape, with a momentum and rapidity, such as might be exhibited

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[1] Jour. Chem. Soc., 1, 174 (1848).

[2] It is given among the references to the literature in Winkelmann's Handbuch der Physik, 1, 498 (1891).

by a highly elastic substance, like a ball of caoutchouc suddenly relieved from enormous pressure. When the acid in its turn is supersaturated with alkali, and flattening again occurs, and by alternating the addition of these reagents, the same globule may be successively flattened and rounded for any number of times.

"It is necessary here to mention that the employment of an acid is not essential to the development of the phenomena described. In distilled water, chloroform exhibits a convexity of upper surface as marked as in the aqueous solution of an acid. The alternate addition to it of water, and removal from it of alkali, are as efficacious accordingly as the successive addition of alkali and acid. But the washing away of the former by repeated effusions and decantations of water, is a tedious and unsatisfactory process, which has the great disadvantage of changing the form of the globule by slow graduations from a flat to a convex surface, whilst an acid effects the conversion *per saltum*. I shall confine my observations, accordingly, to the action of alkalies and acids, although the effect of the latter in altering the shape of the chloroform globule, is not greater but, as I incline to think, less than of water.

"Change in configuration, however, is not the only alteration which the globule of chloroform undergoes. Some of the other physical properties are markedly altered by its contact with acids and alkalies. These changes are best seen when a deep white saucer, or flat-bottomed porcelain basin, is made use of as the containing vessel. When acidulated water is placed in this, and chloroform let fall into it, the denser fluid is scarcely wetted and, although nearly half as heavy again as pure water, sinks reluctantly. If the drops indeed be small, they never reach the bottom but, by floating on the surface, evaporate away. Those which descend form globules very mobile, and readily obeying the solicitation of gravity. When separate globules melt, they rapidly flow together, and scarcely one is to be seen without a bubble of air attached to its upper surface and adhering tenaciously.

I have already referred to the brilliancy of the drops of chloroform at the bottom of the water; they retain this character when the water is acidulated.

"When the water, on the other hand, is alkaline, the chloroform is quickly wetted, and sinks swiftly. The drops, if small, become circular discs with rounded edges; if large, they are oval, or spread out into elongated, irregularly ovoidal, or flattened cylindrical forms. Their shape, however, is changed by the slightest impulse, or inclination of the containing vessel, in a way which, perhaps, I may best illustrate by comparing it to the ever-varying elongation, contractions and irregular swellings, which alter the configuration of an active living leech in a glass of water. The flattened globule, moreover, is much less mobile than the rounded one in acid. The former moves sluggishly, even down an inclination, clings to the vessel; and when compelled to move rapidly, leaves a tail behind it, like foul mercury. No air-bells attach themselves to it and its brilliancy is sensibly diminished, as if its refractive index had altered."

Some further experiments were made by Swan[1], who obtained the following results:

1. Olive oil floating on the surface of water or of hydrochloric acid has its under surface convex, but with solution of potash its surface is apparently flat. It has also, in contact with alcohol or sulphuric ether, a much flatter surface than with solution of potash.

2. Spermaceti oil also exhibits a convex surface in contact with water and hydrochloric acid, and a flat surface with solution of potash.

3. Oil of cloves sinks in water and has a highly convex surface, which becomes nearly flat on the addition of alcohol to the water; but the liquids mingle so readily that their mutual surface is not very well defined.

4. Oil of cassia sinks in water; and its surface, which is very convex, is considerably flattened by adding potash or

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[1] Phil. Mag., (3) 33, 36 (1848).

alcohol to the water. The addition of acid in the former case, or of water in the latter, restores the convexity of the surface.

5. Oil of lavender floats on water, with its under surface convex. If alcohol is poured upon it, its upper surface is nearly flat.

Swan also made some experiments to see "whether the results were modified by altering the nature of the containing vessel. I have found that on immersing a slip of recently ignited platina foil, or clean iron or brass wire in the liquids, the surface of the chloroform is highly convex in contact with them under water or hydrochloric acid, but apparently flat under solution of potash. If the metal is not perfectly clean, the surface of the chloroform is apt to become concave in contact with it under water or acid. On lining a glass tube with a thin coating of wax, I found that chloroform placed in it under hydrochloric acid had a very *concave* surface, while on supersaturating the acid with solution of potash the surface became sensibly flat. Similarly chloroform under water in a quill has a very *concave* surface which becomes sensibly flat on the addition of potash, and the concavity is restored by adding a sufficient quantity of hydrochloric acid. It will be observed that the coating of wax, or the substitution of a tube of quill for one of glass, while it completely reverses the curvature of the chloroform in contact with water and acids, exerts apparently no influence on the power of the alkali to flatten its surface; and the conclusion seems inevitable, that this effect depends upon a mutual action of the liquids, and is quite independent of the nature of the containing vessel for it takes place equally in contact with surfaces of glass, platina, iron, wax, or quill."

Having eliminated everything else, as he thought, Swan concluded that the flattening of the surface must be due to the affinity between caustic potash and the organic liquid, an affinity which is shown independently by the fact that caustic potash reacts with chloroform and with vegetable oils. Swan says: "In conclusion it may be remarked, that if the phaenomenon of the flattened surface of two immiscible liquids has received a correct explanation on the hypothesis of a strong mutual attraction of their molecules, and if this phaenomenon is found to appear only in cases where the liquids have a decided chemical affinity for each other, an interesting connexion is thereby established between chemical affinity and the mechanical force of adhesion, tending to prove that they are modifications of the same force; while the whole subject of the mutual attractions of two liquids opens up an interesting, and, so far as I am aware, a new field of inquiry in capillary attraction."

Swan's hypothesis, that the flattening takes place only when chemical action is possible, is proved to be wrong by the fact that benzene behaves in exactly the same way.[1] While the flattening is clearly due to a change in surface tension, it cannot depend on the absolute value of the surface tension of the water phase because Wilson found the effect of alkali to be the same qualitatively whether sodium chloride was present or not, whereas the addition of salt increases the surface tension of the water phase. What happens is that hydroxyl is adsorbed at the dineric interface lowering the surface tension and causing the organic liquid to flatten. This is confirmed by the experiments of von Lerch,[2] who determined the surface tension between benzene and water by means of the rise in capillary tubes. The surface tension between pure benzene and pure water was found to be 32.6 dynes/cm at 15°-16°. With M/4 NaOH the value dropped to 20.7 and with M/2 NH_4OH to 27.3. The lowering of the surface tension is greater with sodium hydroxide than with ammonia owing to the greater electrolytic dissociation of the former. The surface tension was also lowered by hydrochloric acid but only slightly, M/2 HCl bring it down to 31.5. This is in accord with Wilson's qualitative conclusions that acids do not increase the surface tension quite as much as

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[1] von Lerch: Drude's Ann., 9, 434 (1902).

[2] Drude's Ann., 9, 434 (1902).

pure water. Von Lerch also found a marked effect due to acetic acid; but this acid is miscible in all proportions with benzene and causes benzene and water to become more miscible, so there is nothing surprising about its behavior. The surface tension measurements are confirmed by the electrical ones, for von Lerch found that benzene drops in caustic soda moved fairly readily under electrical stress, whereas there was almost no movement in presence of sodium chloride or hydrochloric acid. It is possible that other ions might be adsorbed markedly by benzene, but I know of no experiments to show this.

The adsorption of hydroxyl means practically a concentrating of alkali at the surface of the benzene and consequently a closely adhering film of water. This accounts for Wilson's observations that the drops of chloroform were readily wetted by an alkaline solution. The presence of the surface film of caustic soda solution also accounts for the decreased mobility observed by Wilson.

The amount of adsorption has not been determined quantitatively in the preceding cases; but Patrick[1] has studied the adsorption of new fuchsine, picric acid, salicylic acid, and mercurous sulphate from solution by mercury. In all four cases the amounts adsorbed varied with the concentration approximately according to the exponential formula and in all four cases the surface tension of the mercury was lowered by the adsorption.

Tomlinson's experiments upon the action of oils on supersaturated solutions would come under the heading of a dissolved salt concentrating at a dineric interface if one were only certain of the accuracy of the work. Tomlinson[2] found that oils start crystallization in supersaturated solutions of sodium sulphate in case the oil spreads out in a film over the water; but do not if it remains lens-shaped. "Four ounces of Glauber's salt in four ounces of water was boiled

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[1] Zeit. phys. Chem., 86, 545 (1914).

[2] Phil. Trans., 161, 51 (1871).

and filtered into four flasks, covered with watch-glasses and left until cold. A clean glass rod was dipped into a bottle of clear, pale seal oil, and the watch-glass being gently removed from off one flask, a drop of the oil was carefully delivered to the surface solution; the glass rod was withdrawn, and the watch-glass restored to its place. The drop of oil expended into a well-shaped film, with a display of iridescent rings; and immediately from the lower surface of the film there fell large well-shaped prisms with dihedral summits of the ten-atom sodic sulphate, being the normal salt. The prisms were an inch or an inch and a half in length, and three-eighths of an inch across. The crystallization proceeded from every part of the lower surface of the film, and as one set of crystals fell off another set was formed, until the whole solution became a mass of fine crystals in a small quantity of liquid. This effect is entirely different from the usual crystallization which takes place when a supersaturated solution of Glauber's salt is subjected to the action of a nucleus at one or two points in its surface, as when motes of dust enter from the air, or the surface is touched with a nuclear body. In such cases small crystalline needles diverge from the point touched, and proceed rapidly in well-packed lines to the bottom, the whole being too crowded and too rapid to allow of the formation of regular crystals. But in the case before us, where the whole surface of the solution and the surface only, is subjected to nuclear action by the spreading of the oil film, the action is not so rapid as in the former case, because it is not downwards but parallel with the surface; the crystals mould themselves, as it were, upon the oil-film, and, falling off, allow fresh portions of the solution to come into contact with the film, until at length a very fine crop of crystals is produced. This experiment was repeated on the solutions in the other three flasks with the same result.

"Similar experiments were tried on solutions of Glauber's salt of different strengths, with drops of ether, absolute alcohol, naphtha, benzole, oil of cajuput, oil of turpentine, and other volatile oils, herring oil, sperm oil, olive oil, castor oil, and some other fixed oils of animal and vegetable origin, with this general result, that, whenever the oil spread out into a film, it acted as a powerful nucleus.... A solution of two parts of Glauber's salt to one part of water was boiled and filtered into three flasks, which were covered with watch-glasses and left until the next day. A drop of castor oil was then placed upon the surface of each; it formed a lens which gradually flattened; but there was no separation of salt, even when the flasks were shaken so as to break up the oil into small globules. The necks of some clean flasks were oiled inside with castor oil, and the boiling solution of Glauber's salt filtered into them; the oil formed into globules, and some of it ran into the solution. Next day there was no separation of salt. The flask was turned round quickly so as to form a whirlpool, in which the globules of oil descended to the bottom and were broken up and diffused so as to form a kind of emulsion; but by repose the solution became clear again, the oil collected into larger globules, and there was no separation of salt. If, while the flask is being turned round, a sudden jerk be given to it, so as to flatten some of the globules against the side into films, the whole solution instantly becomes solid; or if by strong pressure with the finger against the interior of the neck a smear of oil be made, the solution crystallizes as soon as it is brought into contact with such smear. But if it be objected that the finger may introduce nuclear matter, then a catharized wire, which, dipped into the solution is inactive, will, if rubbed against the side so as to flatten some of the small oil globules, leave a number of minute crystals of a chalky white color filling up the lines traced by the wire, and these serve as nuclei to the rest of the solution."

While discussing these and other experiments, Tomlinson[1] says: "It can be shown experimentally that a clean inactive rod immediately becomes active simply by drawing it through the hand: so also a clean surface, such as the inside of a flask, smeared with a little oil, becomes power-

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[1] Phil. Trans., 161, 66 (1871).

fully nuclear; but if the smear on the surface of the rod or on the inner wall of the flask can gather itself up into globules, these are not nuclear. Phenomena of this kind seem to be explained by reference to the surface tension of liquids. In the case of a film formed by depositing a drop of an oil on the surface of a supersaturated saline solution, the surface tension of such solution being diminished at the point touched by the oil, the surface of the solution surrounding the point touched exerts a tractive force on the oil, and spreads it into a film, with adhesion to the surface and a nuclear action on the solution; because being brought into contact with the saline particles, but not with the aqueous (seeing that oil and water do not combine, while adhesion readily takes place between oil and salt), the saline molecules are separated from the aqueous, and the action once begun is propagated. When, on the other hand, an oil deposited on the surface of the solution assumes the form of a well-shaped double convex lens, or even a disk, there is no adhesion properly so-called, and no nuclear action, since the lens is separated from the solution by surface tension, and is not nuclear because it is really not in contact with the solution. Even when the solution is shaken so as to break up the lens into globules and to submerge them, each globule is as completely separated by surface tension from contact with the solution as if it were outside the flask, at least so far as any nuclear action is concerned. Whether a drop of oil form a film or a lens depends on several variable circumstances, such as the temperature of the solution, its degree of supersaturation, its surface viscosity, and so on."

In a series of papers Tomlinson[1] brought forward further evidence in support of his views and answered the objections of others. He found that many oils did not cause crystallization when freshly distilled; but did after standing a sufficient length of time or after being exposed to ozone for a short

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[1] Proc. Roy. Soc., **20**, 342 (1872); **21**, 208 (1873); **27**, 121, 189, 290 (1878); **29**, 24, 326 (1879).

time. It is therefore the oxidized oils which are active in overcoming supersaturation. The accuracy of Tomlinson's experiments has been questioned by Liversidge,[1] Gernez,[2] and Violette;[3] and Ostwald[4] speaks very contemptuously of Tomlinson's work. There is, however, nothing theoretically impossible about Tomlinson's experiments. If a given oil adsorbs sodium sulphate very strongly, it might easily raise the concentration at the dineric interface to such a point that solid salt would separate spontaneously. It is rather surprising that Tomlinson's experiments coincide very closely with what we might expect from our knowledge of colloid chemistry. On the other hand, Tomlinson was more sceptical as to the existence of particles of sodium sulphate in the air than was safe. As I see it, the whole thing turns on the question whether there is or is not marked adsorption at the dineric interface. Tomlinson[5] states that oil adheres much more strongly to salt than to water; but he gives no evidence in support of this statement. If it were true, very fine crystals of sodium sulphate ought to be raised by oil either to the dineric interface or should be carried out of the water phase into the oil phase.[6] Some experiments were made in my laboratory. Finely ground crystals of sodium sulphate were added to to a saturated solution of this salt and the whole shaken with kerosene and with commercial olive oil. With the kerosene there was no sign of the sodium sulphate being carried up by the oil. The experiments were not quite so convincing with olive oil; but the amount of salt carried up by the oil is either zero or very small. It is therefore probable that Tomlinson's results with olive oil are due to experimental error, which naturally throws doubt on his experiments with the other oils. It is always possible, however, that some

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[1] Proc. Roy. Soc., 20, 497 (1872).

[2] Comptes rendus, 75, 1705 (1872).

[3] Ibid., 76, 171 (1873).

[4] Lehrbuch allgem. Chemie, 2nd Ed., 2 II, 739.

[5] Proc. Roy. Soc., 29, 328 (1879).

[6] Hofmann: Zeit. phys. Chem., 83, 385 (1913).

of the other oils may show marked adsorption effects with sodium sulphate. It has seemed to me worth while to discuss Tomlinson's results in spite of their probable inaccuracy, because the theory involved is sound and a case illustrating it satisfactorily may be found some day.

We can now consider the second division of the subject, the adhesion of small particles to the dineric interface. A careful study of this phenomenon has been made recently by Hofmann.[1] As a typical case he cites the behavior of finely divided red lead when shaken with chloroform and water. The red lead adheres to the surface of the benzene or of the chloroform forming a practically continuous coating around the organic liquid in case proper relative amounts of red lead and organic liquid are taken. The theory of the phenomenon is that given by Des Coudres[2] though I am going to put it in a somewhat simpler form than Hofmann does. If a given solid is wetted by water much more strongly than by benzene or chloroform the water will displace the benzene or chloroform and will form a water film around the particles. Owing to the adhesion of water to water, work must be done on the particle to carry it out of the water phase into the organic liquid. In other words, the particle will tend to stay in the water phase. If the other liquid is less dense than water, benzene for instance, the solid particles will stay in the water phase irrespective of size. If the organic liquid is more dense than water, chloroform for instance, the particles will stay in the water phase unless they are so large that the force of gravity carries them down out of the water phase through the chloroform to the bottom of the containing vessel. If, on the other hand, the solid under consideration is wetted more strongly by chloroform or benzene than by water, a surface of chloroform or benzene will form round the particle and will tend to prevent the carrying of the particle from the organic liquid into the water phase. The solid particles

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[1] Zeit. phys. Chem., 83, 385 (1913).

[2] Arch. Entwicklungsmechanik, 7, 325 (1898).

will therefore pass into the water phase only when the water is the more dense of the two liquid phases and when the particles are so large that the force of gravity overcomes the adhesion of the liquid film to the organic liquid.

Since the solid particles tend to remain in the non-aqueous liquid when they are wetted exclusively by the non-aqueous liquid and since they tend to remain in the water phase when they are wetted exclusively by the water, it follows logically that they will remain in the surface separating the two liquids if they are wetted partially[1] by each liquid. This is the conclusion drawn by Des Coudres and by Hofmann. While this is perfectly sound as a matter of logic, it seems to me somewhat unsatisfactory from a physical point of view unless we specify clearly what we mean by partial wetting by each liquid. We may mean that the surface of the solid particles is arranged like a checker board with the organic liquid adhering to the red squares and the water to the black squares. I think that this is Hofmann's conception of the matter so far as he has one, though I admit that he does not say so. This seems probable because Freundlich cites dirty glass as a case of partial wetting, the water wetting the clean places and not wetting the greasy ones. This cannot be what occurs with our solid particles because they are not dirty. If we are not to have the two liquids scattered over the surface of the solid particles as distinct phases, they must be present as a single phase. It seems to me therefore more satisfactory to say that the solid particles tend to go into the water phase if they adsorb water to the practical exclusion of the other liquid; they tend to go into the other liquid phase if they tend to adsorb the other liquid to the practical exclusion of the water; while the particles tend to go into the dineric interface in case the adsorption of the two liquids is sufficiently intense to increase the miscibility of the two liquids very considerably at the surface between solid and liquid.

These conclusions as to the way a given pair of liquids

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[1] Cf. Freundlich: Kapillarchemie, 18 (1909).

will behave with a given solid refer to the relations prevailing under the conditions of the experiment. Hofmann's experiments with two liquid layers in glass test-tubes (soda-lime glass) showed that the time factor might be an important one. If a few cubic centimeters of an aqueous potassium bichromate solution are shaken up in a carefully cleaned glass test-tube, there remains on the walls of the test-tube a continuous uniform coating of solution recognizable by its yellow color. This film gradually becomes thinner and paler but does not break at any point until the water disappears completely through evaporation. If one adds a layer of xylene or kerosene to the aqueous bichromate solution in the test-tube, it is easy to see that there is a coating of aqueous solution between the organic liquid and the glass. If water is allowed to flow in at the bottom of the test-tube, the organic liquid can be forced out at the top and there will be no sign of its having adhered to the glass wall at any point. If, however, the test-tube containing the aqueous bichromate solution and the xylene or kerosene be left standing quietly for a long time, 6–10 hours, it will be found that the organic liquid has diffused through the water film to some extent and now adheres firmly to the glass wall nearly everywhere, having displaced the aqueous film almost completely. If the contents of the test-tube are shaken violently, the water displaces the organic liquid from the glass surface practically completely. The glass is therefore wetted more readily and more rapidly by water than by xylene or petroleum; but a large mass of xylene or petroleum will gradually displace a water film from the glass surface. One would therefore expect to get a slightly different behavior with glass powder according as one treated at first with water or with the organic liquid. This was exactly what Hofmann found. If the glass powder were treated first with water and then shaken with kerosene, practically all the glass went into the water phase. If the glass powder were allowed to stand a long time with kerosene, or if it were heated with it to hasten the removal of the air film, some of the glass powder would remain in the dineric interface. Vigorous shaking would, of course, cause the water to displace the kerosene. Chloroform behaves towards glass and water somewhat like xylene or kerosene though the tendency to displace the water layer from the glass is less than with kerosene. Small drops of chloroform do not break through the water film at all. With increasing amounts of chloroform the force of gravity causes it to break through at the bottom of the test-tube, the surface wetted by the chloroform increasing as the column of chloroform increases in height.

Hofmann[1] describes a number of interesting experiments with thin plates and with powder. "If a freshly-split molybdenite (molybdenum bisulphide) scale be placed on water, it floats on the surface. If it is pushed quickly under water, bubbles of air remain clinging to it. If the air film on the scale is removed by boiling with water, the molybdenite scale sinks under the water and does not remain in the surface. If a layer of xylene or kerosene is placed over the water or a layer of chloroform under it, the molybdenite scale is held fast at the dineric interface when brought in contact with it. If the scale is brought from the air into chloroform, xylene or kerosene, it sinks at once, but adheres to the liquid interface when brought into contact with it. The adhesion at the dineric interface is evidently very great, for if one brings merely a portion of the surface of the scale in contact with the interface the plate is drawn up at once. A molybdenite scale therefore behaves with these pairs of liquids like a small glass plate which has been heated in kerosene.... If one shaves some molybdenite off a fresh cleavage plane, one gets a powder made up of little plates of different sizes and can therefore compare the behavior of these directly with that of the larger plates or scales. At the foam interface only the finest powders are held up; the coarser ones sink at once in the water, showing that the adhesion at the water surface is very small indeed. These finest particles sink also if they are shaken with the water and still more

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[1] Zeit. phys. Chem., 83, 409 (1913).

readily after boiling.[1] The powder can be shaken out of the water phase quantitatively by xylene, kerosene, or chloroform, the powder forming a film round these liquids. Even the coarser particles cannot be shaken off from the interface without carrying drops of the second liquid with them.... We thus find that, in this case where the clinging of the larger plates at the interface pointed to a marked surface adhesion, the powder goes quantitatively into the interface when it is shaken with the two liquids.

"While molybdenite is a typical instance of the simultaneous partial wetting by water and the other liquid, gypsum behaves more like clean glass. When thin plates of gypsum are brought out of water[2] into a xylene or kerosene interface, the gypsum plate is not held there but remains entirely covered with a thin film of water. On the other hand, if one puts a gypsum plate first into kerosene or xylene and then brings it carefully into the water interface, it adheres to this though not very firmly. A slight blow causes it to sink into the water, after which it will not adhere to the interface.... When calcium sulphate powder, suspended in water, is shaken with kerosene, a very small amount of powder does unquestionably cling to the interface and this also happens if a sodium sulphate solution is added to a calcium chloride solution and the mixture is shaken with kerosene at once. There is no question therefore but that occasional particles will adhere to the interface when a powder is shaken with two liquids even though thin plates of the same substance remain covered with a continuous film of the two liquids when brought into the interface. A possible explanation is that the viscous emulsion layer which forms under the petroleum layer after vigorous shaking with water, slows down the rate of sinking of the powder so much that there is time for the thin adher-

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[1] During the boiling the molybdenite powder and also many others are carried up in relatively large amounts to the surface.

[2] In order to make this experiment comparable with those with powdered gypsum, a saturated solution of calcium sulphate was used instead of water.

ing water film to be removed by the kerosene. It is also possible that the particles are held fast by the surface film[1] which forms when kerosene is shaken with pure water. It is also conceivable that the water films around the grains of gypsum are broken mechanically by shaking with kerosene. At the water-chloroform and the water-xylene interfaces there adhere only traces of a calcium sulphate powder suspended in water. In the water-chloroform system the chloroform which does not wet the gypsum, is the more dense liquid and consequently the particles, on standing, settle apparently upon the interface; but they are not really in contact with it as is shown by the fact that a mild shaking whirls them up into the body of the upper liquid. If one suspends gypsum powder first in kerosene, xylene, or chloroform, and then adds water carefully, the same phenomena are obtained as in the similar experiment with glass powder. The powder clings at first to the interface with the exception of the coarser particles which fall at once from the xylene or kerosene into the water. When the tube is shaken, nearly all the gypsum goes into the water phase and only a little is left at the interface. Just as with glass powder, the amount remaining at the interface is greater the longer the powder is left in contact with the organic liquid. If the gypsum were only suspended for a couple of minutes in the organic liquid, the amount that remained in the interface was scarcely larger than if the gypsum had been suspended in water from the first. If the gypsum is left several weeks in the organic liquid, distinctly more powder remains in the interface. Just as with glass, heating the gypsum with the organic liquid cuts down the time enormously.

"Calcium carbonate behaves entirely differently from calcium sulphate. If one brings a plate of Iceland spar out of water[2] into a xylene or kerosene interface, it adheres there

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[1] [This is due to impurities in the kerosene and should have been eliminated in these experiments. W. D. B.]

[2] When these pieces are laid on the surface of water they float there but sink into the water if jarred. The finest particles of calcium carbonate powder also float at the foam interface but can easily be shaken into the water.

even when considerably thicker than a gypsum plate, and is not easily shaken off. From this experiment the adhesion of Iceland spar to xylene or kerosene must be considerably greater than that of gypsum. In accordance with this is the fact that calcium carbonate powder suspended in water goes quantitatively into the dineric interface provided the coarser particles have been removed by sedimentation. The experiment comes out the same way with olive oil in place of kerosene or xylene, the powder being retained quantitatively at the interface.[1] On shaking, a fine emulsion is formed which carries the whole of the powder up with it. When calcium sulphate is used, only a small amount of powder clings to the oil."

TABLE I

Water and	Ether	Chloroform	Butyl alcohol	Benzene	Kerosene	Amyl alcohol	Paraffin oil
$CaSO_4$	*w*	*w*	*w*	*w*	*w*	*w*	*w*
SnO_2	*w(s)*	*ws*	*ws*	*s(w)*	*s(w)*	*sw*	*sw*
$Al(OH)_3$	*w(s)*	*ws*	*ws*	*s*	*s(w?)*	*sw*	*s(w)*
SnS	*ws*	*ws*	*ws*	*s(w)*	*s(w)*	*s*	*ws*
$BaSO_4$	*ws*	*ws*	*ws*	*s*	*s*	*s(w?)*	*s(w?)*
ZnS	*w(s)*	*ws*	*ws*	*s*	*s(w?)*	*s*	*s(w?)*
ZnO	*ws*	*ws*	*s(w)*	*s*	*s*	*s*	*s*
$CaCO_3$	*ws*	*ws*	*s*	*s*	*s*	*s*	*s*
$Mg(OH)_2$	*s(w?)*	*ws*	*s*	*s*	*s*	*s(w)*	*sw*
Al	*sw*	*s(w)*	*s(w)*	*s*	*s*	*s(w)*	*s*
$BaCO_3$	*ws*	*ws*	*s*	*s*	*s*	*sw*	*s*
CuS	*ws*	*s(w)*	*s*	*s*	*s*	*s*	*s*
$PbCrO_4$	*ws*	*s(w?)*	*s*	*s*	*s*	*s*	*s*
Cu_2O[?]	*ws*	*s*	*s*	*s*	*s*	*s*	*s*
MoS_2	*s(w?)*	*s*	*s*	*s*	*s*	*s*	*s*
PbS	*ws*	*s*	*s*	*s*	*s*	*s*	*s*
Fe_3O_4	*ws*	*s*	*s*	*s*	*s*	*s*	*s*
$BaCrO_4$	*ws*	*s*	*s*	*s*	*s*	*s*	*s*
Pb_3O_4	*sw*	*s*	*s*	*s*	*s*	*s*	*s*
C	*sw*	*s*	*s*	*s*	*s*	*s*	*s*
PbI_2	*s*	*s*	*os*	*s*	*s*	*os*	*s*
HgS	*s*	*s*	*s*	*s*	*s*	*s*	*s*
HgO	*s*	*s*	*s*	*s*	*s*	*s*	*o*
HgI_2	*s*	*s*	*s*	*s*	*s*	*o*	*os*
AgI	*s*	*s*	*o*	*s*	*s*	*o*	*os*

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[1] Of course the free acids in the rancid oil convert some of the calcium carbonate into the calcium salts of the fatty acids.

In Table I are given some of Hofmann's results. The letter *w* means that the liquid goes nearly completely into the water phase, while *o* denotes that it goes almost completely into the organic liquid; *s* means that the powder collects nearly quantitatively in the interface. Two letters, such as *sw*, mean that the powder goes partly into the interface and somewhat less into the water phase; the use of a parenthesis, *s*(*w*) or *s*(*o*), signifies that there is a good deal more powder in the interface than in the bracketed phase. Benzene and xylene behave alike so only one is given. In the experiments tabulated, the powder was placed in water and then shaken with the organic liquid.

Much the same conclusions have been worked out by Reinders[1] independently of Hofmann. Some of his data are given in Table II. The powder was placed in the water phase and then shaken with the organic liquid.

TABLE II

Water and	Paraffin oil	Amyl alcohol	CCl_4	Benzene	Ether
Kaolin	*w*	*w*(*s*)	*w*(*s*)	*w*	*w*(*s*)
CaF_2	*ws*	*ws*	*w*(*s*)	*w*(*s*)	*w*(*s*)
Gypsum	*w*	*ws*	*w*	*sw*	*ws*
$BaSO_4$	*w*(*s*)	*ws*	*ws*	*sw*	*ws*
Magnesium	*ws*	*ws*	*ws*	*ws*	*ws*
PbO	*s*	*s*	*sw*	*s*	*sw*
Malachite	*so*	*s*	*s*	*s*	*sw*
ZnS	*s*	*s*	*s*	*s*	*sw*
PbS	*so*	*so*	*s*	*s*	*s*
HgI_2	*so*	*s*	*s*	*s*	*s*
Carbon	*so*	*s*	*s*	*s*	*s*
Selenium	*so*	*so*	*so*	*s*	*s*
Sulphur	*so*	*so*	*o*(*s*)	*so*	*s*

Similar results were obtained with colloidal solutions. Isobutyl alcohol was added to a colloidal gold solution obtained by reducing gold chloride with carbon monoxide. When the two liquids are shaken, the gold forms a thin film

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[1] Zeit. Kolloidchemie, 13, 235 (1913).

at the interface. This film is violet blue to blue green by transmitted light and golden by reflected light. A thin water film forms between the isobutyl alcohol and the glass, and the gold concentrates in the dineric interface thus formed, making the alcohol appear uniformly gold-plated. With ether the gold film rises high above the level of the two liquids. With carbon bisulphide the adherent film of gold appears blue. When the carbon bisulphide is broken into drops by shaking, each drop appears blue. When a blue gold was obtained by reducing gold chloride with phosphorus dissolved in ether, the gold went into the dineric interface. When a brownish red gold was obtained in this way, it remained in the water phase and showed no tendency to pass into the interface. This difference is undoubtedly due to an adsorption of something at the surface of the gold because Reinders found that 0 005 percent gum arabic prevents colloidal gold from passing into the ether-water interface. With carbon tetrachloride, carbon bisulphide, and benzene, the gold goes to the interface as before; but the gum arabic prevents its changing from red to blue.

With colloidal ferric oxide practically no iron went into the interface with any of the organic liquids. It seems probable that this is due to Reinders using a ferric oxide solution which was a year and a half old, because hydrous ferric oxide is ordinarily a pretty good emulsifying agent.[1] Colloidal arsenic sulphide goes into the dineric interface with amyl alcohol or butyl alcohol; but stays in the water phase when carbon tetrachloride, benzene, or ether is the second liquid. India ink goes completely into the interface with amyl alcohol, carbon tetrachloride, or benzene; it goes partly into the interface with isobutyl alcohol and stays entirely in the water phase when ether is the second liquid.

An interesting experiment, which has been done in my laboratory,[2] is to shake copper powder or aluminum powder

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[1] Briggs: Jour. Phys. Chem., 19, 296 (1913).

[2] Bancroft: Trans. Electrochem. Soc., 23, 294 (1913).

with kerosene and water. The metallic powder goes into the kerosene and into the interface, producing an effect of molten copper or molten aluminum as the case may be. When the bottle is allowed to stand after having been shaken, the metallic powder in the interface creeps up the side of the bottle above the surface of the liquid, rising higher if a little alcohol has been added. I have seen an apparently coherent metallic film rise two or three inches above the surface of the upper liquid phase. If too much copper or aluminum be added the kerosene cannot hold it all up and a portion falls to the bottom of the flask carrying drops of kerosene with it. If the mixture be poured out on a piece of wood, the copper spreads over the surface of the wood just as it did over the surface of the glass. This experiment illustrates the principle involved in all bronzing liquids. A bronzing liquid consists of a volatile liquid which will hold up the metal, and some substance which will keep the metallic powder from rubbing off too readily after it has been applied. This second substance also serves the purpose of keeping the metallic powder in a better state of suspension in the volatile liquid. According to Worden[1] the best of these bronzing liquids consist essentially of pyroxylene dissolved in amylacetate, to which the metallic powder is added. For bronzing radiators and steam pipes, a pure pyroxylin would not do since it would decompose, disintegrate and allow the metallic coating to peel off. To prevent this, boiled linseed oil and resin may be added. Such preparations are of course much slower in drying than pyroxylin bronzing liquids; but that is not a serious objection for these special purposes. A much cheaper form of bronzing liquids consists of rosin dissolved in benzine while the cheapest of all is apparently a solution of sodium silicate in water. The aluminum and copper powders on the market are coated with stearin; but special experiments in my laboratory have shown that the behavior of copper and aluminum with kerosene is the same qualitatively whether the stearin coating is removed with ether or not.

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[1] Nitrocellulose Industry, 1, 310–320 (1911).

Instead of using a bronzing liquid to coat a solid, it can also be used, according to Worden,[1] to make imitation gold and silver leaf. "Soluble cotton (1/4 lb.) is dissolved in one gallon amyl acetate, and this combination mixed with 25 percent bronze. After very thorough mixing, the preparation is poured over a liquid heavier than the bronzing solution as water, glycerol, or carbon tetrachloride, depending upon the weight of bronze. The amyl acetate evaporates and leaves a thin film or leaf on the surface of the water. It is not stated in what manner the amyl acetate layer is placed on the water without causing precipitation of the pyroxylin before the latter assumes the solid form. By substituting aluminum powder for the bronze, it is claimed, silver leaf can be produced with equal facility.

"In the United States, this patent has passed through the experimental stage and considerable quantities of this imitation gold leaf, or 'Oriental Tissue' and 'Japanese Leaf,' as it is more often called, is prepared in the following manner: The formula stated above by the patentee has been found unduly expensive and may be replaced by amyl acetate 45 percent, refined fused oil 8 percent, and benzine (62°) 47 percent, the pyroxylin and bronzes being substantially as stated above. No readily water-soluble solvents or non-solvents must enter the formula on account of danger in rendering the film white, opaque and devoid of strength when the solution is floated on the surface of the water. A long vat of wood, from 50–75 ft. in length and about 2 ft. wide, is filled with water from 6–12 inches in depth. A hopper carrying the bronze and solvent mixture, and having a slit in the bottom which is adjustable, is filled with lacquer-bronze mixture, the diameter of the slit adjusted, and this hopper rolled over the surface of the water, but not touching, the sides of the vat acting as a track on which the hopper runs. By varying the diameter of the slit in the hopper and the speed of the movement over the surface of the water, the depth

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[1] Nitrocellulose Industry, 1, 312 (1911).

of the film may be varied within wide limits. That gold bronze found most applicable is known in the trade as Dutch gold or 'blue elephant.' There is thus deposited on the surface of the water a gold film of some 50 ft. in length and of a width so that when trimmed it is 1 ft., and in this manner appears in commerce. The thickness is about the same as a sheet of ordinary writing paper. This imitation gold leaf is finding extensive use in the book-bindery trade in the place of real gold leaf for lettering titles."

Winkelblech[1] has proposed making use of the tendency of certain substances to go into the dineric interface in a method of analysis.

"If a solution of glue is shaken violently with benzine, the glue is precipitated. There is formed a sort of stiff emulsion of glue, benzine, and water, which separates from the water on standing, partly in consequence of entangled air. When the solution is rich in glue, a voluminous product is obtained in large lumps. If, however, a very dilute solution is taken, a number of bubbles of various sizes may be noticed resting for a considerable while on the surface of the water phase. When they break, there is left a permanent, whitish ring of very small bubbles adhering to the walls of the vessel. The further study of the phenomenon was carried out with pure gelatine.

"The following data will show that mere traces of gelatine can be made visible or precipitated in this way. A heavy precipitate was obtained when 10 cc of a solution containing 0.234 g gelatine per liter was shaken with benzine. Precipitates were also obtained when the gelatine solution was diluted tenfold, twentyfold and even fortyfold, provided 10 cc solution were taken for the test. At the highest dilution the concentration of the gelatine was 0.06 g per liter and there were consequently 0.06 mg in the 10 cc taken for the test. This seemed to be about the limit at which a precipitation could be detected definitely. The possibility of recog-

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[1] Zeit. angew. Chem., 19, 1953 (1906).

nizing small amounts of substance is due, as stated, to the fact that these come out in the very voluminous form of very small bubbles. In order to get these last portions out, a very energetic shaking is necessary. In order to concentrate the precipitate in the smallest space, the containing vessel should not be wider than an ordinary test-tube, at any rate at the surface between the benzine and the water. For handling small amounts of liquid, a 50 cc measuring flask with a relatively wide neck was used. After shaking, the flask was inverted and the two liquid phases collected in the neck. Later a small stand glass with a glass stopper was substituted for this.

"By means of this limiting figure for the amount of gelatine which can be detected, gelatine determinations were made fairly successfully with solutions prepared by others. It was only necessary to dilute samples of the solution until the same slight amount of precipitation occurred and no precipitation occurred on further dilution. Gelatine behaves in slightly acid or slightly alkaline solutions much as it does in pure water, though the volume of the precipitate seems somewhat less in the first case and somewhat greater in the second. Such small amounts of gelatine cannot be detected, however, in presence of larger amounts of acids, alkalies or salts. Larger amounts of solution might be taken, however. If a dilute, acidified solution of gelatine be boiled for a short time, it gives no precipitate when shaken with benzine.[1]

"Some other colloids behave like the glue colloid (glutin) and can be shaken out of their solutions. Other hydrocarbons are also effective so that the phenomenon seems to be a general one. Precipitation was obtained with solutions of albumin, water-soluble starch, and soap, as well as with rosin dissolved in very dilute caustic soda. The colloids grouped as mucin can be precipitated from urine and the pro-

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[1] In making up the solutions to be diluted, heating was avoided so far as possible. The gelatine was allowed to swell in cold water and was then dissolved by shaking with warm water.

teins from beer. It is worth noting that tannin can be precipitated but not gallic acid.

"Among organic substances slight precipitates were obtained from a dilute solution of sulphur in caustic soda and from a dilute solution of water glass. With water glass the precipitate rapidly became granular and dropped into the water phase. Acidified water-glass solutions gave clear layers.[1] A sample of concentrated ammonia solution, when diluted, gave a test for silica.

"The hydrocarbons which can be used are: kerosene, liquid paraffin, benzene, chloroform, and carbon bisulphide [in addition to benzine]. The result varies somewhat from case to case. With the hydrocarbons which are lighter than water, the precipitate floats on the water; with the denser hydrocarbons the precipitate is below the water layer. The emulsions which form seem to have very nearly the same density as the organic liquid used. It is not possible to get the precipitation with all liquids which are non-miscible or slightly miscible with water. Experiments with ether were entirely unsuccessful.

"If one asks why these things happen, the most plausible explanation seems to be the following, which recognizes the surface tension as the important factor. The violent shaking breaks the second liquid into a large number of drops, which evidently have the power of condensing on their surfaces the tiny, wet, colloidal particles. The particles then coalesce to larger complexes and there is formed a rigid emulsion which also contains enclosed water.

"When the gelatine concentration was nearly down to the minimum recognizable, a few large, completely transparent and fairly permanent bubbles (drops) appeared, which were filled with hydrocarbon except for a tiny air bubble. From this it follows that the wet colloidal particles are able in some way to form surface films. This seems to be a special

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[1] Flemming found that acidified water-glass solutions gelatinize much less rapidly than alkaline ones, Zeit. phys. Chem., 41, 427 (1902).

case of the familiar phenomenon of the foaming of many liquids when stirred, a phenomenon which also always depends on the separation of small amounts of colloids and perhaps of traces of fatty substances.

"When a colloidal solution contains suspended impurities these are carried out more or less completely with the colloidal material, so one can use this method as a means of purifying certain waters though not as a means of purifying colloids.

"As a complement to the action of hydrocarbons on aqueous colloidal solutions it was found that fats dissolved in hydrocarbons or similar liquids can be precipitated in the surface film by shaking with water. The fats therefore form colloidal solutions. Precipitations were obtained with butter, olive oil, lanolin, and vaseline. It was also found that the emulsions of heavy hydrocarbons or carbon bisulphide with the fats of low specific gravity also accumulate below the water layer, only a small portion being carried to the surface by adhering air bubbles. When water is used for shaking out, the precipitation is very slight. With a slightly alkaline solution such as dilute lime water, heavy voluminous precipitates were obtained while a transparent layer of fat is obtained when a slightly acid solution is used. With concentrated alkali or acid solutions, viscous emulsions are obtained which hold fast considerable amounts of solution."

These results of Winkelblech are exactly what one would expect for substances which pass into the interface. The failure to obtain results with ether is undoubtedly not a general phenomenon. A glance at Table I will show that ether was found by Hofmann to be one of the least effective liquids for carrying substances into the interface; Winkelblech happened to use substances which stayed in the water phase. Reinders shook out colloidal gold with ether; but also found that very small amounts of gum arabic prevented the gold going into the interface. If one is to use Winkelblech's method to detect small amounts of gelatine, it is essential to test the pure reagents. We tried to repeat Winkelblech's experiments once, using benzene as the organic liquid. There seemed to be no limit to the sensitiveness of the reaction until we found that the benzene alone gave a faint film when shaken with water. This was apparently due to a slight trace of rosin or similar matter dissolved in the benzene. Carefully purified benzene did not give any film. This test can be used as a means of detecting small amounts of such material in benzene.

Winkelblech's results seem not to have appeared normal or natural to other people. At a meeting of the Bunsen Society,[1] Jordis said that Winkelblech had made the very remarkable observation that all so-called colloids can be precipitated if one shakes an aqueous colloidal solution with hydrocarbons such as benzine, kerosene, etc. He wondered whether any of the members had made any experiments, for he himself could think of no explanation for the phenomenon. Biltz replied that he could confirm and amplify Winkelblech's observations. "Independently of Winkelblech, a most interesting and, at first, inexplicable observation had been made in the technical research laboratory at Mansfield during the titration of copper solutions with alkali sulphides, namely that the colloidal solution of copper sulphide clears up instantaneously if shaken with chloroform or any similar liquid. The finely divided copper sulphide coagulates and precipitates, leaving a clear solution suitable for titration.[2] I have also made a number of experiments with other colloidal solutions. Gold and platinum, for instance, can be precipitated wonderfully well, and apparently all liquids which are not miscible with water act equally well. Winkelblech has patented the use of such organic liquids as kerosene for clearing sewage. We have made tests to see how much of the putrefiable matter in the sewage can be precipitated by shaking with an organic solvent. About 20 percent was thus precipitated."

Luther remarked that "not only colloids but suspensions

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[1] Zeit. Elektrochemie, 13, 540 (1907).

[2] Koch: Zeit. anal. Chem., 46, 31 (1907).

of microscopic particles can be made to settle wonderfully when the water is shaken with a second non-miscible liquid. The earliest experiments on the subject, so far as I know, are those of the physiologist, Prof. Hofmann (now in Innsbruck). The experiments were made in Leipzig and were published in abstract in Pflüger's Archiv. The whole paper has not been published. The phenomenon can be shown admirably by shaking an aqueous suspension of lead oxide with toluene or chloroform."

It is not clear whether Luther means that the suspended matter coagulates and settles, or whether it passes into the interface. The two phenomena should be kept quite distinct.

The application of Winkelblech's method to the purification of sewage has been studied by Biltz and Kröhnke.[1] "Several years ago we[2] showed that a large portion of the oxidizable material in city sewage is in a colloidal state. The putrefiable material which was isolated by dialyzing acted in so many ways like colloidal material that there could be no doubt about its colloidal nature. This seems for the first time to give an answer to the question as to the way in which the purifying agents really act in the technical purification of water. Although Dunbar and his co-workers[3] have expressed the opinion that the removal of putrefiable substances by the purifying agents was analogous to dyeing and therefore an adsorption phenomenon, there was no explanation for the degree and specific nature of the purification. The development of colloid chemistry has shown that the power of combining by adsorption is one of the most general characteristics of colloids. Once the colloidal nature of the sewage material was established, our general knowledge in regard to colloids could be applied to this special case and it could be brought into line....

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[1] Zeit. angew. Chem., **20**, 883 (1907).

[2] Ber. deutsch. chem. Ges. Berlin, **37**, 1745 (1904).

[3] Cf. Dunbar: Vierteljahrschrift für gerichtliche Medizin und öffentliches Sanitatswesen (3) **19**, Suppl. Bd., 178 (1900).

"Winkelblech[1] and Koch[2] have recently called attention to an adsorption phenomenon which seems to be peculiar to dissolved colloids. If one shakes an aqueous colloidal solution with an organic solvent which is not miscible with water, the finely divided drops of the organic liquid carry down with them the colloidal particles in the solution and form a foam film separated sharply from the water layer. This observation has been made successful use of technically in copper analysis to clear up copper hydrosols (Koch); independently of him Winkelblech has recommended purifying turbid water in the same way. The following experiments show that some purification is obtained when sewage is shaken with an organic liquid.[3]

"Spandau sewage was shaken for three hours on a shaking machine in 100 cc lots together with 5 cc organic liquid and 1 cc 30 percent H_2SO_4; it was then allowed to stand for an hour and a half. In order to determine the degree of purification, acidified samples of sewage were shaken by themselves and 100 cc lots of pure water were shaken with the organic liquids. The content of oxidizable material after shaking was the difference between the permanganate consumption of the sewage samples and the pure water samples, for the water required perceptible amounts of permanganate after being saturated with aliphatic solvents. In order to remove any drops of organic liquid the pipetted samples were filtered through a dry filter. The sewage samples seemed perfectly clear after being shaken and filtered. A film like an oil emulsion had formed out of organic solvent and the adsorbed albuminoids.

"Since the electrical charge on a colloid is known to be of importance in determining the precipitation of colloids, organic liquids were used having very different dielectric constants; but there was no apparent connection with this and there is really no evidence that there is any difference of

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[1] Zeit. angew. Chem., 19, 1953 (1906).

[2] Zeit. anal. Chem., 46, 31 (1906).

[3] Cf. Winkelblech: D. R. P. 180493 (1907).

behavior between the organic liquids because the value for carbon bisulphide is uncertain, owing to the high permanganate consumption for water saturated with this liquid."

Adsorption of Undialyzed Sewage by Organic Liquids

	Oxidizable matter in mg $KMnO_4$ per liter		Percentage adsorbed
	not adsorbed	adsorbed	
Benzene	165	60	27
Chloroform	174	51	23
Nitrobenzene	156	69	31
Kerosene	147	78	35

Adsorption of Dialyzed Sewage by Organic Solvents

	Oxidizable matter in mg $KMnO_4$ per liter		Percentage adsorbed
	not adsorbed	adsorbed	
Benzene	108	27	20
Carbon bisulphide	72	63	47
Nitrobenzene	98	37	27
Kerosene	89	46	34

Biltz considered the phenomenon as a straight adsorption and therefore believed that the adsorption isotherm should apply. For this reason, he did not try to find out why the purification was not more complete. Briggs[1] has shown recently that the adsorption varies with the surface exposed, as of course it should do. If the surface of the organic liquid were made sufficiently large, there seems to be no reason why the extraction should not be increased very much over the figures obtained by Biltz. If the precipitated material could be obtained in a coagulated form which was not readily peptonized by water there is no apparent reason why there should not be practically complete precipitation. I therefore

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[1] Jour. Phys. Chem., 19, 210 (1915).

look upon Biltz's paper as a valuable bit of preliminary work but as being far from the last word on the subject. It seems to me that there is here a very important field for research.

Robertson[1] has described some experiments which emphasize the emulsion formation. "If one shakes solutions of caseine, gelatine, or protein with chloroform, fine particles or drops are formed which, when numerous, form a milky layer at the bottom of the vessel; by transmitted light, they appear completely clear. These drops are extraordinarily stable and do not coalesce no matter how long they are left in contact. They can be washed repeatedly with water until all traces of protein are removed from the supernatant liquid but they remain completely stable and separated one from the other. They can even be shaken with chloroform or with $N/10$ potassium hydroxide without loss of stability. If the drops are heated under a water layer to about the boiling-point of chloroform, they burst, coalesce, and form a continuous layer of chloroform. When treated with alcohol, they dissolve at once and leave a fine filmy precipitate of protein floating on the water. If we shake chloroform with twice its volume of a one percent protamin sulphate solution, allow it to stand, separate the chloroform drops by decantation, wash them repeatedly with water, add about an equal volume of water, and stir cautiously, the drops swell and burst; and we see the fine membranes which surrounded them sink through the aqueous alcohol. If we add several volumes of alcohol, the drops of chloroform disappear completely and what we now obtain is a clear, homogeneous solution in which numberless very thin membranes can be seen floating."

From the experiments that have been described we see that wherever a suspended substance is wetted simultaneously by two liquids it will pass into the dineric interface and will therefore tend to form an emulsion. If the particles of the suspended substance are incapable of coalescing to form a coherent film, the emulsion will be very short-lived. An admira-

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[1] Die physikalische Chemie der Proteine, 308 (1912).

ble illustration of this is to be found with copper, kerosene, and water. On shaking the three substances together we get a copper-plated emulsion which soon breaks down because the copper powder does not form a coherent film. We then have two liquid layers with the copper powder adhering to the liquid interface. By adding gum or something which would cause the copper particles to stick together, it would probably be possible to make a permanent emulsion if that were worth while. I don't myself know what I could do with a permanent copper-plated emulsion even if I had one, so I have not tried to get one. The surprising thing to me has always been that the copper emulsion did not break down much more rapidly than it actually does. The copper powder gives a surprisingly good imitation of a coherent film. This seems to be a general phenomenon for Metcalf[1] says that "apparently any solid, which is distributed uniformly over a liquid surface, has the power of forming a solid film. When a small amount of talc powder or lycopodium is scattered uniformly over a liquid surface, there is formed a solid film showing distinct signs of elasticity and strength."

The other extreme is represented very well by sodium oleate, kerosene, and water. By shaking these three substances vigorously, we get a fairly permanent emulsion of kerosene in water. This is because the sodium oleate forms a fairly permanent, coherent film under ordinary conditions. With ordinary soap (and probably also with sodium oleate), kerosene, and water, one can revert to the instable form of emulsion by adding sodium chloride or sodium hydroxide. These substances tend to precipitate soap from aqueous solutions; in other words, they tend to make soap cone down less hydrous. A film of less hydrous soap is brittle and lacks elasticity. For this reason it is quite impossible to get a good soap emulsion if the water contains considerable quantities of sodium chloride or caustic soda.

Briggs[2] has shown that more soap is adsorbed by a given

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[1] Zeit. phys. Chem., 52, 45 (1905).

[2] Jour. Phys. Chem., 19, 210 (1915).

amount of benzene the greater the surface of the benzene, in other words, the smaller the drops. It seems to be very probable that the soap film is less hydrous the more surface a given amount of soap is required to cover. While there is no direct experimental proof of this as yet, it is made very plausible by the general behavior of emulsions. Emulsions with an excess of liquid to be emulsified seem usually to be less stable than those with a marked excess of the emulsifying liquid. This hypothesis is of assistance in accounting for Winkelblech's experiments. When he shook a dilute solution of gelatine with benzene for instance, the gelatine tended to emulsify the benzene; but the benzene was present in relatively large amounts and consequently the gelatine film round the drops contained relatively little water and was correspondingly brittle. When the drops coalesced again, the gelatine was left in a precipitated or coagulated form not readily peptonized by water. Winkelblech's experiments therefore differ from those of a man making an emulsion in that Winkelblech worked, unconsciously of course, under conditions which tend to make the film form as a non-coherent mass not readily peptonized by either liquid. It does not follow that the emulsion always cracks completely. In Robertson's experiments, the drops apparently remained emulsified. The principle underlying Winkelblech's work is the partial emulsification of one liquid by a small amount of an emulsifying agent present in the other liquid. If the emulsion is moderately stable, we see it as a cream. If the emulsion is instable we may still see the membranes which had formed round the drops, provided these films are not peptonized too rapidly by either of the liquids.

There ought to be a special term for substances which pass into the interface. It is not satisfactory to call them emulsifying agents, because that term should be kept for substances which really form moderately stable emulsions and I should hardly care to call copper powder, for instance, an emulsifying agent for kerosene and water though this might be done. I suggest, therefore, that the general term be "interfacial," a substance being interfacial for two liquids when its finely divided particles pass into the dineric interface of those two liquids. A substance which was held firmly in the interface would be strongly interfacial.

Winkelblech's method is then a test for interfacial substances. As such it seems to me capable of wider application than has yet been made. It seems to me that it may prove a valuable method for detecting colloidal solutions. Hydrous ferric oxide is strongly interfacial for benzene and water and we can show the presence of hydrous ferric oxide in a ferric chloride solution by shaking with benzene.[1] It seems to me that the method might be used for research work, to show the existence or non-existence of colloidal oxides when hydrous chromium, aluminum, or zinc oxide is apparently dissolved in an excess of alkali. Deductions from the data must be made cautiously, because the second liquid may increase perceptibly a hydrolysis which is otherwise negligible; but a correction can doubtless be made for this in any given case. I hope to be in a position before long to report on some such experiments as these.

The general results of this paper are as follows:

1. Many organic liquids adsorb hydroxyl ions from an aqueous alkaline solution.

2. Although it is theoretically possible that oils may make supersaturated solutions of sodium sulphate crystallize, it seems probable that Tomlinson's work along this line is inaccurate.

3. When shaken with water and a non-miscible organic liquid, solid particles tend to go into the water phase if they adsorb water to the practical exclusion of the other liquid; they tend to go into the other liquid phase if they adsorb the organic liquid to the practical exclusion of the water; and they tend to pass into the dineric interface in case they adsorb the two liquids simultaneously.

4. The simultaneous adsorption of two liquids probably

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[1] Briggs: Jour. Phys. Chem., 17, 296 (1913).

produces a homogeneous liquid phase at the surface of the adsorbing particle.

5. A substance which passes into the dineric interface is called interfacial for those two liquids.

6. An interfacial substance can be shaken more or less completely out of its suspension in one liquid by adding a second liquid for which the substance is interfacial.

7. When an interfacial substance can form a coherent, and fairly stable, film we get a fairly stable emulsion.

8. Winkelblech's method of shaking out colloids is a method for detecting interfacial substances. It is effective in case a fairly stable emulsion is formed or if the interfacial substance is left, when the drops coalesce, in a form not readily peptonized by either liquid.

9. It seems probable that an interfacial substance comes out of the aqueous phase less hydrous, the greater the surface of the other liquid phase.

10. It seems probable that Briggs is right in suggesting that Winkelblech's method can be used as a method of research to detect peptonized substances in presence of dissolved substances.

Cornell University

FLAME REACTIONS, IV

BY WILDER D. BANCROFT AND HARRY B. WEISER

Salts in Oxygen and Chlorine Flames

All the salts of the alkali metals impart a marked color to the Bunsen flame and the object of this investigation was to determine, if possible, what reactions were involved. Experiments have been made with the Bunsen flame, with hydrogen burning in chlorine, and with chlorine burning in hydrogen.

When studying the luminescence produced by the addition of salts to the Bunsen flame, it is essential to have some method of getting a uniform and continuous distribution of the salt in the flame. The primitive method of putting salt in the loop of a platinum wire and holding the wire in the flame is satisfactory only for the purposes of qualitative analysis because it does not color the flame uniformly and because the intensity varies as the salt disappears. Most of the sprayers which have been devised[1] are complicated to make. The form devised by Gouy[2] is very satisfactory so far as giving a uniform and continuous luminescence is concerned. In this apparatus the salt solution is broken up into a fine spray by air passing through a sprayer under pressure. The spray saturates the air which is subsequently mixed with illuminating gas. When the gas is lighted, it burns with a flame which is colored brightly and uniformly throughout. We have found that the spraying apparatus as used by Gouy is far more complex than is necessary. From the spraying chamber Gouy led the air into a system of glass bulbs where it was mixed continuously with the requisite amount of gas. The mixer is bulky and difficult of construction; a fluctuation in the gas or air pressure might lead to an explosive mixture being formed in the apparatus. A special provision for ob-

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[1] Cf. Beckmann and Lindner: Zeit. phys. Chem., **82**, 641 (1913).

[2] Ann. chim. phys., (5) **18**, 1 (1879).

taining a mixture of gas and air in the right proportions seems superfluous in view of the fact that we already have such an apparatus in the ordinary Bunsen burner.[1] We have obtained very satisfactory results with a modification of Gouy's apparatus. It may be made without difficulty in any laboratory. It is compact and simple; requires only a moderate amount of salt solution; and will run for hours with a minimum of attention. The apparatus is shown in Fig. 1. The spraying device *S* consists of two concentric glass tubes drawn out to jets. The other tube is preferably about one centimeter internal diameter and from eight to nine centimeters in length. The opening should be about 1.5 mm in diameter. For the best results it is essential that the tube be drawn down uniformly and that the opening should be exactly concentric with the tube. About 5 cm from the tip a small hole *A* is blown. The tube is then fitted through the small one-hole rubber stopper *B*. The inner tube is 3–4 mm internal diameter and is likewise drawn out to form a jet with an opening one millimeter in diameter. This inner tube is held firmly in place concentrically by means of the rubber stopper *B*. The tip of the inner tube must be a short distance below that of the outer tube. Experiment will show what adjustment is necessary to give the best results with any particular sprayer. The inner tube is connected with the laboratory supply of compressed air.

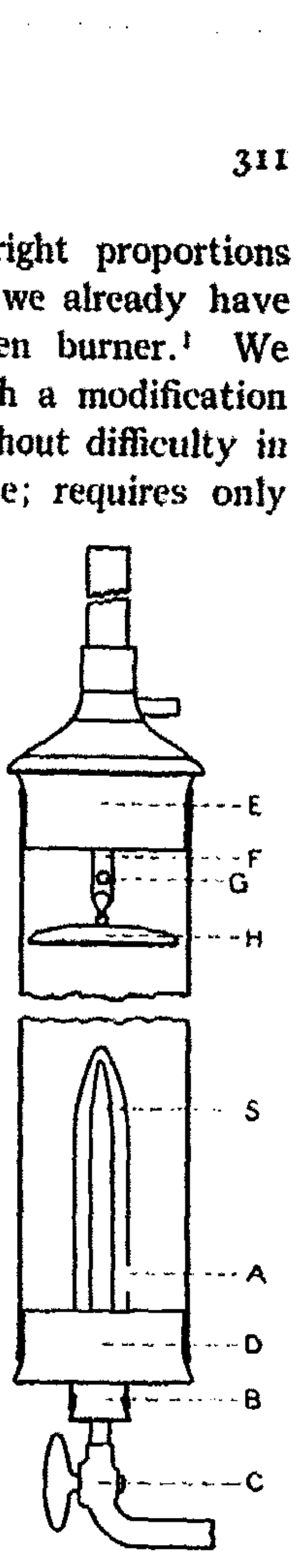

Fig. 1

The spray chamber surrounding the spraying tubes is a glass tube from 4–4.5 cm in diameter and 25 cm in length. It is closed at the two ends by the one-hole rubber stoppers

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[1] Cf. de Watteville: Phil. Trans., **204A**, 140 (1904).

D and *E*. The spraying tubes pass through the lower stopper and the air saturated with the salt solution passes through the hole in the upper stopper to the burner. It was found that a compartment of this size was quite ample to secure thorough saturation of the air. If glass tubing of the size designated be not available, an ordinary straight lamp chimney from a grocery store will serve the purpose admirably.

A very simple type of Bunsen burner, with no holes in the side for the entrance of air, was found to be satisfactory in all cases when it was not necessary to have the flame near the desk. In this type of burner the hole for the admission of air is at the lower end of the tube through the base of the burner. At first it was thought possible to connect the spray chamber with the air hole of the burner by means of a straight glass tube. This did not work well, for a drop of liquid would soon collect in this tube causing the flame to burn unsteadily, or even to go out. To overcome this difficulty a piece of ordinary glass tubing, 4 mm internal diameter, was filed to a point as shown in Fig. 1 so as to prevent a drop of liquid being held in the tube by capillarity. A hole *G* was cut through this tube near the end. The pointed end extends not more than a centimeter into the spray chamber. By means of a platinum wire the cover *H* of a porcelain crucible is hung so that the ring of the cover just touches the point of the glass tube. For the best results the diameter of the spray chamber should not exceed that of the crucible cover by more than 3–4 mm. The burner is fastened to the upper end of the glass tube by means of a small rubber stopper.

When starting the apparatus the sprayer is first fastened into the large glass tube and this latter is then clamped perpendicularly to an iron stand. Connection is made with the supply of compressed air and a screw clamp *C* is put on the rubber tubing as close to the lower end of tube *B* as possible. A concentrated solution of the salt to be examined is poured into the spray chamber until the level is above the end of the inner tube and below that of the outer tube. The solution runs in the hole in the side of the outer tube and fills the space between the two tubes. The Bunsen burner is then connected with the spray chamber and with the gas supply. After the gas is lighted, the air is turned on and the screw clamp is opened. The rush of air through the tip of the sprayer carries the solution up as fine spray which strikes against the suspended crucible cover and against the sides of the spray chamber. The air becomes thoroughly saturated with the salt solution and passes through the tube *F* to the burner. The relative amounts of gas and air are regulated so that a smoothly burning, uniformly colored flame is obtained. Even when the salt is not very soluble, a sufficient amount is carried up to give a brightly colored flame. With soluble salts the color is very intense. Of course the method is not suitable for insoluble salts. No experiments have been made with other solvents than water though this could be done if desired.

The efficiency of this simple spray device as a means of saturating the air may be shown by allowing it to run after removing the stopper *E*. A fog will rise from the end of the tube to a height of a foot or more. The sprayer has the additional advantages that it is very compact, that no parts are liable to break, and that only a little solution is needed.

The method of conducting the saturated air to the burner was found to work admirably for almost any reasonable length of time. The apparatus has been run for five hours, stopping only long enough to replenish the salt solution. During all that time the flame burned smoothly and was colored uniformly. It would be possible to modify the apparatus so as to permit replenishing the salt solution without stopping if that were desired. It would only be necessary to have a second hole in either stopper *D* or *E*, through which a glass tube could be connected with a reservoir of salt solution. If this were done the screw clamp *C* would not be absolutely necessary because the level of the solution need not be brought up above the tip of the inner tube until the air had been turned on; there would then be no danger of the solution flowing down the inner tube. While this would have certain merits, it would make the apparatus somewhat more complicated and we have not found any need for it. Since the apparatus furnishes such a ready means for securing continuously colored flame, its use as a source of monochromatic light suggests itself. We have not made any experiments using oxygen instead of air or using acetylene instead of gas; but there appears to be no reason why the apparatus could not readily be modified to meet either of these requirements in case it were desired to work at higher temperatures.

Instead of having the burner stationary on the top of the spray chamber, it is sometimes desirable to have it standing on the desk and connected with the source of air by tubing in such a way that the burner can be moved from place to place. An arrangement for doing this is shown in Fig. 2. A Bunsen burner is taken which has holes in the side for the admission of air. These holes are then enclosed by means of a glass tube about 3.5 cm in diameter and 4.5 cm in length. The flat corks *J* and *K* serve the double purpose of holding the glass tube in place concentric with the tube of the Bunsen burner and of making a closed compartment *L*. Air saturated with the salt solution enters this compartment through the tube *M* and passes through the holes in the Bunsen burner up to the flame. A small glass bulb *N* opens into *L*. Into this bulb will run any excess of liquid which may condense in the compartment when the apparatus is kept running for a considerable length of time. Using this apparatus the burner may be placed in any desired position and a uniformly colored flame secured for as long a time as may be desired.

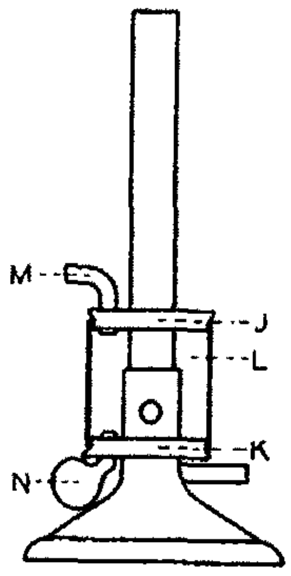

Fig. 2

When a saturated solution of sodium chloride in water is placed in the sprayer, the flame becomes brilliantly yellow because a relatively large amount of salt is distributed uniformly in very fine particles throughout the flame. When this flame is viewed through the spectroscope one notices, in addition to the brilliantly yellow lines, a continuous spectrum with a maximum in the blue.[1] When the Bunsen flame containing a sodium salt is looked at casually the blue luminescence is not seen because it is masked by the very much brighter yellow. A similar continuous spectrum in addition to the familiar line spectrum may be observed when lithium or potassium salts are introduced into the flame; but in these cases the blue or blue green luminescence is also masked to a great extent by the more intense light due to the line spectrum. This fainter luminescence has actually been observed by Lenard[2] without the use of the spectroscope, particularly in that portion of the flame separating the reducing zone from the oxidizing zone. It was of course very difficult to observe definitely the predominating color in this region of the flame because of the intense color in the oxidizing zone through which the light had to pass. In the case of sodium and potassium salts the apparent luminescence in this region was greenish yellow, and with lithium salts it was blue. This is about what one might expect to find by a rough observation with the unaided eye. Particularly is this true in the case of sodium salts, for a bright yellow superimposed on blue would give greenish yellow as Lenard observed.

Lenard also made some observations on the color of beads of salts after these were heated above the melting-point and then removed from the flame. He found that fused salts of the alkaline metals glow with a color which varies with the metal and which is for the most part independent of the acid radical present. Sodium salts glow with a sky-blue color, lithium salts with a blue color, potassium salts with a green color, and rubidium and caesium salts with a yellowish green color. This phenomenon of the luminescence of fused salts has been observed by us on a large scale with sodium chloride. In connection with another experiment altogether

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[1] Cf. Kirchhoff and Bunsen: Pogg. Ann., 110, 161 (1860); 113, 337 (1861); Gouy: Ann. Chim. Phys., (5) 18, 1 (1879).

[2] Drude's Ann., 17, 199 (1905).

several pounds of sodium chloride were fused in an electric furnace. A light-blue luminescence was noted, which was visible even in daylight, particularly when the cooling melt was stirred. At the time of this experiment we were unable to account for the blue luminescence; but it seems now to have been an observation on the large scale of the phenomenon described by Lenard.

Since the line spectra and the continuous spectra shown by the salts of the alkalines in the Bunsen flame are apparently independent spectra,[1] there must be at least two reactions involved. The best way of attacking the problem as to what the reactions are is to find what conditions are favorable to the production of one spectrum rather than the other and to cause chemical reactions to take place if possible, which will duplicate one or the other of the spectra. Most of the experiments have been made with sodium salts. The natural starting point is the hydrogen-chlorine flame.

Mitscherlich[2] showed that when a mixture of sodium chloride with considerable ammonium chloride is introduced into the Bunsen flame, the yellow color characteristic of sodium salts disappears almost completely. He also showed that the yellow color is not obtained when sodium chloride is introduced into a hydrogen flame burning in chlorine in any oxyhydrogen burner.

Smithells[3] repeated Mitscherlich's experiments using an oxyhydrogen burner with hydrogen burning in chlorine and with chlorine burning in hydrogen. He states however that he was able to obliterate the D lines only once. He considered that in entire absence of oxygen—in a pure hydrogen-chlorine flame—the yellow color would doubtless disappear completely.

In our experiments we have found that the modified Gouy sprayer could be used to considerable advantage for observing qualitatively the effect of hydrochloric acid on the

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[1] Lenard: Drude's Ann., 17, 208 (1905).

[2] Pogg. Ann., 116, 304 (1862).

[3] Phil. Mag., (5) 32, 245 (1894).

spectrum of salts of the alkalies introduced into the Bunsen flame burning in air. A concentrated solution of equal parts of ammonium chloride and of the salt under consideration was put into the sprayer. The flame fed into this mixture is colored much less intensely than a flame fed with the same concentration of the salt in question with no added ammonium chloride. An excellent lecture experiment is obtained by placing two sprayers close together with a dilute solution of lithium chloride in one and the same concentration of lithium chloride plus a large amount of ammonium chloride in the other. The first flame burns crimson and the second almost colorless.

With salts that are quite soluble in concentrated hydrochloric acid the sprayer furnishes a very convenient method of introducing hydrochloric acid into the flame. The effect of the acid may be shown strikingly by using salts of copper.[1] Into one sprayer is placed a saturated solution of cupric chloride in water and into the other a saturated solution of cupric chloride in concentrated hydrochloric acid. The first flame burns with the very bright grass-green color usually regarded as most characteristic of the salts of copper while the second shows no green to the unaided eye but is entirely blue. It has been shown in a previous paper[2] that the green luminescence is due to the change from copper to cuprous ion and the blue luminescence to the change from cuprous ion to cupric ion or cupric salt. The fact that the color is intense when the concentration of the hydrochloric acid is high is an argument in favor of the color being due in part at least to the change to undissociated cupric salt. The reason for the difference in the reactions in the two cases is quite simple. The hydrochloric acid forces back the dissociation so that practically no free copper is formed. If one looks carefully at the blue flame, one sees a purplish sheath. This is not really a new luminescence though it looks like one. It is merely the color of undissociated cupric chloride vapor.

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[1] Bancroft and Weiser: Trans. Am. Electrochem. Soc., 25, 121 (1914).

[2] Bancroft and Weiser: Jour. Phys. Chem., 18, 331 (1914).

The two methods, just described, for introducing hydrochloric acid into the flame are of general application and may be used in all cases where a so-called "chloride" spectrum is being investigated.

In their experiments with a hydrogen-chlorine flame Mitscherlich, Smithells, and Fredenhagen[1] used an oxyhydrogen blast lamp. While such an apparatus is convenient, it is not entirely satisfactory for obtaining a pure hydrogen-chlorine flame. We found this particularly true for a flame of chlorine burning in hydrogen. Two forms of apparatus were therefore designed, one for burning hydrogen in chlorine and the other for burning chlorine in hydrogen. When burning hydrogen in chlorine a glass tube 38 cm long and 5–6 cm in diameter served as the chlorine compartment in which the hydrogen flame burned. It is preferable to have this cylindrical tube of thin glass so as to minimize the danger of breaking when it is being subjected to more or less localized heating. In the side of the tube and 6 cm from one end there was blown a hole, 1 cm in diameter; this was closed by a cork through which passed a glass rod with a platinum wire sealed into the end. By means of this wire salts could be introduced into the flame. The ends of the tube were fitted with good corks. A piece of hard glass tubing passing through the lower cork served to introduce the hydrogen into the chlorine chamber. This tube was drawn out to a suitable jet and was tipped with platinum foil. The end of the jet was placed about one centimeter above the opening in the side of the chlorine chamber. Chlorine was brought in by means of another glass tube passing through the lower cork near the hydrogen tube. To keep the hydrogen flame from being fanned by the stream of chlorine, a centrally perforated watch-glass having a diameter only slightly less than that of the chlorine chamber was passed down over the hydrogen tube and held firmly in place horizontally, a few millimeters above the cork bottom of the chlorine compartment, by means

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[1] Drude's Ann., 20, 133 (1906).

of a cork fitting the hydrogen tube and the hole in the watch-glass. As the stream of chlorine entered the chlorine chamber, it impinged on the watch-glass and then passed round it up into the region of the flame. The hydrogen chloride formed by the combustion was led off, together with the excess of chlorine through a glass tube extending from the upper cork to a well-ventilated hood. The hydrogen was made in a Kipp generator by the action of hydrochloric acid on zinc; chlorine was obtained from a cylinder. Glass connections were used throughout.

The apparatus was clamped in an upright position to an iron stand at such a height that the body of the flame was in line with the slit of the spectroscope. The lower stopper was removed, the hydrogen lighted at the jet and the flame made as low as possible. The stopper was then replaced in the tube and a rather rapid stream of chlorine was at once allowed to flow into the chlorine chamber. This soon swept most of the air out so that very little moisture was formed and condensed on the wall of the compartment. After the chlorine had been allowed to flow for several minutes more hydrogen was run in until a flame of the desired size was obtained. The flame burned very smoothly. A bead of the salt to be studied was fused to the end of the platinum wire which later was bent upward in such a way that the salt bead did not stick into the flame but could be made to do so whenever desired by rotating slightly the glass rod into which the wire was sealed.

When using this apparatus there was no danger of corroding the spectroscope since no fumes escaped into the laboratory. When making observations the slit of the spectroscope was placed about two millimeters from the glass so that the metal should not become heated. A Hilger spectroscope with photographic attachment was used in these experiments. This was kindly loaned to us by the Department of Physics.

With lithium or potassium chloride in this hydrogen-chlorine flame, the characteristic lines of the metals were not to be seen with the spectroscope. When sodium chloride was introduced into the edge of the flame, the D lines were often obliterated completely for several seconds; but when the bead was thrust into the center of the flame where hydrogen was in excess, faint flashes of yellow were visible. A bead of salt was held in the edge of the flame while a photographic plate was exposed for several minutes. The D line did not appear when the plate was developed. Fredenhagen[1] mentions that the faint, continuous spectrum of the hydrogen-chlorine flame appears to be intensified when sodium chloride is introduced into this flame. We confirm this statement.

An apparatus for burning chlorine in hydrogen must provide a simple means of lighting the gas and must exclude all air. A large test-tube, 35 cm in length and 5.5 cm in diameter served as the hydrogen compartment in which the jet of chlorine burns. This tube was fastened vertically with the closed end up, while a good cork was fitted into the lower end. A small hole was blown in the side of the tube about 5 cm from the lower end. Through this the bead of salt could be introduced into the flame in the same way as in the other apparatus. A small oxyhydrogen blast-lamp tube with an outer jacket less than a centimeter in diameter served the double purpose of furnishing a ready means of lighting the gas and of providing a jet at which the chlorine flame burned. The stem of the blast lamp was removed from the stand and was passed through the cork in the lower end of the test tube, the tip being placed one centimeter above the hole in the side of the tube. The inner tube of the blast lamp was connected with the chlorine cylinder. By means of a Y-tube the hydrogen could be made to pass either through the outer tube of the blast-lamp or through a small glass tube running through the cork and extending along the wall of the hydrogen chamber to the top of it. Hydrochloric acid and the excess of hydrogen were carried off through still another tube at the bottom of the hydrogen compartment. This tube was bent up after coming out through the cork and was drawn out to a jet at which the escaping hydrogen could be burned.

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[1] Drude's Ann., 20, 145 (1906).

To start the apparatus the cork was removed, chlorine was passed slowly through the inner tube of the blast lamp and hydrogen slowly through the outer tube. The mixture was lighted, giving a small flame, and the cork holding the blast-lamp was fastened securely into the lower end of the test-tube. The hydrogen was gradually cut off from the outer tube of the blast-lamp and at the same time the tube leading to the top of the hydrogen chamber was opened. The hydrogen was allowed to flow quite rapidly for several minutes and then was lighted at the tip of the exit tube. The chlorine flame was then made as large as desired and the supply of hydrogen regulated so that there was always sufficient excess to keep the flame burning at the tip of the exit tube. In this way a steady stream of chlorine was burned in a surrounding atmosphere of hydrogen. If desired, the hydrogen may be allowed to pass through the outer tube of the blast-lamp continuously; but, if so, the flame is very narrow, the shape being more like that of the oxyhydrogen blast. It was therefore found desirable to pass the hydrogen in at the top of the test-tube after the flame was once started. Five large Kipp generators were connected together in order to ensure an excess of hydrogen at all times.

When potassium chloride was introduced into the flame of chlorine burning in hydrogen, the violet color, characteristic of the Bunsen flame, was lacking entirely; neither the blue nor the red line could be seen in the spectroscope. With sodium chloride in the flame, the yellow luminescence was very faint but never disappeared completely. In fact we were able to get a photograph showing the D lines faintly. We thus see that the D lines persist faintly in a hydrogen-chlorine flame with hydrogen in excess whereas they can be made to disappear completely when chlorine is in excess. From the analogous behavior of the copper salts the natural assumption to make is that the yellow luminescence, which is so strong in the Bunsen flame, is due to a reaction of sodium metal, while the blue luminescence, which persists in the hydrogen-chlorine flame, is due to the change from sodium ion to undissociated salt. Our own experiments and the experiments of others confirm this hypothesis.

Since both sodium and potassium oxidize very readily in the air, it was thought that this reaction might take place sufficiently rapid to give a luminescence. The observations were made in a dark room after the eyes had become sufficiently sensitive. When a large piece of potassium was cut so as to expose a fresh surface to the air, this surface glowed with a bluish light. When sodium was treated in the same way, no luminescence could be detected. If, however, the metal is placed in a glass mortar and is ground so that very thin bits are obtained, a faint glow can be seen. If a piece of sodium be thrown into water in the dark, it rolls round over the surface of the water and a trail of bluish luminescence follows it. Wilkinson[1] studied the luminescence produced when oxygen was passed slowly over metallic sodium. So long as the oxidation took place slowly, a blue luminescence was obtained. When the oxidation took place rapidly, the luminescence gave place to—or was masked by—the bright yellow flame so characteristic of sodium. Wilkinson tried a similar experiment substituting chlorine for oxygen. "When a slow current of chlorine is passed over metallic sodium in the form of fine wire placed in the combustion tubing, it [the sodium] gives quite a bright luminescence and the brightness increases with the strength of the chlorine until the sodium bursts into flame with the usual color." A similar result was obtained with potassium. When allowed to burn slowly in an atmosphere of chlorine a deep blue luminescence was produced that was quite different from the characteristic violet color obtained when potassium burns rapidly. Slow combustion in an atmosphere of bromine gave a blue-white luminescence with sodium and a bluish green one with potassium, whereas the yellow sodium flame and the violet potassium one were obtained when the combustion was rapid.

Fredenhagen[2] considered that the yellow luminescence

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[1] Jour. Phys. Chem., 13, 691 (1909).

[2] Drude's Ann., 20, 150 (1906).

obtained with sodium salts in the Bunsen flame was due to the presence of sodium oxide and he attributed the absence of the yellow luminescence when sodium chloride was fed into the hydrogen-chlorine flame to the absence of sodium oxide. If this were true, then sodium burning in pure chlorine should not give a yellow luminescence even when burning rapidly. We have tested this in as careful a manner as possible. A piece of metallic sodium about 3 cm long and 5 mm square was cut from the inside of a large piece of the metal. A stream of hydrogen was directed against the sodium while it was being cut, so that the small piece was obtained with as little oxidation as possible. The sodium was then placed in a small, bright, iron boat and the latter brought to the end of a horizontal piece of combustion tubing through which a rapid stream of dried hydrogen was passing. While thus in the atmosphere of hydrogen, the metal was scraped to remove any oxide and then the boat was pushed way into the tube. The stream of hydrogen was then replaced by a rapid stream of chlorine. The sodium glowed with a blue luminescence for a moment and then the bright yellow flame appeared. This simple experiment is fairly conclusive that the yellow luminescence is obtained when sodium burns sufficiently rapid in chlorine. Of course one cannot deny the presence of oxygen in some form because Wanklyn[1] showed that sodium may be melted in perfectly dry chlorine without any combustion taking place, the surface of the molten metal remaining bright and lustrous. A trace of water vapor is sufficient to make the reaction take place rapidly. In view of the intense color obtained when sodium burns in chlorine, it seems hardly probable that the flame is due solely to the formation of sodium oxide, especially since a perfectly satisfactory explanation is available for the faintness of the yellow luminescence in the hydrogen-chlorine flame.

Wiedemann and Schmidt[2] decided that the luminescence produced by the action of cathode rays on salts was due

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[1] Jour. Chem. Soc., 43, 153 (1885).

[2] Wied. Ann., 54, 662; 56, 203 (1895); 64, 78 (1908).

either to the decomposition of the salts or to the recombination of the decomposition products. It was shown by Wilkinson[1] that, in almost all cases, the luminescence was due to the recombination and not to dissociation. When sodium chloride or bromide is exposed to cathode rays, the luminescence is bluish and there is no sign of a yellow luminescence. With potassium chloride or bromide the luminescence is blue and with the iodide it tends towards the green. When cathode rays act for a considerable time on the alkaline halides, a colored mass is obtained. Wiedemann and Schmidt were inclined to consider the color as due to a sub-salt; but it now seems probable that we have colloidal metal dispersed in the salt.[2] When cathode rays act on sodium chloride, it seems certain that the salt is decomposed to a certain extent into sodium and chlorine, these decomposition products reacting slowly and producing the blue luminescence. If some chlorine escapes as gas, the free metallic sodium in excess colors the salt. A further proof of decomposition and slow recombination is the fact that salts which have been exposed to cathode rays can be made luminescent temporarily by heating. The heating serves to increase the rate of recombination and consequently the intensity of the light emitted. The color of the light emitted is identical with the fluorescence produced when cathode rays are acting on the salts.[3]

Anode or canal rays likewise cause some salts to luminesce. The canal rays are more violent in their action than the cathode rays and it is therefore not surprising that different reactions may predominate and that different luminescences may occur. Both Arnold[4] and Schmidt[5] found that sodium salts emitted a reddish yellow light when exposed to canal rays, the D lines being plainly visible when the light was examined spectroscopically. Schmidt noticed that the

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[1] Jour. Phys. Chem., 13, 691 (1909).

[2] Zsigmondy: Kolloidchemie, 29 (1912).

[3] Farnau: Jour. Phys. Chem., 17, 644 (1913).

[4] Wied. Ann., 61, 326 (1897).

[5] Drude's Ann., 9, 703 (1902).

action of the canal rays first gave rise to the bluish luminescence characteristic of cathode rays; but this was soon replaced by the yellow luminescence. After the exposure to canal rays, heating causes a bluish thermoluminescence, which is exactly what ought to happen.

J. J. Thomson[1] has made a striking observation of the relative effects of cathode and anode rays on lithium chloride. The salt was subjected alternately to the action of anode and cathode rays in the same tube. The anode rays produced a bright red luminescence showing the characteristic lithium line, while the cathode ray luminescence was steely blue giving a faint continuous spectrum.

Bandrowski[2] found that luminescence was obtained when certain salts were precipitated rapidly from solution. This work was confirmed and extended by Farnau.[3] A bluish white luminescence was obtained with sodium chloride and a greenish white with potassium chloride. We have repeated these experiments on a large scale using hydrochloric acid as precipitating agent. As much as 500 cc of a saturated salt solution were used in a single experiment. Under these conditions the luminescence was relatively quite bright. The glow became visible shortly after the addition of the hydrochloric acid. It was faint at first but increased gradually in brightness up to a maximum intensity, then fading away gradually until it was no longer visible. The glow lasted for several seconds. With sodium chloride the glow was a bluish white color and less blue than we had hoped to find it. This difference is probably due to the white color of the precipitated salt, for the intensity of the light was quite sufficient to make the white salt dimly visible and thus change the apparent color of the luminescence from blue to bluish white. All of the reactions giving the blue luminescence involve the change from sodium ion to undissociated

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[1] Conductivity of Electricity through Gases, 2nd Ed., 646 (1902).

[2] Zeit..phys. Chem., 15, 325 (1894).

[3] Jour. Phys. Chem., 17, 649 (1913).

salt or else the slow burning of sodium. If we postulate that the formation of sodium ion is an intermediate step in the slow burning of sodium, we see that the blue luminescence is due to the change from sodium ion to undissociated sodium salt while the yellow luminescence is due to some stage in the change from sodium metal (perhaps as vapor) to sodium ion. This is the same conclusion that was drawn from the analogy between the sodium flames and the copper flames.

It may be well to run over the special cases briefly, taking the blue luminescence first. Apparently the only reaction possible in the case of the fused salt is the change from dissociated to undissociated salt. When sodium chloride is precipitated from aqueous solution, the change is from dissociated salt to undissociated solid salt. When sodium chloride is introduced into a flame of hydrogen burning in chlorine, the temperature of the flame is high enough to cause dissociation of the salt into sodium metal and chlorine; but this dissociation is cut down by the chlorine and the hydrochloric acid just as in the case of the copper salt and we get dissociation to sodium ion. Some dissociation to sodium must take place because we get some yellow with a chlorine flame burning in hydrogen, where the chlorine is not in excess. Owing to the extreme sensitiveness of the sodium reaction it is probable that the dissociation to sodium is very small in the hydrogen-chlorine flame.

If the burning of sodium involves the formation of sodium ion as intermediate product, it is easy to see why we get the blue luminescence when sodium burns in chlorine and oxygen or when sodium chloride is exposed to cathode rays. It is not so obvious why we do not always get the yellow luminescence since we start from sodium in each case. It seems to be a question of relative reactions. It has been shown[1] that all reactions tend to emit light and that they do emit light if the reaction velocity is high enough. The intensity

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[1] Trautz: Zeit. phys. Chem., 53, 1 (1905); Bancroft: Internat. Congress Applied Chemistry, New York, 20, 25, 37 (1912).

of the light increases with the reaction velocity while the quality of the light is independent of it. The critical reaction velocity at which a reaction emits light visible to the eye varies enormously from reaction to reaction. To account for the phenomena we have only to postulate that the reaction from ion to undissociated salt is the only one to emit light at low reaction velocities while the reaction which gives the yellow luminescence becomes the predominant one when the reaction velocity increases. We therefore get the blue luminescence with slow combustion, either directly, or indirectly as the result of the cathode rays.

The more violent action of the anode rays gives us the yellow luminescence, which we also get during the rapid combustion of sodium, either directly or indirectly, as a result of dissociation in the Bunsen flame. Since sodium vapor is itself colored, there will undoubtedly be a thermal luminescence just as there is with heated iodine.[1] This would account for part of the luminescence observed in the Bunsen flame and this luminescence would have to be substracted before one could determine quantitatively the luminescence due to the chemical reaction. It is quite possible that the concentration of sodium vapor in the Bunsen flame is so small that the thermal luminescence due to this is negligible; but only a quantitative study would settle that point.

Since Lenard[2] has shown that there are several sodium spectra and since the experiments of Wood and Galt[3] on the fluorescence of sodium vapor confirm this, it is not safe to say that the change from electrically neutral sodium vapor to sodium ion is the reaction causing the yellow light which we ordinarily associate with sodium. All that we can do as yet is to say that the yellow light is due to some stage in the change from electrically neutral sodium vapor to sodium ion, leaving it undecided as to how many stages there are.

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[1] Bancroft and Weiser: Jour. Phys. Chem., 18, 302 (1914).

[2] Drude's Ann., 11, 636 (1903).

[3] Astrophys. Jour. 33, 72 (1911).

The conclusions in regard to sodium flames apply of course to potassium and lithium flames equally well. The so-called chloride spectra of barium, strontium, and calcium must of course be analogous to the blue luminescence of sodium, though we have only made preliminary experiments on these. The conclusions as to the sources of the line spectra and the continuous spectra of the alkali metals are in agreement with Lenard's experiments on electrical migration. With lithium salts Lenard[1] showed that the sources of emission of the line spectrum did not move under electrical stress and were therefore electrically neutral, which is what one would expect if the reacting substance is electrically neutral lithium vapor. On the other hand, the sources of emission of the continuous spectrum moved to the cathode and were therefore charged positively. We have shown that the reacting substance is the positively charged ion.

The general results of this paper are as follows:

1. A simple and easily constructed modification of the Gouy sprayer has been described.

2. An apparatus has been constructed for burning hydrogen in chlorine and another for burning chlorine in hydrogen.

3. Salts of lithium, potassium, and sodium give two distinct spectra in the Bunsen flame. One is a continuous spectrum and the other a line spectrum.

4. The introduction of hydrochloric acid into the Bunsen flame cuts down the intensity of the line spectra of the alkali metals. With the flame of hydrogen burning in a surrounding atmosphere of chlorine the line spectra disappear completely. The D lines are obtained faintly when sodium chloride is introduced into a flame of chlorine burning in a surrounding atmosphere of hydrogen.

5. The blue luminescence of sodium is obtained without the yellow luminescence: when sodium salts are introduced into a flame of hydrogen burning in chlorine; when metallic

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[1] Drude's Ann., 17, 223 (1905).

sodium burns slowly in oxygen, chlorine, or bromine; when a sodium salt is fused; when cathode rays act on sodium chloride; when anode rays first act on sodium chloride; when one heats the colored residue obtained by the action of anode rays or cathode rays on sodium chloride; when sodium chloride is precipitated rapidly from aqueous solution with hydrochloric acid or alcohol.

6. The yellow luminescence of sodium is obtained, accompanied by the fainter blue luminescence: when a sodium salt is introduced into the Bunsen flame; when sodium burns rapidly in oxygen, chlorine, or bromine; when canal rays act on sodium chloride. It is claimed that the yellow luminescence is obtained when sodium vapor is heated; but it is very difficult to be certain that no burning takes place under these conditions.

7. The blue luminescence of sodium is due to the reaction from sodium ion to undissociated sodium salt.

8. The yellow luminescence is due to some stage in the reaction from sodium vapor to sodium ion. Until we can account for all the sodium spectra, it is unsafe to try to specify the reaction more closely.

9. Since sodium vapor is colored, it will give a thermal luminescence and this must of course be taken into account. It is not known whether the concentration of the sodium vapor in the Bunsen flame is sufficiently high to make the purely thermal luminescence an important factor or not. In so far as solid sodium salts may be present in the Bunsen flame there will theoretically be thermal luminescence due to them.

10. To account for the absence of the yellow luminescence when sodium burns slowly, we postulate that the light intensity for this reaction is very slight when the reaction velocity is low.

11. The diminished intensity of the line spectra in the hydrogen-chlorine flame, or in the Bunsen flame to which hydrochloric acid has been added, is due to the forcing back

of the dissociation of the salts. The salts dissociate to ions and only slightly or not at all to free metal.

12. Since the reacting substance is the electrically neutral vapor of the metal in the case of the line spectrum, there is no migration under electrical stress. Since the reacting substance is the positively charged ion of the metal in the case of the continuous spectrum, there is a migration to the cathode under electrical stress, as found by Lenard.

Cornell University

HYDROUS CHROMIC OXIDE

BY C. F. NAGEL, JR.

Bunce and Finch[1] have described a number of conditions under which chromic oxide jellies can be obtained. They obtained a good jelly by adding caustic potash to a potassium chrome alum; but were not able to get one by adding caustic potash to a chromic sulphate solution. The most plausible explanation of the difference was that the sulphate concentration was not high enough in the second case to permit of a good jelly being formed. They say: "The time at our disposal did not permit us to test within what ratios of potassium sulphate to chromium sulphate it was possible to get a jelly on adding caustic potash, nor have we made any experiments to see whether these jellies behave as do the jellies made with acetate, when subjected to heating, freezing, acids, etc. We did try one experiment with a solution of one part sulphate in ten of water. On adding KOH a precipitate formed at first; but this dissolved in an excess of caustic potash yielding a clear green solution. After standing for several hours this solution began to get viscous; the next day it was very viscous. While the solution did not set to a jelly, it showed a decided tendency to do so and we think that it may be possible to cause a chromic sulphate solution to form a jelly simply by adding caustic potash."

At the suggestion of Professor Bancroft I undertook to find out what relative amounts of potassium sulphate were necessary to give a good jelly. As a preliminary I repeated the work of Bunce and Finch using chrome alum (1 : 9) and KOH (1 : 1) since these concentrations were said to give the best results. While I confirmed the results of Bunce and Finch, I found that their directions were not sufficiently explicit to enable one to repeat their experiments the first time. In order to get a good jelly it is essential to avoid an

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[1] Jour. Phys. Chem., 17, 769 (1913).

undue excess of caustic potash, and the amount of potash necessary to dissolve or peptonize the pale green precipitate varies with the way in which the potash is added. If the KOH is added very slowly with frequent and vigorous shaking, a large excess can be run in without dissolving the precipitate satisfactorily. The pale green color persists and the solution remains thick. If allowed to stand, this solution sets to a kind of jelly but the pale opaque green color remains. If KOH is added in considerable excess, the clear green color, mentioned by Bunce and Finch, is obtained together with a precipitation of potassium sulphate; but this type of solution would not jell even after standing several days. The solutions giving the best and firmest jellies had a green color though of a lighter shade than that produced with excess of KOH. The best results were obtained by adding quickly about 10 percent by volume of KOH solution and shaking just sufficiently to cause the precipitate to disappear. Sufficient KOH has been added if the pale green color just disappears. A slight excess is permissible but the greater the excess of KOH the longer the jelly takes to form. As has been stated, too great an excess prevents the formation of the jelly absolutely. When the solution is in proper condition to jell, the color of the solution is a trifle darker than a grass-green and is somewhat cloudy.

Chrome alum and chromic sulphate solutions were mixed in such proportions that the chromic sulphate content remained practically constant, while the potassium sulphate content varied. The chrome alum solution contained about 135 grams per liter, the chromic sulphate solution about 20 g $Cr_2(SO_4)_3$ per liter, while the KOH solutiom was 1 : 1. The data are given in Table I.

Good jellies were thus obtained with all the relative concentrations of K_2SO_4, which made it seem doubtful whether the alum was needed at all. Experiments were therefore made with solutions containing about 34 g $Cr_2(SO_4)_3$ per liter and KOH, 1 : 1. Good jellies were obtained using 50 cc of the sulphate solution and 10–11 cc KOH. It seems probable that the failure of Bunce and Finch to obtain a jelly was due to adding too much caustic potash. After the jellies had stood for a few days in an open beaker the potassium sulphate began to crystallize. When kept in a closed bottle, the jelly contracted, leaving a colorless supernatant liquid layer.

TABLE I

Ratio	Alum cc	Sulphate cc	KOH cc	Result in 20 hours
1 : 1	9.1	30	4.5	good jelly
1 : 1	9.1	30	6.5	no jelly (excess KOH)
1 : 3	4.55	45	4.0	good jelly
1 : 3	4.55	45	3.5	good jelly
1 : 5	3.0	50	3.3	good jelly
1 : 5	3.0	50	3.3	good jelly
1 : 7	2.1	49	3.7	good jelly
1 : 7	2.1	49	3.5	good jelly
1 : 9	1.8	54	3.7	good jelly
1 : 9	1.8	54	3.9	good jelly

Northcote and Church[1] have recorded some interesting facts in regard to hydrous chromic oxide. "The influence of the association of sesquioxide of chromium with metallic oxides, which by themselves are insoluble in solution of caustic potash, is well known; the insoluble oxides being in some cases rendered soluble when thus associated, while in the other cases, they communicate their insolubility to the otherwise soluble oxide of chromium. The object of the inquiry instituted with reference to these results was to ascertain the exact conditions under which complete solution or precipitation of the associated oxides occurs. It was found that complete solution takes place when the chromium as sesquioxide is associated with 40 percent of iron as sesquioxide; with 12.5 percent of manganese, 20 percent of cobalt, or 25 percent of nickel as protoxides; and that complete precipitation takes place when the chromium as sesquioxide is associated with 80 percent of iron [as sesquioxide], 60 percent

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[1] Jour. Chem. Soc., 6, 54 (1854).

of manganese, 50 percent of cobalt, or 50 percent of nickel as protoxide. When cobalt and nickel, however, are thus rendered soluble, the result is not permanent; and ultimately, not only does the oxide of cobalt or nickel become insoluble but it carries down with it some of the oxide of chromium. The other metallic oxides soluble in caustic potash were not found to be influenced in their relations with caustic potash by the presence of sesquioxide of iron, or to exert any influence upon that oxide."

Knecht, Rawson and Loewenthal[1] say: "Chromic hydroxide in its alkaline solution has the curious property of dissolving other metallic oxides, such as the ferric and the cupric oxides. Ferric oxide dissolves readily, and the brown solution remains clear for weeks without any precipitate forming. The alkaline solution of chromic and cupric oxide is blue; on heating to incipient boiling, red cuprous oxide is precipitated and sodium chromate formed."

Roscoe and Schorlemmer[2] say: "Like alumina, chromic oxide acts as an acidic oxide towards strong bases, yielding salts termed the chromites. Thus a green compound of chromic oxide with an alkali is thrown down on the addition of potash or soda to a solution of a chromic salt, and the alkali cannot be removed even by boiling water. This precipitate is, however, easily soluble in an excess of the precipitant, but can be thrown down either by partial neutralization with acids or by boiling the solution. When caustic soda is added to a solution of a chromic salt and a salt of magnesium, a precipitate is obtained of a compound of magnesia and chromic oxide which does not dissolve in an excess of alkali."

Although there was no reason to question the accuracy of any of these experimental data it seemed desirable to check at least one set qualitatively. Stock solutions of ferric chloride and chromic sulphate were mixed in varying proportions and then an excess of KOH (about 1 : 10) added. The results are given in Table II:

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[1] A Manuel of Dyeing, 1, 241 (1910).

[2] Treatise on Chemistry, 2, 1000 (1907).

TABLE II

$FeCl_3$ cc	$Cr_2(SO_4)_3$ cc	Remarks
10	50	Solution clear green; no precipitate
10	30	Solution less green; slight precipitate
20	20	Solution brown green; more precipitate
30	10	Solution brown green; still more precipitate
60	10	Solution paler; precipitate brown
80	10	Solution nearly colorless; precipitate brown
150	5	Solution like pure water; precipitate brown

In the first experiment the iron has all been dissolved or peptonized and in the last experiment the chromium has all been carried down by the iron. These experiments are admirably adapted for lecture experiments, though it would probably be better to use chromic chloride or to substitute caustic soda for caustic potash to do away with any possibility of potassium sulphate crystallizing. Since Grimaux[1] has shown that, when potassium hydroxide is added to a mixture of glycerine and ferric chloride, a colloidal solution of hydrous ferric oxide is formed, the last three experiments in Table II were repeated after adding 10 cc glycerine to each mixture before treating with alkali. In all three cases a reddish brown solution was obtained and no precipitate. Magnesium hydroxide was found not to precipitate in presence of an excess of chromic salt when caustic soda was added.

The explanation of the phenomena is now fairly simple. Fischer and Herz[2] have shown that the apparent dissolving of hydrous chromic oxide in caustic alkali is really a peptonization, all or nearly all of the chromic oxide being present as a second phase in colloidal solution. Hydrous ferric oxide is not peptonized or dissolved by caustic alkali. Hydrous chromic oxide and hydrous ferric oxide each adsorb the other. Consequently the iron is trying to take the chromium out of the liquid phase, while the chromium is trying to carry

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[1] Comptes rendus, 98, 1485 (1884).

[2] Zeit. anorg. Chem., 31, 352 (1902.

adsorbed iron into colloidal solution. When the chromium is in excess all the iron is peptonized; when the iron is in excess none of the chromium is peptonized. This can be shown in another way by precipitating the oxides separately. A considerable quantity of ferric chloride was precipitated with alkali and washed a couple of times by decantation. The hydrous ferric oxide thus obtained was shaken with a small amount of a green solution of chromic oxide peptonized by alkali. The green solution became colorless owing to the chromium oxide being adsorbed completely by the iron oxide.

Prud'homme[1] has shown that chromic oxide dissolves in ammonia when a salt of copper is added and cupric oxide dissolves in caustic potash if a salt of chromium be present. The case of the cupric oxide in caustic potash is the same as that of the ferric oxide. The cupric oxide is adsorbed by the peptonized chromium oxide. If we are going to follow out the analogy, we ought to conclude that the apparent solubility of chromium oxide in ammonia is due to the adsorption of chromic oxide by peptonized cupric oxide, which would be very interesting indeed. This does not necessarily follow however because hydrous chromium oxide dissolves in ammonia when sufficient sodium acetate is present and sodium acetate is certainly in true solution. The matter is nevertheless interesting enough to warrant further study and I hope before long to be able to report on this point and also on the question to what extent the apparent solubility of oxides of the heavy metals in alkaline sugar solutions, etc., is or is not a case of peptonization.

1. Hydrous chromic oxide is peptonized by caustic alkali. It can adsorb the hydrous oxides of iron, manganese, cobalt, nickel, copper, and magnesium to some extent without coagulation. It thus carries these oxides into colloidal solution.

2. The hydrous oxides of iron, manganese, cobalt, nickel,

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[1] Bull. soc. chim. Paris, (2) 17, 253 (1872).

copper, and magnesium adsorb chromium oxide and therefore tend to take it out of colloidal solution in alkali. When these hydrous oxides are present in sufficient amount, they decolorize practically completely a green solution of chromic oxide peptonized by alkali.

3. In presence of glycerine hydrous iron oxide is peptonized by alkali and consequently does not tend to carry down the chromium oxide.

4. In presence of a copper salt hydrous chromium oxide is peptonized by ammonia; but it is not yet known whether this means that an ammoniacal copper oxide solution is a colloidal solution or not.

5. The question has been raised to what extent we are dealing with colloidal solutions when hydrous oxides of the heavy metals appear to dissolve in alkaline sugar solutions, etc.

6. A good jelly can be obtained by adding caustic potash to a chromic sulphate solution; but the alkali must be added quickly and not in great excess.

Cornell University

THE DIELECTRIC CONSTANT OF LIQUID HYDROGEN IODIDE

BY HERMAN SCHLUNDT AND JULIUS UNDERWOOD

In 1909 Schaefer and Schlundt[1] reported the following values for the dielectric capacity of liquid hydrogen iodide: 2.90 at 22°, 2.88 at —50°, and 3.95 at —70° for the solid. The greater value of the solid as well as the zero temperature coefficient of the liquid are exceptional, and therefore cast doubt upon the above values.[2] We have now made another series of measurements with the Drude-Schmidt apparatus formerly used, and have obtained values that are in accord with the general variations in dielectric capacity with temperature and condition. The following values were obtained: 2.65 at 19°, 3.61 at —50°, and 3.05 for the solid at —70°. These values represent the average of three determinations in cells of somewhat different electric capacities. It is seen that the dielectric constant increases with lowering of temperature by approximately 0.5 percent per degree and that the solid has a lower value than the liquid.

The samples of hydrogen iodide used for the measurements were nearly colorless, and had been redistilled *in vacuo*.

To reduce the possible displacement of the electrodes of the cells as a result of volume changes that accompany solidification and fusion, new cells with heavier platinum wires were used. After all we are still somewhat doubtful about the accuracy of the value found for hydrogen iodide in the solid state.

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[1] Jour. Phys. Chem. 13, 669 (1909).

[2] Kraus and Bray: Jour. Am. Chem. Soc. 35, 1420 (1913).

NEW BOOKS

The Chemistry of the Radio-Elements. *By Frederick Soddy. Second Edition, Part I; First Edition Part II; Two Parts in One Volume. 22 × 14 cm; pp. v + 151 + 46. New York: Longmans, Green & Co., 1915. Price: $1.75 net.*—The first edition of Part I was reviewed in 1912 (16, 341) and the first edition of Part II in 1914 (18, 695). The present volume consists of a new edition of Part I bound with the first edition of Part II.

In the preface to the new edition of Part I, the author says: "In 1914 a new edition of Part I being called for, the present volume was written. The whole subject can now be presented much more clearly and completely than in 1911, and in consequence Part I has had to be largely rewritten from the new point of view. But while the general mode of presentation has been much modified the ground already covered in detail in Part II has been, as far as possible, avoided in the present volume, which concerns itself rather with the practical consequences than with the theoretical significance of the new generalizations.

"In addition, much new matter has been added, especially in connection with the X-rays and recent electro- and colloido-chemical researches on the radio-elements. Some of the topics but briefly dealt with before have been considerably amplified, and many new members of the disintegration series, unknown in 1911, have had to be included. There is reason to hope that something approaching completeness has now been attained with regard to these numerous and involved successive products, and though much remains to be done, it is unlikely that many more will be discovered."

The subject is presented under the headings: general description of radioactivity; radioactive constants, periods of average life, and radioactive equilibrium; enumeration and nomenclature of the radio-elements—preliminary description of the disintegration series; physical methods of separation; the chemical character of the radio-elements; adsorption, electro- and colloido-chemistry of radio-elements; systematic description of the radio-elements.

There is a very interesting account, p. 14, of the chemical action of the rays.

"In addition to the photographic effect, the rays produce many other chemical actions. The most notable is the decomposition of water, which renders it dangerous to seal up radium or other highly radioactive preparations, either in solution, or in an imperfectly dried condition for indefinite periods, owing to the possibility of the vessel bursting and the contents being scattered. For pure radium salts dissolved in water, under which condition the α-rays are operative, the amount of hydrogen and oxygen evolved is some 15 cc per day per gram of radium. Much the same rate would be initially produced from the emanation dissolved in water. When the β- and α-rays only are operative, as when the radium or the emanation is contained in a sealed glass tube immersed in water, the evolution of gas is 0.115 cc per day per gram of radium, and it consists of pure hydrogen, hydrogen peroxide being also formed, in accordance with the equation:

$$2H_2O = H_2O_2 + H_2 - 90{,}000 \text{ calories}$$

"This may account for the fact that in the mixed gases evolved from a solution of radium, the hydrogen is always in slight excess. If the rays from the emanation act on water vapor this excess of hydrogen attains 50 percent by volume. Whereas for ice at —180° there is no excess of hydrogen, but the amount of decomposition is only 5 percent of that which would be produced in liquid water. Conversely, when hydrogen and oxygen, in presence of phosphorus pentoxide, are exposed to the rays, the gases combine to form water.

"The same type of reversible reactions occurs with most other gases. Ammonia is rapidly decomposed, whereas a mixture of hydrogen and nitrogen, in presence of a reagent that absorbs ammonia, contracts in volume. Carbon dioxide is decomposed into carbon monoxide, carbon, and oxygen, whereas carbon monoxide forms carbon dioxide, carbon, and oxygen. Nitrogen, in presence of oxygen, is oxidized. If air, containing emanation, is stored over mercury, nitrous oxide will be found to be formed. No doubt the formation of combined nitrogen from the air, hitherto attributed to silent electric discharges, is largely due to the radium emanation and other radioactive products invariably present in minute amount in the air.

"The general chemical action of the rays seems to be of the nature of a shattering of the molecule and the transient formation of free atoms, which, as in the so-called nascent state, readily recombine and enter into new combinations, which the same elements in the molecular condition are unable to effect. It would appear also, at least as a first approximation, that an extension of Faraday's law of liquid electrolysis controls the action of these rays on the quantitative side. The rays in the gas produce a certain amount of ionization. If this amount be expressed in faradays, it will be found to be of the same order as the amount of chemical action expressed in moles. Thus, in the decomposition of liquid water, for example, the number of molecules decomposed is approximately the same as the number of pairs of ions formed when the rays traverse a gas. This holds even more accurately when the gas in question is water vapor or electrolytic gas rather than air. The numbers of ions produced in various gases by the same rays are not very different, varying over a range of from 1 to 1.3.

"Other chemical actions of the rays which have been studied are the decomposition of hydrogen peroxide, the liberation of iodine from iodides of the alkali-metals, especially in acid solution, the reduction of silver nitrate solution to metallic silver, the oxidation of organic acids, such as acetic acid, and of ethyl alcohol to acetaldehyde and acetic acid, the inversion of sterilized solutions of cane sugar and many others. Many of these changes are produced by ultra-violet light, and it must be remembered that the quantities of material decomposed by the radium rays is always relatively very small.

"Lastly, the coloring action of the rays on common glass and on many gems may be referred to. Ordinary soft laboratory glass is colored usually a purple tint, but sometimes brown according to its composition. Hard glasses are colored brown. Diamonds of the purest water are probably not colored (Beilby), but ordinary stones frequently assume more or less brilliant colors, in one remarkable case, observed by Sir William Crookes, a very fine green being developed. Pure silica is rapidly disintegrated under the rays, and for this reason should not be used to contain radium preparations permanently. Probably owing to the formation of nitric acid from the air, paper and fabrics in which radioactive preparations are wrapped are reduced to powder in the course of time, even when the radium is in sealed glass tubes."

In the chapter on the chemical character of the radioactive elements, p. 43, the first section is worth quoting in full.

"It has always been a matter for surprise, not to say scepticism, that it should be possible to investigate the chemical character of the evanescent products of radioactive changes, few of which are, or ever can be, studied in weighable or spectroscopically detectable quantities, and only one of which, radium, has been obtained pure in quantities sufficient for an ordinary atomic weight determination. Nevertheless the complete chemical character of the successive products has been steadily unravelled, and very simple and surprising general principles have been found to underlie the whole subject, which have notably enlarged our conceptions of elements in general.

"Uppermost in the mind of any one approaching the subject from the point of view of chemistry is the question as to how far such knowledge as can be acquired of the chemical properties of these short-lived radio-elements can be accepted literally, and used as a basis of classification of the radio-elements in the same way as the common elements have been classified in the Periodic Law, for example. It may be urged that although an infinitesimal quantity of ionium, to take one case, behaves, when mixed with a relatively enormous excess of thorium, like the element thorium itself in all respects, the chemical nature of ionium, if it were possible to prepare it free from thorium, might be quite different.

"The vague idea that infinitesimal amounts of radioactive matter may possess a chameleon-like nature, reflecting the properties of the substances with which they are mixed rather than their own, is not justified. The properties of the radio-elements, and with certain reservations with regard to adsorption, their behavior under any defined set of conditions, is at least as definite as those of the common elements. The statement that ionium cannot be separated from thorium, and many similar ones to be detailed in the sequel, is tantamount to saying that these radio-elements *can* be separated completely from all the other elements differing in chemical reactions from the one specified. Admittedly many have not, and, probably, never will be separated from the element they most resemble. But it is inconceivable that a radio-element when pure might possess chemical properties, allied most closely to those of, say, lanthanum, and be capable of being separated from lanthanum but not from, say, thorium out of a mixture containing both of these elements.

"In the first place, we must define more clearly the term "pure" in connection with the radio-element. First, there is the usual sense conveyed by the words "chemically pure," denoting an ideal rather than an attainable condition, be it with radio-elements or any other, a sense that may be rightly used, possibly, for radium preparations, such as those on which atomic weight estimations have been made. Secondly, there is the sense of "radioactively" pure, meaning that the substance is free from all other radioactive substances, though mixed with a possibly minute, but nevertheless overwhelming absolute preponderance of inactive matter. Lastly, there is another and very important sense, which may conveniently be termed "radio-chemically" pure, in which the radio-element, though mixed, possibly, with any quantity of inactive matter of totally different chemical nature to act as a vehicle for its transport, is yet free from substances chemically analogous to, or identical with itself. Such is frequently the condition of short-lived products repeatedly separated from their parents, and of those prepared as active deposits or by recoil and analogous methods.

"As the methods of detection and measurement are based wholly on radio-active phenomena, the presence of inactive matter does not necessarily interfere apart from secondary considerations involved in the absorption of the rays therein and the weakening of the activity on that account. A simple example will perhaps make this clearer. The properties of the radium emanation by which it is studied are not shown by any common gas, and it is a matter of indifference with what gas it may be mixed. By passing it through various absorbents, in each case in presence of sufficient of another gas, not adsorbed by the reagent, to serve as a vehicle to transport it, it is a simple matter to prove that the emanation is not absorbed by any known reagent, and that it is, therefore, a new member of the argon family of gases occupying the zero group of the Periodic Table. To thus characterize the chemistry of the radium emanation, a quantity millions of times less than would be visible as a bubble, or could be spectroscopically detected, or weighed on the micro-balance, did actually, as a matter of historical fact, suffice in 1902. Though, since then, enormously large quantities have been available, and it has been worked with in a state of approximate purity, nothing has been added in consequence to our knowledge of the chemical properties of this radio-element. The example is, of course, a negative one, as it were, because it concerns the absence of all chemical properties in this particular case, but it will perhaps serve as a step towards the understanding of how it is that the absolute minuteness of the quantities involved are not in themselves a barrier to the study of the chemistry of the radio-elements.

"In the next step, let us neglect any inactive matter present and concentrate our attention on the case of separating two chemically different radio-elements from one another. Such separations are effected as completely and simply as ordinary chemical analysis, always provided that, if such a mechanical operation as filtration is involved, there must always be sufficient quantity of matter to form a filterable precipitate. Under such conditions it is always found, for example, that polonium is completely precipitated in acid solution by sulphuretted hydrogen. Ionium is not so precipitated, but is by ammonia, while radium is precipitated by neither reagent, but is completely by sulphuric acid. So that, in presence of precipitable quantities of any of the members of these three analytical groups, the complete separation of these three radio-elements, chosen as examples, from one another is as easy with absolutely unweighable quantities as ordinary analysis. Going further, it is equally possible to show that polonium resembles bismuth more nearly than any other of the metals of Group II, but does not resemble it absolutely, and is in fact a new type of chemical element, though it has never yet been obtained in quantity sufficient to be worked with, apart from inactive material to serve as a vehicle for its transport. Similarly, radium resembles barium more nearly than it does any other of the metals of Group IV, but does not resemble it absolutely, and is, in fact, another new type of chemical element. It is fortunate, but not essential to this conclusion, that in this one case sufficient radium can be got to be weighable and visible by itself as a new chemical element, and almost as full information can be obtained for it as for the inactive elements.

"Lastly, ionium not only resembles thorium more nearly than any other member of Group III, but is found to be chemically identical in properties with it. Ionium, in presence of sufficient thorium to act as a vehicle, may in quantities, however infinitesimal, be completely and simply separated from any mixture containing any or every known element by the simple device of separating the thorium therefrom by known methods. Ionium is a new *radio*-element, but is not a new *chemical* type of element. This is a new conception. In every detail of its radioactive properties, the velocity of range of its α-rays, its period of change, the character of its product and of its parent, ionium is distinct and different from every other radio-element. But in its chemical nature it is not new. On account of its identity in this respect with the element thorium, every detail of its chemical nature is known "by proxy" as completely as though it were obtainable, like thorium, by the ton. Ionium cannot be obtained "radio-chemically pure" on account of its long period and the presence of thorium in all minerals from which it may be obtained. This is in contrast to many of the radio-elements, similar to ionium in not being chemically new, for they can usually be "grown", often *via* the gaseous emanation, in a condition of complete radio-chemical purity.

"Before pursuing this remarkable new line of development, let us push the question of chemical separations a little further to such operations as do not involve mechanical processes like filtration. Volatilization is such a case, already considered. The extraction of one liquid by another is one not yet considered. Extract a uranyl nitrate solution with ether, for example, and it will be found that the uranium can be extracted from the aqueous solution completely by a sufficient number of extractions, but this uranium, so extracted, gives only α-rays, whereas the β-rays of the original uranium come from a constituent, really a product, called uranium X, which remains in the aqueous layer completely. Now if such a thing as pure uranium nitrate or pure ether were practical, rather than ideal existences, then it would be easy to evaporate away the ether and obtain this β-ray product of uranium, which is quite non-volatile, in the pure state. But, unfortunately, however "pure" the materials used might be, the impurities so extracted would probably outweigh a millionfold the uranium X so obtained, of which, in a ton of uranium, it may be calculated these never can exist much more than one-hundredth of a milligram. A very insignificant part of such a quantity would make an X-ray screen in the dark visible to a thousand people in a large hall, even though it were mixed with millions of times its own weight of foreign impurities

"But if, relying on such *radioactive* evidence and neglecting such unavoidable impurities, we study the chemical nature of uranium X, again we reach a surprising conclusion. In chemical nature it also is *identical* with thorium and with nothing else. In radioactive nature it is unique, and as different from ionium, on the one hand, giving β- and not α-rays, being short-lived instead of long-lived, and so on, as it is from thorium on the other. But in chemical character it is not unique. Differing recognizably from every other known element, it yet resembles one with such undeviating fidelity that processes which are capable of removing from it every other known element always leave the concentration of the substance relatively to this one element unchanged."

The colloidal properties of solutions of the radio-elements are distinctly interesting, p. 64.

"Although, in sufficiently concentrated acid solution, it is probable that the radio-elements exist as positive ions, and their transport to the cathode during the passage of a current is analogous to ordinary electrolysis, with the differences already alluded to, the researches of Godlewski and Paneth have shown that frequently the radio-elements exist as colloidal rather than ionic solutions, and their electro-chemical transport is allied to electrophoresis rather than electrolysis.

"To take first a very striking and simple case. Polonium (radium F) may be separated from radium D and E by dialysis of a nearly neutral solution of the radio-lead nitrate through animal membranes or thin parchment paper. The lead, radium D and E, pass through as crystalloids, but the polonium remains behind in the cell in a pure condition.

"Further work showed that in neutral solution the velocity of dialysis of radium E, and in an ammoniacal solution of thorium B, may be much reduced. In general, according to the degree of acidity, both hydrosols and ions of the same radio-element may exist together in the solution. The change from crystalloid to colloid is accompanied by a change of sign of the electric charge, and the colloid particles migrate in an electric field to the anode instead of to the cathode. If a parchment membrane is inserted in such a solution containing both forms, the cathode deposition is not prevented but only hindered, whereas the anodic deposition is completely suppressed.

"Much work has also been done on the radium active deposit formed in pure water containing dissolved emanation. Under these circumstances all the products, radium A, B and C are present as hydrosols, but the A member is deposited on the anode, the B member on the cathode, and the C member on both electrodes. In other words, the A member exists as a negative hydrosol, the B member as a positive hydrosol, and the C member as a mixture of both varieties. It has been suggested that the radium A starts with a negative charge as a negative hydrosol. In its α-ray change the radium B atom produced is expelled by recoil from the colloidal aggregate and forms a negative hydrosol, but in the β-ray change of radium B the radium C atom is not expelled. According as the colloidal aggregate contains excess of radium B atoms or radium C atoms, it is negative or positive, and migrates accordingly. As time goes on, and the majority of the B atoms are transformed into C atoms, the sign of the charge on the colloidal aggregate changes from negative to positive.

"On these solutions many of the consequences of the general theory of colloids, such as arsenious sulphide and platinsol, neutralize the positive hydrosols present and reverse their sign, so that in their presence cathode deposition is prevented, and all the products make their appearance at the anode. Positive colloids like ferric oxide act exactly oppositely.

"Some practical suggestions have been made for employing these facts in the separation of the radio-elements. If the added colloid is precipitated by addition of a suitable precipitant, such as aluminum sulphate, all the radioactive products are precipitated with it. It is easy in this way to concentrate a very powerful radioactivity upon a few milligrams of a precipitated hydrosol of gold or platinum. Again, positive hydrosols are precipitated in the pores of filter paper, whereas negative hydrosols pass through with the aqueous solution. According as aluminum sulphate or hydrochloric acid, on the one hand, or citric acid on the other, is added to the colloidal solution, the amount of positive or negative hydrosol, respectively, is increased, and the amount retained by filter paper may be increased or diminished. As very pure filter paper may be used and burnt after it has adsorbed the radio-element, a method of concentrating the latter is suggested. It has been found possible to separate uranium X from a uranyl nitrate solution, at a dilution of 10 g per liter, by simple filtration and ignition of the filter paper."

The author considers, p. 141, that recent papers "seem to establish definitely the variation of the atomic weight of lead and are favorable to the view that the isotope derived from thorium has an atomic weight some two units higher than that derived from uranium. The atomic weight of ordinary lead accords with the view that it may be a mixture of the two isotopes in very similar proportions."

Wilder D. Bancroft

Metallurgy. *By Henry Wysor. Second Edition. 23 × 16 cm; pp. iii + 391. Easton: The Chemical Publishing Co., 1914. Price: $3.00.*—The title page tells us that this is "a condensed treatise for the use of college students and any desiring a general knowledge of the subject." The preface states that the primary object of the book is to supplement a course of lectures given to engineering students at Lafayette, and that it is also designed as a textbook for other colleges. The author then goes on: "a book may be far from profound and rudimentary to a fault, but nevertheless, successful if it presents fundamental subjects in a style that arouses interest and therefore commands attention.... In elementary courses the text should be used from cover to cover and the expediency of omitting certain chapters or articles should not be felt from either the academic or the technical point of view.... No criticism is made of compendiums or of texts in which subjects are dealt with exhaustively. These have their indispensable places in special courses and as works of reference."

The book is hence not designed to be a reference book or even a textbook for advanced students in metallurgy, but merely as an elementary textbook for engineering students. The marks, not aimed at by the author, have not been hit, so he has at least been successful in not doing what he set out not to do.

It is a question in the reviewer's mind if the author has more than nicked the edge of the bullseye, he did aim at that of writing an interesting elementary textbook. He mentions that impurities in metals affect the crystalline structure as shown by the microscope. A couple of photomicrographs to illustrate the point would increase the interest. Speaking of magnesite under "Basic Materials," the author says, "This substance is highly refractory and it is the most satisfactory material known for some purposes." This is condensation with a vengeance, as the only further explanation given is that it is used in "basic furnaces."

On the other hand, there is a full page illustration and another page of description of the mechanism of a certain recorder for pyrometric use, which space, it seems to the reviewer, might have been more entertainingly, at least, used in giving some definite information as to just what metallurgical processes are pyrometrically controlled in practice, and as to which types of instrument are suited to the various uses.

Under "Crucible Steel—the melting furnace" we find the following paragraph: "The furnaces used for melting steel in crucibles are often of very simple construction, consisting of a melting hole in which the crucibles are placed and in which coke is burned, and a tall chimney for creating a draft. The melting hole is covered with a fireclay lid during the operation. Gas-fired furnaces employing regenerators are also in use." Even if it is not desired to give the student any clearer mental image than he can form from this, why not also mention the use of fuel oil?

Five pages cover the subject of electric steel. Copper is said to "diffuse" readily with most of the common metals, by which the author means that it alloys readily. Bronze is said to be prepared by melting the copper and tin separately, pouring them together and stirring the mixture to give uniformity. This may possibly be the practice in one foundry out of five hundred.

The bulk of the book, however, seems to be better than the particular portions in which the reviewer has most interest, and its study would give a student a pretty good idea of the fundamentals of ferrous and non-ferrous metallurgy, although a sketchy one. If metallurgy were a high school subject, or taught as a cultural study for general information in an A.B. course, this would be a good textbook. Nevertheless, the reviewer does not believe it is fair to an engineering student to make him buy a textbook that is of no real value in his library after the examination in the course is passed. There are but forty-three references given to the literature in this book. Whatever be an author's ideas on the proper degree of detail for a textbook, there can be no excuse for his failure to tell the student where more specific information can be found.

H. W. Gillett

Physical Chemistry, its Bearing on Biology and Medicine. *By James C. Philip. Second Edition. 13 × 18 cm; pp. v + 326. New York: Longmans, Green & Co., 1913. Price: $2.10 net.*—The first edition was reviewed four years ago (15, 416). The chief changes in this edition are the addition of a chapter on electromotive force and the inclusion of Czapek's work on the surface tension of the cell membrane, p. 85*a*. There is an interesting discussion on diffusion of gases, p. 18, in connection with transpiration by leaves.

"The gas exchange between the atmosphere and the assimilating cells of a leaf is at one stage simply a process of diffusion through the stomata alone, for Blackman has shown that if these are blocked up no appreciable diffusion of carbon dioxide into the leaf takes place. This being so, the diffusion of carbon dioxide through the stomata must be relatively rapid; indeed, in the case of a certain leaf examined by Brown and Escombe the stomatic openings were found to absorb per sq. cm. of their area as much as 7.77 cu. cm of carbon dioxide per hour, a figure which is about fifty times as great as the absorption per unit area of a freely exposed solution of caustic alkali. The question whether this was possible led Brown and Escombe to study the free diffusion of carbon dioxide through small apertures into cavities with a comparatively large absorbing surface....

"When a diffusion tube, such as that already described, is covered with a diaphragm containing many small apertures, the diffusion flow is checked to a remarkably small extent. In Brown and Escombe's experiments diaphragms were employed containing 100 perforations (0.38 mm in diameter) per sq. cm of diaphragm surface. Although the area of the apertures was in this case only about one-ninth of the total area of the diaphragm, the amount of diffusion through the perforations was as great as when there was no diaphragm at all. The obstruction, therefore, which is offered to a diffusion flow by a multi-perforate diaphragm may be nil, and is certainly very small. This striking result is to be referred to the intensification of the diffusive flow which, as shown by the figures already quoted, accompanies the decrease of aperture. Provided that the perforations in a multi-perforate septum are not too close, each aperture acts independently of the other according to the diameter law."

"On p. 24 we read that 'the power of water to dissolve oxygen and carbon dioxide is an all-important fact in connection with aquatic plants. The possibility of gaseous interchange between the air and the cells of the submerged plant depends in the first place on the diffusion of oxygen and carbon dioxide through the medium surrounding the plant, for if the medium is freed and kept free from air the plant dies. In general the epidermis of the submerged leaf is not cuticularised, and is unprovided with stomata. It is, however, impregnated with water, and the exchange of oxygen and carbon dioxide between the surrounding medium and the interior of the leaf consists in a diffusion across this water-logged layer. It has been shown that this diffusion across the walls of submerged plants is subject to the same laws as regulate the passage of gases across a film of water. The gaseous interchange of aquatic plants must, therefore, be a comparatively slow process, but in the characteristic development of intercellular spaces there is a mechanism which deals with this difficulty. By this means the oxygen and carbon dioxide liberated in the processes of assimilation and respiration respectively are kept available for future use. Thus it is that those parts of aquatic plants which lie in the mud at the bottom are supplied with oxygen without depending on the slow diffusion of this gas through the surrounding water.

"Another point of interest in connection with the gas exchange of aquatic plants is the fact that marine algae flourish more luxuriantly in arctic than in tropical waters. This is due to the greater solubility of carbon dioxide in water at low temperatures and the resulting increase in the facilities for gaseous interchange."

On p. 37 the author points out that "an interesting case of a semipermeable membrane in the vegetable world was described lately by Brown. He has shown that certain barley grains (*Hordeum vulgare* var. *coerulescens*) have a covering which exhibits selective action when placed in aqueous solutions of sulphuric acid and various other substances; water is absorbed by the grains while the dissolved substance cannot gain an entrance. That sulphuric acid cannot penetrate the covering of the grain is shown by the fact that a blue pigment which is present in the aleurone cells and which is turned red by acids, remains unaffected when undamaged barley grains are soaked in sulphuric acid. On the other hand, any grain, the covering of which is imperfect or has been purposely perforated, at once begins to exhibit the color change denoting the access of acid to the interior. Grains which have been exposed to the action of boiling water for thirty minutes, and which, after this treatment, have lost all power of germinating, behave in the same way as untreated grains, so that the semi-permeable character of the covering does not depend on the activity of living protoplasm."

Wilder D. Bancroft

Chimie physique élémentaire. *By E. Ariès. Vol. I. 19 × 13 cm; pp. v + 212. Paris: Herman et Fils, 1914. Price, 4 francs.*—In the preface the author says: "Everybody recognizes that credit for the unexpected development of chemistry in the last forty years belongs to J. Willard Gibbs. In several famous memoirs this remarkable genius based chemical statics on the principles of thermodynamics. People have admired his works and have quoted him as authority but very often on hearsay and without having really appreciated what he has done. As a matter of fact the work of Gibbs has secured, at any rate in France, very few disciples eager to defend it against attacks which might tend to decrease its importance."

The subject is treated under the general headings: introduction; thermo-elastic properties of substances; chemical energy and chemical equilibrium; four important inequalities; laws of chemical equilibrium and conditions for stability; the laws of Le Chatelier and of van't Hoff; the laws of mass action; the formula of Clapeyron and the phase rule; osmosis and semipermeable membranes. The title of the book is somewhat misleading. The book is not an elementary physical chemistry at all; but rather an elementary chemical thermodynamics. No data are given. The author is very much opposed to the views of Duhem and misses no opportunity of saying so. *Wilder D. Bancroft*

Handbuch der Mineralchemie. *By C. Doelter. Vol. II, Part VII. 25 × 18 cm; pp. 160. Dresden: Theodor Steinkopff, 1915. Price: 6.50 marks.*—The most interesting pages in this number are those on ultramarine. While ultramarine consists normally of alumina, silica, sodium, and sulphur, the silicic acid can be replaced by titanic acid, the alumina by boric acid, and the sodium by silver, which leaves sulphur as the one essential constituent. In accordance with this we have the hypothesis that the color is due to colloidal sulphur, which at first sight seems very plausible. On the other hand, the color changes when the amount of sulphur is kept constant while the sodium concentration varies. Since it has not been shown that the color of colloidal sulphur changes with changing sodium content, there is always the possibility that the color is due to a colloidal sulphide or polysulphide. What one ought to do is to prepare colored colloidal sulphur or sulphides in aqueous solution analogous to the ultramarines and then one would know something definite about the subject. We seem to be in somewhat the same position towards the ultramarines that we should be toward the photochlorides if the variously colored silvers were unknown. Whatever hypothesis is adopted it seems probable that the hypothetical aluminum silicates are primarily peptonizing media. *Wilder D. Bancroft*

THE COAGULATION OF ALBUMIN BY ELECTROLYTES

BY WILDER D. BANCROFT

The recent work on albumin has been to the effect that definite compounds are formed with acids and bases.[1] In so far as albumin is present as a second phase, conclusions based on conductivity measurements are subject to serious error, and conclusions based on electrometric measurements may be in error. In so far as albumin is present as a second phase, adsorption phenomena must play some part. It seems desirable therefore to see to what extent the coagulation of albumin by electrolytes can be accounted for without postulating the formation of definite compounds. It will then be possible to see to what extent one must postulate the existence of compounds. In other words, we will give up, for the time being, the dogma that albumin is an amphoteric electrolyte.

We start with the assumption that a slightly acid or slightly alkaline solution of albumin is a two-phase colloidal system which is least stable when electrically neutral. When the albumin adsorbs the anion relatively more than the cation, as in alkaline solutions, it becomes charged negatively and consequently moves to the anode under electrical stress. When it adsorbs the cation more than the anion, as in acid solutions, it becomes charged positively and consequently moves to the cathode under electrical stress. If we take a negatively charged albumin, in neutral or slightly alkaline solution, and add a salt solution, the effect of an adsorption of the anion will simply be to increase the negative charge and consequently to make the colloidal solution more stable. The more strongly adsorbed the anion is, the less readily will the albumin be precipitated by cations. On the other hand, the adsorption of a cation decreases the electrical charge and con-

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[1] Pauli and Hirschfeld: Biochem. Zeit., 62, 245 (1914).

sequently makes the albumin less stable. The more readily adsorbed the cation, the lower will be the concentration at which it will cause precipitation. In any given case we shall therefore be able to arrange the cations and the anions in series, depending on the way in which they precipitate albumin. It must be remembered that in many experiments with white of egg, the globulin has not been removed,[1] in which case the data refer to the globulin rather than to the albumin. In Table I are some data by Hofmeister[2] for a neutral or slightly alkaline solution. The solution contained 0.2 g albumin per 10 cc; the salt concentrations are given in gram equivalents per liter; the temperature was 30°–40°; the numbers in parenthesis give the valences of the anions:

TABLE I

Concentration in gram equivalents per liter

		K	Na	NH_4
Tartrate	(2)	1.51	1.56	2.72
Sulphate	(2)	—	1.60	2.03
Phosphate	(2)	1.61	1.65	2.51
Citrate	(3)	1.67	1.68	2.71
Acetate	(1)	1.67	1.69	—
Chromate	(2)	2.67	2.61	—
Chloride	(1)	3.53	3.63	—
Nitrate	(1)	—	5.42	—
Chlorate	(1)	—	5.52	—
Iodide	(1)	No precipitate in saturated solutions		
Sulphocyanate	(1)	" " " " "		

The ammonium salts precipitate at distinctly higher concentrations than the sodium and potassium salts and therefore, by definition, are adsorbed less than these. There is not much difference between the sodium and potassium salts, and it is probably wiser to attribute what little difference there is to experimental error, at least temporarily. This is the more advisable because Pauli[3] considers that potassium

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[1] Pauli: Pflüger's Archiv., 78, 315 (1899).

[2] Pflüger's Archiv., 24, 247 (1887).

[3] Hofmeister's Beiträge zur chem. Physiol., 3, 225 (1903).

salts are less effective than sodium salts, whereas Hofmeister's data point to their being somewhat more effective. Since Hofmeister found that lithium sulphate precipitated albumin at an equivalent concentration of 1.54, we conclude that lithium salts are adsorbed slightly more than sodium and potassium salts. Magnesium sulphate precipitates at 2.65, which seems to imply that magnesium salts are adsorbed less than ammonium salts. Whether we draw this conclusion or not depends on whether we take the equivalent concentration or the ion concentration as the standard. For equivalent concentrations of sodium sulphate and magnesium sulphate the precipitating concentrations are 1.60 and 2.65. The gram molecular concentrations of sodium and magnesium ions are 1.60 and 1.35, respectively, assuming complete dissociation. On this basis magnesium ions precipitate at a lower concentration than sodium ions. If we do not postulate complete dissociation, the effect is even more striking because magnesium sulphate is dissociated less than sodium sulphate. It seems to me that the ion concentration is the important one because it is the ion which is adsorbed. Consequently I deduce that the order of precipitation and of adsorption is

$$Mg > Li > Na, K > NH_4$$

when referred to ion concentrations, magnesium ions being adsorbed the most and ammonium ions the least. This point has been overlooked entirely so far as I know, all people putting the precipitating power of magnesium salts below that of ammonium salts. The present way of looking at the matter seems to be more sound theoretically, and it has the advantage of bringing the magnesium salts more nearly in line with the salts of the other bivalent metals.

If we deduce the order of adsorption of the anions from the data in Table I we get: sulphocyanate, iodide > chlorate > nitrate > chloride > chromate > acetate, citrate > phosphate > sulphate > tartrate, the sulphocyanate ion being adsorbed the most and the tartrate ion the least. Pauli[1] finds that the

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[1] Hofmeister's Beiträge zur chem. Physiol., 3, 243 (1903).

tartrate comes in between the acetate and citrate. If so, Hofmeister's determinations with the sodium and potassium tartrates must be in error. Freundlich[1] considers that the concentrations should be given in gram molecular weights per liter instead of gram equivalents in which case one gets Table II:

TABLE II

Concentration in gram molecules per liter

	K	Na	NH_4
Citrate	0.56	0.56	0.90
Tartrate	0.75	0.78	0.91
Sulphate	—	0.80	1.01
Phosphate	0.80	0.82	1.25
Chromate	1.33	1.30	—
Acetate	1.67	1.69	—
Chloride	3.53	3.63	—
Nitrate	—	5.42	—
Chlorate	—	5.52	—
Iodide	No precipitation in saturated solutions		
Sulphocyanate	" " " " "		

On the basis of these data the order is sulphocyanate, iodide > chlorate > nitrate > chloride > acetate > chromate > phosphate > sulphate > tartrate > citrate, the sulphocyanate ion being adsorbed the most and the citrate ion the least. Since we are agreed that the ion concentration is what counts, this seems at first the more rational way of arranging the data for a study of the anions. It has the further advantage that ammonium tartrate fits in as it should, whereas it was abnormal in Table I. On the other hand there is the difficulty when comparing chromate with acetate for instance, that the concentration of sodium or potassium as ion is double in the gram molecular solution of chromate what it is in the acetate solution. Since the albumin is negatively charged, it is precipitated by cations and consequently the error introduced in Table II by doubling the concentration of the cation, may be more serious than the error introduced in Table I

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[1] Kapillarchemie, 425 (1909).

by an inaccurate formulation of the anion concentration. There was a similar error for the cations when comparing $MgSO_4$ with $Na_2SO_4/2$, but the error due to the change in concentration of the sulphate is relatively small, because this anion is not adsorbed to any great extent. With the anions the case is different and it seems to me that the evidence is not sufficient to enable us to decide conclusively between Tables I and II. It will therefore be safer for the present to consider only those anions which come in the same order in both tables. The order of these anions is: sulphocyanate, iodide > chlorate > nitrate > chloride > acetate > phosphate > sulphate > tartrate, the sulphocyanate ion being adsorbed the most and the tartrate ion the least.

These deductions as to the order of adsorption of the cations and anions are made specifically to fit the facts and are therefore worthless unless confirmed independently. We can get the needed independent confirmation by considering the behavior of albumin in slightly acid solution. Here the more strongly adsorbed cation will increase the electrical charge and will consequently make the albumin more stable, while the more strongly adsorbed anion will cut down the electrical charge the most and will precipitate the albumin the most readily.

With an acid concentration of 0.01–0.2 *N* HCl Pauli[1] found that the order of anions and of cations reversed, the order for the anions becoming: sulphocyanate > iodide > bromide > nitrate > chloride > acetate. This is as it should be, and the same relation holds with a stronger acid, 0.03 *N* HCl. The behavior of the cations becomes abnormal, however, in the 0.03 *N* HCl solution, the ammonium salts precipitating at a higher concentration than the corresponding sodium salts, just as they did in the slightly alkaline solutions. I do not pretend to account for this unexpected shift. The most that can be done at present is to formulate the general principles. A careful experimental study of each case will be necessary

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[1] Hofmeister's Beiträge zur chem. Physiol., 5, 27 (1904).

before one can be certain what is the cause of special alleged discrepancies.

Copper and zinc salts precipitate negatively charged albumin even at concentrations of $M/1000$ or less, from which we conclude that these cations are adsorbed very markedly. From what we have seen in regard to sodium and potassium salts, we should expect that a higher concentration of zinc iodide would be necessary to coagulate albumin than if one added zinc sulphate. The experiment has not been tried in just this form so far as I know; but Pauli[1] found that addition of sodium iodide or sulphocyanate cut down the precipitation when a very dilute zinc sulphate (0.005 N) was used. The order of anions was chloride > nitrate > bromide > iodide > sulphocyanate, the most precipitate occurring with the chloride and the least with the sulphocyanate. Curiously enough, it was found that iodide kept the solution clear when 0.02 N $ZnSO_4$ was used, while sulphocyanate caused a heavy precipitate. With 0.1 N $ZnSO_4$ the addition of sodium salts caused a precipitate decreasing in the order: sulphocyanate > iodide > nitrate > chloride > sulphate. This is what one would expect if one had a positively charged albumin instead of a negatively charged one. Unfortunately this point was not thought of by Pauli. I am inclined to believe that this reversal of the anions is connected with the fact that zinc sulphate does not precipitate albumin at all when present in normal to double-normal concentrations.

If we start with a negatively charged albumin and add acid, we neutralize the negative charge and precipitate the albumin. On adding more acid we get the albumin charged positively and peptonized. There is no reason to suppose that this action is confined to the hydrogen cation, and I believe that albumin which is not precipitated by a gram molecular solution of zinc sulphate will be found to be charged positively. In that case the order of the anions would be reversed, as Pauli found. With lower concentrations of zinc

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[1] Hofmeister's Beiträge zur chem. Physiol., 6, 233 (1905).

sulphate we should expect the reversal to occur first with the sulphocyanate which is exactly what happened. Szilard[1] finds that thorium and uranyl nitrates peptonize albumin, which is what they should do in case these cations are adsorbed very strongly.

If we start with an acidified solution the addition of zinc sulphate or copper sulphate should have very little effect. Werigo[2] reports that copper sulphate does not precipitate albumin in presence of hydrochloric acid. Unpublished experiments by Mr. H. I. Cole showed that 0.2 cc $M/10$ $ZnSO_4$ produced a distinct cloudiness when added at 30°–40° to 10 cc of a slightly alkaline albumin solution (containing globulin). When the solution was acidified it was necessary to add more than 10 cc $M/10$ $ZnSO_4$ to produce the same cloudiness. Mr. Cole also confirmed Pauli's results that addition of potassium iodide to a slightly alkaline solution of albumin cut down the precipitation by zinc sulphate. He also found that in acidified solutions potassium iodide precipitated at much lower concentrations than sodium chloride.

Pauli's results with calcium, strontium, and barium salts[3] confirm the hypothesis put forward to account for the effect produced by zinc sulphate. He found that with these salts the order of the anion reverses, and becomes: sulphocyanate > iodide > bromide > nitrate > chloride > acetate, the sulphocyanate causing the most precipitation and the acetate the least. If we assume that the calcium ion is adsorbed sufficiently to make the albumin positively charged,[4] the behavior of the anions becomes normal. As a matter of fact Pauli observed that the solutions became slightly acid, indicating the adsorption of lime.

We have still to consider the reversibility of the precipitation. In neutral or slightly alkaline solution the precipi-

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[1] Jour. chim. phys., 5, 495 (1907).

[2] Pflüger's Archiv., 48, 132 (1891); cf. Hardy: Proc. Roy. Soc., 66, 110 (1900).

[3] Hofmeister's Beiträge zur chem. Physiol., 5, 27 (1901).

[4] Billitzer states that the albumin does move to the cathode, Zeit. phys. Chem., 51, 155 (1905).

tation by the salts of the alkalies is reversible; the precipitation by the salts of the alkaline earths is reversible if the precipitate is washed at once with water but is irreversible if the precipitate is allowed to stand for a short time in contact with the solution; the precipitation by dilute solutions of salts of the heavy metals is irreversible. In acidified solutions the precipitation by sulphocyanates and iodides is irreversible, while the precipitation by actetates and sulphates is reversible if the acid concentration is very low; for concentrations of 0.03 N HCl the precipitation is irreversible.[1]

The precipitation of a colloid is always reversible in case no coalescence or agglomeration takes place, because one of the standard methods of preparing a colloidal solution is to wash out the excess of the precipitating agent. Now the more strongly the precipitating agent is adsorbed, the harder it is to wash it out and consequently the more nearly irreversible the precipitation is. We could use this qualitatively to account for the difference between precipitation by potassium sulphate and zinc sulphate; but we know that there must be agglomeration or coalescence when albumin is precipitated by lime salts because the precipitate can be peptonized when first formed and cannot be later. Even if we got round this, as we undoubtedly could, it is difficult to see how to apply this explanation satisfactorily to the case of precipitation in acidified solution. It seems more probable that the physical properties of the precipitates vary under different conditions of precipitation and that the irreversible precipitates are more gelatinous than the others. We know that the so-called Péan de St. Gilles ferric oxide is precipitated by hydrochloric acid or nitric acid in a sandy form which is readily peptonized by water and is precipitated by sulphuric acid in a more gelatinous form which is not readily peptonized by water.[2] There are no data bearing directly on this point; but Pauli[3]

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[1] Pauli: Pflüger's Archiv., 5, 27 (1904); Freundlich: Kapillarchemie, 425 (1909).

[2] Bancroft: Jour. Phys. Chem., 19, 236 (1915).

[3] Pauli and Handowsky: Biochem. Zeit., 18, 340 (1909); Pauli and Falck: Ibid., 47, 269 (1912).

has suggested in several papers that salts may change the hydration of suspended albumin.

The only other point to be considered is the behavior of so-called electrolyte-free serum albumin.[1] This shows no perceptible diffusion under electrical stress and is therefore apparently electrically neutral without being instable. Addition of sodium, barium, or calcium chloride does not make the albumin electrically positive or electrically negative. It is not precipitated by salts of zinc, copper, mercury, iron or lead. A mixture of $CaCl_2$ + NaSCN causes no precipitation, though precipitation takes place if the albumin solution is acidified before the mixture is added. The only way that I see to account for the stability of the electrolyte-free albumin is to postulate that in the absence of salts the peptonizing action of water is enough to keep the albumin in colloidal solution.[2] To this extent the electrolyte-free albumin behaves like gelatine. This is not impossible, because Denaeyer[3] claims that when albumin is heated in water under a pressure of one atmosphere it becomes soluble again and reacts uncoagulated albumin. Granted that the electrolyte-free albumin is stable and electrically neutral, as Pauli claims, there is no reason why it should be precipitated by salts of zinc, copper, lead, mercury, iron, or lead because these salts would give it a positive charge and make it even more stable. I do no know why the chlorides of sodium, barium or calcium do not give it an electrical charge of one sign or the other, nor why the mixture of calcium chloride and sodium sulphocyanate does not precipitate it. The obvious assumption to make is that in the course of purification the albumin had been so changed by hydration, dehydration or otherwise, that it did not adsorb sodium, calcium, barium, chloride, or sulphocyanate ions to an appreciable extent; but does so after contact with an acid. Colloidal silver bromide has ap-

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[1] Pauli: Hofmeister's Beiträge zur chem. Physiol., 7, 531 (1906).

[2] It is possible, however, that the electrolyte-free albumin is the external phase in the solution. If so, this would account for some of its peculiarities.

[3] Jour Chem. Soc., 60, 1269 (1891).

parently practically no adsorbing power for potassium ions or nitrate ions whereas it does adsorb silver ions or bromide ions. All this is purely speculative and not worth much until there is some experimental evidence forthcoming. It does seem to me, however, that it will be an easier task to account for the properties of electrolyte-free albumin on the basis of varying adsorption than on the basis of an amphoteric electrolyte.

It is usually considered that albumin constitutes a special case[1] and that it differs fundamentally from colloidal gold, let us say, or colloidal ferric oxide. We are told that positively charged colloids are precipitated by anions and that the nature of the cations is immaterial; we are also told that the cation is the all-important factor in the case of a negatively charged colloid, the nature of the anion being immaterial. This seems to be hopelessly wrong. My whole argument will apply to any colloidal solution where the suspended phase becomes instable when electrically neutral; and consequently the nature both of cation and of anion is important. The error has come about very naturally because it was very difficult to prepare a positive gold sol for instance or a negative ferric oxide sol. With a positively charged sol the cations which are less readily adsorbed than the ion causing the charge—usually hydrogen—naturally have very little effect.[2] With a negatively charged sol the anions, which are less readily adsorbed than the ion causing the charge—usually hydroxyl, except perhaps in the case of the metals—naturally have very little effect.[2] Once the erroneous belief had taken root, it grew, because other people either did not test large numbers of cations and anions or ignored the evidence in case they did. I shall discuss this matter more in detail in another paper.

The general conclusions of this paper are as follows:

1. So far as the data go, the coagulation of albumin by salts can be accounted for more satisfactorily on the assumption that we are dealing primarily with adsorption rather

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[1] Freundlich: Kapillarchemie, 434 (1909).

[2] In extreme cases the adsorption may be so slight as to be negligible.

than on the assumption that we are dealing primarily with an amphoteric electrolyte.

2. Slightly acid or slightly alkaline solutions of albumin are least stable when the dispersed phase is electrically neutral.

3. Since the sign of the electrical charge depends on the preferential adsorption of cation or anion, the nature of both anions and cations is important.

4. When albumin is charged positively, the more strongly adsorbed anion will be most effective in causing precipitation and the most strongly adsorbed cation in preventing precipitation.

5. When albumin is charged negatively, the most strongly adsorbed cation will be most effective in causing precipitation and the most strongly adsorbed anion in preventing precipitation.

6. If one adds to negatively charged albumin a salt consisting of a readily adsorbed cation and a slightly adsorbed anion, we shall get precipitation at low concentrations and no precipitation at higher concentration; but in this latter case the albumin will be charged positively.

7. While the reversibility of precipitation depends in part on the ease with which the precipitating agent can be washed out, it seems probable in the case of albumin that the physical properties of the precipitate are important as determining coalescence and agglomeration. There are no data on this point.

8. In the case of the electrolyte-free albumin one must apparently assume that the stability of the solution is due to the peptonizating action of water in the absence of electrolytes.

9. The coagulation of albumin by electrolytes is a typical and general case, whereas the coagulations of gold sols and ferric oxide sols are special cases.

Cornell University

ORGANIC LIQUIDS AND ALKALINE SOLUTIONS

BY T. J. TWOMEY

Wilson[1] has shown that drops of chloroform, carbon bisulphide, or other liquids denser than water tend to become spherical in contact with water or an acidified solution, but flatten considerably when the solution is made alkaline. At the suggestion of Professor Bancroft I have repeated some of these experiments and have done some others to make sure that the phenomenon was not due to impurities. The room temperature was about 21° C. All experiments were done in glass beakers, carefully cleaned.

Into 100 cc water 0.5 cc chloroform was dropped from a 5 cc pipette. The drops sank to the bottom and a round bubble of air appeared in the middle of the upper surface of each. On shaking continuously for two or three minutes, the air bubble was dislodged and rose to the surface of the water, carrying with it a little chloroform. Some of this chloroform remained on top of the water and the rest sank to the bottom. The chloroform that remained on the surface evaporated in the course of time. After the first air bubble had been removed from the chloroform at the bottom of the beaker, another formed. The chloroform must take up air dissolved in the water.

Into 100 cc approximately normal KOH solution 0.5 cc chloroform was dropped from a 5 cc pipette. The chloroform did not seem to spread out on the surface before sinking so much as it did with water. The globules sank to the bottom and flattened out; they were distinctly not very mobile and seemed to stick to the bottom of the vessel. When the chloroform was dropped into the water, it broke up into a number of drops which did not agglomerate so easily as in the water solution. In fact quite a little shaking was necessary in order to make them coalesce. At first no air bubbles could be detected, but after standing for five minutes a very small bubble appeared on the chloroform. Sulphuric acid was then added until the solution became acid. The flattened drop of chloro-

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[1] Jour. Chem. Soc. 1, 174 (1848); Bancroft: Jour. Phys. Chem. 19, 276 (1915).

form at once assumed the shape of a round ball and became mobile. An air bubble also appeared in the center of the drop.

Into 100 cc approximately normal sulphuric acid solution 0.5 cc chloroform was dropped as before. The chloroform spread all over the surface and then sank through the solution in small drops, forming round globules with air bubbles clinging to each. It was hard to get rid of the bubbles on the chloroform drops by shaking; as soon as one was driven off, another bubble appeared exactly in the center of the drop. When the bubbles were dislodged from the drops they rose to the surface carrying with them some chloroform, a part of which remained on the surface until it evaporated, while the rest sank back to the bottom of the solution. The globules were very mobile and coalesced readily. Caustic potash was added to the solution, making it alkaline. The chloroform globule flattened immediately and the air bubble in the center disappeared. In still another experiment an acid solution was made alkaline, then acid, and then alkaline again. The result confirmed Wilson's experiments, for the drop of chloroform was always flat in alkaline solution and round in the acid solution. There is scarcely any difference to be noted between the shape of the drop in acid solution and in pure water. The same results were obtained when NaOH and HCl were substituted for KOH and H_2SO_4.

In one experiment in a nitric acid solution the temperature was raised to about 40°. Bubbles seemed to shoot from all parts of the solution to the chloroform drop. When they had formed a large bubble in the center of the drop of chloroform, the air bubble rose to the surface of the solution as in the other cases.

Since it is possible theoretically that the alkali may have decomposed the chloroform somewhat and thus have caused the phenomena,[1] some experiments were made with carbon tetrachloride. The results were substantially the same as with the chloroform, the only difference being that the carbon tetrachloride seemed to sink more readily in all the solutions than did the chloroform. Owing to the higher density of

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[1] Cf. Swan: Phil. Mag., (3) 33, 36 (1848).

carbon tetrachloride this was to be expected. Since traces of grease might give rise to a soap in presence of alkali, some experiments were made adding potassium cyanide solution to dissolve the grease. In the first experiment 0.5 cc CCl_4 was added to 50 cc *N* NaOH diluted to 125 cc. The drop flattened and ceased to be very mobile. There was then added 50 cc KCN solution (15 g KCN in 300 cc water). The appearance of the drop remained the same even after vigorous shaking and stirring. In another experiment 0.5 cc CCl_4 was added to 100 cc of the KCN solution. The drops of chloroform flattened perceptibly, but had small air bubbles clinging to them. On adding 50 cc *N* NaOH solution the drops flattened much more and the air bubbles became detached. The slight flattening when the potassium cyanide solution was added was probably due to the hydrolysis of the cyanide. When the solution was made acid (under the hood) the drops of chloroform became round again and each one had an air bubble clinging to it. On making the solution alkaline again, the globules of chloroform flattened once more.

There was a possibility that this experiment was not conclusive. One does not know exactly what potassium cyanide does to grease in presence of carbon tetrachloride. For this reason some experiments were made with carefully purified benzene. It was purified from thiophene and the subsequent distillations were performed in glass which had been cleaned carefully with a chromic acid cleaning mixture. In order to make the experiments comparable with the others, a small beaker full of water was inverted in a larger beaker of water and then the benzene was introduced into the smaller beaker by means of a curved pipette. There was therefore no surface between benzene and air to be considered. When the water was made alkaline, the benzene drop flattened, becoming spherical again when the solution was acidified. The flattening of the organic liquids is evidently due to an adsorption of alkali and is not due to a partial decomposition of the organic liquid nor to the formation of soap by the action of the caustic alkali on traces of grease.

Cornell University

NEUTRALIZATION OF ADSORBED IONS

BY WILDER D. BANCROFT

Any substance may be brought into a state of colloidal solution provided we make the particles of that phase so small that the Brownian movements will keep the particles suspended, and provided we prevent agglomeration of the particles by a suitable surface film.[1] Coalescence may be prevented by a non-electrical film, by an electrical film (electrical charge), or by any combination of the two. An electrical suspension is due to the preferential adsorptiom of some ion. So long as the particles are all charged positively or all negatively they will repel each other and will not coalesce. Neutralization of the charge causes precipitation through agglomeration.

If we have a suspension which is stabilized by the preferential adsorption of hydrogen ion from hydrochloric acid solution, we have in the solution free hydrogen ions, free chlorine ions, and the adsorbed hydrogen ions which make the suspension behave like a cation though with a different migration velocity from that of hydrogen. If the suspension adsorbs an anion in an amount equivalent to the hydrogen ion adsorbed, the suspended particles will be electrically neutral. We get this by adding an electrolyte, preferably with a readily adsorbed anion. Since we are dealing with selective adsorption, the concentration in the solution of the added anion necessary to cause an adsorption equivalent to the hydrogen adsorption will vary with each anion. Since we are dealing with preferential adsorption, the nature of the cation must have an effect. To put the matter more generally, the amount of an electrolyte necessary to precipitate any given suspension will vary with the nature of the cation, the anion, and the disperse phase. This is not the usual way of stating the case. It is usually considered that only cations count in the case of

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[1] Bancroft: Jour. Phys. Chem., 18, 552 (1914).

negatively charged sols, that only anions count in the case of positively charged sols, that the univalent ions all cause coagulation at approximately the same concentration, the bivalent ions at a lower concentration which is practically the same for all bivalent ions, and the trivalent ions at a still lower concentration.[1] The matter has been stated pretty clearly by Höber.[2] "Some general rules apply, among them the law first formulated by Hardy[3] that the precipitation of positive colloids depends chiefly on the anion and the precipitation of negative colloids chiefly on the cation; and also the law formulated a long time ago by Schulze[4] that the precipitating power of the active ions is a function of its valence or of the number of electrical charges, which it carries. Of course there are other factors besides these two rules and these factors will now be discussed more carefully; the especial effect of organic ions has already been mentioned."

Everybody recognizes that hydrogen and hydroxyl ions are not to be classed with the other univalent ions because they are usually adsorbed much more strongly,[5] and everybody recognizes that there are other exceptions; but I have found no clear recognition of the fact that Schulze's law is merely a first approximation. In case of doubt it is generally safe to assume that an ion of higher valence will be adsorbed more than one of lower valence; but it is a mistake to consider this so-called law anything more than a guide. Since we are dealing with selective adsorption we shall expect to find that some univalent ions will be adsorbed by some substances more than some bivalent or trivalent ions. This is shown clearly in data by Odén on colloidal sulphur, given in Table I. In the second column are given the liminal concentrations in gram atoms of the cations per liter necessary to coagulate

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[1] Cf. Freundlich: Kapillarchemie, 350, 354 (1909); Zsigmondy: Kolloidchemie, 54 (1912); Hatschek: An Introduction to the Physics and Chemistry of Colloids, 33 (1913).

[2] Physikalische Chemie der Zelle und Gewebe, 283 (1914).

[3] Zeit. phys. Chem., 33, 385 (1900).

[4] Jour. prakt. Chem., (2) 25, 431 (1882); 27, 320 (1884).

[5] Freundlich: Kapillarchemie, 354 (1909).

the sulphur; in the third column are given the reciprocals of these values, the atomic precipitating power so-called.

TABLE I

Coagulation of Sulphur at 18°–20°

Salt	Liminal value gram-atoms. Cations per liter	Atomic precipitating power of cation
HCl	6	0.16
LiCl	0.913	1.1
NH_4Cl	0.435	2.3
$(NH_4)_2SO_4$	0.600	1.7
NH_4NO_3	0.506	2.0
NaCl	0.153	6.1
Na_2SO_4	0.176	5.7
$NaNO_3$	0.163	6.1
KCl	0.021	47.5
K_2SO_4	0.025	39.7
KNO_3	0.022	45.5
RbCl	0.016	63
CsCl	0.009	108
$MgSO_4$	0.0093	107.5
$Mg(NO_3)_2$	0.0080	125
$CaCl_2$	0.0041	245
$Ca(NO_3)_2$	0.0040	247
$Sr(NO_3)_2$	0.0025	385
$BaCl_2$	0.0021	475
$Ba(NO_3)_2$	0.0022	461
$ZnSO_4$	0.0756	13.2
$Cd(NO_3)_2$	0.0493	20.3
$AlCl_3$	0.0044	227
$CuSO_4$	0.0098	102
$Mn(NO_3)_2$	0.0096	105
$Ni(NO_3)_2$	0.0446	22.4
$UO_2(NO_3)_2$	0.0137	73

Under the conditions of Odén's experiments, sulphur is a negative colloid and the precipitation is therefore due to an adsorption of cations. The first thing to be noticed is that hydrogen ion is not adsorbed strongly by sulphur, the precipitating power of hydrochloric acid being much less than that of lithium, ammonium, sodium, potassium, rubidium, or caesium chloride. Instead of these univalent cations precipitating at the same concentration, the required concentration of lithium chloride is in round numbers one hundred times that of caesium chloride. The liminal values for barium and strontium are nearly equal, but calcium chloride requires a distinctly higher concentration. If we take the different bivalent ions the values range from 0.0756 for zinc to 0.0022 for barium, a ratio of over thirty to one. The univalent ion caesium has a greater precipitating power than the bivalent zinc, cadmium, nickel, and uranyl; and about the same precipitating power as the bivalent copper, manganese, and magnesium. The trivalent ion aluminum has about the same precipitating power as the bivalent calcium and distinctly less precipitating power than bivalent strontium and barium. The specific nature of the adsorption comes out extraordinarily clearly with sulphur, practically the only orthodox thing being that nitrate, chloride, and sulphate behave practically alike, though even here Odén considers that sulphate has a slight protecting action. This specific nature appears more clearly perhaps if we arrange the cations in order, the one with the greatest precipitating power coming first: Ba, Sr $>$ Ca, Al $>$ Mg, Cs, Mn, Cu $>$ UO_2 $>$ Rb $>$ K $>$ Ni, Cd, Zn $>$ Na $>$ NH_4 $>$ Li $>$ H.

Sulphur is admittedly an extreme case, but Freundlich[1] gives data for colloidal platinum from which I deduce the order: Al, Pb $>$ Ba, UO_2 $>$ Ag $>$ K, Na. Bivalent lead has practically the same precipitating power as trivalent aluminum. Univalent silver is nearer to bivalent uranyl and barium than to univalent potassium and sodium. If more cations had been studied we should very likely have got more distinct evidence to specific action. As it is, it takes 130 millimols NaOH per liter to coagulate the platinum and only 2.5 millimols NaCl. The change from chloride to hydroxide has a more marked effect than the change from sodium to barium. It seems very probable that barium hydroxide would have no greater precipitating power than sodium chloride. From Pappadà's experiments with colloidal silver[2] I deduce the fol-

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[1] Kapillarchemie, 352 (1909).

[2] Pappadà: Gazz. chim. ital., 42 I, 263 (1912).

lowing order of adsorption: Al > Ba, Sr, Ca > H > Cs > Rb > K > Na > Li. From these data Pappadà concludes that the migration velocity is the determining factor with the univalent cations; but this cannot be true. The difference between aluminum and hydrogen is not very great, one drop of $M/10$ HCl producing a coagulation and one drop $M/20$ $AlCl_3$. In tenth-normal solutions potassium iodide, nitrate, and sulphate produce no coagulation. The reason given by the author is that these anions react with the colloidal silver. In normal solutions the iodides, nitrates, and sulphates are said to precipitate at the same concentrations as the corresponding chlorides and bromides. The effect of concentration is a little obscure in other respects since 5 or 6 drops of normal KCl precipitate 2 cc 0.06% Ag, whereas it takes only 30 drops $N/10$ KCl to produce precipitation. The essential thing from my point of view is that the different univalent cations have different liminal values; the difference between hydrogen and lithium is greater than that between hydrogen and aluminum.

From experiments on mastic[1] we get the data given in Table II.

TABLE II
Coagulation of Mastic

Salt	Liminal value, gram atoms	Atomic precipitating power of cation
NaCl	1.0	1
$AgNO_3$	0.125	8
$HgNO_3$	0.00125	800
HCl	0.010	100
$CaCl_2$	0.025	40
$BaCl_2$	0.025	40
$ZnSO_4$	0.050	20
$Al_2(SO_4)_3$	0.0004	2500
$Al_2(NO_3)_2$	0.0004	2500
$FeCl_3$	0.0003	3300

If we consider the mercury in mercurous nitrate as a univalent ion, it is very much out of place, precipitating at

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[1] Freundlich: Kapillarchemie, 367 (1909).

much lower concentrations than the barium, calcium and zinc salts. Of course the formula should be written $Hg_2(NO_3)_2$ with Hg_2 as a bivalent ion.[1] In this case the precipitating power becomes 1600 instead of 800, which puts it up much nearer the trivalent cations than the bivalent ones. The order of cations is: Fe, Al > Hg_2 > H > Ba, Ca > Zn > Ag > Na. Only three anions are given in the table, so it is impossible to tell what effect the anions have. A good many experiments have been made on mastic with different acids but the degree of electrolytic dissociation varies so as to make these results inconclusive. With Prussian blue Pappadà[2] found the order of the cations to be: Fe, Al, Cr > Ba, Cd > Sr, Ca > H > Cs > Rb > K > Na > Li. Sulphates, nitrates, chlorides, bromides, and iodides all behaved alike. Practically the same order of cations was obtained for copper ferrocyanide.[3] In the cases studied by Pappadà the specific adsorption appears to play a very small part. The data for arsenic sulphide,[4] however, give us variety enough. The order of cations is Ce, In, benzidine, Al > new fuchsine, crystal violet > quinine > morphine, UO_2 Sr, Ca > Be, Zn, Ba > Mg > *p*-chloraniline, toluidine > aniline > strychnine > guanidine > H > K > Na > Li. The organic cations come in where they please and play havoc with any rule as to valency. The chlorides and nitrates give practically the same values and the sulphates are not far out of line, though it seems probable that the restraining power of sulphate is rather greater than that of chloride or nitrate. The liminal values in gram atoms of the cation per liter are 0.0056, 0.0066, 0.0086, 0.110 and >0.240 for potassium nitrate, sulfate, formate, acetate, and citrate, from which one can deduce that the order of adsorption of anion is: citrate > acetate > formate > sulphate > nitrate, chloride. It is a great pity

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[1] Ogg: Zeit. phys. Chem., **27**, 285 (1898).

[2] Zeit. Kolloidchemie, **6**, 83 (1910).

[3] Pappadà: Ibid., **9**, 136 (1911).

[4] Freundlich: Kapillarchemie, 351 (1909); Freundlich and Schucht: Zeit. phys. Chem., **80**, 564 (1912).

that Freundlich did not try other combinations, such as barium acetate for instance.

From the experiments on hydrous ferric oxide,[1] the order of adsorption of the precipitating anions appears to be $Cr_2O_7 > SO_4 > OH >$ salicylate > benzoate > formate > $Cl > NO_3 > Br > I$, while the order for the cations is: $H > Ba > Mg > Tl$, Na, K. The univalent ions do not all behave alike and neither do the bivalent ones; but the upholders of Schulze's law can comfort themselves with the fact that the two sets do not overlap except in the case of hydrogen. There is no such comfort in the case of albumin. I have shown[2] that the probable order of adsorption of anions, so far as known, is: sulphocyanate, iodide > chlorate > nitrate > chloride > acetate > phosphate > sulphate > tartrate, the sulphocyanate ion being adsorbed the most and the tartrate ion the least. Here there is nothing even to suggest Schulze's law and the firm belief which most people have in Schulze's law is probably one reason for the marked failure to account satisfactorily for the phenomena with aluminum. With the cations albumin appears to be fairly orthodox for the order of adsorption appears to be Th, $UO_2 >$ Cu, $Zn > Ca > Mg > Li > K$, $Na > NH_4$, though even here the lithium stands higher in the series than it has been found with other substances.

While there is unquestionably a tendency for ions of a higher valence to be adsorbed more strongly than ions of a lower valence, the experiments which have been cited show that there are many exceptions and that the fundamental rule is that the adsorption is specific both as regards the adsorbing substance and the ion adsorbed.

Since the important thing in the neutralization of an adsorbed ion is the adsorption of an ion of the opposite charge, we may get neutralization when we have a colloid with the opposite charge. In other words, we may neutralize an adsorbed ion with another adsorbed ion instead of by a free ion.

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[1] Freundlich: Kapillarchemie, 352, 358 (1909); Zsigmondy: Kolloidchemie, 181 (1912); Pappadà: Zeit. Kolloidchemie, 9, 233 (1911).

[2] Bancroft: Jour. Phys. Chem., 19, 352 (1915).

The usual statement is that sols having the same charge do not affect each other perceptibly, while sols having opposite charges precipitate each other.[1] Neither of these statements is as accurate as it should be. I shall take up first the case of sols having opposite charges. Positive and negative colloids will precipitate each other when in proper proportions and provided adsorption takes place.[2] I see no theoretical reason why we should not have a positively charged and a negatively charged sol, neither of which adsorbed the other to any appreciable extent. In that case these two sols would not precipitate each other. Since complete neutralization takes place only when one sol has adsorbed the amount of the sol carrying an equivalent amount of the ion having the opposite charge, it follows that the amount of one sol necessary to precipitate a given amount of another sol will vary with the degree of adsorption; it will therefore be a specific property and not an additive one. This can be tested experimentally on data by Biltz given in Table III.[3]

Table III

1.4 mg gold completely precipitated by

CeO_2	Fe_2O_3	ThO_2	ZrO_2	Cr_2O_3	Al_2O_3
4	3	2.5	1.6	0.3	0.1–0.2 mg

28 mg Sb_2O_3 completely precipitated by

Fe_2O_3	ThO_2	CeO_2	ZrO_2	CrO_3	Al_2O_3
32	20	11	6.5	3.0	2.0 mg

24 mg Ag_2S_3 completely precipitated by

Fe_2O_3	ThO_2	CeO_2	ZrO_2	Al_2O_3	Cr_2O_3
13	6	4	2	2	0.5 mg

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[1] Freundlich: Kapillarchemie, 444 (1909); Zsigmondy: Kolloidchemie, 56 (1912); Höber: Physikalische Chemie der Zelle und Gewebe, 294 (1914).

[2] Bancroft: Jour. Phys. Chem., 18, 555 (1914).

[3] Freundlich: Kapillarchemie, 445 (1909).

Alumina is more effective than chromic oxide in precipitating antimony sulphide and much less effective in precipitating arsenic sulphide. The alumina must therefore be adsorbed more by antimony sulphide than chromic oxide while the reverse must be true for arsenic sulphide. Cerium oxide is less effective than ferric oxide and thorium oxide in precipitating gold, but is more effective than either of these in precipitating the sulphides of antimony and arsenic. The phenomenon is thus specific, varying with the nature of the two colloids. This seems not to have been realized before. In fact Freundlich[1] says definitely that "one seems to find approximately the same order regardless of what sol is to be precipitated." This statement is true, but it misses the important thing in the experiments which was that the order was not always the same.

We can now take up the case of sols having the same charge. The statement that neither has any perceptible effect on the other is based solely on the fact that no precipitation occurs. We know, however, that cases of adsorption are not limited to colloids or electrolytes having opposite signs. Charcoal adsorbs both bases and acids. Silver bromide adsorbs silver ions or bromine ions as the case may be. There is therefore no theoretical reason why precipitated hydrous ferric oxide might not adsorb chromic oxide and vice versa. If the precipitated substance will do this there is no reason why the peptonized substance should not. Nagel[2] has recently shown that this does occur and that it accounts for the behavior of mixtures of chromic and ferric salts with excess of alkali. Hydrous chromic oxide is peptonized by caustic potash while hydrous ferric oxide is not. If the chromium salt is present in large amount relatively to the iron salt, the ferric oxide will adsorb the peptonized chromic oxide and be peptonized by it, going apparently into solution. If the ferric salt is present in excess, it will adsorb the peptonized chromic oxide carrying it out of the liquid phase.

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[1] Kapillarchemie, 445 (1909).

[2] Jour. Phys. Chem., 19, 331 (1915).

It is to be noticed that the chromic oxide, when in excess, acts as a so-called protecting colloid to the iron oxide. Everybody is familiar with the fact that gelatine is adsorbed by colloidal gold, for instance; but that is usually treated under the heading of protective colloids rather than under the heading of mutual action of two colloids. The case of chromic and ferric oxides is merely another illustration of the fact that the distinction between a suspension colloid and an emulsion colloid is now arbitrary and unsatisfactory.[1]

Coming back for a moment to the behavior of two oppositely charged colloids, there is a special hypothetical case which is perhaps worth mentioning. Suppose we have two sets of finely divided particles neither of which adsorbs the other appreciably, and let us also suppose that one set of particles adsorbs a given cation very strongly, while the other set of particles adsorbs a given anion very strongly. If we take a mixture of these two sets of particles and add a small amount of the salt of the given base and the given anion, we shall have a colloidal solution which will conduct electricity very well but which will contain no free ions to speak of because, by definition, the cations have been practically completely adsorbed by one set of particles and the anions by the other set of particles. This particular case has not been realized, but an intermediate one seems to have been found by McBain and Martin[2] in sodium palmitate solutions.

"Most authors since Kahlenberg and Schreiner[3] have, as a matter of course, ascribed the conductivity exhibited by soap solutions largely to free alkali hydroxide. In previous papers from this laboratory the same tentative suggestion was made, but it was each time clearly stated that it was only a working hypothesis until these experimental data should be ascertained. Now it is certain that the conductivity of soap solutions is, only to a very minor extent, due to hydroxyl ions. Further, on account of the fact that the rise of boiling

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[1] Bancroft: Jour. Phys. Chem., 18, 556 (1914).

[2] Jour. Chem. Soc., 105, 965 (1914).

[3] Zeit. phys. Chem., 27, 552 (1898).

point in certain soap solutions is practically all required to account for the sodium ions alone,[1] the conductivity cannot be wholly ascribed to simple palmitate ions. The suggestion we made is that we have here a new type of aggregate or micelle, the mobility of which, owing to the reasons given in the paper cited, is comparable with that of a true anion. Of course, further investigations are proceeding in this laboratory in order to bring this to the test of direct experiment. Incidentally, the above shows, further, that undissociated soap is present chiefly or entirely in colloidal form."

As I see the matter the sodium palmitate is hydrolyzed and the hydroxyl ions are adsorbed to a great extent by the undissociated palmitate and possibly by the insoluble palmitate acid also, though this seems less probable. The adsorbing substance thus becomes the anion, owing to the adsorbed hydroxyl. Because of electrometric measurements, McBain[2] considers that there is practically no hydrolysis. Electrometric measurements only show the concentration of hydroxyl ions in solution. I do not believe for a moment that an adsorbed hydrogen ion or hydroxyl ion behaves electrometrically like a free hydrogen or hydroxyl ion. An adsorbed chlorine ion, for instance, would not give a test with silver nitrate. Under these circumstances the electrometric measurements are satisfactory for showing the concentration of hydroxyl ions in the solution, but they are utterly worthless for showing the degree of hydrolysis of sodium palmitate. For the same reason I am very sceptical as to any conclusion in regard to albumin solutions which is based on electrometric measurements.[3]

The adsorption of an ion by a colloid gives us an electrically charged colloid with a migration velocity of its own. This migration velocity, so far as studied, is of the general

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[1] McBain: Trans. Faraday Soc., **9**, 99; Zeit. Kolloidchemie, **12**, 256 (1913).

[2] McBain and Martin: Jour. Chem. Soc., **105**, 957 (1914).

[3] Bancroft: Jour. Phys. Chem., **19**, 349 (1915).

order of magnitude of free ions.[1] Consequently, the presence of a colloid may increase or decrease the conductivity of a solution. Raffo and Rossi[2] found that colloidal sulphur cuts down the conductivity of sulphuric acid and sodium sulphate solutions very much. Games and Cingola[3] also found a marked decrease when tannin was added to a potassium chloride solution. In many cases, however, there was no apparent effect. Of course, if the colloid adsorbs both ions or the undissociated salt, the conductivity will necessarily decrease[4] and we do not know whether the marked change with tannin, potassium chloride and water is due to a change of migration velocity or to a wholesale removal of potassium chloride from the solution. Patten once described what always seemed to me a very interesting experiment. He placed a coarse powder in a dilute solution of an electrolyte, allowed the powder to settle, and measured the conductivity of the supernatant liquid. He then stirred the solution and measured the conductivity again while the powder was suspended between the electrodes, finding an increase in conductivity. The powder adsorbed one ion and of course carried the other down with it when it settled. So far as I know, this experiment has never been published and I cannot give numerical data. My impression is that the paper was presented at the Toronto meeting of the American Chemical Society.

The general results of this paper are:

1. The neutralization of an adsorbed ion is due to specific adsorption. The concentration of a given electrolyte necessary to neutralize the charge on a given colloid will therefore depend on the nature of the cation, the anion, and the colloid.

2. It is inaccurate to say that the cation is negligible in the precipitation of a positive colloid and the anion in the

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[1] Zsigmondy: Kolloidchemie, 46 (1912).

[2] Gazz. chim. ital., 42 II, 326 (1912).

[3] Ibid., 44, I, 36 (1914).

[4] Wolfgang Ostwald: "Gedenkboek aangeboden aan Van Bemmelen," 269 (1910).

precipitation of a negative colloid, though this statement is often approximately true.

3. Univalent ions are not all adsorbed alike; nor are bivalent ions or trivalent ions. The order of adsorption is specific with each colloid and is not determined exclusively—and perhaps not at all—by the migration velocity or solution pressure of the ion.

4. Since the adsorption is specific, Schulze's law is only an approximation. Certain univalent ions are adsorbed by certain colloids more than certain bivalent or trivalent ions. In many cases there is, however, a marked tendency to increased adsorption with increasing valence.

5. Mixtures of two sols will not precipitate each other unless adsorption takes place.

6. Since adsorption is specific, the order of precipitation of a negative sol by a number of positive sols will not necessarily be the same for any two negative sols.

7. It is not accurate to say that two sols having the same sign have no effect one upon the other. Adsorption may, and often does, take place.

8. Hydrous chromic oxide, which is peptonized by caustic potash, may act as a protecting colloid for hydrous ferric oxide, which is not peptonized by caustic potash.

9. Since an adsorbed ion does not necessarily give the reactions of a free ion, electrometric measurements may, and do, lead to false conclusions when applied to colloidal solutions.

10. It is probable that sodium palmitate solutions are hydrolyzed to a very much greater extent than appears from electrometric measurements.

11. If two colloidal sols did not adsorb each other appreciably and if one adsorbed the cation of a given electrolyte very markedly, while the other adsorbed the anion of the same electrolyte very markedly, the addition of a small amount of the electrolyte to a mixture of the two colloids would produce a solution which would conduct electricity without there being any appreciable amount of substance in true solution.

12. In sodium palmitate solutions, it seems probable that the hydroxyl ions set free by hydrolysis are adsorbed practically completely by the colloidal soap.

13. Addition of a colloid to a solution will increase or decrease the conductivity if the adsorbed ion has a greater or lesser migration velocity than the ion adsorbed. In so far as both ions are adsorbed the conductivity will decrease.

14. When adsorption by a colloid causes hydrolysis, the conductivity will depend also on the nature of the products of hydrolysis.

Cornell University

A COLLODION DIFFUSION CELL FOR USE IN DIALYSIS.

BY T. R. BRIGGS

Collodion membranes for use in dialysis have been described and studied by Bigelow and Gemberling,[1] who, having reviewed the literature very completely, recommend the preparation of collodion sacs for dialysis by Novy's method. Recently, however, I found myself called upon to separate several colloid and semi-colloid dyes by the diffusion method and, on attempting to prepare collodion sacs according to Novy's directions, found that the operation required considerable practice before it could be carried out successfully. Parchment diffusion thimbles were not conveniently at hand, so the following procedure was adopted:

A large Soxhlet extraction cartridge (80 x 25 mm) composed of rather thick filter paper was filled with a collodion solution (Kahlbaum's Ph.G.V), and emptied again as soon as the solution had completely impregnated the pores of the paper. The cartridge was allowed to "dry" for a few moments until the collodion had set; thereupon, the filling and emptying process was repeated. In this way three coats of collodion were applied to the interior of the cartridge.

Baranetzky[2] has observed that a collodion membrane *which has completely dried out* is practically impervious to water, while if the freshly prepared membrane be placed into water before the alcohol present has completely evaporated, the result is a film of pyroxylin quite permeable to water. Accordingly, the cartridge prepared as described cannot be allowed to dry out in the air, but must be immersed in water and kept under water until used. After the third coat of collodion has been applied, the cartridge is dried in a current of air until practically all the ether of the mixed solvent is removed, about ten minutes being required for this to occur.

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[1] Jour. Am. Chem. Soc., 29, 1576 (1907).

[2] Pogg. Ann 147, 219 (1872).

Thereupon, on immersing the cartridge in distilled water, the alcohol retained in the pores of the collodion is displaced quickly and completely by diffusion, and the cell is ready for use.

The diffusion cells were tested qualitatively for imperfections and leaks in the collodion membrane by carrying out diffusion tests, as follows: A cartridge was filled to within half an inch of the top with a mixed solution of sodium chloride and congo red, a dye which forms non-diffusing and distinctly colloidal solutions.[1] On partially immersing the cell in distilled water it was found that the sodium chloride dialyzed out while not a trace of congo red appeared in the diffusate; since the liquid stood higher inside the cell than outside, any leak would have been detected at once by the appearance of the red dye in the outer liquid.

Comparative tests were next made of two parchment and two collodion diffusion cells by determining the amount of sodium chloride diffusing through the walls in twenty-four hours under carefully controlled and very nearly identical conditions. Four cells of practically the same dimensions were employed, partly filled with 20 cc of standard (approximately $N/10$) sodium chloride solution plus 25 cc of distilled water and placed in running tap water in a specially designed apparatus. After twenty-four hours the amount of salt left behind in each thimble was determined by titration with standard silver nitrate. The results follow.

TABLE I—COMPARATIVE TESTS

Parchment diffusion thimbles previously well soaked in water
Collodion extraction thimbles (C. S. & S. No. 603)

	Parchment cells		Collodion cells	
	No. 1	No. 2	No. 1	No. 2
Time of test (hrs.)	23	23	23	23
Volume of solution (cc)	45	45	45	45
NaCl originally present (g)	0.118	0.118	0.118	0.118
NaCl removed by diffusion (g)	0.092	0.092	0.112	0.113
Percent NaCl removed by diffusion	77.9	77.9	94.9	94.8

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[1] Freundlich: Kapillarchemie, 564 (1909).

The results of the test were very favorable to the collodion membranes as the data indicate. The only apparent disadvantage possessed by the collodion cells is a tendency to overflow because of water entering by osmosis, a phenomenon which is absent in the case of parchment. Bigelow has observed the same behavior.

I have already called attention to the fact that collodion membranes lose their permeability if they are allowed to dry completely. This is due, without doubt, to irreversible changes leading to the collapse of the pores in the material. It would seem, according to this theory, if one were to add to the original collodion solution some *non-volatile* liquid (or solid) soluble both in water and the ether-alcohol pyroxylin solvent, that under these circumstances the collodion film might be dried in the air and still retain the property of being permeable to water, on replacement of the non-volatile liquid in the pores by immersion in water. Experiment confirmed this most satisfactorily.

Glycerine dissolves readily in collodion solution and was employed in the following experiments: Three different collodion solutions were used to prepare the diffusion shells according to the method just described: Solution 1 contained no glycerine; No. 2 contained 4 percent glycerine by volume; Nos. 3 and 4 contained 6 and 10 percent, respectively. Soxhlet thimbles were coated on the inside with three layers of each solution and then dried in the air, thereupon the removal of volatile solvent was completed by heating in a water-oven for several hours. After several weeks had elapsed, the usual comparative tests were made, each cartridge being soaked in water to remove the glycerine from the membrane, before the tests were begun. The data follow.

TABLE II—COMPARATIVE TESTS

(*a*) Cartridge with three coats of collodion No. 1. Dried in air. Weight of collodion when dry: 0.430 g. Percent NaCl removed by diffusion in 24 hrs.: 45.8.

(*b*) Cartridge with three coats of collodion No. 2. Dried in air. Weight of collodion when dry: 0.580 g. Percent NaCl removed by diffusion in 24 hrs.: 75.

(*c*) Cartridge with three coats of collodion No. 3. Dried in air. Weight of collodion film when dry: 0.886 g. Percent NaCl removed by diffusion in 24 hrs.: 89.2.

(*d*) Cartridge with three coats of collodion No. 4. Dried in air. Weight of collodion when dry: 1.089 g. Percent NaCl removed by diffusion in 24 hrs.: 88.4.

(*e*) Parchment thimble. Percent NaCl removed by diffusion in 24 hrs.: 83.6.

(*f*) Collodion thimble made according to Novy's method without use of filter-paper Soxhlet thimble. Percent NaCl removed by diffusion in 24 hrs.: 99.6.

These data show that the amount of glycerine in the dried collodion membranes varied up to approximately 60 percent by weight, and that the permeability of the cells increased as the glycerine content rose to about 50 percent, after which it remained practically constant. The collodion cells are more efficient than parchment thimbles, though they are less so than the beautiful transparent sacs formed directly from collodion. The ease with which the cartridges are prepared and their durability more than makes up for the lower efficiency. Several cartridges prepared with glycerine have been kept for more than eight months without losing their effectiveness as dialyzing cells.

The results of this paper may be summarized as follows:

1. Collodionized Soxhlet extraction thimbles have been suggested as convenient cells for dialysis.
2. The construction of such cells has been described and comparisons have been made with parchment diffusion shells.
3. By the addition of a small amount of glycerine to the collodion solution the cells may be prepared so that they may be dried completely without losing their permeability to water. Such cells may be kept for a long time before using.
4. The new form of collodion diffusion cell is more efficient than the ordinary type of parchment thimble, but is less efficient than collodion sacs prepared by Novy's method.

Worcester Polytechnic Institute
Cornell University

ON THE REACTIONS OF BOTH THE IONS AND THE MOLECULES OF ACIDS, BASES AND SALTS

ON THE CONDUCTIVITY AND IONIZATION OF SODIUM ETHYLATE, POTASSIUM ETHYLATE, LITHIUM ETHYLATE, SODIUM PHENOLATE, POTASSIUM PHENOLATE, LITHIUM PHENOLATE, SODIUM PHENYLTHIOURAZOLE, SODIUM IODIDE, SODIUM BROMIDE AND MIXTURES OF THESE ELECTROLYTES IN ABSOLUTE ETHYL ALCOHOL AT 0°, 25° AND 35°

BY H. C. ROBERTSON, JR., AND S. F. ACREE

[Nineteenth Communication[1] on Catalysis]

The investigation now in progress in this laboratory on the mechanism of the reactions of alkyl halides with urazoles, ethylates and phenolates has indicated that, in these reactions, both the molecules and the ions of the last three take part. It has, therefore, become necessary to measure the dissociation of all these electrolytes in absolute ethyl alcohol; and since, in the course of the reactions studied, halogen salts are formed, a study of the conductivities of mixtures of these salts with both ethylates and phenolates was also advisable.[2]

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[1] For references to the earlier work see Am. Chem. Jour., 49, 474 (1913). (We have been aided in this investigation by two grants from the Bache Fund of the National Academy of Sciences and by a grant from the Carnegie Institution of Washington.)

[2] The experimental portion of this investigation was done by Dr. H. C. Robertson in 1909–10. We have delayed publication until we could finish this entire chapter on catalysis; although this is not yet complete it is thought best to publish now the incomplete data. Work is being continued now by more accurate methods on the conductivities, viscosities, specific gravities, indices of refraction, and reaction velocities of all the solutions used in this study of catalysis. We are indebted to Mr. W. A. Gruse and Dr. W. A. Taylor for many of the calculations.

In discussing the conductivities of individual electrolytes in nonaqueous solvents reference should be made to the work of Carrarra,[1] Goldschmidt,[2] Lapworth,[3] Bredig,[4] Jones[5] and others on the conductivities of electrolytes in alcohols, to the work of Franklin,[6] Kraus and others on ammonia, and amines as solvents, to a discussion by Kraus[7] and Bray of a number of investigations of nonaqueous solutions and a general dilution formula, and to the work of Walden[8] and of Sachanov[9] on organic solvents having small dielectric constants. Especial attention is called to the recent work and to the dilution formula of Kendall.[10]

It is a deplorable fact that very few investigators of conductivity have striven to make the measurements with the greatest accuracy, and we have therefore attempted to improve upon the technique employed by studying the conductivity cells, the baths, temperature regulation, the bridge and resistances, the methods of making and handling the solutions, and the so-called electrode phenomena. We are indebted to Dr. Curtis[11] and Dr. Wenner, of the National

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[1] Gazz. chim. ital., **26**, I, 119 (1896); **33**, I, 241 (1903); Ahrens' Sammlung, **12**, 403 (1908).

[2] Zeit. Elektrochemie, **15**, 6 (1909); Zeit. phys. Chem., **60**, 728 (1907); **70**, 627 (1910); **81**, 30 (1912).

[3] Jour. Chem. Soc., **93**, 2163, 2203 (1908); **97**, 21 (1910); **99**, 1417, 2224 (1911); **101**, 2249 (1912); **103**, 252 (1913).

[4] Zeit. Elektrochemie, **9**, 118 (1902); **10**, 586 (1903); **11**, 528 (1907); **18**, 535. 539 (1908), and recent papers by Miller, Braune and Snethlage.

[5] See the articles in the Am. Chem. Jour. and the Publications by the Carnegie Institution of Washington.

[6] Am. Chem. Jour., **23**, 277 (1900); Jour. Am. Chem. Soc., **26**, 499 (1904); **27**, 191 (1905); **29**, 1389 (1907); Zeit. phys. Chem., **69**, 290; Jour. Phys. Chem., **15**, 675 (1911); Proc. A. A. A. S., **51**, 366.

[7] Jour. Am. Chem. Soc., **35**, 1315 (1913).

[8] See Jour. Am. Chem. Soc., **34**, 1631 (1908), for a general review. Bull. Acad. Imp. Sc. de St. Petersbourg, **1912**, 305, 1055.

[9] Zeit. phys. Chem., **80**, 20 (1912); **83**, 129 (1913); **87**, 441 (1914); Jour. russ. phys. chem. Ges., **42**, 683; **43**, 526.

[10] Proc. Roy. Soc., **85A**, 200; Meddel. från K. Vet. Akads. Nobelinstitut, **2**, Nos. 25 and 38; Jour. Chem. Soc., **101**, 1275 (1912); Jour. Am. Chem. Soc., **36**, 1069 (1914).

[11] Curtis and Grover: Bureau of Standards Bulletin Vol. **8**, No. 3.

Bureau of Standards, for much valuable advice, and the fine work of Washburn[1] and Bell shows what great improvements can be made in this line.

Dr. W. A. Taylor is now using the excellent equipment of the Bureau of Standards in making a fundamental study of a large number of factors, some of which have already been investigated, while others have not heretofore been studied experimentally in conductivity work by physical chemists. As a result of this work he has already greatly improved the methods. With our suggestions and aided by Dr. Curtis, he has studied: (1) the current from (*a*) induction coils, (*b*) a Holzer-Cabot wireless generator, (*c*) a General Electric Company large generator, (*d*) a Siemens-Halske generator for conductivity work, and (*e*) a Vreeland oscillator, which we have found to be the best source of current yet tried, as it gives a pure sine wave of uniform frequency which can be varied very widely; (2) the voltage, which when varied from 0.25 to 8 volts, has shown no influence on the resistance of the solutions measured so far *in very clean cells*, but is very important in cells not entirely clean; (3) the size and shape of the electrodes, which have a very large influence on the change of resistance and capacity of the cell with change in frequency; (4) the material used in making the electrodes (Pt, Au, Ag, Cu, Zn, etc.), which is very important; (5) the state of aggregation of the surface of the electrode, as in plain, gray and platinized electrodes, which has a very great influence on the capacity of the cell and change of resistance with change in frequency; (6) the frequency of the alternating current, which when varied may change the resistance of some solutions in some cells as much as 3 percent; (7) the high capacity of the cell as a condenser, which is very important in decreasing the change of resistance with change in frequency and in obtaining a perfect minimum in the telephone; (8) the valence and velocities of the different ions; (9) the influence of the concentration and the character of the elec-

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[1] Jour. Am. Chem. Soc., 35, 177 (1913).

trolyte and the solvent on the change of resistance with change in frequency; (10) the proper use of a condenser or inductance in balancing the capacity of the cell, and its influence on the resistance and minimum in the telephone; (11) the construction of the cell in such a way that no errors from evaporation and concentration can be produced; (12) the use of a tuned telephone attached to a Stethoscope or of double wireless telephones; (13) the construction of a Wheatstone bridge with Curtis resistance free from inductance and capacity, kept automatically at constant temperature, and arranged so that every resistance can be checked against the others and against standard enclosed resistances; (14) the development of especially good constant temperature baths for such work; (15) the use of weight methods and special apparatus for making, keeping and transferring solutions; (16) a number of points connected with the proper use of all of the apparatus, especially the electrical equipment, to prevent errors arising from induction, capacity, electrical leaks, and other factors; (17) our criterion of excellent cells, namely, that each one must be independent of the above sources of error and give readings constant to within 0.01 percent, and especially that, *whatever the solution used, the ratios of the resistances in any two such cells must be constant to within 0.01 percent.* Only in this way can we be certain that the electrode effects have been practically eliminated and that we are measuring the true electrical resistance of the solution with great accuracy. By studying the electrode phenomena and other sources of error and correcting them we have now reached a precision of 0.001 percent and an accuracy of about 0.01 percent. The details of all this work will appear shortly in another article by Dr. W. A. Taylor.

It is not difficult to duplicate measurements with the same solution to within 0.1 percent and we have therefore made separate measurements on duplicate solutions in all cases, and often on three or four solutions. In work of the

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[1] See *Science* for Taylor's address before the Physical Chemical Section of the American Chemical Society, New Orleans, April, 1915.

highest character all solutions should be made and analyzed by gravimetric instead of volumetric methods. Such procedure, however, takes a great deal of time and is not warranted by the present investigation in which the values of the reaction velocities, K_N, cannot, with the analytical method employed, be duplicated by the same or different observers to within much less than 1 percent. With this error, however, we can easily test our theory that both ions and molecules react. We have therefore contented ourselves with the more rapid volumetric method for the present and an inspection of Table XXXVIII shows that the sum of the conductivities for all the concentrations up to $N/1024$ in a given series agrees with the duplicate to within 0.35 percent, the average deviation being 0.15 percent. The duplicates for the individual concentrations rarely differ more than 0.5 percent, although in a few cases it may reach 1 percent. Although we believe that the individual values of μ_v are correct to within 0.5 percent for the more concentrated solutions, the error naturally becomes larger for the extremely dilute solutions. This phase of the work is of very great importance because we must know the limiting conductivity, μ_∞, in order to calculate the ionization, α. Many workers have tried to extrapolate μ_∞ and we show at the bottom of Tables VIII, IX, X, XXX, XXXI and XXXII that the use of the formula[1] $\mu_\infty = \frac{V_1\mu^2\mu_1 - V\mu^2_1\mu}{V_1\mu^2 - V\mu^2_1}$ and the data from lithium ethylate and lithium phenolate prove them to be "weak" enough electrolytes to give nearly the same average value for "calc. μ_∞" as we get by direct measurement. But this formula and others do not apply well to the other electrolytes and in the present investigation we have attempted to determine the maximum molecular conductivities by actual measurement rather than by calculation. The difficulties involved in such measurements have been demonstrated by the poor agreement between the values found by different

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[1] See especially the excellent article by Derick: Jour. Am. Chem. Soc. 36, 2268 (1914).

observers. Turner[1] has measured the conductivity of potassium iodide in ethyl alcohol at dilutions of several hundred thousand liters and has discussed the possible sources of error in these measurements. In our work, we have tried to eliminate these sources of error as far as was practicable. Alcohol of low conductivity, accurately measured, should be used and protected from the moisture and carbon dioxide of the atmosphere in such an apparatus as the one illustrated in Fig. 1, below. The style of ground glass joint prevents fine particles of glass from contaminating the alcohol, while the soda lime and phosphorus pentoxide keep out acid and alkaline vapors. The cells and cell electrodes must be clean and free from adhering solvent, electrolyte, or liquid left from more concentrated solutions.

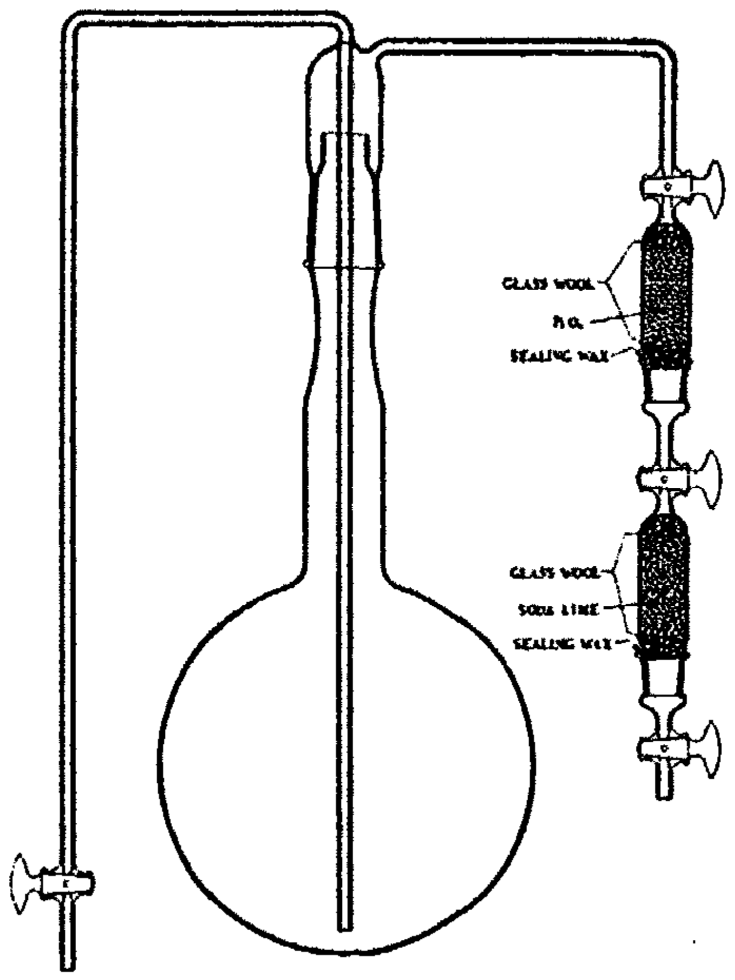

Fig. 1

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[1] Am. Chem. Jour., 40, 558 (1908).

By great care the conductivities can be made to duplicate at $N/1024$ or $N/2048$, or beyond, well enough to obtain the limiting values of μ_∞ to within 1 percent. It is seen in the tables that good values can be obtained up to $N/8096$ and fairly good measurements were made even up to $N/262,144$. In solutions of both sodium iodide and sodium bromide, the maximum molecular conductivity was reached at a dilution of about 4000 or 8000 liters. In the case of sodium, potassium and lithium ethylates μ_∞ was apparently reached at a dilution as low as 2000 liters. From earlier work this was hardly expected, although when we consider the analogy of the latter with sodium hydroxide it is not surprising. Sodium, potassium and lithium phenolates were found to reach their maximum at a slightly greater dilution. By plotting the limiting values of μ_v we can by inspection choose the values of μ_∞ for the different electrolytes at 0°, 25° and 35° and these are given in Table XXXVII. In order to test these values further we have made use of the idea that the temperature coefficients for the dilute solutions of all these electrolytes in alcohol are the same. We have added all the chosen values of μ_∞ at 0° for the different salts and likewise at 25° and at 35°. By comparing these sums we find that on the average the value for μ_∞ at 25° is 1.662 times that at 0°, while at 35° the ratio is 1.979. By adding 19.90, 33.20, and 39.20, the three chosen values of μ_∞ at 0°, 25° and 35° for sodium ethylate, for example, we obtain 92.30, and by dividing this in the ratios 1.000 : 1.662 : 1.979 we obtain the "calculated μ_∞" at 0°, 25° and 35°, namely, 19.89, 33.05 and 39.36, respectively. This was done for all the electrolytes, as shown in Table XXXVII, and it is seen that these "calculated" values of μ_∞ correspond closely to those chosen, the deviation being generally less than 0.5 percent, although reaching 1 percent in a few cases. We have used the chosen value throughout for calculating α, which is given in Column V of each table; the data for α are significant only to the third figure, but we give four. A calculation on our work shows that in the reaction of ethyl bromide with sodium ethylate an error of 0.6 percent in the value of μ_∞ makes a change of only 0.3 percent in the value of K_i and no change in K_m, whereas the other experimental errors make the values of K_i for the sodium, potassium and lithium ethylates and ethyl bromide vary much more. Any error in the μ_∞ chosen is therefore much less than the sum of the other errors. It is clear, therefore, that the values of μ_v, μ_∞ and α are about as accurate as the deviations in K_N make it necessary to have them, and *that the work allows us to prove the crucial point of our theory that both the ions and molecules of acids, bases and salts must be examined for chemical activities.* In the study of "salt catalysis" and the effects of physical factors such as viscosity we shall repeat this work by the use of the more accurate methods.

Two series of conductivities of sodium phenolate were measured. The first were made on solutions prepared by mixing equal volumes of solutions of sodium ethylate and of phenol of the same normality. The volume change due to mixing was found to be too small to affect the results appreciably. In the second series an excess of phenol was present and this excess was increased in constant ratio to the dilution. In this way, alcoholysis of the phenolate should be prevented. A comparison of the two series shows that sodium phenolate is probably slightly alcoholized in solution, the values of the latter series being, in general, somewhat lower than in the first, though not more than 0.3 percent, as can be seen from the summaries of the two series in Table XXXVIII. An excess of phenol was used with both the potassium and lithium phenolates.

Another phase of this work of great importance was the question whether in any case the ionization follows the Ostwald dilution law, as in such instances we cannot tell[1] whether the nonionized molecule or both ions together react. In all the tables we give the constant calculated by the formula

$$\frac{\alpha^2}{(1-\alpha)V} = K$$

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[1] Am. Chem. Jour., 43, 516 (footnote), 519 (1910); 48, 372–377 (1912); 49, 477–480 (1913).

and it is seen that the lithium ethylate and lithium phenolate are the only electrolytes "weak" enough to give an approximate constant. The errors discussed above are so great that the data are significant only to the second figure, but we give three. The Ostwald constant for all the other electrolytes decreases steadily and we shall present in another paper the application of the formulas of Kendall and of Bray and Kraus to the more completed data. Even in the case of the lithium salts the constants for the *N*/1 and *N*/2 solutions are somewhat smaller than the others, and this may be connected with both the viscosity and the use of a volume standard[1] instead of a weight standard.

We have suspected[2] for some time that the differences in the viscosity of the different solutions will be found to have an influence on the velocity of movement of the different substances in solution and hence alter the reaction velocities in certain cases, and change the apparent percent of ionization of the various salts in the solution. If the ions of sodium ethylate move more slowly in the more viscous normal solutions than they do in the *N*/8 solutions, the conductivity measurements will not give us a true measure of the relative percent of ionization in the two cases. We should be compelled, therefore, to make a correction for the viscosity of the more concentrated solutions. No method is known at present, however, for doing this with certainty. One of us wrote of this problem to Professor A. A. Noyes, who at once kindly sent us two pages of a manuscript which he has since published.[3] Noyes' method is to multiply the apparent percent of ionization of the salt in a given solution by some

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[1] Morse and Fraser: Am. Chem. J., **26**, 80 (1901); **28**, 1 (1902); **29**, 173 (1903); **32**, 93 (1904); **34**, 1 (1905); **36**, 1, 29 (1906); **37**, 324, 425, 558 (1907), and later papers. Carnegie Institution of Washington Publication No. 198. Lewis: J. Am. Chem. Soc., **30**, 668 (1908). Acree and coworkers: Ber. deutsch. Chem. Ges., **41**, 3222 (1908); Kendall: J. Am. Chem. Soc., **36**, 1069 (1914).

[2] Am. Chem. Jour., **39**, 231 (1908); **41**, 480 (1909), and later papers.

[3] Noyes, Lombard and Falk: Jour. Am. Chem. Soc., **33**, 1424 (1911); **34**, 454 (1912); Washburn: Ibid., **33**, 1464 (1911); Johnston: Ibid., **31**, 1010 (1908); Green: Jour. Chem. Soc., **93**, 2049 (1908).

power of the ratio of the viscosity of this solution to that of the pure solvent. The power chosen by them as a first approximation was unity. We believe, however, that this correction is far too large. Table XXXIX gives a summary of some measurements of the relative viscosities of solutions of sodium ethylate, sodium phenolate, sodium iodide and of various mixtures of these at 25° and 35°. These were made for us by Dr. J. Sam Guy, to whom we are greatly indebted for this and other favors. Tables III, IV, XII, XIII, XXII, XXIII and XXXIX show that the relation of the viscosities and the conductivities of *N*/1, *N*/2 and of *N*/4 solutions of sodium iodide, sodium phenolate and sodium ethylate at 25° and 35°, for example, are such that if we were to apply Noyes' method we should arrive at the conclusion that the percent of ionization is practically the same for the *N*/1, *N*/2 and *N*/4 solutions of each salt. Such a conclusion is, however, not in harmony with all of the known facts of physical chemistry and certainly is not borne out by our other experimental results.

To illustrate in another way, the Ostwald constant for the *N*/4, *N*/8 and *N*/16 solutions of lithium ethylate and lithium phenolate at 0°, 25° or 35° given in the tables are practically identical with those for the more dilute solutions. If the ratio μ_v/μ_∞ used for each were multiplied by the corresponding viscosity ratio Z_v/Z_∞ the Ostwald constant would be much too large, as would also those for *N*/1 and *N*/2 solutions. It may be that the influence of viscosity should be expressed as a function of the *difference* of the viscosities Z^v and Z_∞ instead of the *ratio* used by Noyes, Washburn and others and that some formula such as

$$\frac{\mu_v\left[1+\left(\frac{Z_v-Z_\infty}{Z_\infty}\right)^n\right]}{\mu_\infty}$$

will be found a closer approximation to the truth. It is clear then that the ratio $\mu_v Z_v/\mu_\infty Z_\infty$ *is much too large* to express the ionization of these concentrated alcoholic solutions, and until further work can be done by the use of methods to give us a direct measure of the real ionic velocities, solvation, etc., we do not see any clear way to correlate viscosity and ionization. We have therefore contented ourselves with the assumption that the ratio μ_v/μ_∞ gives a much closer approximation for α in our concentrated alcoholic solutions than does the expression $\mu_v Z_v/\mu_\infty Z_\infty$ used by Noyes, and we have made all our calculations accordingly. When we have completed all of our studies on viscosity, conductivity, ionic mobility, solvation, and the other relating factors, we can then make the proper corrections in K_i and K_m and the other constants.

It was of interest to us in studying the relation of the isohydric principle to viscosity and the influence of the ions and the molecules of electrolytes on viscosity to learn whether the viscosity of mixtures of electrolytes can be calculated from the viscosities of the separate solutions. This should be the case whenever the ionizations of the electrolytes remain unchanged on mixing and no other physical or chemical changes occur. The data in Table XXXIX show that the viscosities of mixtures of equal volumes of sodium iodide and sodium ethylate having the same concentration, and of sodium iodide and sodium phenolate having the same concentration, are close to the average of the viscosities of the separate solutions provided that they are not more concentrated than $N/2$. This was also found to be the case for the conductivities in Tables XVII, XVIII, XIX, XX and XXIII. The viscosities of the mixtures of $N/1$ solutions are *less* than the average of the separate viscosities and it is notable that the conductivities of the mixtures of $N/1$ solutions of sodium iodide and sodium ethylate are also less than the calculated, as is shown in Tables XVII and XX. The viscosities of the sodium iodide solutions increase directly in proportion to the concentration whereas the viscosities of the solutions of sodium ethylate and sodium phenolate increase more rapidly than the concentrations. This, then, gives us another way to study all these relationships and with more complete data we expect to try to see if the differences between the viscosity of the solvent and the viscosities of solutions of electrolytes can be expressed as functions of the concentrations of both the ions and the molecules, as we do the reaction velocities: namely, $Z_N = Z_i\alpha + Z_m(1 - \alpha)$.

Following the classical investigations of Arrhenius, Barmwater,[1] working with aqueous solutions, has shown that the conductivities of mixtures of both strong and weak electrolytes may be calculated from the known conductivities of the components by assuming that, in such solutions, the solvent is divided between the component electrolytes in proportion to their respective molecular concentrations. Barmwater has studied the conductivities of mixtures of potassium chloride, sodium chloride and potassium nitrate, as well as of mixtures of weak acids such as acetic, propionic, butyric, valerianic and glycollic acids. More recently he has studied the conductivity of mixtures of salts of weak acids, using sodium acetate and potassium acetate. In all of these cases it was found that the agreement between the observed results and those calculated from his theory was very satisfactory, excepting in the more concentrated solutions. In solutions of high concentration, the values observed were generally lower than those calculated.

MacGregor,[2] in his study of the conductivity of mixed electrolytes, has observed the same discrepancy. MacGregor has shown that the conductivities of mixtures of salts of acids could be calculated from the conductivities observed for the separate components. In a study of the conductivities of mixtures of sodium chloride and potassium chloride it was found that, in dilute solutions, the agreement between the calculated and observed values was within the limits of experimental error. In higher concentrations the agreement was not so good. He pointed out that, while his method of calculation assumed that there were no changes in the ionic velocities of the constituents, due to the mixture, such changes

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[1] Zeit. phys. Chem., 28, 424 (1899); 45, 557 (1903); 56, 225 (1906).

[2] Trans. Nova Scotia Inst. Sciences, 9, 101.

might occur and would account for the discrepancies observed.

McIntosh[1] has continued the work of MacGregor, investigating in particular these abnormal values. This investigator has studied the conductivities of very concentrated mixtures of sodium and potassium chlorides, as well as of mixtures of sodium chloride with hydrochloric acid, in which the ionic velocities of the constituents vary more than in the former case. In saturated aqueous solutions of mixtures of sodium chloride and potassium chloride the value observed was lower by 6.4 percent than that calculated. The discrepancy became less and less with increasing dilution and finally disappeared, the agreement being within the limits of the errors of observation. McIntosh discussed the probable causes of these abnormal results, suggesting changes in ionic velocities. He made no measurements of the viscosities of his solution before and after mixing.

Although a considerable amount of work has been published, dealing with the conductivity of mixed electrolytes in aqueous solutions, these conductivities in other solvents have been almost neglected. Philip and Courtman,[2] working with organic solvents, have shown that the conductivities of mixtures of electrolytes can be calculated as suggested by Barmwater. These authors have measured the conductivities of mixtures of potassium iodide and tetraethyl-ammonium iodide in methyl alcohol, methyl-ethyl ketone, aceto nitrile and nitro-methane. In all cases their solutions were quite dilute and the agreement with the calculated values was very satisfactory. On the other hand, recent work by Sachanov[3] on conductivities of mixed electrolytes in organic solvents having small dielectric constants shows that the conductivity of the mixture is larger than the calculated: the electrolytes seem to tend to increase the ionization of other electrolytes. As a very able discussion of the earlier work of

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[1] Trans. Nova Scotia Inst. Sciences, **9**, 120.
[2] Jour. Chem. Soc., **97**, 1261 (1910).
[3] Zeit. phys. Chem., **87**, 441 (1914).

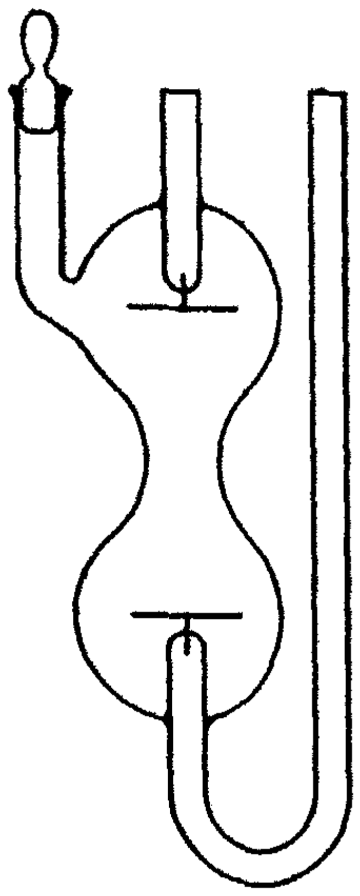
Arrhenius, Euler and the more recent investigations by others is given by Sachanov, further consideration of this subject can be omitted here.

In Tables XVII, XVIII and XXXIII the observed values for the conductivities of the mixtures of equivalent quantities of sodium ethylate and sodium iodide, of sodium ethylate and sodium bromide, and of sodium ethylate and sodium phenolate are given, as well as the values calculated by Barmwater's method. All results are expressed in molecular conductivities. In the tables "V" represents the reciprocal of the molecular concentration of *sodium, potassium or lithium*. Consequently, the molecular conductivities of a mixture of two electrolytes of any given concentration of sodium in a mixture may be calculated by averaging the sum of the conductivities of the components at the same concentration. We give a short series of conductivities in Table XIX, in which two volumes of sodium ethylate were mixed with one volume of sodium iodide, and another in Table XX, in which seven volumes of sodium iodide were mixed with one volume of sodium ethylate of the same concentration. In the first series the molecular conductivities of the mixtures were calculated on the assumption that the ethylate occupies two-thirds of the solution and the iodide one-third of the solution, while in the second the ethylate was assumed to occupy one-eighth of the solution. As may be seen from the tables, the observed values in the more concentrated solutions are slightly lower than those calculated; it was shown in Table XXXIX that the same is true of the viscosities. A closer approximation to the truth is probably the assumption of the isohydric principle used first by Arrhenius, and later by Walker, Noyes, Acree, Bjerrum and others, that each electrolyte occupies a fraction of the whole solution corresponding to the percentage which that electrolyte has contributed to the total number of ions present. We cannot interpolate the available data closely enough to decide this question and are making other measurements to this end. We may therefore conclude that these mixtures obey the isohydric principle and that in the reactions of ethylates and phenolates with the alkyl halides the ethylate or phenolate does not change appreciably in ionization as the reaction proceeds.

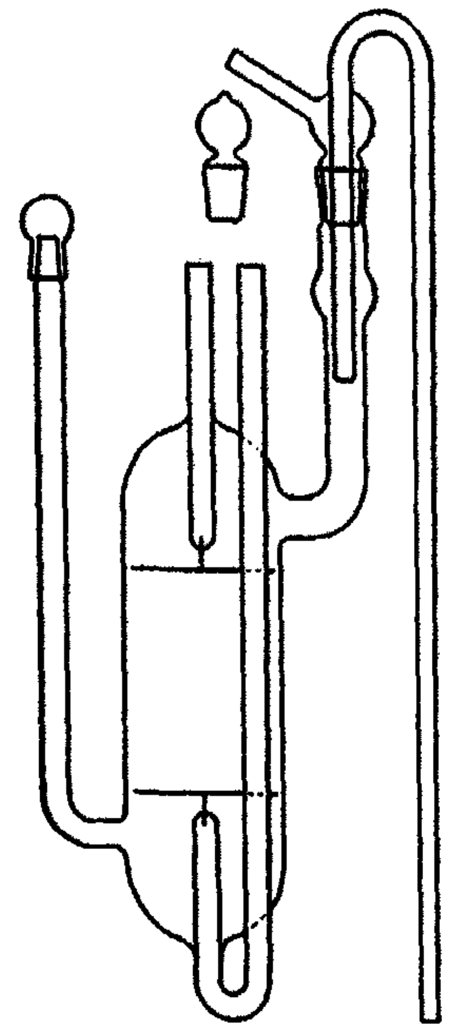
Conductivity Cells

During the first part of the present investigation the cells used were of the Ostwald type in which the platinum electrodes are supported at one edge. This type has been in use in this and other laboratories for a number of years. While, possibly, these cells are not subjected to great changes in constant if handled with the greatest care, it was found very difficult, if not impossible, to prevent changes in their constants from time to time. These sometimes amount to several percent when the plates had been accidentally scraped against the sides of the cell while inserting or removing them, as can be seen in Table I. We have, therefore, spent considerable time designing and investigating cells of somewhat different type, which have been found very satisfactory and with very little tendency towards abrupt changes of cell constant, even when handled more or less carelessly. Twelve of these cells are shown in the accompanying sketches, some of them having been used by others, and Table I gives a few of the constants typical of each.

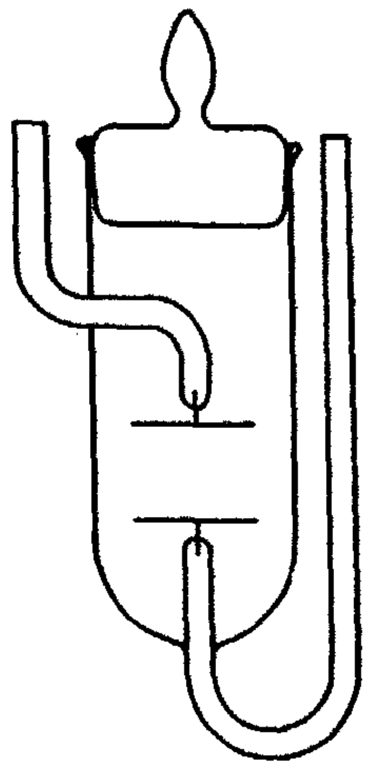
Cell I is of a dumb-bell form, the object of the constriction being to increase the resistance of the cell and to give a high constant. This cell has been found very useful in working with solutions more concentrated than $N/8$. The plates being entirely enclosed and consequently protected from accidental jarring or touching, cells of this type are extremely constant, as will be seen from Table I, in which some of the constants of all the cells used in this work have been tabulated, so as to show the changes from time to time. It is readily filled with the siphon described with Cell II. The total change of constant in this cell during six months of use was 0.2 percent, which is hardly more than the experimental error involved in its measurement. All of our recent more



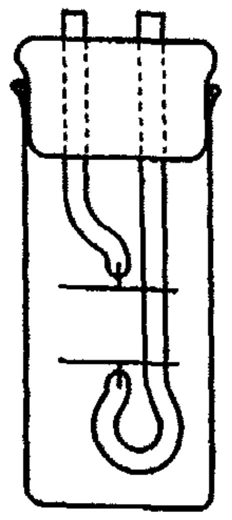
CELL I



CELL II



CELL III



CELL IV

accurate work with cells I and II shows the "cell constant" not to change more than 0.01 percent.

The sketch of Cell II gives an illustration of a modification of Cell I which we devised to allow us to fill the cell directly from the flask in which the solution is made and hence to measure the conductivity of the solution without exposing it to the air or allowing appreciable evaporation, as can also be done with Cell I. The siphon on the right is dipped into the flask containing the desired solution and a small rubber tube is placed on the tube above: suction causes the cell to fill quickly. The siphon is removed and the stopper is inserted in its place. When necessary, sealing wax can be used to seal the two stoppers in place and exclude carbon dioxide and moisture and prevent any changes in the solution such as Lapworth[1] observed in his fine work on the conductivity of alcoholic hydrochloric acid. These cells can be washed out easily by a stream of water or alcohol and then dried by leading air through them. As the bright platinum plates are only 0.5 inch in diameter and the cell is very narrow the uncertainties due to temperature changes are small. Two of these cells have proven extremely valuable and constant, as shown in Table I.

In Cell III the plates are not removable from the cell, but are attached to glass tubes which are sealed in through the sides of the vessel and so bent that the plates are supported at their centers. An open top, instead of the narrow tubes in Cells I and II, allows the cells to be filled, emptied and cleaned readily. Although, as is seen from Table I, cells of this type can be depended on to 0.1 percent, they have not proved so satisfactory on account of their fragility.

Cell IV is a modification of the Arrhenius cell, and has a closed top like those devised in H. C. Jones' laboratory. In this, as in all circular plate cells which have been found satisfactory, the plates are joined to the glass tubes by fairly heavy platinum posts fixed at the *exact centers* of the plate instead

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[1] Jour. Chem. Soc., 93, 2163, 2203 (1908); 97, 21 (1910); 99, 1417, 2224 (1911); 101, 2249 (1912); 103, 252 (1913).

of at *one side* as in the Arrhenius-Jones cell. The bend in the glass tube supporting the lower plate serves the purpose of protecting the plates from scraping against the sides of the vessel while being introduced or withdrawn. As is seen, this bend projects beyond the edge of the plates and affords very good protection to them if one allows the "point" of the bend to slide along in contact with the side of the vessel when opening or closing the cell. As can be seen from the table of cell constants, these cells are also very satisfactory, one cell showing no change greater than 0.1 percent.

A modification of Cell IV is shown in the sketch of Cell V, in which the lower plate only is shown, the upper plate being like that in cell IV. In addition to the bend shown in Cell IV, three spurs or projections have been added, radiating at right angles to each other in a plane parallel to the electrode and projecting beyond the edges of the plate in all four quadrants. With this arrangement it is impossible to scrape the electrode against the sides of the vessel at any time. A record of cells of this type is also given in the table of cell constants, the two cells showing no change greater than 0.1 percent.

A cylindrical type of cell was devised and first described by Turner,[1] working in this laboratory. In the original cell made by Turner, only two cylinders were used, as in Cell VI, and these were kept apart by small beads of glass fused between them. Occasionally some of these beads dropped off, leaving the cylinders less rigid or, perhaps, causing a change in the cell constant. We suggest as an improvement that corresponding holes be bored through both cylinders at four to six places at the top and bottom and that the glass beads of Jena 397^{III} be fused through the holes as in Cell VI. Cells of this type do not lose the beads and remain very constant, the variation of 0.1 percent shown in Table I being within the experimental error involved in measuring cells with such small constants.

We are now testing Cell VII, a modification of Cell VI,

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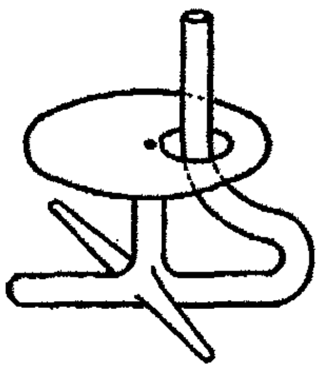
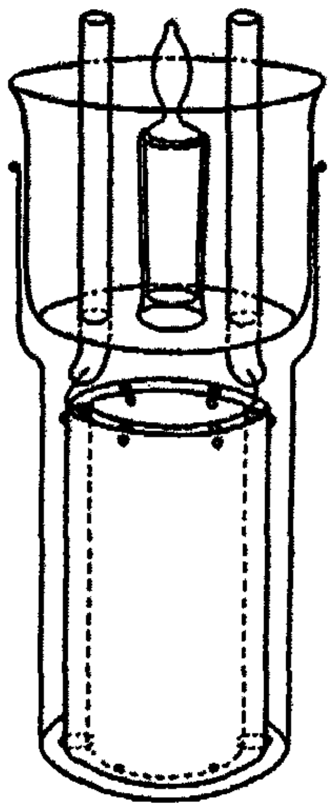
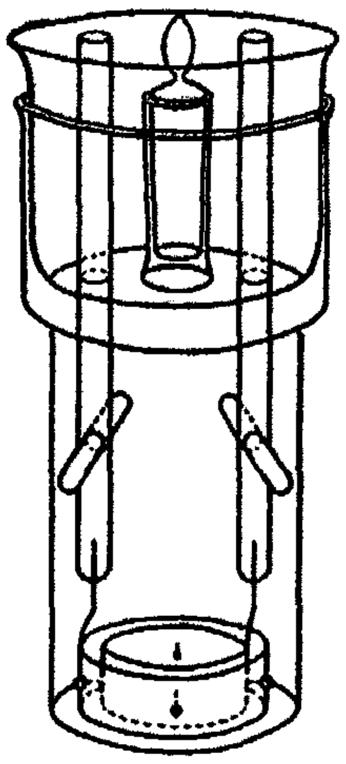
[1] Am. Chem. Jour., 40, 558 (1908).



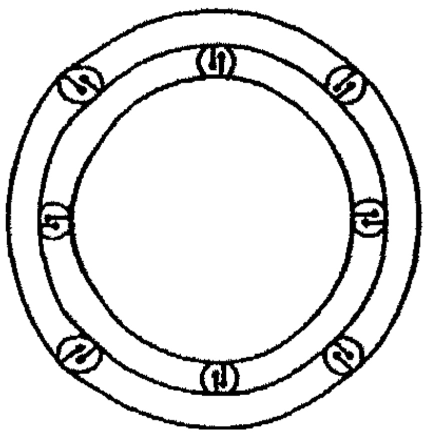
CELL V



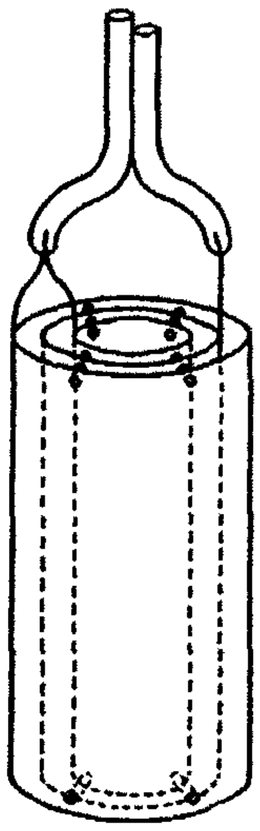
CELL VI



CELL VII



CELL VIII



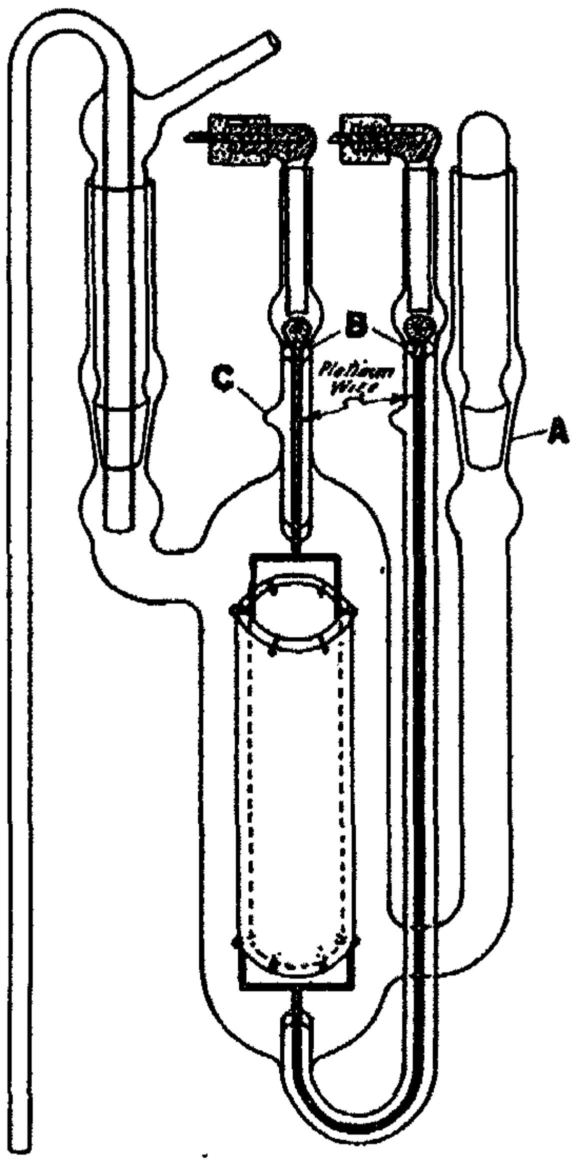
CELL IX

with much shorter cylinders which are fixed at a greater distance apart so as to give a higher constant. Four heavy platinum wires fused on the inner cylinder slip into much larger holes in the outer cylinder. The glass beads, shown as small black circles in the figure, insulate these wires from the outer cylinder and hold the electrodes rigid. Four glass arms attached to the vertical glass tubes of the top prevent the electrodes from striking the sides. The cell constant has not varied more than 0.15 percent.

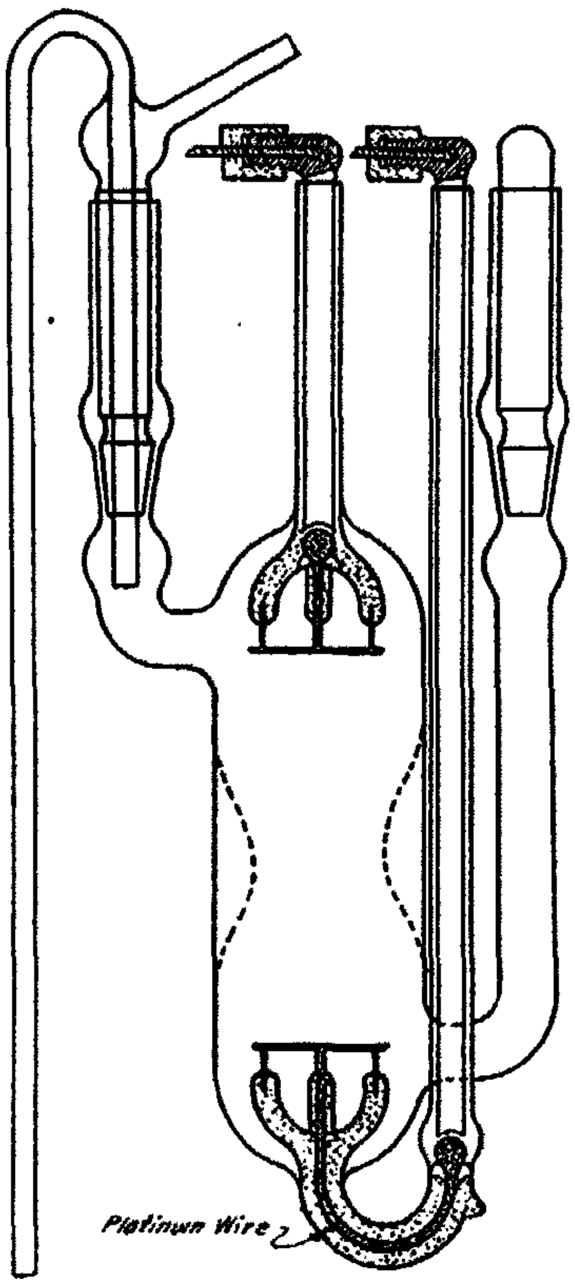
In Cell VIII, which is illustrated only in cross-section, the plates are three long cylinders, like those in Cell VI. The inner and outer cylinders are connected by a heavy platinum wire and form one electrode, while the third cylinder between them is the other electrode. The electrodes are fixed at a distance of about 1 mm apart. In the first cell made, glass beads were used to hold the cylinders, as Turner has done. In the next one made we began the use of very short platinum wires fixed at the top and bottom of the cylinders and at right angles to the cylinders and serving as supports for the glass beads, as illustrated in Cell VIII. The ends of the wires are fused, forming small knobs, which prevent the beads becoming loosened. The short wires on the middle cylinder are exactly opposite those on the outer cylinders and a small globule of glass is fused between these wires. When the cylinders are very close together the wires must overlap as illustrated. The addition of these short wires costs several dollars but is well worth the extra expense. These cells and others with only two cylinders, as shown in Cell VI, have been used extensively in this investigation and, having very low constants, they have been of very great service in working with solutions of high dilution or in determining the conductivity of the pure solvent. They are very constant, as may be seen from Table I, the total change being almost within the experimental error involved in measuring such small constants. We can especially recommend the deep, open top of Cells VI, VII and VIII, as they allow the worker to obtain a firm hold in opening and closing the cells, catch any mercury which might otherwise overflow into the bath and cause damage through amalgamation, and allow the cell to be placed deep in the water of the bath and attain the correct temperature.

A dip cell of type VIII, shown as Cell IX, with a long stem is very useful for measuring the conductivity of a large quantity of the solvent in a bottle.

Cells X, XI and XII show our suggestions how to make excellent cells, measurements with which will be described in detail later. With large, bright or platinized electrodes fixed



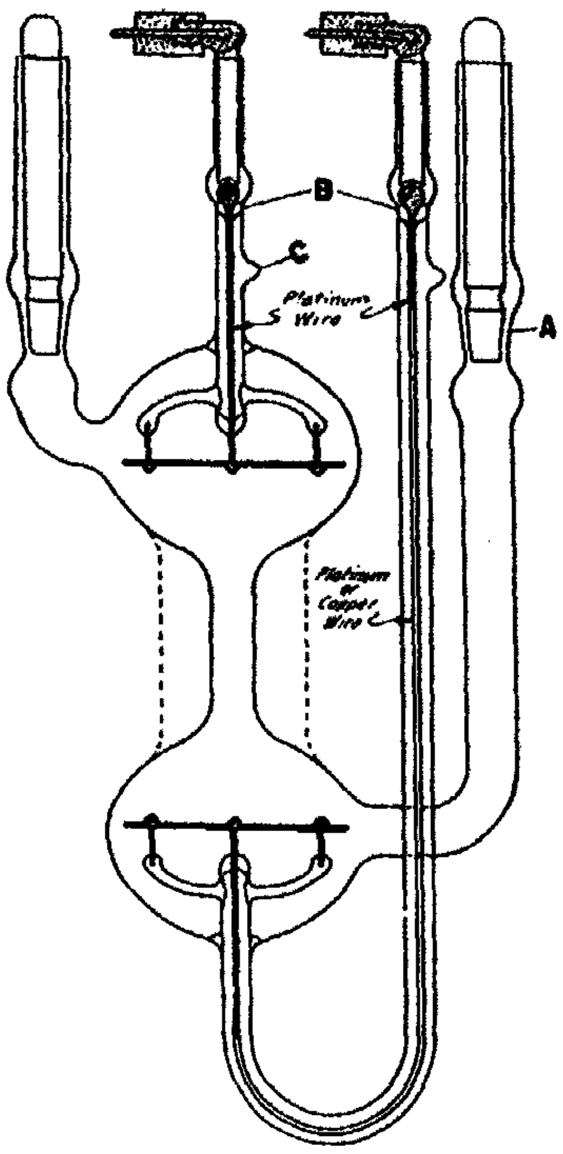
CELL X



CELL XI

in position and ground joints under the surface of the liquid in the bath, it is possible to measure conductivities with a precision of 0.001 percent and an accuracy close to 0.01 percent, the resistance sometimes varying not more than 0.001 percent in 24 hours.

In all of this work we have employed electrodes of bright platinum since it was found that certain solutions, particularly dilute solutions of sodium phenolate, change rapidly in conductivity on standing in cells whose electrodes were coated with platinum black. No difficulty was experienced in obtaining sharp minima when using these bright platinum electrodes, as long as the solutions were used in cells of high enough resistance. A Kohlrausch condenser was of no great aid in securing a minimum in our earlier work, but is of the very greatest importance in all of our recent work having a precision of 0.001 percent and an accuracy of 0.01 percent. An inductance in series with the cell gives the same excellent results.



CELL XII

It is evident that changes in cell constants must be caused almost entirely by increase or decrease in the mean distance between the electrodes, caused either by scraping them against the sides of the containing vessel or by careless handling. In the cells we have described, it is practically impossible to bring the plates into contact with the vessel. However, it was found that, in cells whose circular electrodes were supported at their *exact centers*, no appreciable change in constants was occasioned even when the electrodes were deliberately bent out of place. In a cell of this type, having circular electrodes 25 mm in diameter and about 24 mm apart, giving a cell constant of 291.2, the edge of one of the plates was intentionally pushed downwards a distance of three millimeters towards the other plate. The opposite edge of the plate was found to have moved upwards a corresponding amount, and the constant, when redetermined with the plates in that position, was found to be 291.0, a change of only 0.07 percent. This would be larger if the plates were closer. A cell of similar dimensions, but of the older type in which the plates are supported near one edge, when treated in an identical manner, showed a change in constant amounting to 5.6 percent. Bracing the plates of such cells by means of slender glass rods sealed between them was found to be useless, since these invariably became loosened and fell off after a time.

Temperature Regulation

The conductivity measurements were carried out at three temperatures: 0°, 25° and 35° Centigrade. For the work at 0° a vessel was filled with crushed ice and in this the cells were immersed as far as possible. For the other temperatures thermostats were used, by which it was possible to keep temperatures constant within 0.02°, which was entirely satisfactory for conductivity measurements. The actual temperatures were determined by thermometers which had been calibrated at the U. S. Bureau of Standards at Washington, and which were undoubtedly correct to within 0.01°.

The solutions were always made up to volume at 25° and their conductivities measured at that temperature, after which they were removed to the 35° bath and finally to the ice bath. The conductivities obtained at 35° were corrected for the increase in dilution due to the change from 25° to 35°, and those measured at 0° were in like manner corrected for their increased concentration at that temperature; a small correction was also necessary for the increased or decreased ionization due to these volume changes. As will be seen from the tables, the data have been recalculated by interpolation so as to give values for the molecular conductivities at concentrations which are exact powers of two, these being the concentrations at which they are generally measured.

Solvent

In all of the present investigations the solvent used was ethyl alcohol. This was purified by boiling with silver nitrate for a time and redistilling, after which it was dehydrated in the usual manner by the use of calcium oxide. Particular care was taken to remove the last traces of water. No alcohol containing more than 0.04 percent water was used at any time, while for the high dilutions, where small traces of water might have an appreciable influence on the results, the alcohol used was considerably better than the above. The best alcohol that was obtained for use in this conductivity work had a specific gravity of 0.785065 $\frac{25^\circ}{4^\circ}$. The specific gravities were determined by means of pycnometers of about 50 cc capacity that had been very carefully calibrated.

The conductivity of the best alcohol used was 0.12×10^{-6}; that of the worst was 0.28×10^{-6}. We have had samples as low as 0.07×10^{-6}.

The physical constants of pure ethyl alcohol are now being investigated at length in this laboratory, and Mr. E. C. McKelvey, of the National Bureau of Standards, is now measuring the conductivity and ionization of pure ethyl and methyl alcohol in special platinum apparatus.

Chemicals

The sodium, potassium and lithium used in making the ethylates and phenolates in this investigation were the best obtainable in Germany, being ordered especially for the purpose. No attempt was made to analyze them.

The phenol used was Kahlbaum's best. It was twice redistilled and boiled at 180.0–180.2°, uncorrected. It was kept in vacuum desiccators over sulphuric acid.

The sodium iodide used was Kahlbaum's. It was first dried in an air bath at 130° C and then dried further in a stream of hydrogen. Two duplicate analyses gave a purity of 99.93 percent and 100.02 percent, respectively.

The sodium bromide was Baker's. It was dried in the air bath and analyzed and showed 99.87 percent purity. It was assumed to be pure as the contaminating salts would give a conductivity partly offsetting the 0.13 percent of impurity.

Conductivity Apparatus

The resistance boxes used in the investigation were furnished by Leeds and Northrup and made with the coils as free as possible from inductance and capacity; they were certified to be accurate within 0.05 percent. The slide wire was of the Leeds and Northrup-Kohlrausch type, in which the bridge wire is mounted upon a marble cylinder, extra resistances at the ends of the wire giving greater accuracy.

All conductivity data are referred to the value 129.7 used as the molecular conductivity of $N/50$ potassium chloride at 25°.

In the following tables duplicates of all measurements are given. In many cases, three or more determinations were made of a complete series of conductivities or of individual concentrations. In such cases, the two values were selected which agreed most closely. Correction has been made in all cases for the conductivity of the solvent, which is especially important when the excess of phenol was present.

TABLE I—RECORD OF "CELL CONSTANTS"[1]

Type I	Type II	Type II	Type III	Type III	Type IV	Type IV	Type V	Type V
1535	1253	2821	455.5	75.48	117.1	39.80	291.0	207.0
1535	1255	2817	454.6	75.45	117.1	39.80	291.1	207.1
1538	1253	2826	455.5	75.54	117.1	39.91	291.2	207.1
1536	—	—	455.1	—	117.0	—	291.0	207.1

[1] These cells have only two cylinders.

TABLE I—(*Continued*)

Type VI[1]	Type VI[1]	Type VII	Type VIII	Type VIII	Cells of Ostwald type (plates supported at sides)		
10.06	10.50	39.61	2.140	2.155	268.0	201.0	210.5
10.06	10.50	39.56	2.147	2.161	269.0	202.2	208.5
10.05	10.48	39.61	2.163[2]	2.159	269.3	202.4	208.0
10.05	10.49	—	—	—	265.1	198.0	209.1

TABLE II—CONDUCTIVITY, DISSOCIATION AND OSTWALD CONSTANT FOR SODIUM ETHYLATE AT 0°

V	Conductivity			Dissociation	Ostwald constant
	I	II	Mean		
1	2.72	2.70	2.71	0.1362	0.0215
2	4.74	4.71	4.72	0.2372	0.0369
4	6.67	6.67	6.67	0.3352	0.0433
8	8.61	8.70	8.65	0.4347	0.0418
16	10.57	10.57	10.57	0.5311	0.0376
32	12.59	12.62	12.60	0.6332	0.0342
64	14.44	14.44	14.44	0.7256	0.0300
128	16.27	16.31	16.29	0.8186	0.0289
256	17.79	17.89	17.84	0.8965	0.0303
512	19.13	19.18	19.15	0.9123	0.0185
1024	19.66	19.77	19.71	0.9905	—
2048	20.00	19.92	19.96	—	—
4096	19.90	—	19.90	—	—
8192	19.76	—	19.76	—	—
16384	—	19.74	19.74	—	—
32768	20.62	20.00	20.31	—	—
65536	19.74	19.12	19.43	—	—
131072	—	20.65	20.65	—	—
262144	—	19.18	19.18	—	—

$\mu_\infty = 19.90$

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[1] These cells have only two cylinders.

[2] The plates of this cell were kept apart by small beads of glass sealed directly to the plates, and one of these had become detached.

TABLE III—CONDUCTIVITY, DISSOCIATION AND OSTWALD CONSTANT FOR SODIUM ETHYLATE AT 25°

V	Conductivity			Dissociation	Ostwald constant
	I	II	Mean		
1	4.93	4.93	4.93	0.1485	0.0259
2	7.79	7.76	7.78	0.2344	0.0359
4	10.36	10.37	10.37	0.3123	0.0355
8	13.03	13.05	13.04	0.3928	0.0318
16	15.98	15.98	15.98	0.4814	0.0279
32	19.16	19.16	19.16	0.5771	0.0246
40	20.10	—	20.10	0.6055	0.0232
64	22.52	22.47	22.50	0.6777	0.0223
128	25.60	25.68	25.64	0.7723	0.0205
256	28.90	28.95	28.93	0.8714	0.0231
512	31.35	31.39	31.37	0.9449	0.0316
1024	32.57	32.64	32.60	0.9819	—
2048	33.20	33.06	33.13	0.9979	—
4096	32.81	—	32.81	—	—
8192	32.72	—	32.72	—	—
16384	—	32.30	32.30	—	—
32768	33.67	32.82	33.24	—	—
65536	32.40	31.94	32.17	—	—
131072	—	33.42	33.42	—	—
262144	—	32.06	32.06	—	—

$\mu_\infty = 33.20$

TABLE IV—CONDUCTIVITY, DISSOCIATION AND OSTWALD CONSTANTS FOR SODIUM ETHYLATE AT 35°

V	Conductivity			Dissociation	Ostwald constant
	I	II	Mean		
1	6.04	6.03	6.03	0.1538	0.0280
2	9.11	9.11	9.11	0.2324	0.0352
4	11.93	11.94	11.93	0.3044	0.0333
8	14.80	14.85	14.82	0.3780	0.0287
16	18.09	18.07	18.08	0.4612	0.0247
32	21.78	21.83	21.80	0.5561	0.0218
64	25.88	25.88	25.88	0.6602	0.0200
128	29.86	29.91	29.88	0.7622	0.0191
256	33.85	33.88	33.86	0.8638	0.0214
512	36.95	36.98	36.97	0.9431	0.0305
1024	38.72	38.90	38.81	0.9900	—
2048	39.54	39.40	39.47	—	—
4096	38.99	—	38.99	—	—
8192	39.09	—	39.09	—	—
16384	—	38.62	38.62	—	—
32768	40.16	39.02	39.59	—	—
65536	38.57	37.38	37.97	—	—
131072	—	38.22	38.22	—	—
262144	—	36.86	36.86	—	—

$\mu_\infty = 39.20$

TABLE V—CONDUCTIVITY, DISSOCIATION AND OSTWALD CONSTANT FOR POTASSIUM ETHYLATE AT 0°

V	Conductivity			Dissociation	Ostwald constant
	I	II	Mean		
1	3.76	3.75	3.75	0.1689	0.0343
2	6.03	6.01	6.02	0.2713	0.0505
8/3	6.95	—	6.95	0.3130	0.0535
16/5	7.42	—	7.42	0.3342	0.0524
4	8.10	8.10	8.10	0.3649	0.0524
16/3	8.89	—	8.89	0.4004	0.0501
8	10.20	10.20	10.20	0.4595	0.0488
32/3	10.91	—	10.91	0.4914	0.0445
16	12.16	12.11	12.13	0.5464	0.0411
32	14.14	14.15	14.14	0.6369	0.0349
64	16.29	16.17	16.23	0.7311	0.0311
128	18.04	18.02	18.03	0.8122	0.0274
256	19.66	19.72	19.69	0.8870	0.0272
512	21.02	21.06	21.04	0.9478	0.0336
1024	21.75	21.69	21.72	0.9784	—
2048	22.27	22.08	22.18	0.9991	—
4096	22.05	—	22.05	—	—
8192	21.95	—	21.95	—	—

$\mu_\infty = 22.20$

TABLE VI—CONDUCTIVITY, DISSOCIATION AND OSTWALD CONSTANT FOR POTASSIUM ETHYLATE AT 25°

V	Conductivity			Dissociation	Ostwald constant
	I	II	Mean		
1	6.54	6.55	6.54	0.1758	0.0375
2	9.80	9.78	9.79	0.2632	0.0470
8/3	10.92	—	10.92	0.2935	0.0457
16/5	11.63	—	11.63	0.3126	0.0444
4	12.43	12.43	12.43	0.3341	0.0419
16/3	13.57	—	13.57	0.3647	0.0393
8	15.26	15.26	15.26	0.4102	0.0357
32/3	16.42	—	16.42	0.4414	0.0327
16	18.27	18.24	18.26	0.4908	0.0296
32	21.54	21.54	21.54	0.5790	0.0249
64	25.13	25.01	25.07	0.6739	0.0218
128	28.55	28.56	28.55	0.7675	0.0201
256	31.71	31.87	31.79	0.8546	0.0196
512	34.36	34.35	34.35	0.9234	0.0217
1024	36.24	36.27	36.25	0.9745	—
2048	37.24	37.11	37.17	0.9993	—
4096	36.74	—	36.74	—	—
8192	37.08	—	37.08	—	—

$\mu_\infty = 37.20$

TABLE VII—CONDUCTIVITY, DISSOCIATION AND OSTWALD CONSTANT FOR POTASSIUM ETHYLATE AT 35°

V	Conductivity			Dissociation	Ostwald constant
	I	II	Mean		
1	7.85	7.85	7.85	0.1768	0.0380
2	11.28	11.31	11.30	0.2545	0.0434
8/3	12.57	—	12.57	0.2831	0.0419
16/5	12.30	—	13.20	0.2973	0.0393
4	14.21	14.22	14.21	0.3200	0.0376
16/3	15.46	—	15.46	0.3482	0.0348
8	17.27	17.25	17.26	0.3887	0.0309
32/3	18.57	—	18.57	0.4182	0.0282
16	20.65	20.68	20.66	0.4653	0.0253
32	24.46	24.50	24.48	0.5513	0.0212
64	28.79	28.79	28.79	0.6484	0.0187
128	33.13	33.07	33.10	0.7455	0.0171
256	37.18	37.34	37.26	0.8392	0.0171
512	40.70	40.75	40.73	0.9171	0.0189
1024	43.08	43.12	43.10	0.9706	—
2048	44.53	44.36	44.44	1.0000	—
4096	43.94	—	34.94	—	—
8192	44.36	—	44.36	—	—

$\mu_\infty = 44.40$

TABLE VIII—CONDUCTIVITY, DISSOCIATION AND OSTWALD CONSTANT FOR LITHIUM ETHYLATE AT 0°

V	Conductivity			Dissociation	Ostwald constant
	I	II	Mean		
1	1.30	1.30	1.30	0.0699	0.0053
2	2.68	2.67	2.67	0.1435	0.0121
4	4.10	4.09	4.09	0.2199	0.0155
8	5.80	5.80	5.80	0.3118	0.0177
16	7.61	7.62	7.61	0.4091	0.0177
32	9.65	9.66	9.65	0.5188	0.0175
64	11.62	11.60	11.61	0.6242	0.0162
128	13.54	13.58	13.56	0.7290	0.0153
256	15.37	15.35	15.36	0.8258	0.0153
512	16.74	16.86	16.80	0.9033	0.0165
1024	18.80	18.86	18.83	—	—
2048	18.47	18.60	18.54	—	—
4096	18.56	—	18.56	—	—
8192	18.51	—	18.51	—	—

$\mu_\infty = 18.60$ Calc. $\mu_\infty = 18.40$

TABLE IX—CONDUCTIVITY, DISSOCIATION AND OSTWALD CONSTANT FOR LITHIUM ETHYLATE AT 25°

V	Conductivity			Dissociation	Ostwald constant
	I	II	Mean		
1	2.50	2.49	2.50	0.0804	0.0070
2	4.38	4.37	4.38	0.1408	0.0115
4	6.39	6.38	6.39	0.2055	0.0133
8	8.59	8.58	9.58	0.2762	0.0132
16	11.21	11.19	11.20	0.3601	0.0127
32	14.18	14.14	14.16	0.4553	0.0119
64	17.51	17.47	17.49	0.5624	0.0113
128	21.09	21.05	21.07	0.6775	0.0111
256	24.49	24.44	24.46	0.7865	0.0113
512	27.43	27.63	27.53	0.8855	0.0134
1024	29.72	29.86	29.79	0.9579	—
2048	30.94	31.05	31.00	0.9968	—
4096	31.06	—	31.06	0.9987	—
8192	30.73	—	30.73	—	—

$\mu_\infty = 31.10$ Calc. $\mu_\infty = 30.10$

TABLE X—CONDUCTIVITY, DISSOCIATION AND OSTWALD CONSTANT FOR LITHIUM ETHYLATE AT 35°

V	Conductivity			Dissociation	Ostwald constant
	I	II	Mean		
1	3.07	3.06	3.06	0.0823	0.0073
2	5.18	5.17	5.17	0.1390	0.0112
4	7.35	7.34	7.34	0.1973	0.0121
8	9.71	9.69	9.70	0.2608	0.0115
16	12.61	12.58	12.59	0.3384	0.0108
32	15.95	15.93	15.94	0.4285	0.0100
64	19.82	19.77	19.80	0.5323	0.0095
128	24.01	24.08	24.04	0.6462	0.0092
256	28.30	28.25	28.28	0.7602	0.0094
512	32.01	32.28	32.15	0.8643	0.0108
1024	34.97	35.15	35.06	0.9425	—
2048	37.12	37.37	37.24	0.0000	—
4096	37.22	—	37.22	—	—
8192	36.91	—	36.91	—	—

$\mu_\infty = 37.20$ Calc. $\mu_\infty = 34.30$

TABLE XI—CONDUCTIVITY, DISSOCIATION AND OSTWALD CONSTANT FOR SODIUM IODIDE AT 0°

V	Conductivity			Dissociation	Ostwald constant
	I	II	Mean		
1	7.02	7.10	7.06	0.2802	0.1080
2	9.15	9.12	9.13	0.3623	0.1029
4	11.04	11.06	11.05	0.4385	0.0856
8	12.78	12.89	12.83	0.5091	0.0660
16	14.76	14.60	14.68	0.5825	0.0508
32	16.69	16.73	16.71	0.6631	0.0408
64	18.61	18.56	18.58	0.7373	0.0323
128	20.40	20.42	20.41	0.8099	0.0270
256	21.84	21.75	21.79	0.8647	0.0216
512	23.29	23.31	23.30	0.9246	0.0221
1024	24.34	24.26	24.30	0.9643	—
2048	25.17	25.05	25.11	0.9964	—
4096	25.36	25.14	25.25	—	—
8192	25.36	—	25.36	—	—
16384	25.04	—	25.04	—	—
65536	24.36	—	24.36	—	—

$\mu_\infty = 25.20$

TABLE XII—CONDUCTIVITY, DISSOCIATION AND OSTWALD CONSTANT FOR SODIUM IODIDE AT 25°

V	Conductivity			Dissociation	Ostwald constant
	I	II	Mean		
1	12.52	12.48	12.50	0.3012	0.1298
2	14.84	14.77	14.80	0.3574	0.0994
4	17.46	17.52	17.49	0.4214	0.0767
8	20.09	20.07	20.08	0.4838	0.0567
16	22.81	22.82	22.81	0.5496	0.0419
32	26.02	26.02	26.02	0.6270	0.0329
64	29.30	29.29	29.29	0.7058	0.0265
128	32.24	32.27	32.25	0.7771	0.0212
256	35.10	35.04	35.07	0.8451	0.0181
512	37.48	37.54	37.51	0.9039	0.0166
1024	39.47	39.41	39.44	0.9504	—
2048	40.88	40.68	40.78	0.9827	—
4096	41.61	41.41	41.51	1.0000	—
8192	41.84	—	41.84	—	—
16384	41.56	—	41.56	—	—
65536	40.88	—	40.88	—	—

$\mu_\infty = 41.50$

TABLE XIII—CONDUCTIVITY, DISSOCIATION AND OSTWALD CONSTANT FOR SODIUM IODIDE AT 35°

V	Conductivity			Dissociation	Ostwald constant
	I	II	Mean		
1	15.21	15.26	15.23	0.3046	0.1334
2	17.37	17.40	17.38	0.3476	0.0926
4	20.38	20.50	20.44	0.4088	0.0707
8	23.50	24.55	23.52	0.4704	0.0522
16	26.55	26.51	26.53	0.5306	0.0375
32	30.30	30.28	30.29	0.6058	0.0291
64	34.19	34.21	34.20	0.6840	0.0231
128	37.93	37.94	37.93	0.7586	0.0286
256	41.40	41.33	41.36	0.8272	0.0155
512	44.15	44.19	44.17	0.8834	0.0131
1024	47.12	47.05	47.08	0.9416	—
2048	48.87	48.72	48.80	0.9760	—
4096	49.92	49.70	49.81	0.9962	—
8192	50.22	—	50.22	—	—
16384	50.01	—	50.01	—	—
65536	49.22	—	49.22	—	—

$\mu_\infty = 50.00$

TABLE XIV—CONDUCTIVITY, DISSOCIATION AND OSTWALD CONSTANT FOR SODIUM BROMIDE AT 0°

V	Conductivity			Dissociation	Ostwald constant
	I	II	Mean		
8	10.70	10.70	10.70	0.4598	0.0489
16	12.49	12.48	12.48	0.5363	0.0388
32	14.42	14.34	14.38	0.6179	0.0312
64	16.39	16.25	16.32	0.7013	0.0257
128	18.18	18.15	18.16	0.7804	0.0217
256	19.77	19.73	19.75	0.8487	0.0186
512	21.26	—	21.26	0.9136	0.0189
1024	22.33	22.30	22.31	0.9587	—
2048	23.24	23.23	23.23	0.9982	—
4096	23.58	23.50	23.54	—	—
8192	23.93	23.79	23.86	—	—
16384	23.29	—	23.29	—	—
32768	23.50	—	23.50	—	—
65536	22.00	—	22.00	—	—
131072	21.78	—	21.78	—	—

$\mu_\infty = 23.50$

TABLE XV—CONDUCTIVITY, DISSOCIATION AND OSTWALD CONSTANT FOR SODIUM BROMIDE AT 25°

V	Conductivity			Dissociation	Ostwald constant
	I	II	Mean		
8	16.30	16.33	16.31	0.4216	0.0384
16	19.04	19.09	19.06	0.4927	0.0299
32	22.12	22.16	22.14	0.5723	0.0239
64	25.52	25.54	25.53	0.6600	0.0200
128	28.65	28.70	28.67	0.7412	0.0166
256	31.58	31.59	31.58	0.8164	0.0142
512	24.23	—	34.23	0.8848	0.0133
1024	36.42	36.36	36.39	0.9407	—
2048	38.15	38.21	38.18	0.9870	—
4096	39.16	39.06	39.11	—	—
8192	39.68	39.60	39.64	—	—
16384	39.18	—	39.18	—	—
32768	40.00	—	40.00	—	—
65536	38.77	—	38.77	—	—
131072	38.11	—	38.11	—	—

$\mu_\infty = 39.30$

TABLE XVI—CONDUCTIVITY, DISSOCIATION AND OSTWALD CONSTANT FOR SODIUM BROMIDE AT 35°

V	Conductivity			Dissociation	Ostwald constant
	I	II	Mean		
8	18.90	18.88	18.89	0.4102	0.0357
16	22.09	21.96	22.02	0.4781	0.0274
32	25.53	25.59	25.56	0.5550	0.0216
64	29.67	29.55	29.61	0.6429	0.0181
128	33.56	33.56	33.56	0.7287	0.0153
256	37.29	37.24	37.26	0.8091	0.0134
512	40.63	—	40.63	0.8823	0.0129
1024	42.20	42.14	42.17	0.9157	—
2048	44.08	44.07	44.07	0.9570	—
4096	45.24	45.12	45.18	0.9811	—
8192	45.47	45.31	45.39	0.9856	—
16384	45.14	—	45.14	—	—
32768	46.20	—	46.20	—	—
65536	44.70	—	44.70	—	—
131072	43.55	—	43.55	—	—

$\mu_\infty = 45.20$

TABLE XVII—CONDUCTIVITY OF MIXTURES OF SODIUM ETHYLATE AND SODIUM IODIDE IN EQUAL PROPORTIONS

V	I	II	Mean	Calc.
		0°		
1[1]	4.76	4.78	4.77	4.88
2	6.86	6.87	6.86	6.92
4	8.86	8.76	8.81	8.86
8	10.66	10.68	10.67	10.74
16	12.58	12.68	12.63	12.62
32	14.72	14.66	14.69	14.65
64	16.56	16.62	16.59	16.51
128	18.31	18.27	18.29	18.35
256	19.87	19.87	19.87	19.81
512	21.24	21.27	21.25	21.22
		25°		
1	8.39	8.38	8.38	8.71
2	11.25	11.23	11.24	11.29
4	13.88	13.82	13.85	13.93
8	16.57	16.46	16.52	16.56
16	19.38	19.46	19.42	19.39
32	22.71	22.63	22.67	22.59
64	25.85	25.85	25.85	25.89
128	28.98	28.85	28.91	28.94
256	31.89	31.95	31.93	32.00
512	34.42	34.43	34.42	34.44
		35°		
1	10.00	10.01	10.00	10.63
2	13.26	13.24	13.25	13.24
4	16.22	16.06	16.14	16.18
8	19.06	19.11	19.09	19.17
16	22.33	22.37	22.35	22.30
32	26.14	26.12	26.13	26.04
64	29.98	29.98	29.98	30.04
128	33.81	33.86	33.84	33.90
256	37.56	37.59	37.57	37.61
512	40.64	40.60	40.62	40.57

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[1] The data for this one concentration are somewhat in doubt because of the uncertainty concerning the purity of the sodium iodide used.

TABLE XVIII—CONDUCTIVITY OF MIXTURES OF SODIUM ETHYLATE AND SODIUM BROMIDE IN EQUAL PROPORTIONS

V	I	II	Mean	Calc.
		0°		
8	9.60	9.60	9.60	9.67
16	11.58	11.45	11.51	11.52
32	13.49	13.57	13.53	13.49
64	15.41	15.49	15.45	15.38
128	17.16	17.22	17.19	17.22
256	18.78	18.78	18.78	18.79
512	20.20	20.16	20.18	20.20
		25°		
8	14.57	14.57	14.57	14.67
16	17.55	17.45	17.50	17.52
32	20.63	20.63	20.63	20.65
64	23.94	24.04	23.99	24.02
128	27.20	27.05	27.12	27.15
256	30.28	30.28	30.28	30.25
512	32.67	32.76	32.72	32.80
		35°		
8	16.70	16.74	16.72	16.85
16	20.08	19.92	20.00	20.05
32	23.70	23.70	23.70	23.68
64	27.64	27.74	27.69	27.74
128	31.78	31.70	31.74	31.72
256	35.52	35.66	35.59	35.56
512	38.69	38.69	38.69	38.80

TABLE XIX

CONDUCTIVITY OF MIXTURES OF TWO VOLUMES SODIUM ETHYLATE WITH ONE VOLUME SODIUM IODIDE

	0°				25°				35°			
V	I	II	Mean	Calculated	I	II	Mean	Calculated	I	II	Mean	Calculated
4	8.14	8.14	8.14	8.13	12.68	12.68	12.68	12.74	14.75	14.75	14.75	14.76
8	10.08	10.06	10.07	10.04	15.28	15.34	15.31	15.38	17.69	17.65	17.67	17.72
16	12.07	12.01	12.04	11.93	18.22	18.22	18.22	18.25	20.92	20.92	20.92	20.89

TABLE XX

CONDUCTIVITY OF MIXTURES OF SODIUM ETHYLATE AND SODIUM IODIDE

Solution	Conductivity $N/1$ ethylate	Conductivity $N/1$ NaI	Calculated for mixtures	Observed	Observed % error
1 part $N/1$ C_2H_6ONa + 7 parts $N/1$ NaI	4.93	12.50	11.55	11.43	—1.0
1 part $N/4$ C_2H_5ONa + 7 parts $N/4$ NaI	10.37	17.49	16.60	16.60	—0.0
1 part $N/16$ C_2H_5ONa + 7 parts $N/16$ NaI	15.98	22.81	21.96	21.94	—0.1

TABLE XXI—CONDUCTIVITY, DISSOCIATION AND OSTWALD CONSTANT FOR SODIUM PHENOLATE AT 0°

V	Conductivity			Dissociation	Ostwald constant
	I	II	Mean		
1	2.46	2.47	2.46	0.1223	0.0170
2	4.00	4.00	4.00	0.1990	0.0247
4	5.73	5.73	5.73	0.2851	0.0284
8	7.68	7.65	7.66	0.3811	0.0293
16	9.54	9.56	9.55	0.4751	0.0269
32	11.51	11.49	11.50	0.5721	0.0239
64	13.43	13.50	13.46	0.6696	0.0212
128	14.92	15.04	14.98	0.7452	0.0170
256	16.72	16.69	16.71	0.8313	0.0160
512	17.96	17.95	17.95	0.8930	0.0146
1024	18.91	18.86	18.88	0.9393	—
2048	19.27	19.40	19.33	0.9616	—
4096	20.43	20.20	20.31	—	—
8192	19.45	—	19.45	—	—
16384	19.15	19.48	19.31	—	—
32768	18.72	—	18.72	—	—
65536	20.22	19.80	20.01	—	—
131072	20.46	—	20.46	—	—

$\mu_\infty = 20.10$

TABLE XXII—CONDUCTIVITY, DISSOCIATION AND OSTWALD CONSTANT FOR SODIUM PHENOLATE AT 25°

V	Conductivity			Dissociation	Ostwald constant
	I	II	Mean		
1	4.14	4.14	4.14	0.1247	0.0178
2	6.41	6.40	6.40	0.1927	0.0230
4	8.75	8.71	8.73	0.2629	0.0234
8	11.41	11.43	11.42	0.3439	0.0225
16	14.15	14.21	14.18	0.4271	0.0199
32	17.16	17.26	17.21	0.5183	0.0174
64	20.42	20.48	20.45	0.6159	0.0154
128	23.34	23.34	23.34	0.7030	0.0130
256	26.31	26.31	26.31	0.7924	0.0118
512	28.96	28.91	28.93	0.8713	0.0115
1024	30.60	30.60	30.60	0.9216	—
2048	32.12	32.08	32.10	0.9668	—
4096	33.21	33.14	33.17	0.9991	—
8192	32.45	—	32.45	—	—
16384	32.80	33.09	32.94	—	—
32768	31.50	—	31.50	—	—
65536	32.44	32.14	32.29	—	—
131072	32.50	—	32.50	—	—

$\mu_\infty = 33.20$

TABLE XXIII—CONDUCTIVITY, DISSOCIATION AND OSTWALD CONSTANT FOR SODIUM PHENOLATE AT 35°

V	Conductivity			Dissociation	Ostwald constant
	I	II	Mean		
1	4.97	4.97	4.97	0.1242	0.0176
2	7.46	7.47	7.46	0.1865	0.0214
4	10.00	10.00	10.00	0.2500	0.0208
8	12.89	12.94	12.91	0.3227	0.0192
16	16.14	16.14	16.14	0.4035	0.0171
32	19.68	19.73	19.70	0.4925	0.0149
64	23.51	23.67	23.59	0.5897	0.0132
128	27.15	26.96	27.05	0.6762	0.0110
256	30.87	30.81	30.84	0.7710	0.0101
512	34.08	33.96	34.02	0.8505	0.0095
1024	36.18	35.99	36.09	0.9022	—
2048	38.25	37.98	38.11	0.9527	—
4096	39.85	39.65	39.75	0.9937	—
8192	38.96	—	38.96	—	—
16384	39.47	39.53	39.50	—	—
32768	37.78	—	37.78	—	—
65536	38.10	37.93	38.01	—	—
131072	37.48	—	37.48	—	—

$\mu_\infty = 40.00$

TABLE XXIV—CONDUCTIVITY, DISSOCIATION AND OSTWALD CONSTANT FOR SODIUM PHENOLATE USING EXCESS OF PHENOL AT 0°

V	Excess phenol	Conductivity			Dissociation	Ostwald constant
		I	II	Mean		
1	0%	2.46	2.47	2.46	0.1224	0.0171
2	10%	3.98	3.99	3.98	0.1980	0.0244
4	20%	5.70	5.70	5.70	0.2836	0.0281
8	40%	7.59	7.61	7.60	0.3781	0.0287
16	80%	9.52	9.51	9.51	0.4731	0.0265
32	160%	11.46	11.44	11.45	0.5696	0.0236
64	320%	13.57	13.47	13.52	0.6726	0.0216
128	640%	15.08	15.19	15.14	0.7532	0.0180
256	1280%	16.90	16.72	16.81	0.8363	0.0167
512	2560%	17.97	17.95	17.96	0.8935	0.0146
1024	5120%	18.78	18.86	18.82	0.9363	—
2048	10240%	19.26	19.49	19.37	0.9637	—
4096	20480%	19.94	20.16	20.05	0.9975	—
8192	40960%	20.16	—	20.16	1.0000	—
32768	163840%	20.07	—	20.07	—	—

$\mu_\infty = 20.10$

Table XXV—Conductivity, Dissociation and Ostwald Constant for Sodium Phenolate Using Excess of Phenol at 25°

V	Excess phenol	Conductivity			Dissociation	Ostwald constant
		I	II	Mean		
1	0%	4.14	4.14	4.14	0.1247	0.0178
2	10%	6.38	6.37	6.37	0.1919	0.0228
8/3	13.3%	7.01	—	7.01	0.2111	0.0212
4	20%	8.70	8.70	8.70	0.2620	0.0233
8	40%	11.30	11.32	11.31	0.3407	0.0220
16	80%	14.12	14.12	14.12	0.4253	0.0197
20	100%	15.13	—	15.13	0.4557	0.0191
32	160%	17.17	17.16	17.16	0.5196	0.0173
64	320%	20.49	20.41	20.45	0.6160	0.0154
128	640%	23.39	23.39	23.39	0.7045	0.0131
256	1280%	26.36	26.20	26.28	0.7916	0.0124
512	2560%	28.80	28.60	28.70	0.8645	0.0108
1024	5120%	30.48	30.57	30.52	—	—
2048	10240%	31.50	31.70	31.60	—	—
4096	20480%	33.17	33.32	33.25	—	—
8192	40960%	33.74	—	33.74	—	—
32768	163840%	31.56	—	31.56	—	—

$\mu_\infty = 33.20$

Table XXVI—Conductivity, Dissociation and Ostwald Constant for Sodium Phenolate Using Excess Phenol at 35°

V	Excess phenol	Conductivity			Dissociation	Ostwald constant
		I	II	Mean		
1	0%	4.97	4.97	4.97	0.1243	0.0176
2	10%	7.46	7.47	7.46	0.1865	0.0214
4	20%	9.98	9.98	9.98	0.2495	0.0206
8	40%	12.84	12.88	12.86	0.3215	0.0190
16	80%	16.05	16.13	16.09	0.4023	0.0169
20	100%	17.16	—	17.16	0.4290	0.0161
32	160%	19.62	19.65	19.63	0.4907	0.0148
40	200%	20.79	—	20.79	0.5198	0.0141
64	320%	23.55	23.55	23.55	0.5887	0.0132
128	640%	27.16	27.18	27.17	0.6795	0.0113
256	1289%	30.90	30.74	30.82	0.7705	0.0101
512	2560%	33.96	33.81	33.88	0.8470	0.0092
1024	5120%	36.23	36.31	36.27	0.9068	—
2048	10240%	37.53	37.68	37.61	0.9402	—
4096	20480%	39.95	40.06	40.00	1.0000	—
8192	40960%	40.28	—	40.28	—	—
32768	163840%	40.02	—	40.02	—	—

$\mu_\infty = 40.00$

TABLE XXVII—CONDUCTIVITY, DISSOCIATION AND OSTWALD CONSTANT FOR POTASSIUM PHENOLATE USING EXCESS PHENOL AT 0°

V	Excess phenol	Conductivity			Dissociation	Ostwald constant
		I	II	Mean		
1	0%	3.16	3.16	3.16	0.1430	0.0237
2	10%	4.97	5.01	4.99	0.2258	0.0329
4	20%	6.71	6.71	6.71	0.3036	0.0331
8	40%	8.57	8.56	8.56	0.3873	0.0306
16	80%	10.52	10.49	10.50	0.4751	0.0269
32	160%	12.47	12.43	12.45	0.5633	0.0227
64	320%	14.42	14.42	14.42	0.6525	0.0191
128	640%	16.40	16.29	16.34	0.7393	0.0164
256	1280%	18.38	18.28	18.35	0.8303	0.0159
512	2560%	19.78	19.69	19.74	0.8932	0.0146
1024	5120%	21.68	21.58	21.63	0.9787	—
2048	10240%	21.83	21.74	21.78	0.9855	—
4096	20480%	22.02	22.30	22.16	1.0000	—
8192	40960%	22.04	—	22.04	—	—

$\mu_\infty = 22.10$

TABLE XXVIII—CONDUCTIVITY, DISSOCIATION AND OSTWALD CONSTANT FOR POTASSIUM PHENOLATE USING EXCESS PHENOL AT 25°

V	Excess phenol	Conductivity			Dissociation	Ostwald constant
		I	II	Mean		
1	0%	5.53	5.52	5.52	0.1529	0.0276
2	10%	7.89	7.91	7.90	0.2188	0.0306
4	20%	10.13	10.13	10.13	0.2806	0.0274
8	40%	12.64	12.58	12.61	0.3494	0.0235
16	80%	15.44	15.42	15.43	0.4274	0.0199
32	160%	18.46	18.40	18.43	0.5105	0.0166
64	320%	21.74	21.73	21.73	0.6019	0.0142
128	640%	25.25	25.22	25.24	0.6993	0.0127
256	1280%	28.57	28.49	28.53	0.7903	0.0116
512	2560%	31.32	31.21	31.26	0.8659	0.0109
1024	5120%	33.41	33.22	33.31	0.9227	—
2048	10240%	35.31	35.02	35.17	0.9742	—
4096	20480%	36.18	36.07	36.12	1.0000	—
8192	40960%	36.03	—	36.03	—	—

$\mu_\infty = 36.10$

Table XXIX—Conductivity, Dissociation and Ostwald Constant for Potassium Phenolate Using Excess Phenol at 35°

V	Excess phenol	Conductivity			Dissociation	Ostwald constant
		I	II	Mean		
1	0%	6.62	6.62	6.62	0.1532	0.0277
2	10%	9.00	9.14	9.10	0.2106	0.0281
4	20%	11.43	11.44	11.43	0.2646	0.0238
8	40%	14.21	14.17	14.19	0.3285	0.0201
16	80%	17.43	17.41	17.42	0.4032	0.0170
32	160%	20.96	20.92	29.04	0.4847	0.0142
64	320%	24.84	24.81	24.82	0.5745	0.0121
128	640%	29.14	29.09	29.12	0.6741	0.0109
256	1280%	33.22	33.03	33.13	0.7669	0.0099
512	2560%	36.87	36.73	36.80	0.8519	0.0096
1024	5120%	39.50	39.27	39.38	0.9116	—
2048	10240%	42.02	41.74	41.88	0.9695	—
4096	20480%	43.17	43.12	43.14	0.9986	—
8192	40960%	43.27	—	43.27	1.0000	—

$\mu_\infty = 43.20$

Table XXX—Conductivity, Dissociation and Ostwald Constant for Lithium Phenolate Using Excess of Phenol at 0°

V	Excess phenol	Conductivity			Dissociation	Ostwald constant
		I	II	Mean		
1	0%	1.17	1.17	1.17	0.0654	0.0046
2	10%	2.37	2.36	2.36	0.1319	0.0100
4	20%	3.87	3.86	3.86	0.2156	0.0148
8	40%	5.61	5.62	5.61	0.3134	0.0179
16	80%	7.45	7.45	7.45	0.4162	0.0185
32	160%	9.30	9.29	9.29	0.5190	0.0175
64	320%	11.27	11.23	11.25	0.6285	0.0166
128	640%	13.04	13.06	13.05	0.7290	0.0153
256	1280%	14.56	14.61	14.59	0.8151	0.0140
512	2560%	15.94	15.89	15.92	0.8894	0.01396
1024	5120%	16.90	16.72	16.81	0.9391	—
2048	10240%	17.65	17.58	17.62	0.9844	—
4096	20480%	17.96	17.91	17.94	1.0000	—
8192	40960%	18.09	17.86	17.97	—	—

$\mu_\infty = 17.90$ Calc. $\mu_\infty = 17.6$

Table XXXI—Conductivity, Dissociation and Ostwald Constant for Lithium Phenolate Using Excess of Phenol at 25°

V	Excess phenol	Conductivity			Dissociation	Ostwald constant
		I	II	Mean		
1	0%	2.09	2.09	2.09	0.0706	0.0054
2	10%	2.83	3.83	3.83	0.1294	0.0096
4	20%	5.90	5.89	5.89	0.1990	0.0124
8	40%	8.30	8.30	8.30	0.2804	0.0137
16	80%	10.99	10.97	10.98	0.3709	0.0137
32	160%	13.82	13.85	13.83	0.4672	0.0128
64	320%	16.96	16.98	16.97	0.5733	0.0120
128	640%	20.08	20.10	20.09	0.6787	0.0112
256	1280%	22.96	23.02	22.99	0.7767	0.0106
512	2560%	25.61	25.61	25.61	0.8652	0.0109
1024	5120%	27.37	27.34	27.35	0.9240	—
2048	10240%	28.95	28.97	28.96	0.9784	—
4096	20480%	29.52	29.63	29.57	0.9990	—
8192	40960%	29.35	29.38	29.36	—	—

$\mu_\infty = 29.60$ Calc. $\mu_\infty = 28.8$

Table XXXII—Conductivity, Dissociation and Ostwald Constant for Lithium Phenolate Using Excess of Phenol at 35°

V	Excess phenol	Conductivity			Dissociation	Ostwald constant
		I	II	Mean		
1	0%	2.50	2.50	2.50	0.0708	0.0054
2	10%	4.47	4.47	4.47	0.1266	0.0092
4	20%	6.75	6.74	6.74	0.1909	0.0113
8	40%	9.40	9.38	9.39	0.2660	0.0120
16	80%	12.37	12.36	12.36	0.3501	0.0118
32	160%	15.65	15.63	15.64	0.4431	0.0110
64	320%	19.38	19.39	19.38	0.5490	0.0104
128	640%	23.11	23.16	23.13	0.6553	0.0097
256	1280%	26.76	26.83	26.79	0.7589	0.0093
512	2560%	30.00	29.98	29.99	0.8496	0.0094
1024	5120%	32.54	32.26	32.40	0.9179	—
2048	10240%	34.49	34.53	34.51	0.9776	—
4096	20480%	35.24	35.33	35.28	0.9994	—
8192	40960%	35.10	35.21	35.15	—	—

$\mu_\infty = 35.30$ Calc. $\mu_\infty = 34.6$

Table XXXIII

Conductivity of Mixtures of Sodium Ethylate and Sodium Phenolate in Equal Proportions

	0°				25°				35°			
V	I	II	Mean	Calc.	I	II	Mean	Calc.	I	II	Mean	Calc.
1	2.61	2.61	2.61	2.58	4.54	4.54	4.54	4.53	5.49	5.49	5.49	5.50
2	4.37	4.40	4.38	4.35	7.07	7.07	7.07	7.07	8.30	8.30	8.30	8.28
4	6.16	6.17	6.16	6.18	9.52	9.52	9.52	9.53	10.91	10.92	10.91	10.95
8	8.16	8.16	8.16	8.12	12.12	12.17	12.14	12.17	13.80	13.84	13.82	13.84
16	10.12	10.06	10.09	10.04	15.10	15.06	15.08	15.05	17.17	17.11	17.14	17.08
32	11.99	12.01	12.00	12.02	18.22	18.17	18.20	18.16	20.73	20.68	20.70	20.71
64	13.95	13.95	13.95	13.98	21.46	21.41	21.44	21.47	24.67	24.61	24.64	24.71
128	15.76	15.71	15.73	15.71	24.65	24.60	24.62	24.51	28.59	28.54	28.56	28.52
256	17.39	17.36	17.37	17.32	27.62	27.59	27.60	27.60	32.38	32.34	32.36	32.34

Table XXXIV—Conductivity, Dissociation and Ostwald Constant for Sodium Thiourazole at 0°

V	Conductivity			Dissociation	Ostwald constant
	I	II	Mean		
2	3.13	3.14	3.13	0.1597	0.0152
4	4.98	4.99	4.99	0.2545	0.0217
8	6.84	6.83	6.83	0.3485	0.0233
16	8.74	8.75	8.74	0.4459	0.0224
32	10.76	10.76	10.76	0.5490	0.0209
64	12.58	12.63	12.60	0.6429	0.0181
128	14.49	14.41	14.45	0.7372	0.0162
256	15.92	15.88	15.90	0.8112	0.0136
512	17.39	17.29	17.34	0.8847	0.0133
1024	18.39	—	18.39	0.9383	—
2048	19.08	18.86	18.97	0.9679	—
4096	19.58	19.27	19.43	0.9913	—
8192	19.82	—	19.83	—	—

$\mu_\infty = 19.60$

Table XXXV—Conductivity, Dissociation and Ostwald Constant for Sodium Thiourazole at 25°

V	Conductivity			Dissociation	Ostwald constant
	I	II	Mean		
2	5.46	5.47	5.47	0.1653	0.0164
4	8.21	8.23	8.22	0.2483	0.0205
8	11.05	11.05	11.05	0.3338	0.0209
16	13.91	13.95	13.93	0.4208	0.0191
32	17.06	16.99	17.03	0.5145	0.0170
64	20.05	20.11	20.08	0.6066	0.0146
128	23.12	23.04	23.08	0.6973	0.0125
256	25.77	25.71	25.74	0.7776	0.0106
512	28.62	28.54	28.58	0.8634	0.0107
1024	30.81	—	30.81	0.9308	—
2048	32.15	31.84	32.00	0.9668	—
4096	33.03	33.04	33.04	0.9982	—
8192	33.21	—	33.21	1.0000	—

$\mu_\infty = 33.10$

TABLE XXXVI—CONDUCTIVITY, DISSOCIATION AND OSTWALD CONSTANT FOR SODIUM THIOURAZOLE AT 35°

V	Conductivity			Dissociation	Ostwald constant
	I	II	Mean		
2	6.54	6.56	6.55	0.1650	0.0163
4	9.60	9.61	9.50	0.2418	0.0193
8	12.91	12.91	12.91	0.3252	0.0196
16	16.28	16.31	16.30	0.4106	0.0179
32	19.86	19.86	19.86	0.5003	0.0157
64	23.54	23.54	23.54	0.5930	0.0135
128	27.26	27.19	27.23	0.6859	0.0117
256	30.52	30.45	30.48	0.7677	0.0099
512	33.95	33.87	33.91	0.8542	0.0098
1024	37.19	—	37.19	0.9368	—
2048	38.49	38.12	38.30	0.9647	—
4096	39.65	39.71	39.68	0.9995	—
8192	40.45	—	40.45	—	—

$\mu_\infty = 39.70$

TABLE XXXVII

Salt		0°	25°	35°
KOC_2H_5	Chosen	22.20	37.20	44.40
	Calculated	22.37	37.17	44.26
$NaOC_2H_5$	Chosen	19.90	33.20	39.20
	Calculated	19.89	33.05	39.36
$LiOC_2H_5$	Chosen	18.60	31.10	37.20
	Calculated	18.72	31.12	37.06
KOC_6H_5	Chosen	22.10	36.10	43.20
	Calculated	21.84	36.30	43.23
$NaOC_6H_5$	Chosen	20.10	33.20	40.00
	Calculated	20.10	33.40	39.79
$LiOC_6H_5$	Chosen	17.90	29.60	35.30
	Calculated	17.84	29.65	35.31
NaI	Chosen	25.20	41.50	50.00
	Calculated	25.15	41.79	49.76
NaBr	Chosen	23.50	39.30	45.20
	Calculated	23.27	38.68	46.05
Sodium thiourazole	Chosen	19.60	33.10	39.70
	Calculated	19.93	33.13	39.45
	Ratio	1.000	1.662	1.979

TABLE XXXVIII—COMPARISONS OF THE SUMS OF THE DUPLICATE SERIES OF CONDUCTIVITY MEASUREMENTS

Salt	Temp.	I	II	Variation in percent
$NaOC_2H_5$	0°	153.19	153.48	0.18
	25°	245.39	245.44	0.02
	35°	286.55	286.78	0.08
KOC_2H_5	0°	173.42	173.06	0.21
	25°	277.07	276.97	0.04
	35°	323.13	323.24	0.03
$LiOC_2H_5$	0°	125.68	125.99	0.24
	25°	198.43	198.65	0.11
	35°	230.10	230.37	0.11
$NaOC_6H_5$	0°	142.13	142.34	0.14
	25°	223.77	223.87	0.04
	35°	261.18	260.62	0.22
$NaOC_6H_5$ + excess phenol	0°	142.27	142.40	0.09
	25°	222.83	222.68	0.07
	35°	260.25	260.36	0.04
KOC_6H_5 + excess phenol	0°	158.89	158.37	0.33
	25°	245.69	244.85	0.35
	35°	285.30	284.37	0.33
$LiOC_6H_5$ + excess phenol	0°	119.13	118.84	0.25
	25°	186.86	186.89	0.01
	35°	217.42	217.23	0.09
NaBr	0°	158.98	158.44	0.34
	25°	252.01	252.21	0.07
	35°	293.95	293.62	0.12
NaI	0°	205.09	204.85	0.12
	25°	328.21	327.91	0.10
	35°	386.97	386.94	0.00
Sodium thiourazole	0°	132.30	131.93	0.28
	25°	216.21	215.74	0.22
	35°	256.14	255.61	0.21
			Average variation	0.15

TABLE XXXIX

VISCOSITIES OF SOLUTIONS OF SODIUM ETHYLATE, SODIUM PHENOLATE, AND SODIUM IODIDE, AND MIXTURES OF THESE ELECTROLYTES IN ABSOLUTE ETHYL ALCOHOL AT 25° AND 35°

Salt	Viscosity at 25°		Viscosity at 35°	
	Found	Calculated	Found	Calculated
N/1 Sodium Ethylate	0.03067	—	0.02398	—
N/2 Sodium Ethylate	0.01866	—	0.01453	—
N/4 Sodium Ethylate	0.01414	—	0.01125	—
N/1 Sodium Iodide	0.01926	—	0.01524	—
N/2 Sodium Iodide	0.01508	—	0.01201	—
N/4 Sodium Iodide	0.01297	—	0.01036	—
Mixtures of Equal Volumes of:				
N/1 Sodium Ethylate and N/1 Sodium Iodide	0.02426	0.02496	0.01852	0.01961
N/2 Sodium Ethylate and N/2 Sodium Iodide	0.01670	0.01687	0.01310	0.01327
N/4 Sodium Ethylate and N/4 Sodium Iodide	0.01368	0.01356	0.01094	0.01080
N/1 Sodium Phenolate	0.03059	—	0.02275	—
N/2 Sodium Phenolate	0.01851	—	0.01436	—
N/4 Sodium Phenolate	0.01423	—	0.01123	—
Mixtures of Equal Volumes of:				
N/1 Sodium Phenolate and N/1 Sodium Iodide	0.02362	0.02492	0.01835	0.01900
N/2 Sodium Phenolate and N/2 Sodium Iodide	0.01661	0.01679	0.01307	0.01319
N/4 Sodium Phenolate and N/4 Sodium Iodide	0.01361	0.01360	0.01079	0.01079
Alcohol	0.01088	—	0.00872	—

Conclusions

1. Alcohol having less than 0.01 percent water and a conductivity around 0.10×10^{-6} was made comparatively easily.

2. When this was used as solvent the conductivities of sodium, potassium and lithium ethylates, sodium, potassium and lithium phenolates, sodium iodide, sodium bromide, sodium 1-phenyl-3-thiourazole, and mixtures of these were measured comparatively easily, duplicate observations agreeing generally within 0.5 percent.

3. The temperature coefficients for the conductivities of the very dilute solutions are practically the same for all the salts and average 2.65 percent per degree between 0° and 25° and 2.8 percent per degree between 0° and 35°. The temperature coefficients for the concentrated solutions are somewhat larger and vary considerably with the different salts.

4. The lithium ethylate and lithium phenolate with solutions more dilute than $N/2$ give a constant when the proper data are inserted in the Ostwald dilution formula. All of the other electrolytes studied give values which gradually decrease as the concentrations decrease.

5. The conductivities of mixtures of the electrolytes studied can be calculated by Barmwater's method for the conductivities of the individual electrolytes, provided that the total concentration of the electrolyte is not more than $N/2$. The conductivities as well as the viscosities of the mixtures of $N/1$ solutions are less than those calculated by Barmwater's method.

6. Electrolytes in ethyl alcohol cause a very much larger percentage increase in viscosity than do the corresponding electrolytes in water. The viscosities of our mixtures of electrolytes are additive, provided that the total concentration is not more than $N/2$. Mixtures of $N/1$ solutions have viscosities smaller than those calculated by this additive principle; the conductivities are also smaller than those calculated by Barmwater's method. The conductivity and the vis-

cosity data show that in these alcoholic solutions having concentrations less than $N/4$ the ratio μ_v/μ_∞ gives a closer approximation to the value of α than does the formula $\mu_v Z_v/\mu_\infty Z_\infty$ used by Noyes, Washburn and others, though neither formula is correct for the $N/2$ and $N/1$ solutions.

Johns Hopkins University
June 1, 1910

NEW BOOKS

Le Froid industriel. *By L. Marchis. 19 × 12 cm; pp. 327. Paris: Librairie Félix Alcan, 1913. Price, 3.50 francs.*—Though the first successful experiments on preserving food by artificial cold were made by a Frenchman, Charles Tellier, the cold storage industry has been developed by English, Americans, and Germans and is of relatively slight importance in France. The author believes that this has been due to the Frenchmen overlooking some of the important conditions during the early development of the industry and it is his object to point out in this book the fundamental principles. The first three chapters deal with the different types of ice machines and the fourth with insulating materials. The fifth chapter describes the construction of a cold-storage warehouse and the sixth the method of keeping different forms of food. Artificial ice is the subject of the seventh chapter, the eighth chapter is concerned with the refrigeration of meat at the packing houses while the ninth chapter deals with the special problem of fish.

On p. 11 the author says: "The success of a warehouse for the cold storage of food depends very largely on the satisfactory thermal insulation of the storage rooms. When once chilled, these must not tend to warm up too rapidly owing to a flow of heat from the outside. As we shall see later, provisions keep their market value only in case all parts of the storage rooms are kept as nearly as possible at a constant temperature. Chilled meat, for instance, must be kept between the limits of +2° and +4° C; a room in which the temperature fluctuated between —4° and +6° would be very unsatisfactory for storing meat. Such a constancy of temperature in different parts of a room is possible only when the room is properly insulated. A carefully constructed insulation is an expensive thing if good materials are used. For this reason people are apt to economize on insulation, and expensive machinery is relied on to counteract defective insulation."

Instead of saying that the vaporization of a liquid absorbs heat, one may say that it produces cold. The author therefore speaks, p. 18, of the production of kilogram frigories instead of the absorption of kilogram calories. On p. 220 the author discusses the conditions for making transparent or opaque ice. The conditions favorable to transparency are agitation, slowness of freezing, absence of dissolved air, and absence of dissolved salts.

Frozen or hard beef must be frozen very slowly if good results are to be obtained. With dry air at —5° it takes several weeks to freeze a quarter of beef, p. 251. With air at —12° to —15° the time is cut down to about four days. Frozen beef is kept at a temperature of —6° to —8° and shows no deterioration inside of six months. Eggs are kept at +2° to +3° and the moisture content of the air must be 75–80% in order to prevent evaporation, p. 208. If properly handled, eggs may be boiled if they have been kept not more than three or four months in cold storage. After four months, however, the evaporation has been sufficient to make it advisable to cook the egg some other way. According to the author six months is as long as an egg should be kept in cold storage.

Wilder D. Bancroft

Chemistry in the High School. *By E. P. Schoch. 22 × 15 cm; Part I, pp. 35. Parts II and III, pp. 210. Bulletins of the University of Texas Nos. 329 and 375. Austin (1914).*—In the preface the author says: "Today our home life, our commerce, and the practice of our trades and professions involve chemical operations so frequently and require so much knowledge of the composition and properties of substances that the acquisition of such knowledge by young people is really a prime necessity. A course in chemistry can give such information. Of course, *training* is the first object of all school work, but in the study of chemistry *training can be given while information of practical value is given.* General facts and principles can be illustrated with material met in daily life as well as, if not better than, with substances rarely met with. A course in chemistry can include more information of practical value than probably any other high school course, and if properly conducted the chemistry course will serve to train young minds just as well as any course primarily designed for this purpose. The study of chemistry gives young people much that is essential in all walks of life and it is an absolute necessity for the great number who deal directly with materials, such as painters, builders, merchants, farmers, housekeepers, etc.

"*The high school chemistry course as generally given up till now does not* attain the above object as nearly as it can be obtained by a course specially designed with this in view. This has just been recognized by a great many chemistry teachers, and the effort to change the chemistry course in accordance with this idea has just begun. Naturally it is very difficult to introduce such a course at this time because there are no text-books on the market which really fit these peculiar conditions. Hence all teachers, even those who are otherwise well prepared in chemistry, must be allowed extra time for planning and executing a course along the new line."

There is no question but that the introductory course in chemistry as given at schools and colleges is not well adapted to those who are not going to take more chemistry. The problem is what to put in its place. The author gives us one solution and a very interesting one. He includes a great deal of material —perhaps too much. It is very doubtful whether such a course should include a chapter entitled: ionization and the general relation between dissolved acids, bases, and salts which results in a metathetical reaction. The following headings to some of the chapters will give some idea of the ground covered: fuels and industrial waters; some experiments on silicates and phosphates—to illustrate some of their industrially important compounds; the effect of forces acting in the surfaces of contact between different substances; the chemical changes at the poles of electrolytic cells; battery cells and oxidation and reduction reactions; the periodic system; the fundamental principles of organic chemistry and the chief types of organic compounds; animal and vegetable fats and oils, carbohydrates, and nitrogenous food constituents.

The object of the author has been rather a condensation than a selection. While this is not exactly the course in chemistry which the reviewer has vaguely in mind, it is an interesting one and it is a distinct step in advance because it is an attempt to adjust our teaching to things as they are. We know perfectly well that only a small percentage of high school students go to college and that only a limited number of the ones who do, go on with chemistry and yet we arrange our introductory course solely for the benefit of those who intend to take other courses in chemistry.

These bulletins have been issued by the University of Texas primarily for the benefit of teachers interested in the teaching of chemistry. In applying for them, teachers should state the positions they hold. No charge is made to teachers in Texas; a charge of fifty cents is made to teachers in other states. Orders should be addressed: Bulletins, University of Texas, Austin. Remittances are payable to the Auditor of the University of Texas.

Wilder D. Bancroft

Leavening Agents. *By Richard N. Hart. 23 × 15 cm; pp. iv + 90. Easton: The Chemical Publishing Co., 1914. Price: $1.00.*—In the preface the author says: "This volume fills a gap in the literature of baking in this country. The baker knows a good deal about his flours and also how they are made, but he knows very little about his yeast and less still about his baking powder. He has been well supplied with literature on the technology and chemistry of flour, but much of the data on his aerating agents has either been much over his head or else has been purposely misleading."

The book deals with yeast, salt-rising fermentation, baking powders, aerated bread, and milk powder. Nowadays, practically all breweries and many distilleries and yeast factories start their mother liquor from a single yeast cell according to one of the pure-culture systems, p. 16. Dry yeast cakes made with fine grain or barley meal were used by the Roman bakers.

The use of yeast runs back a long ways, p. 43. "Barley bread four thousand years old, taken from the tombs of Egypt, showed yeast cells under the microscope. This ancient yeast came from the 'leaven' which was merely a portion of dough taken from a previous batch, and well crowded with all manner of yeasts, wild yeasts and bacteria. As a result leavened bread contained its full share of lactic and other flavors which these mixed ferments set up. This kind of ferment starter has been standard for centuries. The Scotch barm and the potato ferment are modifications of the leaven, in which the mixed yeasts from an original spontaneous fermentation are so treated that bread yeasts become predominant: lactic acid bacillus, which seems to have its function in giving a buttermilk flavor, is encouraged in the barms. After the bakers began to go to the brewer for his top or bottom yeasts, they found that they could save themselves time and money; and later the industry of compressed yeast making has driven barms and potato mixtures out of progressive regions. Compressed yeasts have also helped to make straight dough and short fermentation recipes more popular."

From experiments by Kohman it appears, p. 50, that "the ordinary salt-rising fermentation is brought about by bacteria, which act principally on the sugars of the flour and milk and especially on milk casein. These bacteria seem to consist of a mixed flora, some of which as spores live through the boiling temperature and would be found in batter from boiling milk, while others, not capable of forming spores, died at a temperature of 77° C. Among these was the variety separated for his pure culture; this was thought to belong to the *coli* group—the same that was called *bacillus levans* by Wolffin and Lehman. None of these varieties was kept in liquid media over 24 hours, but could be made up in a dry starchy cake for indefinite future use."

Under baking powders, the author says, p. 62: "The first requirement of a baking powder, of course, is that its reaction in the dough, and its residues, shall be harmless to the consumer. If the 'baking powder controversy' was of special value to the world it was in showing there is no record as yet of injurious result from using any baking powder well made by any of the standard formulas. In a baking powder it is not a question of whether 'alum' is harmful or phosphate and cream of tartar wholesome but of whether their residues in bread are deleterious. Using the three primary powders according to recipe, one would have to eat the following number of biscuits to take a dose of residual salts:

	Biscuits
Cream of tartar	48–96
Phosphates	120–240
Alum	80–160"

The baker and housewife must bear in mind that when a good baking powder is mixed in the dough, "it will be a different substance in the baked bread. Neither 'alum,' phosphate nor cream of tartar will remain."

On p. 69 we read that "the first aerated bread patent was taken out in England in 1832 by Luke Wright. In 1856, Dr. John Dauglish brought forth the process which bears his name. He made bread by mixing flour and water charged with carbon dioxide under pressure. The releasing of the dough in the pans and the heat of the oven expanded the gas in solution and raised the dough. Thus he obtained bread without yeast or fermentation. The primary claims of Dr. Dauglish for his process were that by doing away with the process of fermentation his bread was cheaper and more nutritious. Both his method and the present American method will be here described, more because of their interest and possibilities than because of economic success."

In regard to milk powder, the author says, p. 75: "The first account of powdered milk is found in Marco Polo's report of his travels in Tartary in the interior of Asia. In about 1290 he found the Tartars drying milk in the sun, pulverizing it into powder and placing it in packs to be carried on their excursions into the territory of their enemies. Powdered milk was again heard of in England about 100 years ago. It has recently come to the front very prominently in this country. It is quite likely that wholesale milk users will in time use milk powder to the exclusion of the original liquid....

"Milk can be successfully reduced to powder by removing a portion of its water by agitation in a vacuum pan; the boiling is thus carried on at a temperature below the coagulation point of albumen. This condensed milk is then sprayed into a current of hot air. This reduces the moisture to less than three percent. It is then sterile to the lactic acid bacteria, and can be kept indefinitely. The albumen has not been cooked and the butter fat has not been broken down, because the rapid evaporation of the milk spray reduces the temperature of each spray drop until dry. The pasty stage (between 10 to 40 percent water) has been passed while in the air in a finely divided state. Lewis C. Merrell estimates that each pint of milk has a spray surface of two acres."

Wilder D. Bancroft

THE DENSITY OF OXYGEN

BY ALBERT F. O. GERMANN

The recent perfections in the experimental technique of the work on gases are so manifold and far reaching in their character that measurements of the highest degree of accuracy may now be made in one-half to one-fourth the time the methods of less than fifteen years ago required. This development is giving rise to renewed activity along these lines on the part of investigators, new fields of work have been attacked, and progress made that would have been impossible fifteen years ago. The most conspicuous example of this is the recent work on atomic and molecular weights by purely physico-chemical methods, such, for example, as the revision of the atomic weight of nitrogen, undertaken and carried to successful completion by Guye[1] and his collaborators.

Since oxygen has by common consent been chosen as the basis of all atomic weights, the accuracy of every method wherein the density of this gas is in any way involved is limited by the accuracy with which the density of oxygen is known. Until recently, however, the density of all gases was referred to that of carbon dioxide free air,[2] weighed under the same conditions, and set equal to unity. Hence the determination of any density presupposed a double operation, the consecutive weighing under the same conditions of air and the gas under consideration. Recent investigation has, however, shown that the limit of accuracy attainable in the weight of a pure gas far exceeds that attainable in the weight of air;

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[1] Ph. A. Guye: "Recherches Expérimentales sur les Propriétés Physico-Chimiques de quelques Gaz." Reprinted from the "Mémoires de la Société de Physique et d'Histoire Naturelle de Genève" of December, 1908. "Nouvelles Recherches sur le Poids Atomique de l'Azote," lecture delivered before the Société Chimique de Paris in June, 1905. "Travaux Récents exécutés à Genève sur la Revision des Poids Atomiques," Arch. des Sciences Phys. et Nat. de Genève, **27**, 557 (1909); Zeit. anorg. Chem., **64**, 1 (1909).

[2] See, for example, A. Leduc: "Recherches sur les Gaz.," p. 27 (1898); Ann. chim. phys., (7) **15**, 27 (1898).

and we have been forced to conclude that slight changes in the composition of the latter take place, depending on certain conditions not yet well established.[1]

It is interesting to note, however, that the earliest determinations of the density of gases were performed so as to give the absolute weight of the unit volume; the results so obtained, however, were not strictly comparable, because there was no agreement as to the temperature, pressure, or the units of measurement that should be used to express the results; and the variety of units in use, not to mention the possibility of various interpretations, made a comparison an exceedingly laborious undertaking. So, for example, Th. de Saussure[2] determined the weight of a liter of oxygen saturated with moisture at 12.5° and under a pressure of 758 mm. to be 1.3563 g. Thomas Thompson[3] calculates from this that the density of oxygen referred to air is 1.13521; Dumas and Boussingault[4] from apparently the same data derive the value 1.1056. From this circumstance arose the custom of referring all gas densities directly to air, for then there was no further chance of misunderstanding, and the results were intelligible to everyone. With the international adoption of the metric system for scientific purposes, this objection was no longer valid; but the custom continued in use, despite the objections of such great men as Regnault, and not until very recent times has the faultiness of the system been generally recognized.

But even the absolute weight of a given volume of gas under given conditions varies from place to place; and so, with the refinement of balances, it became necessary to define the place of weighing by indicating the latitude and the height above sea level; in other words, to give the value of the gravity constant "g" at the place where the measurements were

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[1] Ph. von Jolly: Wied. Ann., **6**, 520 (1879); Morley: Am. Jour. Sci., **22**, 417 (1881); Guye, Kovacs and Wourtzel: Comptes rendus, **154**, 1424 (1912).

[2] Annales de Chimie, **71**, 254 (1809); Nicholson's Journal of Natural Philosophy, **26**, 161 (1810).

[3] Comptes rendus, **12**, 1048 (1841).

[4] Ibid., **12**, 1013 (1841); Ann. chim. phys., (3) **3**, 275 (1841).

carried out; this again necessitates annoying calculations to make the results of various experimenters comparable. The most modern usage is that introduced by Morley, in which the density of a gas is the weight in grams of the normal liter, that is, the weight of a liter of the gas under consideration at the temperature of melting ice, under a pressure of 760 mm of mercury, at sea level in latitude 45° N; the expression "normal liter" will be used in the above defined sense in this paper, and designated by the abbreviation *L.N.*

Historical Survey

Galileo in the first half of the seventeenth century had proven that air had weight; but the actual operation of weighing it presented unusual difficulties. However, the first measurements of the weight of air were made a little later by Otto von Guericke, after he had in 1650 invented the air pump. Such early attempts must have been very unsatisfactory, as even the efforts of such great masters as Lavoisier, Berthollet, and Davy, over a century later, were still very crude. Lavoisier makes frequent reference in his works to the densities of oxygen and air, without going into the details of their measurement. This is true of most of the earlier experimenters, and is not to be wondered at, for it was thought that all that was necessary for the determination was to weigh a flask, first empty, and then filled with the gas in question, noting the temperature and the height of the barometer—a very simple operation indeed. Even the method described by Biot in his "Traité de Physique,"[1] a method in use for many years, was anything but accurate, despite the author's recommendation. In its essential details, the method included the following points: A glass globe of five or six liters capacity, provided with a metallic stopcock capable of holding a vacuum, is evacuated as well as possible, the residual pressure measured, and the globe weighed on a good balance. Then the stopcock is slowly opened and the globe allowed to fill with air; the globe is again weighed, and the barometer,

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[1] Biot: Traité de Physique, Paris, 1, 347-398 (1816).

thermometer and hygrometer are read. Finally the globe is again evacuated and filled with the gas whose density is to be determined, and which has been stored over water; the globe is weighed, and barometer, thermometer and hygrometer readings again made. To arrive at the density, a long series of corrections are necessary: air displaced by the globe, cubical expansion of the globe, residual pressure, hygroscopic condition of the gas, reduction to standard temperature and pressure. Further, Biot suggests that the true weight of the globe is best expressed by the average of the weights empty, before and after the weighings full. The quotient of the weight of air into the weight of gas under consideration gave the density relative to the former. The globe was calibrated by means of water, and corrections made to reduce to zero. Then a simple calculation gave the absolute weight, which was reduced to sea level and 45°. It is interesting to note that Biot recognized the danger of filling the globe with a gas saturated with water vapor; for the gas, on expanding in the evacuated globe, cools off to such an extent that a large percent of the water vapor is precipitated on the walls of the globe, which necessarily results in a density that is much too high. Biot indicates that this may be avoided by the desiccation of the gas, but adds that this is less certain, and that by following certain precautions he believes no precipitation takes place.

That Biot erred is plainly shown by the results obtained by him and Arago,[1] for the inexact values of the physical constants in use a hundred years ago would not alone suffice to give the uniformly high values they obtained:

$$L_{N\ air} = 1.299075 \text{ gm.}$$
$$L_{N\ oxygen} = 1.43353 \text{ gm.}$$

The method of Biot and Arago in its essential details remained the standard for a period of forty years; and the high esteem in which it was held may be seen from a remark made by Berzelius and Dulong[2] in choosing a method for similar

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[1] Biot et Arago: Mémoires de l'Institut, 7, 301 (1806).

[2] Ann. chim. phys., 15, 386 (1820).

work: "......après que M. M. Biot et Arago eurent apporté dans la mesure des pesanteurs spécifiques des principaux gaz les soins les plus minutieux." These authors, however, prefer weighing the gas dry, and recommend collecting it over water covered with a layer of oil to prevent impurities dissolved in the water from contaminating the gas, and subsequently passing the gas over desiccating agents. Notwithstanding these precautions, they arrive at a density for oxygen relative to air much lower than the true value, *viz.*, 1.1026, though it is in the sense that one would suppose; for Biot and Arago had weighed oxygen saturated, or nearly so, with moisture, and air as it was furnished by nature, so that the error on the latter must have been less than in the case of oxygen; this would lead to a higher relative result than when the two gases are weighed in the same state of humidity, or dry, as in the case of Berzelius and Dulong.

During the greater part of the first half of the nineteenth century the values given by Biot and Arago remained classic; and this is not surprising, if we consider for a moment a list of values of the density of oxygen referred to air found by the most careful experimenters, as given by Dumas and Boussingault:[1]

1.087	Foucroy, Vauquelin and Seguin.[2]
1.088	Allen and Pepys.[3]
1.1026	Berzelius and Dulong.[4]
1.103	Kirwan.[5]
1.1036	Biot and Arago.[6]
1.1056	de Saussure.[7]
1.1111	Thomas Thomson.[8]
1.128	Davy

of which the value found by Biot and Arago, 1.1036, happens to be the exact mean.

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[1] Ann. chim. phys., (3) 3, 257 (1841).

[2] Annales de Chimie, 8, 230 (1791).

[3] Phil. Trans., 97, 267 (1807).

[4] Ann. chim. phys., 15, 386 (1820).

[5] Phil. Trans., 71, 7 (1781).

[6] Mémoires de l'Institut, 7, 301 (1806).

[7] Annales de Chimie, 71, 254 (1809).

[8] Annals of Philosophy, 16, 161 (1820); Comptes rendus, 12, 1048 (1841).

Dumas and Boussingault[1] in 1841 brought certain noteworthy perfections to the method. They, like Berzelius and Dulong, weighed the gases dry, and even avoided collecting the gases in tanks over water by choosing a suitable reaction for their preparation as needed, and passing them directly from the generator through desiccating tubes into the globes. The difficult question of the temperature was partially solved by them, in that they suspended an accurate thermometer on the interior of the globe, and placed the globe itself in an air bath whose temperature was kept constant by a layer of water filling an annular space in the walls. They did not start weighing until after the second filling of the globe. In wiping the globe preparatory to weighing it, they noticed that the surface became electrified, which seriously hampered the weighing, for the electricity was but slowly dispersed; they found no remedy. Up to this time weighings had been made on open balances; Dumas and Boussingault rendered their weighings more exact by allowing the globe to hang in a chest beneath the balances. With these precautions, they succeeded in finding a value for the density of oxygen relative to air equal to 1.1057; they did not determine the absolute weight of the liter.

With the work of Regnault[2] a new era in the determination of the density of gases begins. With wonderful insight, he saw the weak points of the methods then in use, and his master mind devised a scheme which so far remedied them that, in its main details, the method is still in use today. The greatest improvement was the introduction of the counterpoise of the same shape, size, weight and material as the globe, which at one blow made the weighings absolutely independent of atmospheric conditions and changes. Of scarcely less importance was the simple expedient of surrounding the globe, during the filling and evacuation, with melting ice, which insured the temperature to at least a hundredth of a degree, and at the same time eliminated all temperature cor-

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[1] Ann. chim. phys., (3) 3, 257 (1841).

[2] Mémoires de l'Academie, 21, 121 (1847).

rections. The pressure was determined as in the older methods —that is, by allowing equilibrium to be established with the atmosphere, and reading the atmospheric pressure; this was read from a special barometer of 20 mm internal diameter. The residual pressure was determined directly on a specially designed baro-manometer of which the barometer above mentioned formed a part. The globe, of about ten liters capacity, was supplied with a brass stopcock, as in the older methods. The volume was determined by filling with distilled water at zero, the whole being plunged in melting ice for a period of from twelve to eighteen hours to attain this temperature, and weighed in a room whose temperature was 4° to 6° C, to keep the water from overflowing. In filling the globe with a new gas, the gas was not considered pure until the globe had been filled with it at least three times, and evacuated as well as possible each time. Then to avoid electrification by wiping, Regnault wiped with a damp cloth. The globe, ready for weighing, was suspended from the beam of a balance and left until the next day, when the weighing was made by observing the deflections of the needle with a telescope.

Regnault arrived at the following values:

Weight of a liter of oxygen in Paris........	1.429802 gm.
Weight of a liter of air....................	1.293187 gm.

This gives us:

$$L_{N\,\mathrm{oxygen}} = 1.42933 \text{ gm.}$$
$$L_{N\,\mathrm{air}} = 1.29276 \text{ gm.}$$

Accepted, as the method was, as the standard of excellence by the scientific world, the numerical results of Regnault's work were the classic values through a long series of years; and a series of articles has appeared in which various corrections have been applied. It would be useless to discuss these corrections here, for experience has shown that where a series of small corrections has been neglected, as was the case in Regnault's work, they tend to neutralize one another, being first positive, then negative. That we may consider this to have occurred, a few points tend to show: no one will dispute that, of all the gases worked on by Regnault, air was the purest, and the value found by him coincides exactly with that found later by Leduc, *viz.*, $L_{N\ air}$ = 1.29273; on the other hand, if we apply the corrections advocated since Regnault's time, his number becomes $L_{N\ air}$ = 1.29306, a difference of two and a half parts in ten thousand,[1] which seems hardly probable. Leduc[2] is probably right when he says that so many corrections are not permissible; hence we will adopt as his number, the result which he himself indicates.

Some years later, Ph. von Jolly made some measurements on oxygen and air, and showed that globes of a capacity of one liter could be successfully used in the determination of gas densities; the globe employed by him was provided with a glass stopcock instead of the classic brass cock, and so the dead weight was reduced from about a kilogram to 150 grams. Von Jolly arrived at the following values for the normal liter:[3]

$$L_{N\ oxygen} = 1.42892 \text{ gm.}$$
$$L_{N\ air} = 1.293085 \text{ gm.}$$

Lord Rayleigh indicates[4] that these values should be corrected for the contraction of the globe when evacuated, and deduces the figures:

$$L_{N\ oxygen} = 1.42924 \text{ gm.}$$
$$L_{N\ air} = 1.29340 \text{ gm.}$$

Von Jolly found differences in the density of air, which he attributed to changes in its composition, depending on the direction of the wind.

The first important work to appear after this was that of Lord Rayleigh,[5] who first called attention to the fact that the compressibility of the globe when evacuated had been neglected by previous experimenters. Besides the question of

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[1] For these notes, see the following: W. Lasch: Pogg. Ann. Ergänzungsband, **3**, 321 (1853); R. Kohlrausch: Ibid., **98**, 178 (1856); Crafts: Comptes rendus, **106**, 1662 (1888).

[2] "Recherches sur les Gaz.," p. 26.

[3] Wied. Ann., **6**, 520 (1879).

[4] Proc. Roy. Soc., **53**, 134 (1893).

[5] Ibid., **43**, 356 (1888); **53**, 134 (1893); Chem. News, **57**, 73 (1888).

contraction, Rayleigh paid much attention to the difficult question of the pressure. He used a special form of manometer, which required that the pressure be always brought to the same value, *viz.*, the distance between two points of an iron rod. The diameter of the barometric tube was 21 mm. Before each reading of the instrument, the vacuum above the upper mercury surface was tested by renewing the vacuum with the mercury pump. The entire apparatus was composed of glass sealed together, a very important innovation. The globe used had a capacity of about 1800 cc. The values found by Rayleigh are as follows:

$$L_{N\ oxygen} = 1.42904 \text{ gm.}$$
$$L_{N\ air} = 1.29284 \text{ gm.}$$

In 1895, E. W. Morley[1] published his great work on the densities of oxygen and hydrogen. He described an extremely carefully conducted series of measurements, using globes of from 8 to 21 liters capacity, and varying the conditions of his experiments very greatly (conditions such as the temperature, the source of the gas, and method of determining the pressure). In three series of determinations, comprising in all 41 experiments, he reached the following results for oxygen:

$$\text{1st series, } L_{N\ oxygen} = 1.42879 \text{ gm.} \pm 0.000034$$
$$\text{2nd series, } L_{N\ oxygen} = 1.42887 \text{ gm.} \pm 0.000048$$
$$\text{3rd series, } L_{N\ oxygen} = 1.42917 \text{ gm.} \pm 0.000048$$

and giving the third series double weight in the calculation of a mean, he reaches the value:

$$L_{N\ oxygen} = 1.42900 \text{ gm.} \pm 0.000034$$

Julius Thomsen[2] in 1896 by a simple volumetric method found for oxygen the value:

$$L_{N\ oxygen} = 1.42906 \text{ gm.}$$

Two years later Leduc published his great researches on the gases.[3] He used globes of about 2.3 liters capacity, an

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[1] Smithsonian Contributions to Knowledge (1895); Zeit. phys. Chem., **20**, 68 (1896).

[2] Zeit. anorg. Chem., **12**, 1 (1896).

[3] Ann. chim. phys., (7) **15**, 5 (1898); reprint, "Recherches sur les Gaz.," Gauthier-Villars, Paris (1898).

apparatus whose parts were connected by lead capillary tubing, and a special barometer of 23 mm diameter. He paid particular attention to the loss of weight of the evacuated globe, taking as its real weight at the moment of weighing the gas under consideration, the mean of the weights when evacuated before and after. Thus he found the weights of the normal liter of oxygen and air to be:

$$L_{N\ oxygen} = 1.42876\text{ gm.}$$
$$L_{N\ air} = 1.29273\text{ gm.}$$

The oxygen was obtained from two sources, electrolysis and potassium permanganate. Leduc believes to have proven that the composition, and hence the density, of air varies from place to place, and from time to time.

Of theoretical interest is the work of J. Giesen,[1] who determined the density of oxygen relative to air, using the microbalance of Salvioni, and applying the principle of Archimedes—the change in equilibrium was found when a light glass bulb floated in air and in the gas studied. The absolute weights were derived by using Leduc's value for the density of air, so that they can hardly be considered as having any great value; besides this, the oxygen used was a commercial sample, carefully dried, but otherwise not purified. Giesen arrived at a density relative to air for the oxygen he used equal to 1.1051.

In Geneva, Jaquerod and Pintza[2] determined the density of oxygen by a volumetric method, but only to test out their apparatus; the oxygen weighed was obtained by heating ordinary potassium permanganate in a vacuum. They arrived at the value:

$$L_{N\ oxygen} = 1.4292\text{ gm.}$$

but believed the result to be too high. Reference will be made in this paper to the probable cause (see page 474).

The following year, R. W. Gray[3] during his work on the atomic weight of nitrogen found occasion to determine the

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[1] Drude's Ann., **10**, 830 (1903).

[2] Comptes rendus, **139**, 129 (1904).

[3] Jour. Chem. Soc., **87**, 1601 (1905).

weight of oxygen gas. He used a globe of about 300 cc capacity, and a barometer measuring 20 mm internal diameter, connected up with a mercury pump as in Rayleigh's work. The gas was obtained by heating pure recrystallized potassium permanganate. From Gray's results, Guye[1] calculated the weight of a normal liter of oxygen to be:

$$L_{N\ oxygen} = 1.42896 \text{ gm.}$$

In Neuchâtel, Jaquerod and Tourpaian[2] worked along lines similar to those of Giesen; working with ordinary precision balances, they were able to apply the principle of Archimedes successfully to the accurate determination of gas densities. By their method they were led to the value:

$$L_{N\ oxygen} = 1.4290 \text{ gm.}$$

Guye, Kovacs and Wourtzel[3] made thirty determinations of the density of air in Geneva, and obtained the mean value:

$$L_{N\ air} = 1.2930 \text{ gm.}$$

They were led to the conclusion already signalled by Morley[4] that the density of air depends on the place, the altitude, and the barometric changes: a rising barometer being accompanied by descending currents of air bringing supplies from the upper strata of the atmosphere less rich in oxygen, and tending to decrease the density of the air; a falling barometer would have the opposite effect.

Table I contains all the more important values attributed to the normal liter of oxygen and air; of these, the values found before Rayleigh's time have little more than historical interest.

The value generally admitted today for the density of oxygen is:

$$L_{N\ oxygen} = 1.4290 \text{ gm.}$$

The little differences found in its density can probably be traced to slight impurities in the gas; the work which forms the basis of this paper was undertaken in the hope of adding

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[1] Jour. chim. phys., **5**, 203 (1907).

[2] Arch. Sci. phys. nat., (4) **31**, 20 (1911).

[3] Comptes rendus, **154**, 1584 (1912); Jour. chim. phys., **10**, 332 (1912).

[4] Am. Jour. Sci., **22**, 417 (1881).

something to our knowledge of this point, and to determine the density of oxygen purified by the best methods at our command.

Table I

Author	$L_{N\ \mathrm{oxygen}}$ Gm	$L_{N\ \mathrm{air}}$ Gm	Sp. gr. oxygen
Biot and Arago	1.43353	1.299075	1.1035
Berzelius and Dulong	—	—	1.1026
Dumas and Boussingault	—	—	1.1057
Regnault	1.42933	1.29276	1.10564
von Jolly	1.42892	1.293085	1.10505
Rayleigh	1.42904	1.29284	1.10530
Morley	1.42900	—	—
J. Thomsen	1.42906	—	—
Leduc	1.42876	1.29273	1.10523
Jaquerod and Pintza	1.4292	—	—
Gray	1.42896	—	—
Jaquerod and Tourpaian	1.4290	—	—
Guye, Kovacs and Wourtzel	—	1.2930	—

As to the density of air, it can no longer be doubted that slight variations in the composition of air do occur, and that its density must, therefore, not be constant; this question forms the topic of an excellent review recently published by O. F. Tower.[1] Two series of determinations of the density of air in Geneva were carried out by the author after the completion of the researches recorded in this paper, using the same precautions as those outlined. The results fully confirm the conclusions of von Jolly, Leduc, Morley, and Guye. The first series, three measurements, made during a period of rising barometric pressure, gave for dry, carbon dioxide free air,

$$L_{N\ \mathrm{air}} = 1.2927 \text{ gm.}$$

corresponding to a deficit of oxygen, if the average weight of the normal liter of air in Geneva be taken as 1.2930 gm, the average value found by Guye, Kovacs and Wourtzel. The second series, four measurements, made during a period of falling barometric pressure, gave:

$$L_{N\ \mathrm{air}} = 1.2932 \text{ gm.}$$

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[1] Western Reserve University Bulletin, 15, 158 (1912); Jour. chim. phys., 11, 249 (1913).

corresponding to a deficit of nitrogen (see discussion on page 447).[1]

The work recorded in this paper was carried out in the laboratory of theoretical and technical chemistry of the University of Geneva, under the direction of Professor Ph. A. Guye, whose interest in the progress of the work I take pleasure in acknowledging here, and to whom, as well as to Dr. G. Baume, I wish to express my thanks for friendly advice.

Method

The choice of a method to be used is largely an arbitrary one, for each method in use has its own peculiar advantages. The globe method, modified as it has been in Geneva, is, however, relatively more rapid than the volumeter method, since a single determination furnishes several values; and, as the value of an average depends in large measure on the total number of values obtained, it was decided to adopt this method.

The most important modification which the method of Regnault had undergone in Geneva was the simultaneous use of several globes of various sizes, requiring a greater number of weighings, but in all other points requiring no extra time or labor. By this scheme several important sources of error are controlled and practically eliminated; it may be well to refer to the most important of these.

Accidental errors of calibration are rendered impossible if they be large, or unimportant if small. That large errors due to calibration are impossible was shown in a striking manner in the course of this work: a large globe used in the measurements had been calibrated by O. Scheuer, and subsequently used by J. Kovacs in the course of his work on the density of air;[2] at its completion, the constants of the globe (volume and contraction) were transcribed on a tag, and the whole stored away. An oversight, however, caused an error of 2 cc to be made in the volume. Consequently, this globe gave results

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[1] See Germann: Jour. chim. phys., 12, 103 (1914), for the details of these measurements.

[2] Jules Kovacs: "Thèse de Doctorat," Geneva (1912).

which differed by nearly a quarter of a percent from the results found with the other globes used in the work. A recalibration showed that the volume was 872.33 cc, while the original notes of Mr. Kovacs showed that Mr. Scheuer had found 872.35 cc, a most remarkable agreement.

Errors due to condensation of the gas on the walls of the globes: since this error is a function of the surface exposed to the gas, it depends on the volume of the globe, but is not directly proportional to it; for small differences in volume it can be shown that

$$\frac{ds}{dv} = \sqrt[3]{\frac{32\pi}{3v}}$$

where s is the surface exposed to the gas, and v is the volume of the globe; and for the differences occurring in the globes used in this work, the numerical difference in surface exposed was approximately equal to one-third the numerical difference in volume. By the use of globes differing materially in size, then, this source of error is reduced to a minimum, and any gross errors arising from it could be detected. As the cause of condensation is probably to be traced to the action of moisture in the pores of the glass, the error must diminish in proportion as this moisture is removed, and the results obtained with different sized globes must theoretically approach the same value.

Errors arising from the adherence to the globe of extraneous matter, such as moisture, minute particles of dust or slight deposits of chemicals readily formed in the atmosphere of a chemical laboratory, or to the introduction into the interior of the globe of dust particles or other finely divided material, are reduced to a minimum and made unimportant.

Small errors in the weights used are eliminated. An example will illustrate this. A set of platinum plated analytical weights made and adjusted by Scholl of Geneva, kindly loaned by G. Baume, was used in this work. The weights from one gram down were calibrated carefully, using the method described by Kohlrausch; individual weights showed errors as high as one-tenth milligram. In order to test the necessity of such accurate calibration, the final calculations of density were made in two ways: (*a*) Assuming the weights to be correct; and (*b*) applying the corrections found. The differences found by applying the two methods varied from zero to 1/3000; after taking the averages, however, of each series of four globes, these differences fell to from 1/20000 to 1/30000, or within the limit of error of the weighings.

A second no less important modification was the method of purification of the gas—its liquefaction and fractional distillation at reduced pressures. This is the only satisfactory way of preparing a perfectly pure sample of any gas, for by any other method traces of air are certain to remain; traces which may be negligible, but as to whose presence and quantity there is no indication; hence the necessity of using a method of purification that will eliminate all traces of air, as well as traces of any other impurity. Gases more volatile than the gas to be purified are gotten rid of in the first fractions, which are discarded; the less volatile products remain in the end portion, and are likewise rejected. Only those gases whose vapor pressure curves are approximately the same as that of the gas to be purified, or which form constant boiling mixtures with it, cannot be eliminated. Usually it is possible to purify from such gases by a chemical process, and this should in all cases precede the physical purification.

An innovation introduced into the method in this work is the simultaneous use of four barometers of different diameters, all set up in an air bath. The advantages of such a method can readily be seen; for by the use of a series of globes certain important errors have been minimized or eliminated, but the error due to any uncertainty in the pressure has not been affected, so that one of our greatest sources of error, and one that has troubled all experimenters working on the density of gases, remained uncontrolled. As long as this great source of error remained, the accuracy of the other operations was a useless precaution. By increasing, then, the number of barometers correspondingly to the number of globes, we can proportionately decrease the error due to a barometer reading, and make this operation approach in its accuracy the operations already enumerated.

Description of the Apparatus

Experience has shown that an apparatus constructed entirely of glass can be much more relied upon to hold a vacuum than one whose parts are joined together by rubber or lead; and yet the experimenter must be on his guard, for even apparently sound glass tubing may allow air to filter slowly through it. This is due to fine capillary openings running the length of the tube, which, after fusion to the apparatus, may have one end opening on the interior, the other on the exterior, offering an easy passage to gases. Such imperfections are detected most easily by moistening the seals suspected of leaking with some highly colored liquid, taking care to have the apparatus evacuated. After some time the liquid will have filtered through the defective seal, coloring the glass on the interior.

The apparatus used here was constructed entirely of glass: only in one place were rubber connections used, namely to attach the density globes. But even here the use of rubber is dangerous, more dangerous, perhaps, than it would be in any other part of the apparatus; for no matter how careful one may be, there is always the chance of introducing foreign material into the globes when attaching them to the rubber connections. A large majority of the discrepancies in the results are probably to be explained in this way. It would seem highly desirable to replace the rubber connections used here by glass; the flat glass joints used by Wourtzel in the determination of the density of nitrosyl chloride[1] meet all the requirements, and the author is preparing to run a series of gaseous determinations with their aid. The use of the flat glass joints involves a little more risk of breaking the apparatus during a measurement, it is true, but the increased accuracy will more than compensate for the added pains and trouble of manipulation.

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[1] Jour. chim. phys., 11, 29 (1913).

The stopcocks, of which there were about thirty-five on the apparatus in its perfected form, were all of the capillary variety; they were the best obtainable: a small size, furnished by Müller of Liverpool, and a larger size, slightly inclined on the tube, made by Geissler of Bonn. In the preliminary work they were lubricated with the rubber grease recommended by Travers,[1] but it was found that this grease slowly absorbed oxygen, particularly near the capillary opening, where it came in contact with the pure gas; that this absorption gave rise to a change in the properties of the grease; and that in a short time the air found an opening around the glass stopper to the interior of the globe, so that a vacuum could no longer be maintained. The first and simplest remedy that suggested itself was to modify the grease so that it could no longer absorb oxygen. Since the base of the grease, rubber, is an unsaturated compound capable of forming an addition product with an element such as oxygen; this was tried, and proved successful. A current of oxygen was passed into the grease at a temperature of about 150° C until no more was absorbed. The grease, which was much more viscous than it had been, retained its desirable properties, and proved to be a perfect lubricating material for stopcocks required to hold a vacuum indefinitely in contact with oxygen. In fact, the stopcocks of two of the globes used were greased with it, and required no attention throughout the duration of the measurements, and at the end of five months were still in perfect condition; the unmodified grease, on the other hand, had to be changed every two weeks. The stopcocks of the other two globes were greased with the chlorinated grease used by Wourtzel in his work on nitrosyl chloride;[2] this grease has as its base stearine and paraffine, and is saturated with chlorine at an elevated temperature; it gave even better satisfaction than the oxygenated grease, for it was less viscous, and the stopper turned more easily in its socket.

As has been mentioned, a new feature of the method em-

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[1] Travers: Experimental Study of Gases (1901).

[2] Jour. chim. phys., 11, 29 (1913).

ployed was the use of a number of barometers equal to the number of globes employed. The barometers were of two types: the first, I and II in Fig. 1, were of the model currently used in the Geneva laboratory; the second, III and IV in the figure, a special type recently described by the author.[1] The chief point of difference between the two types was in the method of making and maintaining the vacuum. As shown in the figure, barometers I and II were connected up with a mercury pump, by means of which the vacuum was made and controlled; III and IV have their vacuum chambers (*A*,*A*) connected to the capillary overflow tubes (*b*,*b*) and reservoir tubes (*N*,*N*), arranged exactly as the similar tubes in the mercury pump shown at *Z* in Fig. 1, making of them a kind of mercury pump. For an accurate description of the barometer, the reader must be referred to one of the references cited.

The cleaning of the barometers, always a difficult but highly important operation, was accomplished as follows: They were filled with a strong solution of bichromic acid and allowed to stand over night; they were then filled with strong nitric acid containing a few drops of alcohol, and allowed to stand for several hours; they were washed with distilled water free from grease, and finally rinsed with freshly distilled alcohol. After the barometers were placed in position, dry air was passed through them for a week to remove all adsorbed moisture; they were then allowed to stand evacuated for several days, and were filled without heating.

For use in the barometer, mercury was specially purified. Ordinary impure mercury was agitated, by bubbling air through it, for a number of hours with 10 percent nitric acid; as an extra precaution it was also passed through a mercury tower containing the same reagent. It was then distilled in a specially constructed still, composed entirely of glass. Two ordinary distilling flasks, whose side tubes were fused to either end of a long condensing tube, served as distilling and receiving flask. The distilling flask had fused into its neck a tube

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[1] Jour. Am. Chem. Soc., 36, 2456 (1914); Jour. chim. phys., 12, 78 (1914).

extending to the bottom of the flask and terminating above in a Y, one branch of which was drawn out to a fine capillary tube, to admit a slow current of air during distillation; the other carried a stopcock and a thistle tube, through which

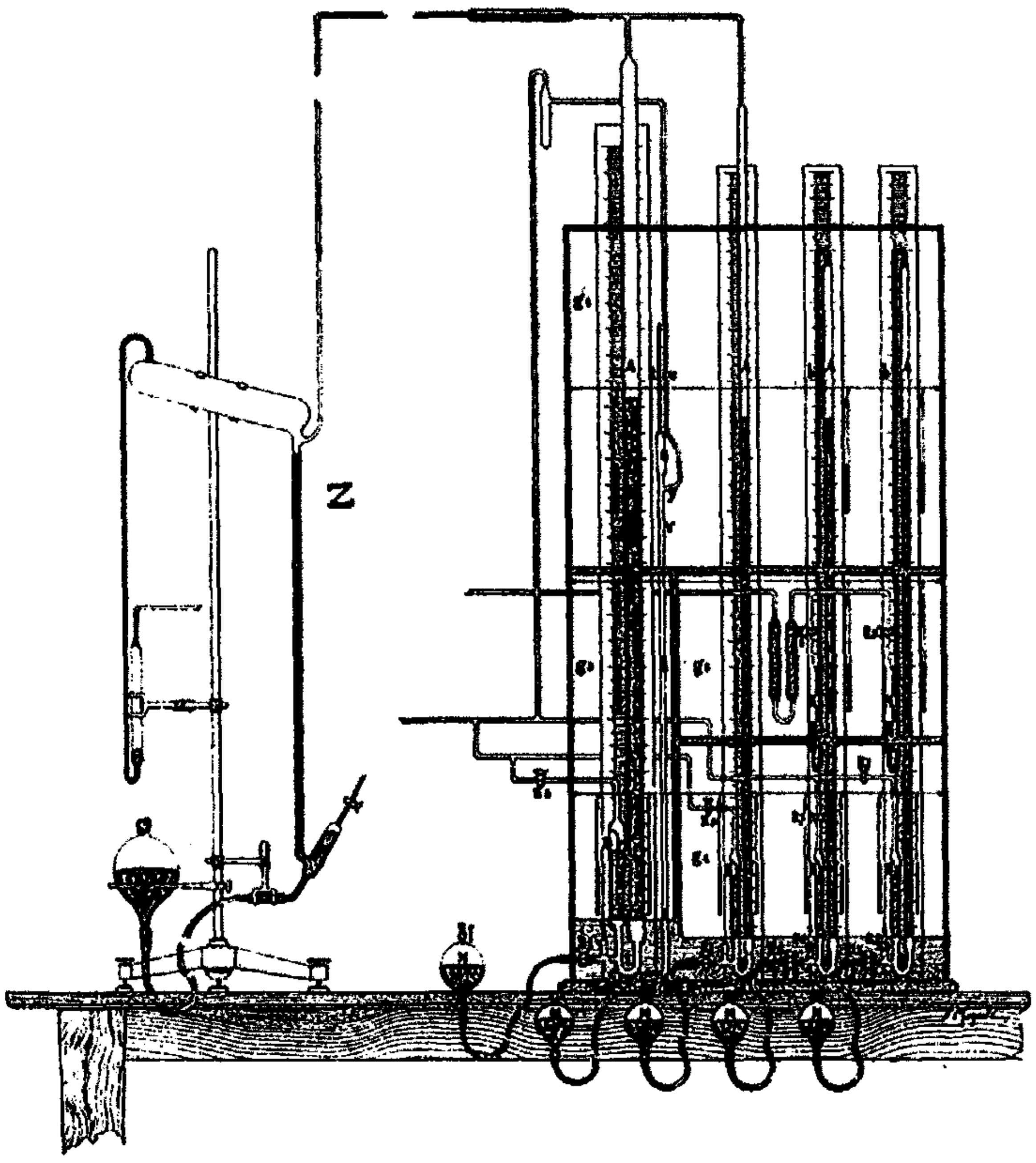

Fig. 1

mercury was introduced into the flask. The lower or receiving flask had a stopcock sealed in the bottom, to permit of drawing the distilled mercury off without tearing down the apparatus; the neck was drawn out and sealed to drying tubes communicating with the water pump and with a mercury manometer; two stopcocks, properly arranged, permitted of interrupting the suction of the water pump and admitting air to the apparatus. The distillation was carried on at about fifteen millimeters pressure; the small amount of air entering the distilling flask and bubbling through the mercury served the double purpose of preventing bumping and of oxidizing any easily oxidizable metals present; at the temperature of the distillation the mercury was not oxidized. The method of operating the still will be evident from the description.

The barometers were mounted on wooden supports placed side by side, and these supports were used as the basis of an air bath constructed about the barometers, as shown in detail in Fig. 1, designed to prevent the rapid changes of temperature caused by an open door or window. The plate glass front was composed of four sections: g_1 and g_2 were stationary, the others, g_3 and g_4, movable so as to admit of access to the stopcocks on the interior of the case. In order to further guard the barometers from the temperature changes caused by the proximity of the ice baths about the globes during the operation of filling, two heavy sheets of asbestos board were interposed between the barometer case and the globes. Over an opening 5 cm wide and the full length of each barometer left in the wooden support behind each instrument was placed an accurately graduated plate glass scale. These scales were graduated on paraffine and etched with hydrofluoric acid by the "Société Genevoise pour la Construction des Instruments de Physique." The scales were divided in millimeters, and could be read to tenths of a millimeter by the unaided eye; by the aid of a telescope the twentieth of a millimeter could be read without difficulty. The internal diameter of barometer I was 25 mm; that of II was 13.5 mm; III and IV were 15 mm. Each barometer was accompanied by four carefully calibrated thermometers, one near the upper mercury surface, one near the center, and two at the bottom; of the last two, one was on each side, to determine any difference in temperature in the two branches. The thermometers were of the ordinary type, with milk glass scale, graduated in degrees from −25° to +110°. The corrections for each thermometer were determined at the temperature of melting ice and at the transition point of sodium sulphate decahydrate; thermometers showing abnormal readings were discarded.

Barometer readings were made with the aid of a small cathetometer. To facilitate the readings, an electric light immersed in a bath of water was arranged on a pulley behind the barometer case, and could be brought into any position desired; the blinding effect of the light was overcome by interposing behind the glass scales a sheet of thin white tissue paper. Both top and bottom of each meniscus were always read.

The corrected barometric reading, P_o, was obtained by substituting in the formula:

$$P_o = G_o\left[P' + c\left(\frac{1}{R_s} - \frac{1}{R_i}\right) - \tau\right]^{1}$$

where G_o is the ratio of the normal acceleration due to gravity to the acceleration at the place of measurement; P' is the observed barometric reading; c is a constant equal to 6.6; R_s and R_i are the radii of curvature of the upper and lower menisci, respectively; τ is the correction for the thermal expansion of the mercury and glass scale.

The residual pressures in the globes were measured with the modified MacLeod vacuometer described by G. Baume.[2] The instrument was set up in the barometer case between barometers I and II. Its readings were verified by comparison with the barometers.

The devices used to obtain a vacuum were the water suction pump, the mercury pump, the rotary oil pump, and the absorption of gases by amorphous carbon at low temperatures. The mercury pumps, two in number (*Z*, Fig. 1), were of the type described by Cardoso and the author.[3] One of them was reserved for use with barometers I and II, while the other served to evacuate the various parts of the apparatus.

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[1] For the derivation and discussion of the formula see the author, Jour. Am. Chem. Soc., **36**, 2456 (1914); this article also contains a table, giving the results obtained with the four barometers in two series of readings.

[2] Jour. chim. phys., **6**, 26 (1908).

[3] Ibid., **10**, 306 (1912).

Evacuation with the mercury pump was always preceded by evacuation with the water suction pump; a vacuum of less than one-tenth millimeter was then attained in a short time. The suction pump was of a simple type, easily blown in the laboratory.

To evacuate large volumes completely, the mercury pump proved to be too tedious; for this purpose the absorbent properties of amorphous carbon at low temperatures were utilized. As is well known, certain forms of amorphous carbon have the property of absorbing large volumes of gas; this property becomes more accentuated as the temperature is lowered, while at high temperatures it ceases to exist. Then it is evident that to prepare a sample of amorphous carbon for this purpose, it must be carefully heated so as to expel all dissolved gases; this also serves to drive out moisture and other volatile impurities, all of which would impair the absorbing qualities of the material. For this work, cocoanut charcoal, as recommended by Dewar,[1] was used; later investigation[2] indicates that animal charcoal is superior. It was enclosed in a tube, *T* (Fig. 4), provided with a stopcock, R_{24}, at its open end, and sealed to the apparatus in close proximity to the volumes to be evacuated. Plunged into a bath of solid carbon dioxide and alcohol, or into liquid air, it was ready for use, and reduced the last fifteen millimeters of pressure due to oxygen in a volume of two liters to one two-hundredth of a millimeter in fifteen minutes when liquid air was used as the cooling agent. The charcoal required frequent burning out to drive off the absorbed gases.

The rotary oil pump was connected as an auxiliary to the mercury pump, but as the latter never failed to give good results the oil pump was rarely used. It was of Siemens-Schuckert manufacture, and easily gave a vacuum of 1/10 mm.

The globes in which the gas was weighed were originally

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[1] Dewar: Comptes rendus, **139**, 261 (1904); Chem. News, **90**, 73 (1904); Ann. chim. phys., (8) **3**, 5 (1904); Proc. Roy. Soc., **74**, 122 (1905); see also Baerwald: Drude's Ann., **23**, 84 (1907).

[2] Hempel and Vater: Zeit. Electrochemie, **18**, 724 (1912).

ordinary round-bottomed flasks; they were drawn out at the neck and glass stopcocks sealed on. Two flasks were selected of the same glass and as nearly as possible of the same volume, and the smaller of them prepared as a counterpoise. The weight of the counterpoise was adjusted by introducing a little water so as to be a trifle heavier than the density globe; the volume was likewise adjusted to within a few cubic centimeters by blowing a bulb on the neck, and was then sealed off.

The method of calibrating a density globe is quite simple, and yet there are certain points that must not be neglected if consistently good results are to be obtained. Fig. 2, in which the globes are sadly out of proportion, shows the form of apparatus used. *A* is the globe whose volume is to be ascertained, *B* is a stout round-bottomed flask of Jena glass. The flask *B* was filled with distilled water, and the water allowed to boil for an hour to expel all air, stopcock *a* remaining open, and *b* closed; *a* was then closed, and the water allowed to cool off. Meanwhile the globe *A* was evacuated by means of the water pump, through stopcock *c*. After *B* had cooled somewhat, *c* was closed, and a little water was allowed to flow into *A* through stopcock *b*. Suction was again applied until a sufficient quantity of water had boiled away to sweep out all the air. Then *b* and *a* were opened and *A*

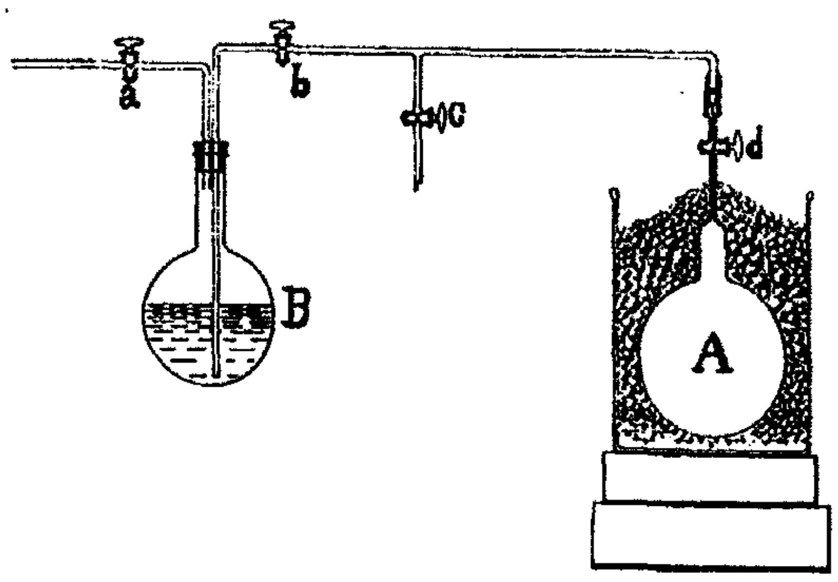

Fig. 2

was allowed to fill completely. Any dissolved gas remaining was boiled out by again lowering the pressure with the water pump. When properly done, no air bubbles remained in the tube connecting the two globes. *A* was surrounded with clean, finely cracked ice, and left until temperature equilibrium was attained, keeping the water siphoned off. The connecting tubes were removed from globe *A*, its stopcock closed, and the capillary above it dried with a bit of filter paper. The stopcock was again opened, and if, after half an hour, no movement of the meniscus was observed, equilibrium was assumed to have been attained, and the globe was removed to the weighing room, after wiping it carefully. A short glass tube drawn out to a capillary was attached to the stem of the globe to provide for the expansion of the water; the globe itself was suspended from the balance arm by means of an improvised basket made of nickel wire. The next morning weighings were made to one centigram, using counterpoises. Finally the globes were emptied, evacuated, and weighed again. The difference was the weight of water contained at the temperature of melting ice.

To find the volume at 0° C the following corrections had to be applied:

1° Correction for the buoyancy of the air on the weights used. The average weight of a cubic centimeter of air in Geneva is 0.00117 gm, then the correction amounted to $\frac{W}{8.5} \times 0.00117$, where W is the weight of water, and 8.5 is the density of brass; the correction is negative.

2° Correction for the volume of water at zero; if the density of water at zero is taken as 0.999868, the correction is $W \times 0.999868$, and is positive.

Correction for latitude and altitude; in Geneva this is equal to $+W \times 0.000016$.[1]

The algebraic sum, Σ, of these corrections becomes:

$$\Sigma = 0.000007\ W + 0.000132\ W - \frac{0.00117}{8.5}\ W = 0.000010\ W$$

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[1] See page 472 for a discussion of this factor.

or ten parts per million; under the conditions outlined, therefore, the weight of the water at zero gives directly the volume at the same temperature.

In the following table are set down the volumes found for the four globes used, which may be numbered, beginning with the smallest, I, II, III, IV; the values given are the averages of at least two calibrations; for purposes of comparison the values found by previous experimenters are also given.

TABLE II

I	252.004 cc Germann	252.04 cc Wourtzel
II	410.27 cc Germann	410.35 cc Wourtzel
III	455.72 cc Germann	
IV	872.33 cc Germann	872.35 cc Scheuer

An important source of systematic error that was neglected until Rayleigh called attention to it in 1888[1] is the contraction of the globe when it is evacuated, causing it to displace less air than before, and hence apparently to weigh more. To correct this error it is only necessary to know the amount of the contraction. Its determination was a simple matter, using the apparatus outlined in Figure 3. The globe was enclosed in a stout metal can, supplied with a lid that could be clamped on tightly; the lid had an inch hole, provided with a two-holed rubber stopper; through one of the holes the stem of the globe protruded (*a*), and through the other a calibrated capillary tube (*b*). The can was filled with water, and the lid clamped on, so that the water stood at some point in the capillary; the globe was evacuated, and the level of the water in the capillary tube noted; then air was allowed to fill the globe rapidly, and the level of the water again noted. The volume of the capillary between the two points noted was the amount of contraction of the globe. The average of several determinations was taken as the final value. The results are included in Table III.

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[1] Proc. Roy. Soc., 43, 361-2 (1888); Chem. News, 57, 74 (1888).

Table III

Globe	Volume Cc	Approximate weight Gm	Contraction Cc	
I	252.004	45	0.002	Germann
II	410.27	67	0.017	Wourtzel
III	455.72	118	0.0001	Germann
IV	872.33	194	0.0051	Scheuer

Each globe and counterpoise was supplied with a nickel wire hook fastened about the stem, to facilitate suspension in the weighing case, and in the balance case.

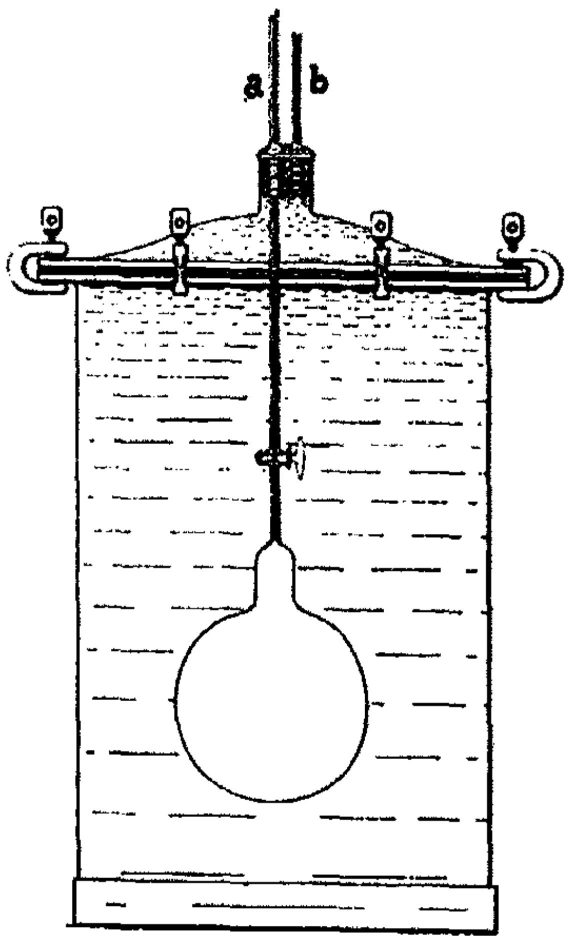

Fig. 3

The balance used in calibrating the globes was of a type used in technical work for weighing heavier objects; it weighed accurately to less than one centigram. For the other weighing—for the actual determination of the weight of the gases—an ordinary Sartorius chemical balance was employed. To increase the accuracy, the pans were removed, and light aluminium trays were suspended close under the knife edges by means of fine platinum wire; these trays were designed to receive the weights, and left the lower part of the balance case free to receive the globes and their counterpoises. The center of gravity was lowered enough to make the time of swing quite long, in order to facilitate the reading of the swings. The balance case itself was surrounded by a much larger glass case with doors opening from the front. Across the top of this outer case was stretched a nickel wire, from which the globes with their counterpoises were hung preparatory to weighing. It was found that this method of disposing of so many articles during the necessarily long process of weighing was much preferable to the method usually used, namely, placing them on a clean, smooth surface at the bottom of the case.

The weights were those used by G. Baume in his work on the gases;[1] they were ordinary, platinum plated analytical weights, constructed by Scholl of Geneva; they were carefully calibrated by the manufacturers and by the author, as has already been mentioned.[2]

For the preparation and purification of the oxygen used special forms of apparatus were employed. The generator was composed of a set of heavy glass tubes, G (Fig. 4), communicating with one another, and filled with the purest potassium permanganate obtainable (Kahlbaum); the permanganate was covered with a heavy layer of glass wool to retain any dust arising from the decomposition of the permanganate. There followed a series of tubes containing the reagents designed to effect the chemical purification of the gas; these comprised a tube containing solid potassium hydroxide in tablet form to remove traces of carbon dioxide; two tubes containing phosphorous pentoxide, to remove moisture; and a system of modified Liebig bulbs, L_1, containing mercury, to break up any ozone that formed at the temperature of decomposition of the permanganate; a shunt tube with stopcock

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[1] Jour. chim. phys., 6, 1 (1908).

[2] See page.

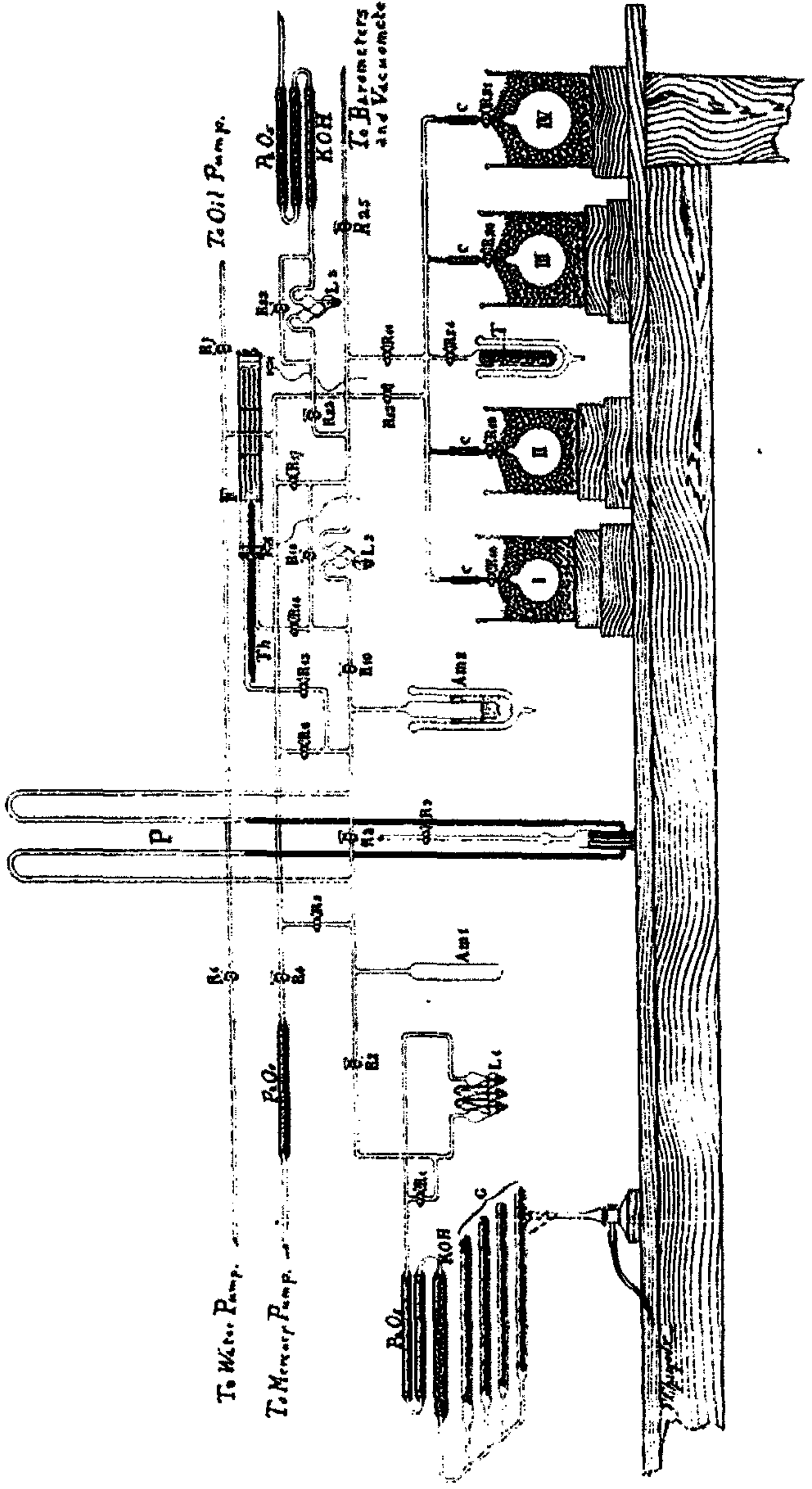
To Oil Pump
P_2O_5
KOH
To Barometers and Vacuometer
Ras
P
F
Th
Ams
I
II
III
IV
T
P_2O_5
To Water Pump
To Mercury Pump
P_2O_5
KOH
G

Fig. 4

R_1 made it possible to evacuate the generating and purification tubes completely in spite of the centimeter or more of mercury in the bulbs.

From this point the gas passed into the apparatus designed for its purification by physical methods. Through stopcock R_2 the gas entered directly into the liquefaction and distilling apparatus, composed of two liquefaction bulbs, Am_1 and Am_2, separated by a stopcock, R_3, and each supplied with a manometer, P, and with vacuum connections through the stopcocks R_5 and R_8; stopcocks R_4, R_7, and R_6 governed communication with the mercury pump, the oil pump, and the water pump, respectively, and any one of these could be turned on by opening the corresponding cock and leaving the others closed. From the liquefaction tube Am_2 the gas could pass through stopcock R_{10}, through the mercury bulb L_2, which served the double purpose of indicating the speed of flow of the gas, and of decomposing any trace of ozone, through stopcock R_{11} into the globes; or else the gas could pass through stopcock R_{13} into a system of tubes F containing platinized asbestos, and thence *via* stopcock R_{14} to the mercury bulb L_2 and so on as before. Vacuum connections to these tubes were supplied by means of stopcocks R_{14}, R_{15} and R_{17}. The platinized asbestos tubes were four in number, and were enclosed in an electric resistance furnace, made by winding a suitable iron tube, covered with a layer of asbestos paper, with nickel wire, and covering the whole heavily with asbestos. The temperature was controlled by means of a rheostat, and the intensity read on a high temperature thermometer, Th.

Manipulation

Before beginning a measurement, the globes were placed in position, and the apparatus was evacuated. Oxygen was then generated by heating one of the permanganate tubes, until the entire apparatus contained several centimeters of oxygen, as indicated on the manometer tubes; this was pumped out, and the process repeated several times. The apparatus was allowed to stand overnight with a pressure amounting to no more than one millimeter of mercury, and the same process continued the next day; any leaks in the apparatus would have made themselves apparent in the interval, and have been corrected. During the evacuation, all parts of the apparatus that could be heated without damage were heated with the bare Bunsen flame to drive out moisture. After several days of such treatment, it was considered that all air and moisture had been removed. The residual pressure, by means of the vacuometer, and the temperature were noted; the stopcocks of the globes and R_{11} were then closed, and the the globes removed. The globes and counterpoises were washed with distilled water and wiped with a piece of good quality white silk, which has the advantage of leaving no lint. The globes and counterpoises were suspended in the outer balance case, and weighed the next morning.

As the great sensibility of the modified balance made it imperative to load the trays to get consistent zero readings, the twenty gram piece was placed in one tray, and the two tens in the other, the screw was adjusted so as to bring the point of equilibrium near the center of the scale, and the exact zero determined by the method of swings, with the rider on the beam, after allowing the beam to swing for five minutes.

The globes were protected from the hands by double-tipped silk gloves. The counterpoise, it will be remembered, was so adjusted as to be a trifle heavier than the corresponding globe; when this was not the case, a constant weight was placed in the tray on the side of the counterpoise—the left side of the balance was chosen for this—large enough to bring about the desired excess of weight. Equilibrium was attained by adding weights to the right tray, the final adjustment to the nearest milligram being made with the rider. The same method was used to determine the point of equilibrium as had been used to find the zero; however, the load was allowed to swing on the knife edges a greater length of time, depending always more or less on the weight of the load; so globe I was always allowed to swing ten minutes; globe II, fifteen minutes; globe III, twenty minutes; and globe IV, twenty-five minutes;

it was found that only in this way could the point of equilibrium be duplicated with a given load; it was also shown to be imperative that the weighing of the lighter globes should precede that of the heavier ones, in other words, that the globe sequence should always be the same, and begin with globe I. The reason for this is probably to be sought in differences in the strain produced in the beam by the different loads; a series of readings, for example, begun immediately after placing globe IV, with its counterpoise on the knife edges, showed a gradual change in a given direction, at first rapidly, then slowly approaching a fairly constant value. As it was found that the sensibility of the balance with the same load varied appreciably from one weighing to another, its determination was never omitted; this necessitated moving the rider; the best results were obtained when this was accomplished without raising the beam. A simple calculation gave the position of equilibrium, and another the exact weight required to bring about equilibrium at the zero point found. The latter was taken as the average of the values found before and after weighing the set of four globes. Three sets of weighings were thus made—the second on the afternoon of the same day, the third on the morning of the next day—and the average of the three weighings taken.

This represented the weight that had to be added to the globe plus the small weight of oxygen it contained at a pressure of p millimeters, to cause equilibrium to be established with the counterpoise. It was necessary to correct, then, for the small amount of oxygen still in the globe; if V be the volume of the globe expressed in cc, p the pressure in millimeters read on the vacuometer, and T the absolute temperature of the gas when the reading was made, the amount of the correction is given by the expression:

$$\frac{1.429 \times 273 \times V \times P}{1000 \times 760 \times T} = 0.0005133 \frac{VP}{T}.$$

This correction is positive and must be added to the weight found.

The globes were then transferred to the laboratory, where they were placed in position, and the vacuum in each measured to be certain that no air had entered in the interval, care having been taken to evacuate and rinse with oxygen several times the space between the stopcocks of the globes and R_{11}.

The afternoon was devoted to the preparation of pure oxygen, and filling the globes with it. The liquefaction bulb Am_1 was immersed in liquid air, while oxygen was generated in one of the permanganate tubes; all stopcocks in this portion of the apparatus were closed except R_2, which governs the communication between the permanganate tubes and the liquefaction tubes. As the gas started to generate, the level of the mercury in manometer P gradually fell to a height corresponding to the vapor pressure of oxygen at the temperature of liquid air, for at this point the gas began to liquefy. About five cubic centimeters of the liquid were collected, that is, five or six liters of gas, the specific gravity of the liquid at its boiling point being approximately 1.53. Stopcock R_2 was then closed. The fractionation of the liquid followed, the operation being carried on between the tubes Am_1 and Am_2, through the stopcock R_3. The first and last fractions (no less than 200 or 300 cc of gas in each case) were always allowed to escape through the manometer P, which also served the purpose of safety valve, its stopcock R_9 being left open. The middle fraction was collected in the second liquefaction tube with the aid of liquid air; at least three such distillations were made, before the gas was considered to be pure. The purified liquid was perfectly limpid, of a pronounced bluish tinge. In the distillation of liquefied gases, a criterion of the purity of the gas is given by the pressure exerted during the distillation; the pressure remains constant as long as the composition of the distillate does not change, and the distillation proceeds quietly.

Meanwhile finely cracked ice had been prepared and placed in the large glass vases about the globes, covering the globes completely up to their stopcocks. The accumulation of water from the melting ice was prevented by siphoning it off every ten minutes or so. All vacuum connections to the globes were now cut off by closing stopcock R_{12} (Fig. 4), and oxygen gas was allowed to evaporate into the globes by opening stopcock R_{10}, without for the moment removing the bath of liquid air, so that the evaporation proceeded quite slowly; the speed of evaporation was indicated by the degree of agitation of the mercury in L_2. As the speed began to diminish, the Dewar tube containing liquid air was slowly lowered, so as to compensate for the increasing pressure, and to maintain about the same rate of evaporation. When the pressure in the globes became near that of the atmosphere, communication was established with the barometers by opening the stopcock R_{25} leading to the barometer case, and the stopcocks of the four barometers, R_5 and R_7 (Fig. 1). The manometer stopcock R_9 (Fig. 4) was then closed, to permit of the attainment of a pressure in the apparatus greater than the atmospheric pressure. The mercury in branch B (Fig. 1) of the barometers was kept as close as possible to the glass points p, by adjusting the mercury bulbs M, and when the difference in level of the two menisci amounted to 762 or 763 mm the supply of oxygen was cut off by closing stopcock R_{10} (Fig. 4); at the same time the manometer stopcock R_9 was opened to relieve the pressure in that part of the apparatus and the bath of liquid air was brought up around the liquid oxygen. After a suitable length of time, that is, when temperature equilibrium had been attained, the mercury of the barometers was adjusted so that the glass points p (Fig. 1) just touched their reflections in the mercury surfaces, and the stopcocks through which mercury was admitted to the barometers, R_1 and R_3 (Fig. 1), were closed. Two series of pressure readings were made on the barometers, and the average of all the readings taken; thermometers accompanying the barometers were read as the pressure readings were made. The globe stopcocks were closed, and then those leading to the barometers, after the oxygen in them had been pumped out to prevent the soiling of the mercury through oxidation.

This ended the operation of filling. The globes were removed from the ice, carefully washed, wiped dry, and placed in the weighing case as before, to remain overnight. Two weighings were made during the next day, and a third on the morning of the following day. The averages of these weighings were the weights of the globes filled with oxygen at the pressure P, read on the barometers. On the afternoon after the third weighing, the globes were again evacuated, and weighed exactly as already described. Now, the real value of the weight that would have been necessary to cause equilibrium had the globes been completely evacuated at the time they were weighed full of oxygen, is best expressed by the average of the weights found before and after filling, if we may consider that any change in weight in the interval was caused by wiping the surface of the globes, and so wearing off or dissolving a minute portion of the glass. Then the difference between the weight of the filled globe and that of the empty globe gave the weight of the oxygen it contained at 0° C and H millimeters pressure. The calculation of the gross weight of the liter followed, by the application of the formula:

$$L_{gross} = \frac{760\, W}{HV}$$

where W is the weight of the gas found, and L_{gross} the uncorrected weight of the liter of gas.

The corrections to be applied were four in number:

1. Correction for the contraction of the globe during evacuation; since this contraction involves an apparent increase in the weight of the globe when it is evacuated, due to the smaller volume of air displaced by it, the value of the correction, C_c, is evidently given by the additional weight of air that would be displaced if the globe were not evacuated; this weight, on the basis of a liter, assuming the average weight of a cubic centimeter of air in Geneva to be 0.00117 gm, and expressing the amount of the contraction in cubic centimeters by C, is given by:

$$C_c = \frac{1000 \times 0.00117 \times C}{V} = 1.17\,\frac{C}{V}$$

Substituting the values for the contraction found for the globes used in this formula, we obtain the following positive corrections:

TABLE IV

	Gm
Globe I	0.00001
Globe II	0.00005
Globe III	0.00000
Globe IV	0.00001

2. Correction for the buoyancy of the air on the weights; since only those weights come into consideration that are used to replace the oxygen when the globes are weighed empty, the gross weights employed may be neglected, and the calculation made on the basis of a liter, 1.429 g. The weight of air displaced, R_v, using as the density of brass 8.5, and assuming that all the weights were made of brass,[1] since in the calibration of the weights a brass kilogram was used as standard, is given by:

$$R_v = \frac{1.429 \times 0.00117}{8.5} = 0.00020 \text{ gm}$$

a negative correction.

3. Correction for the altitude, or reduction to sea level and 45° N latitude. The correction factor for the altitude is expressed with sufficient approximation by the formula:

$$1 + \frac{2h}{R}$$

where h is the altitude above sea level, and R the average radius of the earth; the factor for the latitude is given by:

$$\frac{1}{1 - \delta \cos 2\phi}$$

where ϕ is the latitude of the point of observation, and δ a constant whose value is given by Lasch[2] as 0.0025935. Combining these two factors, we have the total correction factor G_0:

$$G_0 = \frac{1 + \frac{2h}{R}}{1 - \delta \cos 2\phi}.$$

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[1] See Gray and Burt: Jour. Chem. Soc., **95**, 1636 (1909).

[2] Pogg. Ann. Ergänzungsband, **3**, 321 (1853).

Taking R = 6367382 meters, the mean of the values given for a and b of Clark's ellipsoide, and assuming that at the École de Chimie in Geneva, h = 400 meters, and ϕ = 46° 12', we have:

$$G_0 = \frac{1 + \frac{800}{6367382}}{1 + 0.0025935 \sin 2^\circ 24'} = 1.000016$$

Then the correction to be applied to the weight of the liter of gas becomes:

$$G = L_{gross}\,(1.000016 - 1)$$

therefore, an additive correction. For oxygen G becomes 0.0000023. This value coincides exactly with that found experimentally at the observatory in Geneva, which is only a short distance from the laboratory. The ratio of the normal acceleration due to gravity, g_n (at sea level and 45° N lat.), to the acceleration due to gravity at the place of measurement, g_m, becomes, for Geneva:[1]

$$G_0 = \frac{g_n}{g_m} = \frac{980.616}{980.600} = 1.000016$$

4. Correction for the compressibility of the oxygen. This correction was very small, because the pressures at which the globes were closed before weighing were always as nearly as possible equal to 760 mm. The correction A, letting A'_0 represent the coefficient of compressibility of the gas, and P_0 the average pressure in the globes, is given by:

$$A = \frac{LA'_0}{760}\,(760 - P_0)$$

The value of A'_0 for oxygen, determined by Jaquerod and Scheuer,[2] is 0.00097.

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[1] Compare the derivation of this value by the author, Jour. Am. Chem. Soc., 36, 2461 (1914). The Recueil de Constantes Physiques, published by the Société française de Physique (1913), gives g_m (Geneva) = 980.599; this value is the result of observations made in 1892; the publications of the Swiss Geodetic Commission, Vol. 7 (1897), indicate that more recent measurements, made in 1894, bring the value of g_m for Geneva to 980.600.

[2] Mémoires de la Société de Physique de Genève, 35, 659 (1908).

Applying these corrections to the gross weight of the liter of gas, we have the expression:

$$L_N = L_{gross} + C_c - R_v + G + A$$

In practice the correction for the contraction of the globes during evacuation, C_c, was applied to the individual results, since the correction varied from globe to globe; the other corrections were applied to the averages obtained.

Results

The results obtained for the density of oxygen purified by fractional distillation as described are tabulated in Table V. The first measurement unfortunately included but three globes, as globe I was inadvertently taken from the ice after filling, before the stopcock had been closed. The barometric readings given in the third column are the corrected averages for barometers I, II and IV, barometer III having suffered an accident. The gross weight noted in the fourth column is the weight of the oxygen contained in the globe at the time of measurement, corrected for the inaccuracies of the weights. The value of the gross liter is that obtained by the simple application of Boyle's law, while the next column tabulates the weight of the liter corrected for the contraction of the globe (see Table IV).

TABLE V

Measurement	Globe	Corrected barometer Mm	Gross weight G	L_{gross} G	$L_{gross} + C_c$ G
I	IV	758.06	1.24345	1.42908	1.42909
I	III	758.06	0.64968	1.42926	1.42926
I	II	758.06	0.58501	1.42956	1.42961
II	IV	762.94	1.25156	1.42920	1.42921
II	III	762.94	0.65400	1.42956	1.42956
II	II	762.94	0.58877	1.42955	1.42960
II	I	762.94	0.36157	1.42925	1.42926
III	IV	763.16	1.25171	1.42896	1.42897
III	III	763.16	0.65409	1.42935	1.42935
III	II	763.16	0.58876	1.42911	1.42916
III	I	763.16	0.36150	1.42856	1.42857

The average of the eleven values is $L_{gross} + C_c = 1.42924$ gm. The formula for the correction for compressibility gives a value for $A = 0.0000002$, which is a negligible quantity. Then the weight of the normal liter becomes, using the values already found for R_v and G:

$$L_N = (L_{gross} + C_c) - R_v + G = 1.42906 \text{ gm.}$$

This value, agreeing so closely with the generally accepted value, 1.4290 g, differs by 1/10000 from the value found some years ago in the same laboratory by another method, that of the volumeter, by Jaquerod and Pintza (see page 446). However, the sources of the gas used in the two researches were identical; the methods of purification were different; the gas used by Jaquerod and Pintza was not subjected to liquefaction and fractional distillation. In order to determine, if possible, the value of this species of purification, and at the same time to determine the possible cause of the higher value found by the authors cited, two determinations of the density of oxygen were carried out on the unliquefied and undistilled gas. The results are set down in Table VI. The pressures given are those read from barometers I and II, III and IV both having been out of commission.

TABLE VI

Measurement	Globe	Corrected barometer Mm	Gross weight G	L_{gross} G	$L_{gross} + C_c$ G
IV	IV	761.53	1.24910	1.42904	1.42905
IV	III	761.53	0.65296	1.42993	1.42993
IV	II	761.53	0.58755	1.42923	1.42928
IV	I	761.53	0.36096	1.42948	1.42949
V	IV	762.92	1.25157	1.42925	1.42926
V	III	762.92	0.65395	1.42949	1.42949
V	II	762.92	0.58849	1.42891	1.42896
V	I	762.92	0.36174	1.42996	1.42997

The average of the eight values is $L_{gross} = 1.42943$ gm. $A = 0.000004$, therefore, negligible. Then

$$L_N = (L_{gross} + C_c) - \mathrm{R}_v + G = 1.42925 \text{ gm,}$$

thus completely corroborating the results found by Jaquerod and Pintza, with oxygen prepared in the same way.[1]

G. Owen[2] has called attention to the formation in air of complex molecules at low temperatures. The same would, in all probability, also happen with oxygen, and such molecules might be capable of persisting for some time at ordinary temperatures, a very small percent of them sufficing to throw the results of a density determination away off. One set of determinations was, therefore, planned to show whether the results had been affected by this source of error. To break up any polymerized molecules, the oxygen was passed from the liquefaction tube Am_2 into the series of tubes containing platinized asbestos (see page 465, and F, Fig. 4), heated to 400° C; from there the gas passed through the mercury bulb L_2, Fig. 4, into the globes. The rest of the operation was as already described. The results are included in Table VII. The pressures given were calculated from readings of barometers I, II and IV.

The average of the four values is $L_{gross} + C_c = 1.429235$ gm. Correction A becomes equal to -0.000005, which may be considered in this case. Then the value of the normal liter becomes:

$$L_N = (L_{gross} + C_c) - R_v + G + A = 1.42905 \text{ gm.}$$

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[1] The reason for the difference found in the density of distilled and undistilled oxygen is rather difficult to determine with any degree of certainty. Among the suppositions that can be made may be mentioned the presence, in the oxygen prepared directly from potassium permanganate, of traces of carbon dioxide (from the combustion of organic substances accompanying the permanganate), or of very finely divided manganese dioxide carried along mechanically. It is possible that the conditions, under which the decomposition of the permanganate is carried out, may be such as to avoid this source of error. So Rayleigh, for example, found no appreciable difference between the weights of his globe when filled with oxygen from various sources, without purification by fractional distillation; the average weight of oxygen contained at 0° C and reduced to 760 mm was:

From electrolysis	2.6272 and 2.6271 gm
From $KClO_3$	2.6269 and 2.6269 gm
From $KMnO_4$	2.6271 gm
Average	2.62704 gm

[2] Phil. Mag., (6) **15**, 746 (1908); **21**, 465; **22**, 563 (1911).

TABLE VII

Measurement	Globe	Corrected barometer Mm	Gross weight G	L_{gross} G	$L_{gross} + C$. G
VI	IV	763.03	1.25123	1.42866	1.42867
VI	III	763.03	0.65417	1.42976	1.42976
VI	II	763.03	0.58866	1.42911	1.42916
VI	I	763.03	0.36164	1.42934	1.42935

Conclusion

The most trustworthy results found for the weight of the normal liter of oxygen are the following:

First, or general series, 11 observations...... L_N = 1.42906
Second, or special series, 4 observations...... L_N = 1.42905
Arithmetical average of the 15 observations.. L_N = 1.42906

This value is nearly identical with the values proposed by Rayleigh (1.42904), Morley (1.42900), Thomsen (1.42906), Gray (1.42896), and Jaquerod and Tourpaian (1.4290); it differs by only one part in ten thousand from that found by Jaquerod and Pintza (1.4292), and by two parts in ten thousand from that found by Leduc (1.42876).

The two most satisfactory series of measurements made in the past are the following:

Morley, 41 observations.................... L_N = 1.42900
Rayleigh, 16 observations.................. L_N = 1.42904

Taking the series of measurements described in the present research into account with these, the average of the three series of results (comprising 72 observations), obtained independently is:

$$L_N = 1.42903$$

which coincides almost exactly with Rayleigh's number. However, in order to take into account the fact that the measurements described in this paper were carried out (1) on oxygen purified by liquefaction and fractional distillation, and (2) with several barometers so that the average of all the pressure readings could be used for each observation, it seems justifiable to give a little more weight to the value found in this research; I propose, therefore, as the most probable value, in the present state of our knowledge, for the weight of the normal liter of oxygen, the number:

$$L_N = 1.42905$$

Summary

A brief historical survey of the more important determinations of the density of oxygen has been made.

A detailed account of the modern methods used in the Geneva laboratory in the determination of gas densities, with particular reference to the purification of the gases used, is given.

An improvement in the globe method, as it has been developed in Geneva, is described, consisting in the simultaneous use of a number of barometers equal to the number of globes employed.

The density of oxygen was revised, operating on gas furnished by the decomposition of potassium permanganate and purified by fractional distillation. Fifteen determinations led to the value:

$$L_N = 1.42906$$

This value, taking into consideration the results of Morley and Rayleigh, leads to the value:

$$L_N = 1.42905$$

which represents at the present time the most probable value for the weight of the normal liter of oxygen.

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EXPERIMENTS ON EMULSIONS. II

BY T. ROLAND BRIGGS AND HUGO F. SCHMIDT

Emulsions of Water and Benzene

The experiments described in this paper are to be regarded as supplementing and continuing Newman's work on emulsification,[1] the theory of which has been reviewed and coordinated by Bancroft.[2] In the majority of his experiments, Newman used benzene and water as liquid components; we shall do the same for the reason that disturbing factors[3] are reduced thus apparently to a minimum.

Newman's experiments were undertaken primarily to study the conditions under which are formed the two theoretically possible types of benzene-water emulsions—emulsions of benzene as disperse phase in water and emulsion of water as disperse phase in benzene. While the first type is well known and has been studied in detail in many instances, surprisingly little has been written about the second type up to the present, although emulsions with water as internal phase are of wide occurrence.[4] It is with regard to the second type of emulsion that Newman's results are most striking and we shall refer to these later.

In the experiments to be described, the emulsions were prepared by direct shaking, and were accordingly comparable with Newman's preparations. Glass-stoppered bottles of 125 cc capacity were used as containers, after being cleaned first in soapy water, rinsed and immersed in hot cleaning mixture for at least one day. By this painstaking treatment

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[1] Jour. Phys. Chem., **18**, 34 (1914).

[2] Ibid., **16**, 177, 345, 474, 739 (1912); **17**, 50 (1913); **19**, 275 (1915).

[3] Insufficient care has been taken in the past to exclude the possibility of phase in the oily impurities, especially of free fatty acids.

[4] Cf. Bancroft, *loc cit.;* also Hofmann: Zeit. Biologie, **63**, 395 (1914). Emulsions of water in oil have been mentioned in pharmaceutical papers from time to time. Cf. Saunders: Pharm. Jour., (3) **5**, 663 (1874); Gerrard: Pharm. Jour., (3) **18**, 431 (1887).

disturbing effects due to contamination of the surface were probably eliminated.

The shaking machine produced very largely a lateral motion approximating 400 oscillations per minute. A special frame was constructed to hold several bottles at a time, and, by accommodating them in a horizontal position, ensured the maximum effect being obtained. Unless it is specified otherwise, shaking was done at room temperature, which did not vary very seriously throughout these experiments, the apparatus being located in the basement of the Salisbury laboratories.

As already stated, the work was confined wholly to two liquids, benzene and water, with the addition of a number of emulsifying agents—some miscible with water only and others miscible only with benzene. The benzene itself was used repeatedly, being recovered from discarded emulsions as follows: the emulsified mixture was "cracked" by adding a little sulphuric acid and the benzene removed and dried over calcium chloride and a stick of caustic potash. The benzene was then distilled carefully.

In preliminary experiments the capacity of the shaking apparatus was ascertained with results that agreed essentially with Newman's. Emulsions of benzene in solutions of sodium oleate were those first prepared. Except when much benzene and little soap solution were mixed, the system separated into two distinct layers on standing after emulsification—into an upper, opaque and very viscous layer of closely packed benzene globules and into a lower clear stratum consisting of soap solution with perhaps a trace of benzene in suspension. When the relative proportion of aqueous liquid was very small, not enough remained in excess to produce the lower stratum and the whole formed a mass like blanc-mange, the viscosity of which increased rapidly with the relative amount of benzene. With incomplete emulsification, however, a third layer made its appearance, consisting of clear and non-emulsified benzene, superposed upon the opaque layer of completely emulsified benzene which comprised a portion of the mixture. In the tables to follow, complete emulsification is indicated by the presence of one-layer or two-layer systems—incomplete emulsification by three layers.

Emulsions of Benzene in Water: Composition and Time of Shaking

By following the procedure established by Newman, a study was made of the degree of emulsification and the composition by volume, according to two different methods. In one case (A) the *concentration* of soap in the aqueous phase was kept constant throughout a given set of emulsions, although the *absolute* amount of soap present varied directly with the volume of solution used. In the second case (B), the *absolute* amount of emulsifier was kept constant, while its concentration in the solution varied inversely as the volume. A third procedure suggests itself for comparison—to maintain a fixed ratio between the quantity of emulsifier and the volume of the disperse phase (benzene). No experiments of this type have been made, however.

A run was made with nine mixtures of benzene and one percent sodium oleate solution. The nine bottles were shaken simultaneously for five minutes. The results follow in Table I:

Table I

Emulsions: benzene in water.
Aqueous phase: one percent sodium oleate.
Time of shaking: 5 minutes.
Room temperature.

No. of bottle	Benzene in 100 cc of original mixture	Remarks
1, 2, 3	90, 80, 70	Three layers
4, 5, 6, 7, 8, 9	60, 50, 40, 30, 20, 10	Two layers

From the table given above it will be seen that shaking for five minutes completely emulsified the benzene in six out of nine of the mixtures. When the benzene in the original mixture comprised 90, 80 or 70 percent by volume, emulsification occurred only partially and three layers were visible.

We next endeavored to carry the emulsification further by longer shaking.

On shaking for ten minutes, No. 3 was transformed into a completely emulsified mixture of two layers, while the intermediate, opaque stratum of emulsified benzene had increased visibly in both No. 1 and No. 2. After fifteen minutes, No. 2 showed two layers only; after thirty minutes even No. 1 succumbed to the persistency of the treatment. There appears thus to be no definite limit beyond which one cannot go in emulsifying directly mixtures of benzene and soap solution, though as a matter of fact no one would ever employ this method of making an emulsion of high benzene content, if he were in a hurry. The method of adding benzene continuously and gradually during the shaking is vastly more satisfactory.

An interesting and characteristic phenomenon was observed to occur as each mixture became completely emulsified and the clear benzene layer disappeared. A sudden development of foam took place, which could be detected during the shaking by the sharp change in appearance of the mixture in the bottle or by the sudden disappearance of the typical "splashing" sound produced by the agitation of the liquid. As long as the benzene is only partly dispersed and there is no foam, the splash is distinctly audible; but, on the production of foam, the latter acts as a cushion and the splash becomes almost inaudible. This behavior seems to indicate a selective emulsifying action on the part of soap, for it appears to exert a greater emulsifying action on benzene as compared with air, and can form an emulsion of air only when the benzene is completely dispersed. Accordingly, the final emulsions prepared by the method undoubtedly contain a certain percentage of emulsified air, which one ought not to lose sight of.

A supplementary series of experiments was carried out according to the second method of procedure (B), already discussed. As the results obtained differed in no respect from those with method A, no data will be given in this paper. In all subsequent work, the first mode of procedure was followed exclusively.

A more detailed study was now undertaken of the time required to emulsify completely mixtures containing different relative amounts by(volume) of benzene, and one percent sodium oleate. As before, the work was done at room temperature. The combined volume of benzene and aqueous solution was kept constant at 50 cc throughout the series, the results of which follow. For part of the data we are indebted to Mr. H. G. Carter, working in this laboratory.

TABLE II

Emulsions: benzene in water.
Aqueous phase: one percent sodium oleate.
Time of shaking variable.
Room temperature.

Percent of benzene by volume	Time required for complete emulsification (Minutes)
99	(Incomplete after 8 hours)
96	125
95	40
90	23 (22)
80	17 (11)
70	10
60	7
50	3
40	2
30	Less than 1

The curve in Fig. 1 is constructed from these data, with times required for complete emulsification as abscissae and parts of benzene by volume as ordinates. From this it is evident that the necessary amount of shaking increases with the percentage of benzene to be emulsified, at first slowly and then with very rapidly increasing speed, until the amount of shaking becomes infinitely great, for all practical purposes. With the particular apparatus employed in these experiments, the limiting value works out to be in the neighborhood of 98 percent of benzene by volume; emulsions containing a greater proportion of benzene cannot be made with the apparatus by mixing the component liquids directly and shaking. Such emulsions can be prepared, however, by adding benzene to the soap solution little by little and by taking care that emulsification is complete before every fresh addition.

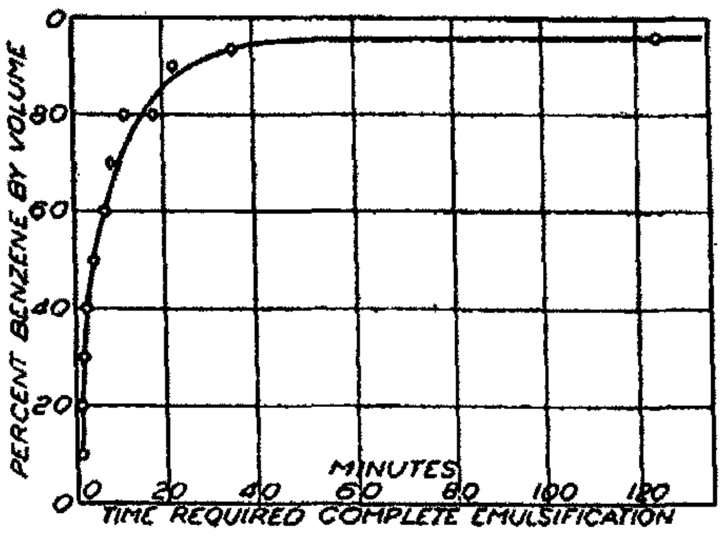

Fig. 1

Of course the position of this curve is dependent not only upon the size and shape of the bottles used as containers, the speed and mode of agitation, etc., but also upon the strength of the soap solution, to a certain extent. What the effect of varying the soap concentration may be, is the subject of the next investigation.

Emulsions of Benzene in Water: Influence of Soap Concentration

According to the method producing the data of Table I, several sets of nine emulsion mixtures were prepared, each set containing a soap solution of definite but changed concentration as external phase. After shaking for five minutes, the progress of events was observed and the sets shaken again for five minutes, making ten minutes as the total. The data follow.

In Fig. 2 these data are graphically treated by using soap concentrations in the aqueous phases as abscissae and for ordinates the percentage of benzene by volume in that emulsion of each set which contains a *maximum* of com-

Table III

Concentration of soap in aqueous phase (percent)	Maximum percent of benzene emulsified (approximate)	
	Shaking 5 minutes	Shaking 10 minutes
0.1	30	30
1.0	60	70
2.0	50	70
4.0	50	70
6.0	50	70
8.0	50	70
10.0	40	60

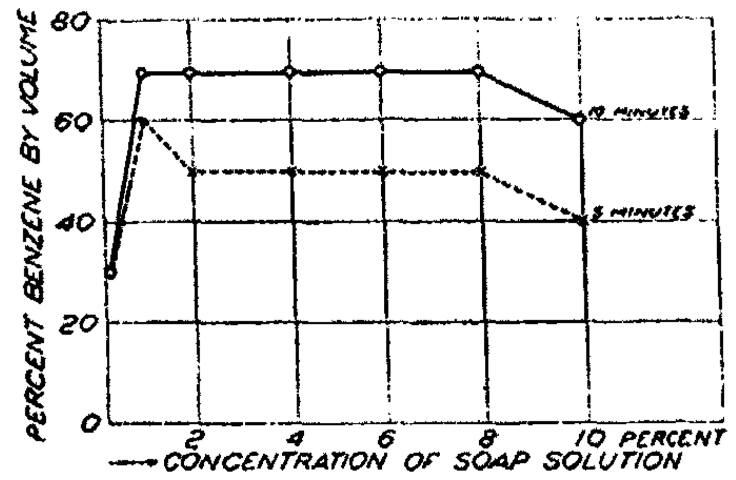

Fig. 2

pletely emulsified benzene. The curves indicate a slight maximum in the peptonizing (emulsifying) action of sodium oleate on benzene as the concentration of the former increases though it is possible that the slight falling off in the emulsifying power as the soap solution becomes very concentrated is due to an increase in viscosity. The optimum concentration of soap seems to be about one percent, which is in agreement with certain qualitative observations made by one of us in a former paper.[1]

Emulsions of Benzene in Water. Study of Some Emulsifying Substances

A comparative study was next undertaken of the emulsifying power of several different compounds, all of which form

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[1] Briggs: Jour. Phys. Chem., 19, 210 (1915).

colloidal solutions in water to a certain extent and are coagulated by benzene. The first of these, if we except sodium oleate as already studied, was sodium resinate—pure resin soap. The data follow:

TABLE IV

Emulsions: benzene in water.
Aqueous phase: one percent sodium resinate.
Time of shaking: 20 minutes.
Room temperature.

No. of bottle	Percent benzene by volume	Remarks
1, 2	90, 80	Incomplete
3, 4, 5, 6, 7, 8, 9	70, 60, 50, 40, 30, 20, 10	Complete

The appearance and behavior of these resin-soap emulsions differed in practically no respect from those prepared with sodium oleate, just as one would expect from the similarity of the emulsifiers. As a matter of accuracy, however, it is only fair to state that the resin soap is slightly, though definitely, less efficient than sodium oleate.

Pickering has described certain inorganic emulsifying agents as follows:[1] "When copper sulphate was added to lime before emulsification, it was noticed that the emulsion produced was altogether different from that with lime alone, and following up this indication, it was found that the basic sulphate of copper, precipitated by the action of lime on the copper sulphate, is, by itself, capable of emulsifying paraffin oil and water almost as finely as, and much more easily than soap.... On the other hand, no connection between emulsification and the nature of the metal present can be traced; copper hydroxide will not emulsify, though the basic sulphate will, whereas both ferrous hydroxide and basic sulphate are good emulsifiers."

In a recent paper,[2] Hofmann has discussed the conditions under which a powdered solid will condense in the interface between two liquids and he has also described some interesting emulsions produced in this way, notably a very permanent

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[1] Jour. Chem. Soc., 91, 2002 (1907).
[2] Zeit. Biologie, 63, 395 (1914).

emulsion of chloroform in water containing silver dichromate.

While on the subject of Pickering's inorganic emulsifiers, it is interesting to note that a certain argillaceous earth, called Tfol,[1] consisting largely of silica, is used by the Arabs of northern Africa as a substitute for soap in washing linen. Not only does it absorb oil but it also strongly emulsifies oil in water.

To illustrate Pickering's inorganic emulsifiers, experiments were performed with aqueous ferric acetate (Merck) as the water phase. Ferric acetate is strongly hydrolyzed in solution, with the production of a very stable suspension of hydrous ferric oxide[2] (or basic acetate). If hydrous ferric oxide in suspension possesses the two prime requisites of an emulsifying agent—the property of condensing by adsorption in the dineric interface[3] and the ability to form under these circumstances a strong and coherent film—it will produce a stable and, in our opinion, a *true* emulsion, having all the properties of Pickering's emulsions with basic copper sulphate.

One percent solutions of ferric acetate were shaken with benzene for twenty minutes as in the preceding case. The results follow in Table V:

TABLE V

Emulsion: benzene in water.
Aqueous phase: one percent ferric acetate.
Time of shaking: 20 minutes.
Room temperature.

No. of bottle	Percent benzene by volume	Remarks
1, 2, 3, 4, 5	90, 80, 70, 60, 50	Incomplete: 3 layers
6, 7, 8, 9	40, 30, 20, 10	Complete: 2 layers

The completed emulsions were quite stable and were light brown in color; in each case foam appeared above the layer of emulsified benzene. One may conclude safely from these experiments that hydrous ferric oxide in aqueous suspension is a fairly good emulsifying agent.

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[1] Pharm. Jour., (4) 6, 1228 (1898).

[2] Péan de St. Gilles: Comptes rendus, 40, 568 (1855), etc.; Reinitzer, Monatshefte, 3, 249 (1890).

[3] Cf. Bancroft: Jour. Phys. Chem., 19, 275 (1915).

A similar conclusion has been reached previously by one of us[1] and it has been suggested in this connection that the production of an emulsion when a pure oil is shaken with a liquid can be interpreted as indicating the presence of a substance suspended in the aqueous phase. But it is well to observe that the *non-production of an emulsion does not prove necessarily the non-existence of a colloid in suspension*, for not all colloids are emulsifying agents. To act as such, they must fulfill the two requirements already stated.

When one prepares a solution of methyl violet in water, a distinct foaming occurs if the liquid is agitated. Foam being an emulsion of air in water, it was to be expected that aqueous methyl violet would act as a strong emulsifying agent toward benzene. On attempting to make emulsions with benzene and a one percent solution of the dye, no satisfactory results were obtained, though evidences of a slight emulsion-formation were not entirely absent. Diluting the solution of the dye to one-fifth likewise produced no emulsions. In this case it is quite probable that, although condensation of dye may occur in the dineric interface, the properties of the film so formed are quite unsuitable to the production of an emulsion. Further experiments of this kind should be undertaken with dyes in solution, for it would be interesting to compare the dyes of undoubted colloidal nature, such as congo-red, with those forming true or semi-colloidal solutions.

Experiments were next carried out with gelatine as emulsifier and the following data obtained:

TABLE VI

Emulsion: benzene in water.
Aqueous phase: one percent gelatine.
Time of shaking: 20 minutes.
Room temperature.

No. of bottle	Percent benzene by volume	Remarks
1, 2, 3, 4, 5	90, 80, 70, 60, 50	Incomplete
6, 7, 8, 9	40, 30, 20, 10	Complete

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[1] Briggs: Jour. Phys. Chem., 16, 281 (1913).

The data given in the table above show that gelatine is not as efficient as the alkali soaps—indeed it is little better than ferric acetate solution. However, a very large quantity of foam was produced in the four completed emulsions. When the quantity of benzene was large relative to the amount of gelatine solution, the attempted emulsification served to precipitate the colloid in large white flocks, which floated in the benzene or stuck to the walls of the bottle. This observation[1] accounts in all probability for the comparative inefficiency of gelatine as an emulsion builder.

In pharmaceutical work gum arabic is used very extensively as an emulsifying agent, not only because of its ability to disperse oil in water, but also because of its harmlessness. Experiments performed by us with a one percent solution showed that the gum possessed even less emulsifying power than gelatine. Evidences of flocculation were obtained in this case also. It is necessary to observe that the pharmacist prepares his gum arabic emulsions, not by shaking, but by trituration in a mortar, so that the conditions of experiment may be quite different.

The Surface Factor. Preliminary Wetting of Glass with Water or Benzene

Wa. Ostwald[2] has observed specific effects, depending upon whether the glass surface is wetted with oil or water, previous to making an emulsion. He writes as follows:

"The purified and dried surfaces (glass cylinder and stirrer) were carefully covered with oil in case an oily emulsion was wanted, and with water in case a watery emulsion was to be made. The other liquid was added and the stirring begun. The short-lived emulsions had very different properties depending upon whether the surface was water or oil......"

Hofmann[3] also discusses the subject. The following is taken from his paper:

"The wetting of the walls of the flask plays an important

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[1] Cf. Winkelblech's experiments: Zeit. angew. Chemie, 19, 1953 (1906).

[2] Zeit. Kolloidchemie, 6, 103 (1910).

[3] Zeit. Biologie, 63, 398 (1914).

part in these researches. It is often possible to change the relationship entirely—that is, to prepare an emulsion of water in the second liquid (chloroform, etc.) if one shakes together both liquids in a flask, in which the water has been displaced from the walls by the second liquid. This can be shown best by dissolving a little lecithin in chloroform and shaking with water or aqueous-bichromate solution. There is thus produced a very fine and permanent emulsion of water in chloroform, in which the water drops are coated with precipitated lecithin and are hindered from re-uniting for a long period of time. On standing quietly, however, the water globules finally coalesce. If the same experiment be performed with a solution of wax in chloroform, there is likewise obtained an emulsion of water in chloroform.... It is especially interesting to observe, in this case, how the wax films about the single water globules gradually melt to larger membranes which float in water, until they collapse together entirely, when the flask is shaken rather vigorously. One may follow the production of the 'haptogen membrane' in such cases very beautifully, even with the naked eye.

"According to the experiments described, that liquid which is displaced from the walls of the flask by the other, is more easily emulsified by shaking, than the better wetting liquid. Still, the wetting of the glass walls is not the only determining factor. There is added also the mutual quantity ratio of the two liquids. If to a clean flask, capable of being wetted easily by water, one adds to a large quantity of chloroform only so little water that the latter floats on the surface of the chloroform in large drops without reaching the glass walls, under these conditions the water is dispersed as minute drops by shaking. On the other hand, chloroform containing dissolved wax is dispersed in water by being shaken in a wax-coated flask, in case the chloroform is not too greatly in excess. These relationships have been discussed by Wa. Ostwald[1] and by T. B. Robertson.[2] It is possible to express

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[1] Kolloid. Zeit., 6, 103 (1910).

[2] Ibid., 7, 7, (1910).

the influence which wetting of the surface exerts, by means of the rule (not always true as we shall see) that with equal quantities of the two liquids the poorer wetting one will be emulsified in the better."

In our experiments the interior of a clean and dry glass bottle was wetted with 40 cc of benzene, 10 cc of one percent sodium oleate were added and the whole shaken until completely emulsified. The time required was nine minutes. A second bottle was wetted with 10 cc of soap solution and 40 cc of benzene were added. Complete emulsification required nine minutes of shaking, as in the previous case. The emulsions produced were both of the benzene-in-water type and absolutely identical in appearance. Furthermore, the results were the same, even when the surface was increased relatively and absolutely by the addition of a given quantity of glass beads to each bottle before shaking. The order in which the components are added to the bottle seems to be unimportant; so also it makes little difference which of the two liquids wets the glass surface in the beginning.

The material composing the surface was next changed by coating the interior of the bottle with substances such as bakelite, collodion, lacquer, shellac, etc. In this case also, just as in the experiments immediately preceding, no important differences were observed in the amount of shaking required to produce a completed emulsion, though perhaps the collodion surface aided the process to a certain extent. At any rate, the emulsions were all of the benzene-in-water type.

Ostwald's experiments are not highly satisfactory, as a matter of fact, for his emulsions scarcely deserve the name, being, as they were, coarse and ephemeral suspensions of oil in water or water in oil, with no emulsifying agent specified. Nevertheless, they undoubtedly point to a determining influence produced by the liquid wetting the walls of the flask. The liquid wetting the walls tends to become the outside phase. The strength of this tendency is small, however.

Hofmann's experiments are complicated by the use of a third substance—lecithin or wax. These being soluble in benzene and insoluble in water and having the ability to concentrate in the interface as a coherent film, one should expect an emulsion of water in benzene to be produced, regardless of which liquid wets the walls of the bottle. Of course, this expectation is warranted only by the assumption that the determining effect of the third substance is much greater than that of the surface wetting. Hofmann's results seem to indicate also that the relative volumes of the two liquids constitute a third factor. This is likewise unimportant, relatively, for it is easily possible to prepare an emulsion of benzene in water containing 99 percent of the former if sodium oleate be used as emulsifier, while almost as great a percentage of water has been emulsified in benzene containing magnesium oleate or in white lead paints containing rosin.

Since the use of an emulsifier of peculiar influence counts against Hofmann's conclusions, so also the same objection applies to our own experiments with sodium oleate emulsions. All that we may conclude with safety is that the nature of the third substance overshadows in its determining effects the two other factors—wetting of the surface and relative volumes of the liquids. How far this conclusion applies to emulsification by other means than shaking, is not certain.

Emulsions Containing Free Alkali

Experiments were performed by Mr. H. G. Carter in this laboratory to determine what effect is produced upon the time required for emulsification by adding free sodium hydroxide to the soap solution. The data appears in Table VII.

These data are made more easily intelligible by the curves in Fig. 3, where the abscissae measure the concentration of free alkali in the soap solution and the ordinates are the average times required to complete the emulsions. Since these last are an inverse measure of the ease with which an emulsion containing a definite quantity of free alkali may be obtained, the curves show that small amounts of free alkali (not exceeding one-tenth of one percent) are distinctly beneficial. As the alkali content increases, however, the emulsions

Table VII—Effect of Free Alkali

(*a*) Aqueous phase: one percent sodium oleate

No. of bottle	Percent benzene by volume	Shaking required in minutes			
		NaOH = 0%	0.01%	0.1%	1.0%
1	90	22	20	19	>30
2	80	11	8	6	>30
3	70	10	6	4	>30
4	60	10	6	4	14
5	50	3	2	1	2
	Average,	10.6	8.2	6.4	>17

(*b*) Aqueous phase: 0.5 percent sodium oleate

1	90	30	19	23	>30
2	80	9	6	8	>30
3	70	8	4	6	>30
4	60	5	1	1	15
5	50	3	1	1	3
	Average,	11	6.2	7.8	>22

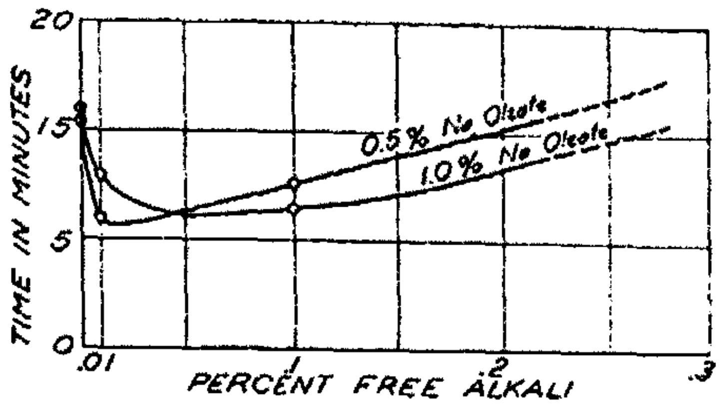

Fig. 3

are produced with greater difficulty. This fact may be connected with the "salting out" of the soap by the addition of sodium hydroxide. The stabilizing action of small amounts of free hydroxide may be due to a true peptonizing action or to the reduction of hydrolysis and the consequent disappearance of the acid sodium oleate, a relatively insoluble substance. It is interesting to note that as the concentration of the soap solution falls off, the value of the optimum concentration of free alkali decreases.

Emulsions of Water

Newman's emulsions of water in benzene were prepared by shaking water up with benzene containing a dissolved third substance of suitable emulsion-building properties. After considerable experimenting it was found that the metallic soaps were eminently useful, especially the oleates of magnesium and calcium, which though insoluble in water are readily dissolved by warm benzene. It is not certain what the nature of these solutions is; it seems quite probable, however, that they are colloidal.

When water and a benzene solution of magnesium oleate are shaken together, if the water is not in too great excess, the latter is completely emulsified in the benzene solution; if the relative proportion of water is large, the emulsification is incomplete. In this respect the similarity between the two types of emulsion is shown very plainly. On the other hand, if water is added little by little with constant shaking its relative proportion may be increased up to ninety percent or more, until a stiff, jelly-like mass is obtained. The emulsions of water in benzene differ strongly from those of the other type by being very much less stable; within a few hours they invariably decompose.

The two types of emulsion are very much alike in outward appearance, especially when the concentration of the disperse phase is relatively high in either case. A very useful test[1] has been devised for the purpose of distinguishing one form of emulsion from the other—a test which depends upon the fact that an emulsion is miscible with an excess of that liquid which forms the external phase but is not miscible in the liquid composing the disperse phase or the drops. If one removes a bit of the opaque cream from a benzene-in-water emulsion with a clean glass rod and stirs it into a drop of *water* on a glass plate, it will be found that the emulsion and the excess of water mix completely and easily. On the other hand, if a second portion be stirred into a drop of *benzene*, no mixing

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[1] Newman: Jour. Phys. Chem., 1, 34 (1914).

at all takes place. If the emulsion is of the water-in-benzene type, however, mixing occurs readily in benzene, but not in water. The test is quickly performed and is exceedingly decisive. In this connection it is interesting to find that Pickering[1] recognized the principle involved when he wrote:

"There are no signs of an emulsion of water in oil [using the alkali soaps]. As a consequence of this, an emulsion—even a 99 percent one—will mix perfectly with water to form a weaker emulsion, but will not mix with more paraffin [oil]."

Magnesium oleate was prepared from the sodium salt and magnesium sulphate, washed until free from soluble impurities and carefully dried. One percent solutions of the oleate in benzene were made up, by heating a mixture of the two on a steam bath in a flask fitted with a reflux condenser. In about an hour solution was complete. In the experiments to follow the concentration of soap in the benzene was kept constant, according to procedure A.

Four sets of emulsions were made—each set containing the usual nine bottles—and the time of shaking was varied as follows: 5, 10, 20 and 30 minutes. No case of three layers was observed, for all the lower water layer seemed to be emulsified in every bottle, though the stability and opacity of the lower layer increased with the duration of the shaking. Two layers only were produced, an upper layer (cloudy) consisting of an excess of benzene, and a lower opaque layer of emulsified water. The appearance of the set was just the reverse of that observed with the set of completed benzene-in-water emulsions, for in the latter case the opaque cream floated on the clear layer while in the present instance the opaque cream settled to the bottom and the clear layer remained on top. In no case was the separation of an excess water-layer observed, unless the emulsions were breaking down, which they did very rapidly when once started. The only visible effect of long-continued shaking, as we have seen, was to increase the opacity of the lower layer; we can infer

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[1] Jour. Chem. Soc., 91, 2003 (1907).

from this that the mean diameter of the water globules was correspondingly lessened.

With a one percent solution of magnesium resinate in benzene (the soap dissolved very easily in this case), the attempt to produce stable emulsions was a failure. The resinate was precipitated in flocculent masses by contact with water. Thus, although this particular substance is able to condense in the dineric interface, it does not possess the necessary ability to produce a suitable membrane and to insure the stability of the emulsion momentarily produced. Copper resinate and lead oleate are also unsatisfactory. Barium oleate is less effective than the magnesium salt.

With aluminum palmitate the emulsions were slightly different in their general aspect. Several hours' heating was necessary to produce an approximately one percent solution of the soap in benzene. After being shaken and allowed to stand, the emulsions did not separate into the usual two layers, but formed a stiff and viscous jelly. This jelly was not very opaque—it was fairly translucent as a matter of fact.

Under the microscope these palmitate emulsions consisted of large and irregular drops of liquid (water), entangled apparently in a voluminous precipitate of a very gelatinous nature. After standing for half an hour, the emulsions broke down spontaneously; but before this took place, they fulfilled the test for an emulsion of water in benzene. These emulsions seem to be analogous with Pickering's "quasi-emulsions,"[1] which he describes as follows:

"The general behavior of these lime emulsions suggests that they are merely coarse mechanical mixtures of lime and paraffin and not true emulsions. An examination under the microscope confirms this view; the oil globules in them are very large and show great variation in size, being, when under the most favorable conditions, ten times the diameter of the globules in a soap solution. They appear to be merely caught by, and entangled in the particles of lime."

Following this suggestion a microscopic examination of

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[1] Jour. Chem. Soc., 91, 2008 (1907).

the various emulsions was undertaken, with the result that interesting differences were discovered. Emulsions of benzene in sodium oleate, resinate, etc., were of the usual form, consisting as they did of small spherical drops of benzene floating in the aqueous medium. While the globules were irregular in size, they could be made smaller and more uniform by homogenization.[1] The interesting thing is that the membranes about the drops must be very elastic and mobile, for no variation from the spherical shape of the globules was to be seen. With the emulsions in aqueous gelatine, however, this was not the case, for the globules were somewhat irregular in shape and the membrane was thick enough apparently to be visible. Here is a case similar to that of the haptogen membrane in milk. One cannot neglect to take into consideration the strength, elasticity, and permanence of the surface membrane.

The internal structure of the water-in-benzene emulsions was found to be of a different nature. The magnesium oleate emulsions seemed composed of a gelatinous material containing a large proportion of water in exceedingly irregular masses; there were no sharply defined water globules as such and the readiness with which the emulsions decomposed while under observation made their study a very uncertain matter. The structure of the magnesium emulsions was the same essentially as that of the aluminum palmitate emulsion described—the difference being one of degree only. The more pronounced development of the gelatinous material in the second case accounts without doubt for the non-formation of two layers on standing.

Emulsification and the Drop Number

Donnan[2] has measured the effect of alkali soaps in lowering the surface tension between oil and water, by counting the number of drops produced when a given volume of oil is allowed to flow through the aqueous solution and by comparing the number so found with that obtained by allowing an equal volume of oil to drop through pure water. The ap-

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[1] Briggs: Jour. Phys. Chem., 19, 223 (1915).

[2] Zeit. phys. Chem., 31, 42 (1899).

paratus required for the purpose is called a "drop pipette," and the number of drops per given volume of oil is the "drop number." As the surface tension is lowered by continued addition of small quantities of soap to water, the drop number of oil is increased until it finally reaches a fairly constant value.

A drop pipette was constructed from a 5 cc pipette by fusing a length of capillary tubing to the stem below the bulb and this was bent into a U and drawn out to a fine point, the whole having the shape of a large fish-hook. The bent portion was placed into a beaker of distilled water or into the solution being studied and a given volume of benzene allowed to flow upward in drops through the solution. The approximate number of drops being ascertained, the following data were produced:

Aqueous phase	Number of benzene drops
Water (distilled)	87
Ditto	89
Sodium oleate 1%	230
Sodium resinate 1%	210
Gum arabic 1%	61
Gelatine 1%	23–32

The soap solutions give data as per schedule, where the greatly decreased surface tension as compared with pure water is indicated by the rise in the drop number. But with gum arabic and gelatine the results are quite different, for here another factor enters in—the great elasticity and strength of the semi-solid films formed about the drops of benzene. This may be seen quite easily, for the films act like small rubber bags, which expand steadily as they are filled with benzene and are detached only with difficulty from the orifice of the pipette. This permitted the drops to become comparatively large in some instances and quite irregular in shape. These observations are entirely in agreement with what we have reported as the result of microscopic examination. Finally, both gum arabic and gelatine are emulsifying agents, so that drop-number measurements are not a fair and sufficient test for an emulsifier in solution.

Having determined the drop number of benzene against a number of aqueous solutions, we decided next to measure the drop number of water against benzene containing the metallic soaps in solution. This was easily done by giving the capillary of the drop pipette an extra bend so that the orifice pointed downwards and allowing the water to flow from the pipette in drops[1] through the benzene solution. The drop numbers follow:

Benzene phase	Number of water drops
Distilled benzene	42
Benzene + 1% Mg oleate	160–180
Benzene + 1% Mg resinate	160–180
Benzene + 1% Al palmitate	48–50

These data seem to indicate that the magnesium soaps in benzene act in a manner that is analogous in all respects to the alkali soaps in water, so far as the drop number is concerned. Actually, however, the film produced by the resinate, though equally effective in the first instance by comparison with the oleate, goes to pieces very quickly and the emulsions produced at first are consequently quite unstable. The aluminum palmitate emulsions, while very coarse, actually were more permanent than those prepared with magnesium resinate. Here again the drop number is not in every case a measure of the ability of a solution to form a permanent emulsion of the liquid under consideration.

The results of this paper are the following:

1. Two types of emulsion are possible with benzene and

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[1] The behavior of the falling water-drops in the benzene solution of magnesium oleate was interesting to watch. As the drops fell, they assumed a spherical shape and became covered with a whitish film, not unlike a scum, which prevented coalescence—at least for a time—when the drops came in contact with one another. This behavior of the freshly formed films was more striking when one observed the drops as they reached the water layer below the benzene. The surface of the water was also covered with a thin, white scum and was separated by it from the benzene solution, so that, as the drops struck the water surface they bounded back like so many small rubber balls. Here and there the film separating the drops from the mass of water became ruptured and coalescence occurred; moreover the strength of the films seemed to decrease with time.

water depending upon the nature of the emulsifying agent and the properties of the films produced in the dineric interface.

2. Emulsions of benzene in water may be prepared if a suitable water-soluble emulsion builder is present; under these conditions the relative amounts of the two phases and the wetting of the walls of the bottle are of very little importance in determining the type of emulsion.

3. Emulsions of benzene in water may be obtained by direct shaking in the presence of small amounts of alkali soaps and other substances; the concentration of benzene in the emulsion varies with the amount and intensity of shaking, approaching a limit which is probably not much below 100 percent.

4. A study has been made of several different emulsifying agents soluble in water. The properties of the emulsions produced depend largely upon the interfacial membrane.

5. The ease with which benzene is emulsified in aqueous sodium oleate increases very rapidly at first as the concentration of soap rises to one one-hundredth of one percent, after which it remains more or less constant. A slight maximum occurs as the soap concentration increases.

6. The ease with which benzene is emulsified in aqueous sodium oleate is strongly affected by free alkali hydroxide. At low concentrations free alkali has a peptonizing action; at higher concentrations it has a very deleterious effect.

7. Emulsions of water in benzene may be prepared if a suitable benzene-soluble emulsion builder is present; under these conditions the relative amounts of the two phases and the wetting of the walls of the bottle are of secondary importance in determining the type of emulsion.

8. The nature of the emulsions of water in benzene depends upon the properties of the film produced in the dineric interface.

9. The drop number cannot be used directly as a measure of the probable efficiency of a substance as an emulsifying agent for a given liquid.

Worcester Polytechnic Institute—Cornell University
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HEAT OF VAPORIZATION AND MOLECULAR ASSOCIATION IN LIQUIDS

BY M. M. GARVER

In a recent paper[1] on "Molecular Association of Liquids," Professor Tyrer takes occasion to condemn as "based on untenable assumptions" two articles of mine, the first on "A Thermodynamic Measure of the Degree of Polymerization of Liquid Substances,"[2] and the second on "The Polymerization of Liquids and a General Method of Determining its Relative Value."[3] While the condemned articles made no claim to being beyond criticism, or to contain the last word on the subject they treated, they were offered as a real contribution to the literature of the subject which should be taken into consideration by any one interested in the molecular constitution of liquids; for the so-called "untenable assumptions" were based on a new, and, as it seems to me, important fact.

The new fact, which, in my judgment, warranted the assumptions *actually made* (I repudiate entirely the condemned assumptions which were imputed to me) was a new equation discovered by me in an investigation on the range of molecular action.[4] The equation, which will be referred to in what follows as equation A, states that

$$\frac{\gamma}{2\epsilon} = \rho \frac{R}{m} T \qquad \text{A}$$

where γ is the surface tension in dynes per centimeter length, ϵ is the range of molecular action, ρ is the density of the liquid, R is the absolute gas constant, m is the molecular weight of the vapor and T is the absolute temperature.

Now the assumptions actually made, not the "fundamental errors" and "unjustifiable assumptions" wrongly

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[1] Jour. Phys. Chem., 19, 81 (1915).

[2] Trans. Roy. Soc. Can., 6, 95 (1912); Jour. Phys. Chem., 16, 454 (1912).

[3] Eighth Int. Cong. App. Chem., 22, 129 (1912); Jour. Phys. Chem., 16, 669 (1912).

[4] Trans. Roy. Soc. Can., 6, 3, 81 (1912); Jour. Phys. Chem., 16, 284 (1912).

attributed to me, were based on my interpretation of this equation which Tyrer entirely ignores, thereby giving the reader the impression that my assumptions were based on some hazy notions about "intrinsic pressure" instead of on facts. Moreover, I doubt whether any reader, however candid and competent, would be able to discover from Tyrer's statement of my assumption just what I did assume, to say nothing of the grounds for the assumption. Scientific fairness, as well as regard for scientific truth, requires that when one unqualifiedly rejects a scientific deduction it should at least be fairly stated, even if no detailed reasons be given for the rejection; for an apparently fair and oracularly delivered verdict against what on the surface seems to be in opposition to accepted doctrine, has great weight in preventing fair and discriminating investigation. I knew perfectly well that the new point of view that I have presented would have against it all those who were influenced by authority instead of fact, for many of the great names in mathematical physics can be cited against me without misrepresenting me in what Professor Tyrer calls my "untenable assumption," or a "fundamental error." But it is not possible to claim as "settled" any scientific problem, or question, so long as any opposing fact or evidence is ignored. Two courses were open to Professor Tyrer, or to any other critic interested in scientific truth: (1) Show that the new equation was faulty, or was incorrectly deduced from the experimental facts, or, (2) show that the assumption, or interpretation, was not warranted by the equation itself, but that quite different conclusions should be drawn from it. Failure to do either one of these two things must inevitably weaken any objections that may be made to the necessary conclusions to which the interpretation may lead.

Of course, an objection, like an assumption, should be based on something tangible and evident; accordingly, Professor Tyrer proceeds to state at some length his reasons for his rejection, but instead of attacking the basis of the assumption he attacked the conclusions to which he *assumed* it led. But, strange to say, he did not correctly apprehend and state the assumptions expressing my interpretation of equation A, which was:

"*The attractive forces which maintain a substance in the free liquid phase are just numerically equal to the pressure the same substance would exert were it a perfect gas, at the same temperature and density.*"[1] Here the "same substance" is to be understood as chemically the same in both liquid and vapor phases and that the film of liquid in contact with the vapor is of the same molecular weight and constitution as the vapor. This may be true even when the liquid is more or less polymerized, or associated. This view of the nature of the equilibrium between a liquid and its vapor is discussed more fully by me in a paper "On the Molecular Constitution of the Free Surfaces of Liquids."[2]

From the preceding remarks it may be gathered that I cannot regard any criticism which leaves the integrity of equation A unimpaired as of very serious consequence, although from the oracular tone in which judgment is pronounced against what is stated to be my scientific method, or theory of procedure, the uninformed might receive the impression that I had violated the mandate known as the "Twelfth Commandment" which declares: "Thou shalt not write about that which thou dost not understand." However, Professor Tyrer points out three specific instances in which he charges me with making fundamental errors or unjustifiable assumptions, and these may be examined and disposed of in detail in order that the reader may judge for himself where the "fundamental error" lies. He says:

"Another method of determining the association factors of liquids has recently been proposed by Garver. This method depends upon the following considerations concerning the latent heat of vaporization of a liquid:

"If L is the latent heat, then

$$L = l + E + H$$

where l is work done against molecular attractions, E is ex-

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[1] Jour. Phys. Chem., 16, 669 (1912).

[2] Ibid., 17, 368 (1913).

ternal work done and H is heat of dissociation of any associated molecules which split up as the liquid vaporizes." He then discusses the determination of these separate quantities, and continues: "The trouble lies in determining *l* and in this Garver makes a fundamental error."

The casual reader of the above excerpts would naturally suppose that the "method" referred to was Garver's, but it is Tyrer's exposition of what he regards as Garver's error. The theoretical considerations presented are Tyrer's; they certainly are not Garver's, for they cannot be inferred from anything that I have written. I care nothing about the value of *l* as distinguished from E and made no effort, or attempt, to determine it. Perhaps Tyrer thinks that I ought to, but that is where he and I differ. On page 678, in the second paper criticized, in reply to a supposed criticism I emphasize and *italicize* this very point. "The *direction of the action* can have no influence on the *magnitude* of the work performed by it. So far as work is concerned it is immaterial whether it be done by a push or a pull or by a combined push and pull." This wording was intended to direct particular attention to my claim that it made no difference whether the heat of vaporization *be attributed to molecular attraction or to external pressure.* Notwithstanding the above explicit statements he proceeds to exhibit *l* as having been determined by the following integral:

$$-\frac{1}{J}\int_{v_L}^{v_V} \frac{RT}{v_L}\,dv = l$$

and then remarks: "This assumption is perfectly unjustifiable for several reasons." In the last statement I most heartily concur, even if the integral does not contain a misprint (*i. e.*, is corrected); for in either case, if it were true my equation could not be true. For, if v_L is a constant in the integral it is nonsense to me, and if a variable, then the right-hand member represents only a hypothetical part of what mine is intended to represent, namely, *the work due to forces, internal or external or both together.* On page 460 of my first paper, under "Theoretical Summary," my equation is given as

$$W = \int_1^2 (p + \gamma)dv = \int_1^2 P\,dv$$

where W is the total work attributable to forces of any character, p is external, and γ is the internal forces. For the parenthesis, one *variable*, P, can be substituted. (Query. Did Tyrer take P to be a *constant?*) But I shall waive the difference in the above two equations and suppose that our critic's objections are directed against the one that I acknowledge to be mine. Professor Tyrer continues: "First, because the Boyle pressure of a perfect gas is caused by the impact of particles of negligible size against the walls of the containing vessel while the intrinsic pressure in a liquid is caused by the impact of particles of comparatively appreciable size against each other. The two phenomena are radically different.[1] The intrinsic pressure must be much greater and can, in fact, be shown to be much greater than RT/v_L. Secondly, assuming for the moment that the intrinsic pressure is really equal to RT/v_L, the expression

$$-\frac{1}{J}\int_{v_L}^{v_V} \frac{RT}{v_L}\,dv$$

is not equal to the internal heat as Garver supposes, for in no case does this agree with facts but gives latent heats much too small."

This is pure imagination, for I have nowhere supposed that that expression should give the internal heat. On the contrary, if the R in Tyrer's equation represents the R/m in my equation, where m is determined from the density of the *saturated* vapor; and for the v_L we write v, for the variable

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[1] The logical reader will please observe that the above statement is made by a writer who claims that the molecules of a "normal liquid" are of the same weight and character as those of the non-associated vapor. Does he not confuse the theoretically deduced law with the experimentally observed law and apply the first to gases and the second to liquids?

to be integrated, *then* it should give the value of that portion of the total heat, L, that *may be attributed to forces.*[1] The remainder of the heat must come from some other source with a corresponding change in the internal kinetic energy. For, if we know the force function and the displacement produced by or against the forces, then we are not permitted to assume forces *ad libitum* to account for heat effects. The heat effects attributable to forces are strictly limited because the forces and displacements are strictly limited. Heretofore it has been the custom of writers to estimate the forces acting during changes in the volumes of fluids from the heat effects observable. However, suppose that the force function becomes known by the direct observation of a force action; then we can determine the quantity of heat which we can consistently attribute to forces—the remainder of the heat, if any, *must of necessity be accounted for otherwise.*

If equation A is correctly deduced from the experimental facts discussed by Kelvin and Poynting and Thomson, then it undoubtedly expresses a law of Nature, and, as such, requires recognition and interpretation in connection with related facts even if it *does seem* to contradict other established facts. The equation itself, if correctly deduced from experimental facts, is not an assumption; it is a fact and cannot be ignored merely because it does not fit in with other equations also regarded as representing facts. Numerous equations

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[1] I find it impossible to determine whether v_L is a misprint for v or only another vagary among many others. If it is a misprint for the variable it represents more nearly my proposed integral. In the discussion which follows I have supposed v_L in the denominator of Tyrer's integral to represent the variable v, but I may be mistaken. He may have imagined that when I wrote $\int_1^2 Pdv$ I meant $P\int_1^2 dv$. This error, however, is hardly excusable, for P, as written in the integral, is an implied function of the variable, not a constant. Also, on a later page (465) I integrated the function, and in another place (p. 669) wrote $\int_1^2 Pdv = K\int_1^2 \frac{dv}{v}$.

claiming to be experimentally verified may be cited against the law of force represented in equation A. However, it will be found that in all such cases the law of force is deduced, either from heat effects or from some *external* force effects. In equation A alone do we measure the direct effects of molecular attractions. The following confirmation, based on experimentally observed values, is interesting and instructive. Consider the following four characteristics of a liquid substance: the surface tension γ, the density of the liquid ρ, the vapor pressure ω and the vapor density σ. The surface film has some thickness. Represent it by τ. Then $\gamma\ \tau\rho$ is the attraction per unit area of the cross-section of the film per unit density and $\omega\ \sigma$ is the pressure of the vapor per unit area per unit density. Call the ratio of these two ratios r. Then $\gamma\ \tau\rho \div \omega\ \sigma = r$. But σ, the vapor density, being known we can find m for the vapor and write $\frac{\omega}{\sigma} = \frac{\mathrm{RT}}{m}$. Solving for the intrinsic pressure (or intrinsic attraction) of the liquid, we get:

$$\frac{\gamma}{\tau r} = \rho \frac{\mathrm{R}}{m} \mathrm{T} \text{......................B}$$

Since all the other values in this equation are the same as those in equation A it is impossible to avoid the conclusion that τr is the same quantity as 2ϵ in equation A; and since τ is a thickness, r is a length, for τr is evidently an area. It is plain that two centimeters of one surface film will have the same area of cross-section as one centimeter length of a film with two surfaces, or $r = 1$.

From this equation, are we not entitled to conclude that the attraction per unit area of cross-section in a liquid film is just numerically equal to the pressure per unit area that would be required to give the substance the density of the liquid if it were a perfect gas of molecular weight m and free from molecular attractions? And is not the equation applicable to all pure liquids in which the vapor has the same chemical constitution as the film with which it is in contact? Again, if the liquid is enclosed and is at a temperature such that the vapor has an appreciable pressure with the two phases in equilibrium in the closed space does not the pressure of the vapor merely supplement the molecular attraction which is insufficient at a temperature that produces the vapor pressure?

No doubt Professor Tyrer found it difficult to accept my interpretation of Equation A which antagonizes a very prevalent belief in the reality of enormous intrinsic pressures in the interior of liquids. Equation A asserts that the attraction in liquid films is proportional to the density while van der Waals' equation requires that the attraction be proportional to the *square* of the density. Which represents the actual truth, or does either? Personal preferences have nothing to do with such questions; it is the truth that we are seeking. I was not content to accept the new equation unquestioningly but sought information on all sides, and only after deriving it in a number of different ways was I convinced that it must represent an important truth. I am free to confess that until I came across this equation I also accepted the prevalent notions regarding immense intrinsic pressures in liquids; and until suggested by this equation I never thought of applying d'Alembert's principle to the equilibrium of a drop of free liquid. But when once suggested, the conviction was overwhelming that the principles of dynamic equilibrium must also apply to equilibrium in fluids. Since the conception of a "normal" liquid involves the same "molecule" as found in the vapor, in what ways can such a liquid, in its interior, differ from a gas of the same density and molecular weight? The reply will be to refer to the great "forces" acting. The fact is, however, that the term "force" is often used in a very loose and indefinite way to account for anything and everything that cannot be accounted for any other way. Clearness and exactness, at the expense of a little conciseness, would be furthered if the term "force" were dropped entirely and the definition were used instead of the single word. For, as applied in kinetics, the term force should always mean "the rate of change of momentum in the given direction." If this conception is adhered to, how is it possible to realize mentally, or express definitely the term "intrinsic pressure" (force per unit area) in the interior of a "normal" liquid conceived of as being made up of discrete, rapidly moving material particles possessing inertia, except as the rate of change of momentum normal to a unit of area immersed in the liquid? If the molecular masses and velocities are the same in both the liquid and vapor phases at the same temperature, then the "molecular pressure" in the interior of the liquid will exceed the corresponding vapor pressure per unit area in the proportion that the liquid density exceeds the vapor density. This conception is included in and is consistent with Equation A.

The above full explanation of my point of view is given because Professor Tyrer waves it aside as an "unjustifiable assumption" and insists that there is an essential difference between gas pressure and intrinsic pressure, for "the two phenomena are radically different." In my judgment, the "intrinsic pressure" in the interior of a liquid that is radically different from the gas pressure in the interior of a gas is not a phenomenon but a conception, and a misconception at that. Taking the Newtonian conception, or definition, of force given above and remembering that a force as applied to a system of freely moving material particles is measured by the *accelerations* of the particles in the direction of the force, perhaps Professor Tyrer will be so kind as to explain the "two radically different kinds of pressures" (forces per unit area) that he claims distinguishes the interior of a liquid from the interior of its vapor. Perhaps at the same time he may be led to explain how, in a drop of liquid, for instance, the accelerations inwards can be greater than the accelerations outwards without producing a continual increase in the density of the drop of liquid.

Another objection (page 85) that I can attribute only to a complete failure on the objector's part to comprehend what he is criticizing is that "Even if we could discover the correct expression for the intrinsic pressure of a liquid * * * * even then we could not employ Garver's method for the simple reason that the force * * * * is not equal to the attractive force when the volume lies in between v_v and v_L, for if it were so it would be possible for liquid to exist in this intermediate state at the same temperature." This last statement leads me to conclude that the v_L previously mentioned is not a misprint but represents a complete failure on the part of Tyrer to comprehend what I meant. At any rate this objection shows that my point of view was not comprehended or its significance grasped, for I have never proposed to find the internal heat of vaporization from the intrinsic pressure of a liquid, by a process of integration. My integral is designed to find the total heat due to *forces* whether external or internal during an isothermal change from a vapor of volume v_V to a liquid having a volume v_L. My division of the total heat L is into two parts, W the heat attributable to forces, and H the heat attributable to change in the internal kinetic energy of the substance. Each of these parts may often with advantage be again subdivided. If we know the force function we can find by integration the part of the total heat due to force, whether external or internal. The reason why the intermediate stage need not be considered is that we are dealing with a force function having a potential. And the proof that we are dealing with a potential is found in the fact that the energy change must be independent of the path, and depend solely upon the initial and final states. All we need to know is the force function along some *one* path. The discontinuity mentioned in the objection has no application whatever to the integral which I proposed, for it is a continuous and single valued force function of the sum of *two* actions, external pressure and internal attraction, one increasing as the other diminishes. And just as the latent heat of vaporization per unit mass is independent of the actual mass undergoing change of phase, so the total heat is independent of whether the whole mass changes phase all at once or gradually. In any case the whole will be equal to the sum of the parts. Hence our summation, or integration, need take no account of the rate of change from one phase to the other. All that is necessary is that it should apply in some *one possible way*. That is where equation A comes in, for from it we may conclude that the only effect of the molecular attraction is to diminish the pressure that would otherwise be necessary.

It is perfectly possible, ideally, to take any vapor below its critical temperature and compress it isothermally and reversibly into a liquid having the same temperature as the original vapor. Is Professor Tyrer prepared to deny that the same quantity of heat would not be given out by all possible changes involving the same change in volume of the same substance in which the initial and final states and temperatures are the same, *i. e.*, whether isothermal or not? And if the total energy change (heat given out or absorbed) depends only upon the initial and final states of the substance, then are we not permitted to choose the simplest path between the two states? In the case of isothermal compression would not the total heat, $L = W_e + W_i + E_v + E_n$, where W_e is external and W_i internal work, E_v any change in molecular velocity and E_i internal energy change due to change in the number of molecules, supposing all quantities to be measured in the same units? In special cases one, or even two of these quantities may be zero, but in general, all four are possible and are to be reckoned with. In my previous work I assumed that Maxwell's law held, or that E_v was zero. Professor Tyrer claims that in some cases, at least, E_v is not zero, CS_2 for instance. If this be true and is generally established, then the surplus heat over what can be attributed to forces, will have to be distributed between the two kinds of internal change.

But to return to the main point. Although we cannot by a process of integration find the "internal heat of vaporization" (as Tyrer claims that I tried to do), I do insist that equation A and d'Alembert's principle enable us to find the sum of the two quantities W_e and W_i by a process of integration. For consider the equation $L = W_e + W_i + E_v + E_n$. Between two isothermal states v_v and v_l, the quantities L,

E_v and E_n are fixed and definite. We cannot vary them in any way; they are constitutional. But the sum, only, of W_e and W_i is fixed and definite. Hence, so long as we use the correct force function for the effect of the *sum* we may imagine either one to be increased or diminished at will and use whichever lends itself best to an isothermal process. It is plainly evident that in the isothermal compression of a vapor to a liquid there would be no liquefaction if there were no molecular attractions; but the *heat effect* must be independent of whether the *force* be an *attraction* or a *compression*. We are at liberty then to assume at will all attraction or all compression, since the only possible effect of the attraction is to diminish the compression that would otherwise be required. Since equation A shows that the attraction in a liquid film is directly proportional to the density of the liquid; and Boyle's law states that in an ideal gas the pressure is also directly proportional to the density, we may, ideally, use the compression law in bringing about the isothermal change in volume from v_V to v_L, and then substitute (ideally, of course) an equal attraction for the force of compression. We would, then, for temperatures at which the vapor pressures are negligible, have our liquid in stable equilibrium without the application of external force. The attractive film would simply replace the retaining walls of the containing vessel because the rate of change of momentum normal to the free surface of the liquid film due to the attractive forces would be numerically equal to what the rate of change of momentum would be normal to the retaining walls if there were no molecular attractions.

Finally, Tyrer calls attention to what he regards as a conflict between my proposals and Dieterici's equation, $l = \mathrm{CRT}\,ln\, v_V/v_L$. It is curious that he did not observe a remarkable similarity between them rather than cite one against the other. When my papers were published I was unacquainted with Dieterici's equation and Richter's experimental investigation of it;[1] but the similarity mentioned

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[1] Inaugural Dissertation, Rostock (1908).

may easily be exhibited. From the published values of $L/W = r$ it may be seen that my values of r are always somewhat higher than Dieterici's values for C. The reason is evident when the two equations are compared. Since $L = rW$, my equation may be written $L = \frac{R}{m} T \ln \frac{v_v}{v_L}$, where L is the *total* heat instead of "internal" heat l as in Dieterici's. In my equation, however, r is not supposed to be a constant, but to have the value unity for a non-associated liquid. Also, $\frac{R}{m}$ is not necessarily the same as the "gas constant R" because it is intended to represent the *absolute*, or hydrogen value of "R" divided by the molecular weight of the *saturated* vapor as determined from the density of the saturated vapor. It is true that I did not always take sufficient care to use the *actual* instead of the *theoretical* value of m in my computations, but except for strongly associated vapors, as acetic acid, for instance, this failure did not lead to large errors. In the case of acetic acid this was partially corrected and special attention called to it.

In my previous work I assumed Maxwell's law to hold, but the value of $r = \frac{L}{W}$ is really, if the separation previously suggested is made, better expressed by $r = \frac{W_e + W_i + E_v + E_n}{W_e + W_i}$, or, $r - 1 = \frac{E_r + E_n}{W_e + W_i}$ if there are two kinds of internal change, as many claim, and as Tyrer claims in the case of CS_2 and some other liquids. Also, in my first paper of the two I called attention to a remarkable relation of the above r to the k of Ramsay and Shields for their normal liquids; r is always smaller than their k just as it is always larger than Dieterici's "C." There is evidently some intimate relation between the three diverse methods, although the reason why r is larger than "C" is perfectly obvious.

State College
March, 1915

THE THEORY OF EMULSIFICATION. VII

BY WILDER D. BANCROFT

It has been noticed that after a while certain colloidal solutions become covered with an apparently solid film. Since this film forms at the foam interface, it might be considered in connection with the adsorption of gases by liquids. Experimentally, however, the phenomenon is more akin to the emulsion formation and consequently I prefer to consider it as an intermediate case.

The best experimental work on the subject has been done by Metcalf in Ostwald's laboratory.[1] When a few drops of a peptone solution are allowed to spread over a surface of pure water, a solid elastic film forms in a short time on the surface of the water. "Siegfried's experiments[2] have made it probable that ordinary peptone is a mixture of different allied substances rather than a definite chemical compound. It was, therefore, desirable to determine whether the formation of a solid film was dependent on the complex nature of peptone or whether a definite chemical compound is able to form such a film. I was fortunate enough to secure a sample of pepsin-fibrinogen-peptone-*a* which had the formula $C_{21}H_{34}O_9$. It was prepared by Professor Siegfried and was kindly presented to me by Dr. W. Neumann. Both Professor Siegfried and Dr. Neumann are convinced that it is a definite chemical compound. A 3.2 percent solution of this substance was prepared and two drops were placed on the surface of pure water. A test with a piece of cork showed that the surface was still mobile. A few more drops were then added, whereupon a solid elastic film was formed. On standing a few minutes this film disappeared completely and the surface became mobile again. On adding another drop, a solid film was formed again but disappeared in time, though more slowly than the preceding one. This was repeated several

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[1] Metcalf: Zeit. phys. Chem., 52, 1 (1905).

[2] Siegfried: Zeit. physiol. Chem., 35, 164 (1902); 38, 259 (1903).

times until at length a permanent film was obtained. This was allowed to stand for twenty hours, at the end of which time it had increased perceptibly in viscosity. This experiment shows conclusively that the formation of solid films of peptone does not depend on peptone being a mixture.

"The experiment also shows that the solid matter, of which the pepsin-fibrinogen-peptone film is formed, is somewhat soluble in water. The film continues to dissolve until at least the upper layers of the water phase are saturated with the substance which forms the film. The film then becomes permanent and even increases in strength with time just as do films of ordinary peptone. At any rate this is the most obvious explanation. This assumption of a slight solubility of the material of which the film is formed accounts for the probable minimum observed with an ordinary peptone film. This explanation is made more probable by the following interesting experiment with a very concentrated peptone solution. When one drop of such a solution is allowed to fall on a water surface, it spreads out somewhat on the surface; but the greater part of the drop sinks to the bottom of the dish. Where the solution comes in contact with water there is formed an easily visible, white membrane. At first the membrane has the form of two discs connected by a vertical tube. This soon disappears and no sign of it remains, because the peptone has dissolved completely in the water. It seems probable that the white membrane is formed of the same substance as the ordinary, invisible surface film of peptone. If so, a certain solubility of the film substance has been shown."

Metcalf found that a film formed at a low temperature is more elastic than one formed at a higher temperature; but the two become alike when brought to the same temperature. The properties of the film vary with the time.

"Immediately after dropping a 0.3% peptome solution on a water surface, the latter was tested by means of a piece of cork. A slight surface viscosity could be detected but no elasticity. The water surface in the blank test was very mobile. The dishes were covered and left for an hour and a half. The surface viscosity had increased perceptibly in the dish containing peptone. Twenty-four hours later a distinct elasticity could be detected, and this increased perceptibly in the next twenty hours. During this whole time the water surface in the blank test remained as mobile as at the beginning. The experiment was repeated a number of times in substantially the same way and there was always an increase of elasticity on standing. This increase often took place more or less irregularly but it was always to be detected. The film always went through all the stages from a very slight viscosity at first to a final distinct elasticity. It made no difference whether distilled or tap water were used.

"When one drop of a 0.15% solution was used instead of a 0.3% solution, no surface viscosity or elasticity could be detected either at first or after forty-eight hours. When two drops of this solution were taken, an elastic film was obtained at any rate in some cases. With a 0.6% solution the film was distinctly viscous from the start but not elastic. At the end of six hours the surface was distinctly elastic and the elasticity had increased appreciably by the end of twenty-four hours. Solutions containing 1.2% and 2.5% peptone differed from the preceding one only in that the films were elastic when first formed. The elasticity of these films increased with time."

A series of special experiments led Metcalf to the belief that diffusion is practically negligible[1] under ordinary conditions. On the other hand the following experiment seems to me to show that some diffusion must take place: "A solid, elastic film was formed by bringing several drops of a 2.5% peptone solution upon a water surface and allowing it to stand for 47 hours. Powdered cork was strewn over the surface and then about a third of the film removed by means of filter paper. Small particles of cork which were left by the filter paper were drawn by capillary action to the edge of the film and thus made this edge a clearly defined line. The undis-

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[1] Zeit. phys. Chem., 52, 25 (1905).

turbed portion of the film was just as strong and elastic as before, while the free water surface was as mobile as ordinary water. After four and one-half hours, the old film was still solid, the new surface mobile, and the line separating them clearly marked. The position of this boundary line had not changed perceptibly. Nineteen hours later the old film was still there and the boundary line was as sharp as ever; but the new water surface was now covered with a distinctly elastic film. The experiment was repeated twice with one drop of a 5.3% solution and also with one drop of a 2.7% solution. These films were left untouched for 89 hours and then a portion removed as described. The result was the same as before.

"A film was prepared by touching the surface of the water with a glass rod which had been dropped into a one percent solution. The liquid below the surface was watched carefully; but there was no sign of any peptone sinking down. The dish was then covered and left for almost four days, after which time a distinctly elastic film could be detected. A portion of this film was removed with filter paper. The edge of the old film moved forward a little over the new water surface. This first rapid movement soon came to an end; but the film continued to spread slowly over the water for about twenty-four hours. At the end of this time, the free water surface had become very small; but was still separated from the old film by a perfectly distinct boundary line. The water surface is, however, covered with a perceptibly elastic film. The old film had thus spread to some extent over the water surface and a new film had formed over the rest of it. There was no sudden spreading of the film over the whole water surface as is the case when a film is first formed."

Since it had been suggested by Schütt[1] that the film might be due to oxidation, Metcalf made some experiments in an atmosphere of hydrogen, getting the same results as in air. While this is satisfactory as a proof that the film is not an

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[1] Drude's Ann., 13, 712 (1904).

oxidation product, it shows nothing as to whether the presence of a gas is essential or not. Metcalf did not consider the possibility of peptone adsorbing air or hydrogen and being floated up by it.

At the end of his paper Metcalf discusses five possible hypotheses to account for the formation of a film when a solution is allowed to stand, or when a drop of solution is allowed to fall on a water surface. The first possibility is that the film is due to oxidation. The films that form on molten lead or on zinc amalgam are due to this cause; but the experiments with hydrogen exclude it in the case of the peptone films. The second hypothesis—due to Marangoni—is that no solid film is formed at all and that it is merely a question of a lowering of the surface tension with increasing surface viscosity. Since ether lowers the surface tension of water without increasing its surface viscosity, there is no necessary connection between these two phenomena. If there were no solid film, the surface tension would keep the surface uniform and we could not long have the phenomenon of part of the surface being mobile and the other part not. The third possibility is that peptone is a mixture of two substances, one of which is soluble in water and the other not, the film being formed of the insoluble substance. This seems to be negatived by the experiment with the peptone which was a definite chemical compound. Of course, Metcalf did not consider the possibility that the peptone is not soluble to any appreciable extent in water. He considered that his 5.3% solution, for instance, contained the peptone in true solution, whereas now we know that he was dealing with a two phase colloidal solution. The hypothesis goes by the board, however, if we can show that the film formation can be accounted for without postulating a mixture of substances.

As fourth hypothesis Metcalf suggests that the surface film may be a saturated solution. Since a dissolved substance concentrates in the surface layer in case it lowers the surface tension of the liquid, it is theoretically possible that the surface layer might be saturated when the mass of the solution was not. Metcalf has overlooked the possibility that the solubility in the surface layer might be greater than in the mass of the liquid, in which case the hypothesis would be untenable. He rejects the hypothesis on a different ground.[1]

"The separation of a solid phase at the surface of an extraordinarily dilute solution is difficult to account for on the basis of this hypothesis alone. The only possible explanation would be that the surface concentration is greater than the saturation concentration, for only under these conditions could the solid precipitate. Since the surface concentration is kept in reversible equilibrium with the concentration in the body of the liquid by the surface tension, saturation in the surface layer seems very improbable when one is dealing with such extraordinarily dilute solutions as were found to give distinct films. In the case of pepsin fibrin-peptone-*a* a perceptibly elastic film was obtained with solutions which contained less than one ten-thousandth the amount necessary for saturation.[2] In this case the ratio between the concentration in the surface and in the body of the liquid must be at least 10,000 : 1 according to the hypothesis. If we consider the molecular weight[3] of the compound as 514, the molar concentration of the solution is about 0.0001 mol per liter. If the law for the osmotic pressure of dilute solutions holds in this case, the osmotic pressure in the body of the solution is about 0.002 atmosphere. The osmotic pressure of the saturated solution must be at least ten thousand times as much or about 20 atmospheres. The difference between these two pressures, practically 20 atmospheres or 20,000,000 dynes, represents the osmotic pressure tending to make the solute diffuse out of the surface layer. The total surface energy of water is only about 81 ergs per square centimeter. The intensity factor of this energy is 81 dynes per square centimeter. It is difficult to believe that this can be in equilibrium with an osmotic

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[1] Metcalf: Zeit. phys. Chem., **52**, 41 (1905).

[2] A saturated solution contains at least 59% substance. In one experiment a solid film was obtained with a 0.0059% solution.

[3] Zeit. physiol. Chem., **38**, 293 (1903).

pressure of 20,000,000 dynes per square centimeter. Other cases could be cited which are even more extreme.[1]

"It is not to be assumed that this calculation is even approximately accurate. It is very probable, however, that the two forces, which are in equilibrium according to the hypothesis, are of quite different orders of magnitude. It seems probable also that a solid film forms over the surface of a peptone solution long before the surface layer can have attained the concentration of a saturated solution."

On this statement of facts, Metcalf was quite justified in rejecting this hypothesis. The difficulty is that his statement of facts is not correct. There is no evidence that the osmotic pressure in a 59% peptone solution is of the order of 20 atmospheres. If we are dealing with a colloidal solution the whole of the hypothetical counter-osmotic force disappears. As I shall show, a modification of this hypothesis is undoubtedly the correct explanation of the phenomenon.

Metcalf himself decides in favor of the hypothesis that pure peptone changes into an insoluble modification. His argument[2] is based on a theorem by Gibbs. "If the substances in a solution are capable of reacting chemically so as to cause a lowering of the surface tension, there is a tendency for this reaction to take place. From another theorem of Gibbs it follows that the reaction product which lowers the surface tension will tend to concentrate in the surface layer more than in the body of the liquid. Such a product of the chemical change may be solid or liquid depending on the experimental conditions; it may be soluble or insoluble. If it is an insoluble, solid substance it will form a solid film. If it is a sparingly soluble substance, its formation in the surface layer will be accompanied by a diffusion into the body of the liquid. If the chemical decomposition is irreversible, the equilibrium

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[1] Ramsden [Proc. Roy. Soc., 72, 158 (1903)] obtained solid films with some solutions which contained only one-millionth of the solute necessary for saturation. The calculation given above was for a solution one hundred times as concentrated.

[2] Metcalf: Zeit. phys. Chem., 52, 44 (1905).

is reached as soon as the solvent is saturated with the film substance or the surface layer has become so thick that a further increase in its thickness has no effect on the surface tension. Under these conditions there will then be no tendency for the chemical reaction to run further. Therefore, the formation of the film substance will cease and the system will be in equilibrium. If the chemical process is reversible, equilibrium will be reached at some point before the increasing thickness of the film ceases to affect the surface tension. In either case equilibrium is reached asymptotically. Whatever is left of the original, soluble substance —and also the soluble portion of the film substance—will be distributed between the surface layer and the mass of the liquid according to the law of physical equilibrium. The solution will be unsaturated for the original solute but saturated for the film substance.

"Let us suppose that the original solution is so dilute that it does not form a saturated solution. In this case it is probable that no solid film would form. There must, therefore, be a minimum concentration for solutions which have the power of forming solid films on their surface. All intermediate stages between the two extremes may occur, corresponding to solid films of different thicknesses and strengths. The rate of formation of the film at any moment will be the resultant of two opposed velocities, the rate of the chemical reaction which forms the film substance in the surface, and the rate at which this substance dissolves. The rate of the chemical reaction depends on at least two factors, the amount of the lowering of the surface tension which is the factor causing the chemical change, and the concentration of the original solute in the surface film. This concentration is dependent both on the concentration of the solution and on the rate at which the solute can diffuse from below into the surface.

"The hypothesis seems to account for the observed phenomena in connection with the formation of solid films on the surface of concentrated and of dilute solutions. It avoids the difficulties which have been pointed out as besetting the other hypotheses. It is easy to account for the formation of solid films on the surface of very dilute solutions. The only assumption that we have to make is that the solubility of the new film substance is extraordinarily small. In that case a very small amount will be sufficient to form a saturated solution and thus give rise to the conditions essential to the existence of a permanent, solid film.

"The solid films form more or less slowly at the surface of the solutions. It may be hours or days before elasticity can be detected, the time varying with the nature of the substance; the concentration, etc. On the other hand solid films form instantaneously when a drop of solution spreads out on a surface, always provided the solution is not too dilute. Our hypothesis accounts for the tremendous difference in the rates of formation of films formed by the two methods. When the drops of solution come in contact with the water surface there are three surface tensions to consider: Water-air, solution-air, and solution-water. Since the first of these is larger than the resultant of the other two, it acts as a force pulling the drops out suddenly to a thin film, whereby the surface is increased enormously. Gibbs[1] and van der Mensbrugghe[2] have deduced independently that a sudden increase of the surface of a liquid lowers the temperature and increases the surface tension. This can be shown simply in a qualitative manner. If work is done upon a system, the intensity factor of the energy against which the work is directed must increase.[3] A force doing work develops in the system a resistance to its own action. If work is done against the volume energy by compressing a gas, the intensity factor of that energy, the pressure, increases. If a drop of peptone solution is suddenly spread out into a thin film by a force, the surface tension of water, work is done against the surface energy.

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[1] Thermodynamische Studien, 319.

[2] Mém. Acad. Belg., 43, 39 (1878).

[3] [He should have said that it may increase and cannot decrease. If the liquid and vapor are compressed, there is no increase of pressure so long as any vapor is present.—W. D. B.]

Therefore, there must be an increase in the intensity factor of this energy, the surface tension. The question as to the relative changes in surface tension, temperature, etc., will depend on the conditions of the experiment; but they must be of such nature as to act against the external force.

"Devaux's brilliant experiments on the limit of expansion of such solutions on a pure water surface are an experimental proof for the increase in the surface tension of the drop caused by the formation of a film. If the water surface is large enough, the drop spreads out rapidly in the form of a complete circle to a definite size and then stops. At first the resultant of the two surface tensions, solution-air and solution-water, is smaller than that of water-air. Therefore, the drop is drawn out until the resultant of the two surface tensions is equal to that of water-air, when equilibrium is reached. While the drop is spreading, an increase in the resultant of the two surface tensions, solution-air and solution-water, must take place. These are the surface tensions at the surfaces of the film.[1]

"We now have theoretical and experimental reasons for the assumption that when a drop is drawn out to a film, there is a distinct increase in its surface tension—the intensity factor of its surface energy—as well as in the surface—the capacity factor of the surface energy.[2] During the formation of the film there is a marked and sudden increase in the intensity factor and capacity factor, both of which affect the chemical action. This, of course, makes itself felt by a more rapid chemical change than would occur at the surface under normal conditions. We, therefore, expect that the reaction velocity will be high at first and will then decrease asymptotically. The cause of the chemical action is the force tending to de-

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[1] It should also be noticed that, with a film of a certain thinness, the capillary forces of the water in the film must have some effect on surface tension, solution-air.

[2] When a gas is compressed, the intensity factor of the volume energy increases but the capacity factor decreases. In the present case both intensity factor and capacity factor increase. The difference is due to the fact that a rise of temperature increases the pressure of a gas but decreases the surface tension.

crease the surface tension. This force decreases in amount as the reaction goes on and as the surface tension becomes smaller.

"Our hypothesis offers an explanation for the previously mentioned maximum and minimum of strength. Such a maximum and minimum calls for at least two factors acting simultaneously. In this case the two factors are the chemical reaction which tends to strengthen the film and the dissolving of the film substance, which tends to weaken it. Through the simultaneous action of these two factors it is easy to follow and account for the alternating increase and decrease in strength. With a drop of fairly concentrated peptone solution, we get solid film at once. Under these experimental conditions, it is probable that the chemical reaction velocity far exceeds the rate of solution. There is therefore a rapid increase in strength. After the first rapid change the chemical reaction of course goes much slower and it is quite possible that for a while the rate of solution might be greater than the chemical reaction velocity. This would cause a decrease in the strength of the film. If the time necessary for the chemical reaction to reach its final equilibrium is greater than that necessary to saturate the solution, the film must begin to grow again after a certain time. It is easy to draw two asymptotic curves whose resultant shows such a maximum and minimum. If the solution is very dilute, the first rapid change of the surface tension takes place relatively slowly and we shall expect a more gradual development of the film. This explanation is purely qualitative; but it is hoped some day to get the necessary data for a quantitative study of the phenomenon.

"It is worth while to consider another characteristic of the film in the light of our hypothesis. It has been shown experimentally that when a thick film is brought in contact with a fresh water surface, it does not spread out instantaneously over it. The film stretches more or less depending on the conditions of the experiment and a new film forms on the fresh surface without masking the boundary line of the old film. The surface tension of the fresh surface is evidently greater than that of the surface on which the film rests. Therefore, there is a distinct tendency for the film to spread over the new surface. A solid film resists the pull for days without any blurring of the boundary line, and the pull ceases finally because of the formation of a new film on the fresh surface and not because the old film finally spreads over the surface. This is a distinct sign that the film acts essentially like a solid and not like a liquid; and also that it is partly soluble in water. Thermodynamic considerations show clearly that a solid and sparingly soluble film must equalize the surface tensions by a sort of distillation through the water, which will carry the film substance from the old film where the surface tension is low to the new surface where the surface tension is higher. The continuation of this process cuts down the high surface tension and increases the low one; it will continue until equilibrium is reached and the two surface tensions have become equal."

I have given Metcalf's views in his own words because this is a very interesting illustration of the way in which a man may start from false premises and yet work out a very plausible explanation of the phenomena. Metcalf starts with the assumption that peptone forms a true solution and consequently he has to account for the film formation by postulating that peptone changes into an insoluble modification. This at once makes the phenomenon a special one and not a general one, which is in itself a defect because a good many substances form these films. While it is legitimate to postulate in regard to any one substance that it occurs in two modifications, a soluble and insoluble one, this becomes very unsatisfactory when the assumption has to be made in regard to a large number of substances. That, however, is a debatable matter. The error in Metcalf's work lies in the assumption—a perfectly proper one at the time he made it—that peptone is really soluble to an appreciable extent in water. We know nowadays that peptone forms a colloidal solution with water and consequently we do not have to postulate an insoluble modification. All we have to do is to get the peptone concentrated in the surface layer.

There are several ways of looking at the matter and it is quite possible that each one of them is partially true. We may consider that the colloid adsorbs gas and is floated to the surface thereby. McBain has shown[1] that it is very difficult to remove all the air from soap solutions and that previous vapor pressure determinations were consequently worthless. If the concentrating of the peptone in the surface layer is due to adsorbed gas, no surface film should be formed in the absence of air. This experiment was not tried by Metcalf. I doubt very much whether a gas adsorption is the sole factor in the formation of a solid surface film. Nagel[2] has shown that a solid film forms over a fuchsine solution even when all air is removed.

Since the surface of a liquid is in a different state from the mass of the liquid, we may consider that we are dealing with two liquid layers, the upper one being infinitely thin. We might then have the colloidal substance concentrating at the dineric interface and coalescing there to a solid film. On this hypothesis, the solid film would theoretically be just below the surface instead of itself forming the surface; but this difference would be very difficult to detect experimentally.

A third possibility is that a substance with a low surface tension may tend to concentrate in the surface even though it be not in true solution. While the Gibbs theorem applies only to substances which are actually in solution, there is nothing to prevent there being a similar theorem in regard to suspended particles. Stark[3] has called attention to an interesting special case where something of this sort takes place.

"If one drops some soot into chloroform in a watch-glass and covers the latter with a glass plate to prevent evaporation of the chloroform, the particles of soot sink because of their higher specific weight and collect into little balls at

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[1] McBain and Taylor: Zeit. phys. Chem., 76, 183 (1911).

[2] Drude's Ann., 29, 1035 (1909).

[3] Wied. Ann., 65, 288 (1898).

the bottom of the watch-glass. At least, this is what happens in the dark. If the watch-glass with the chloroform is brought into the sunlight, the balls of soot begin to move vertically upwards. When they reach the surface, the particles scatter suddenly and spread themselves uniformly over the surface, remaining thus scattered so long as no shadow falls upon them. If a shadow from a knife or a lead pencil, for instance, falls upon the chloroform surface which is coated with soot, the particles of soot in the shadow and on the edges of it jerk together forming a thicker mass in the shaded surface than in the illuminated surface. If the optical shadow is made to move sufficiently slowly, the soot shadow moves with it. If one removes the object which is casting the shadow, the soot particles which were in the shadow scatter again instantaneously.

"The three processes of the rising of the soot particles, the scattering at the surface, and the concentrating in the shadow are not hard to account for. The soot is heated more by the sunlight than the transparent chloroform. The liquid immediately in contact with the soot is therefore heated more than the rest of the chloroform. The chloroform in contact with the soot becomes less dense than the rest of the chloroform and rises, carrying to the surface with it the soot which is only a little denser. Wherever there is a ball of soot the heating is correspondingly greater and there is a lowering of the surface tension. At the points of higher surface tension the surface contracts, expanding where the surface tension is low and, thereby, ripping the ball of soot to pieces. In this way the soot is scattered over the surface. If a portion of the surface is shaded, the particles of soot in the shadow lose heat by conduction and radiation, while the surface exposed to the sun is heated continually. We have, therefore, a colder portion with a higher surface tension bordering on a warmer portion with a lower surface tension. The cooler surface contracts, carrying with it the particles of soot and concentrating them. The force of gravity and the surface tension act together both when the particles of soot are scattered and when they are brought together; but the rapidity of the action seems to show that the surface tension phenomena are the dominating ones."

While the difference in density between the soot and the chloroform is not great, this is not the important factor because Quincke[1] has observed a somewhat similar action with silver in a silvering solution and has accounted for it in exactly the same way, by postulating increased heating of the silver particles and consequent decrease of the surface tension of the solution in contact with them.

Once we admit that suspended particles tend to concentrate in the surface, Metcalf's results become quite obvious. With very small amounts of peptone, the disintegrating or peptonizing action of the mass of the liquid is the predominating factor and the film disappears. With higher concentrations of peptone, the concentration of the peptone in the surface is the important factor and the film gets stronger on standing, partly because more peptone is brought up from the bottom and partly probably because the coalescence to a solid film becomes more perfect with time. Metcalf would have adopted this explanation if he had not been frightened out of it by the bugbear of an overwhelming osmotic pressure. That disappears as soon as we recognize that we are dealing with a two-phase system throughout and not with a true solution. Once the film is fairly formed, it does not disintegrate readily or rapidly and consequently a fresh film forms over half the surface through peptone brought there from the mass of the liquid rather than through a spreading of the old film though this latter may occur to some extent.

The peptone solutions differ fundamentally from mercury surfaces or surfaces of zinc amalgam which become coated with a solid film of oxide when exposed to air.[2] On the other hand the cases of albumin, ferric acetate, and saponin are analogous to that of peptone. Aqueous solutions of fuchsine

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[1] Drude's Ann., **7**, 89 (1902).

[2] Schutt: Ibid., **13**, 743 (1904).

and of crystal violet have been studied by Rohde[1] who found that solid surface films were formed which could easily be recognized by their metallic luster. "The surface of the liquid becomes more concentrated, then viscous, and lastly solid and brittle, so that finally the solution is covered with a film of solid dye. There is nothing to conflict with the assumption that the molecular forces which cause the precipitation of the solid dye are the same which give rise to the surface tensions of liquids.... The strong photoelectric action of aqueous solutions of fuchsine and methyl violet is due exclusively to a surface which has aged. Statements as to the photoelectric action of these solutions are, therefore, worthless unless the degree of ageing is taken into account."

Nagel[2] has studied the formation of solid films with many different solutions. In the case of cobalt chloride solution he showed that the film was a cobalt carbonate due to ammonium carbonate either in the water or in the air. With potassium permanganate solution, the color showed that the film was an oxide of manganese, presumably hydrated. With iron salts we know that the surface film is due to hydrous ferric oxide. Of the solutions studied by Nagel the following gave rise to solid surface films on standing: $NiCl_2$, $Ni(NO_3)_2$, $CoCl_2$, $CoSO_4$, $FeCl_3$, $FeSO_4$, $K_4Fe(CN_6)$, $MnSO_4$, $MnCl_2$, $Pb(NO_3)_2$, $AgNO_3$, $KMnO_4$. In all these cases the film was undoubtedly an insoluble salt which had been formed by oxidation, hydrolysis, or by interaction with some salt in the air or in the water.

With colloidal silver, Nagel observed a gradual formation of a silver film. This appears to furnish satisfactory evidence that colloidal particles tend to concentrate on the surface. In this particular case no experiments were made to determine whether a gas adsorption played any part or not; but Nagel did show that a solid film forms over a fuchsine solution even when all air is removed. In the case of fuchsine solutions, Nagel considered that there had been a change to another and insoluble modification; but the proof of this is

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[1] Drude's Ann., 19, 935 (1906).

[2] Ibid., 29, 1029 (1909).

distinctly far from satisfactory. The formation of solid films by electrolysis is, of course, not analogous to the formation of solid films with peptone and there are still so many obscure points in regard to these films[1] that it is scarcely worth while to discuss them now.

The general results of this paper are as follows:

1. The Gibbs theorem in regard to the concentration in the surface film of substances which lower the surface tension applies only to the substances in true solution. It is probable that a similar theorem holds for suspended particles and it is probable that this second theorem accounts for some of the discrepancies observed when people have tried to apply the theorem of Gibbs quantitatively.

2. Since peptone does not dissolve in water to any appreciable extent, the concentration of peptone in the surface film does not give rise to the enormous differences of osmotic pressure calculated by Metcalf.

3. While the presence of adsorbed gases may be a factor in causing the formation of a solid film, it is not the sole factor and is probably a minor factor in most cases.

4. The solid film which forms over mercury or over liquid zinc amalgams is an oxide. When solid films are formed in solutions of ferric salts, the film is undoubtedly hydrous ferric oxide. With cobalt chloride solutions the film is a carbonate of cobalt formed by the action of ammonium carbonate.

5. There is no reason for postulating the formation of a special insoluble modification with peptone. The peptone particles concentrate in the surface and coalesce to form a solid film. A similar result can be obtained with colloidal silver. It is not quite certain to what the solid film is due in the case of solutions of fuchsine.

6. The formation of a solid film at the surface of a liquid is an intermediate case between the adsorption of solids at a dineric interface and the flotation of solids by adsorbed gases.

Cornell University

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[1] Gubkin: Wied. Ann., **32**, 114 (1887); Mylius and Fromm: Ibid., **51**, 593 (1894); Freundlich and Novikow: Zeit. Elektrochemie, **16**, 394 (1910).

NEW BOOKS

A Text-Book of Physiological Chemistry. *By Olaf Hammarsten with the collaboration of S. G. Hedin. Seventh English Edition translated from the Eighth German Edition by John A. Mandel. 17 × 22 cm; pp. viii + 1026. New York: John Wiley and Sons, 1914. Price: Cloth $4.00 net.*—The subject is treated under the headings: general and physico-chemical; the proteins; the carbohydrates; animal fats and phosphatides; the blood; chyle, lymph, transudates and exudates; the liver; digestion; tissues of the connective substance; the muscles, brain and nerves; organs of generation; the milk; the urine; the skin and its secretions; respiration and oxidation; metabolism.

It used to be thought that ferments were living organisms and that enzymes were chemical substances which could be separated from the cells and whose activity was not dependent on the life of the cell, p. 41. The experiments of Buchner have shown that alcoholic fermentation is caused by a special enzyme or mixture of enzymes called zymase. There is now no way of differentiating sharply between organized ferments and enzymes. "The metabolic processes of the living organisms which we recognize as fermentation phenomena must as a rule be ascribed to enzymes acting within the cell." The names enzyme and ferment are now generally used in the same sense.

On p. 95, the author says that when proteids are precipitated by salts of the heavy metals, the precipitates (often called metallic albuminates) are not definite compounds but are rather to be considered as loose adsorption compounds of the proteid with the same. On p. 103 is the statement that "a sharp line cannot be drawn between the albumins and the globulins from their properties and this is shown from the researches of Moll, which show that by the action of dilute alkalies and warmth upon seralbumin it attains the properties of serglobulin. It is evident that we are here dealing with a change of the external properties of the albumins to a greater similarity to those of the globulins, and not with a true transformation of the albumin, which is free from glycocoll, into globulin which contains glycocoll.... This is an instructive example of the subordinate importance [that] the solubility and precipitation properties have in the differentiation of various groups of proteids." This is confirmed by the statement, p. 259, that "a water-soluble globulin can be transformed into a globulin insoluble in water by careful purification, and also....a globulin insoluble in water can sometimes be converted into one soluble in water by allowing it to lie in the air. An insoluble protein like casein can also, according to Hammarsten, have the solubilities of a globulin due to the contamination with the constituents of the serum."

The alcoholic fermentation of sugar is accelerated by the addition of disodium phosphate, p. 204, and it is claimed by some that a hexose phosphoric acid ester is an intermediate product. There is still much difference of opinion on this point and it seems to be a matter which should be taken up by the physical chemist.

The question as to honeycomb structure or sponge structure is a disputed one in the case of the blood corpuscles, p. 272. "The blood-corpuscles consist principally of two chief constituents, the stroma, which forms the real protoplasm, and the intraglobular contents, whose chief constituent is haemoglobin. We cannot state anything positive for the present in regard to a more detailed arrangement, and the views on this subject are somewhat divergent. The two following views are more or less related to each other. According to one view the blood-corpuscles consist of a membrane which encloses a haemoglobin solution, while the other view considers the stroma as a protoplasmic structure soaked with haemoglobin. This latter view is in accord with the assumption as to an outside boundary-layer. Thus according to Hamburger the stroma forms a protoplasmic net in whose meshes there exists a red, fluid or semifluid, mass which consists in great measure of haemoglobin. This mass represents the water-attracting force of the blood-corpuscles, and besides this it is also considered that the outer protoplasmic boundary is semi-permeable.... The researches of Köppe, Albrecht, Pascucci, Rywosch, and others indicate the presence of a special envelope or boundary layer, and there is no doubt that the outer layer contains so-called lipoids, such as cholesterin, lecithin, and similar bodies."

On p. 486 the author discusses the question why the stomach does not digest itself during life but without coming to any definite conclusion. On p. 558 he gives data as to the composition of the teeth and then says: "According to Gassmann, the teeth among themselves have different composition, and in man the wisdom teeth are poorer in organic substance and richer in lime than the canine teeth. The great tendency of the first to caries is probably explained by this fact. The reason for the degeneration of the teeth is considered by C. Röse to be a lack of earthy salts, and according to him one finds the best teeth in localities where the drinking water has high permanent hardness." If this is correct we apparently have to choose between hardening of the arteries and softening of the teeth.

Those who have read Kipling's "At the End of the Passage" will be interested in the paragraph on p. 616 in regard to visual purple, the pigment of the rods in the retina. "As the visual purple is easily destroyed by light, it must, therefore, also be regenerated during life. Kühne has also found that the retina of the eye of the frog becomes bleached when exposed for a long time to strong sunlight and that its color gradually returns when the animal is placed in the dark. This regeneration of the visual purple is a function of the living cells in the layer of the pigment epithelium of the retina. This may be inferred from the fact that a detached piece of the retina which has been bleached by light may have its visual purple restored if it is carefully laid on the choroid having layers of the pigment-epithelium attached. The regeneration has, it seems, nothing to do with the dark pigment, the melanin or fucsin, in the epithelium cells. A partial regeneration seems, according to Kühne, to be possible in the retina which has been completely removed. On account of this property of the visual purple of being bleached by light during life we may, as Kühne has shown, under special conditions and by observing special precautions, obtain after death, by the action of intense light or more continuous light, the picture of bright objects, such as windows and the like—so-called optograms."

On p. 873 there is an interesting paragraph on oxidases. "Irrespective of whether the division of the oxidation enzymes into oxygenases and peroxidases can be carried out in all cases, there are various oxidation processes, whose occurrence by a combination of oxygenase (or peroxide) with peroxidase (or metallic salt) can be explained only with difficulty. According to Bertrand's view the action of plant oxidation enzymes is connected with their manganese content. Nevertheless Bach has been able to prepare enzymes from plants which were entirely free from iron as well as manganese salts. Starting from Bertrand's viewpoint, Trillat has prepared solutions of manganese salts, alkali and colloidal substances, which acted like oxidizing enzymes. Dony-Hénault has prepared artificial 'oxidases' from a faintly alkaline solution of gum treated with a solution of manganese salt. According to Euler and Bolin the salts of certain organic acids have the ability of setting the oxidation power of manganese salts free. Similar observations have been made by Wolff. In the oxidation of auto-oxidisable substances the presence of extremely small amounts of iron salts may be of advantage, for example with the lecithins as well as in the oxidation of certain thio-compounds."

One may congratulate the translator on his diligence and on the promptness with which he has brought out the new edition; but the actual translation might easily have been done better. *Wilder D. Bancroft*

An Introduction to the Study of Physical Metallurgy. *By Walter Rosenhain. 14 × 22 cm; pp. xxii + 368. New York: D. Van Nostrand Co., 1914. Price: $3.50.*—In the preface the author says: "The present volume is intended to serve as an introduction to the subject of Physical Metallurgy for those who are interested in the physics and physical chemistry of metals, whether as scientific investigators, manufacturers or users of metals, or students of metallurgy, engineering and allied subjects in which a knowledge of metals plays an important part. The volume also serves as an introduction to the Metallurgical Series which is in course of publication by Messrs. Constable under the editorship of the author. In the various volumes of this series will be found that more detailed treatment of many of the principal subjects touched upon in this book which is required by those particularly interested in any one metal or alloy or in some special aspect of the subject. With these more detailed volumes in view, the treatment of the whole subject in the present work has been intentionally kept somewhat general, the object of the author being to awaken interest and to stimulate thought and ideas rather than to communicate a great mass of detailed data."

The book is divided into two parts. Under the general heading of the structure and constitution of metals and alloys, the chapters are entitled: the microscopic examination of metals; the metallurgical microscope; the micro-structure of pure metals and of alloys; the thermal study of metals and alloys; the constitutional diagram and the physical properties of alloys; typical alloy systems; the iron-carbon system. The second part of the book deals with the properties of metals as related to their structure and constitution, the chapters being entitled: the mechanical testing of metals; the effect of strain on the structure of metals; the thermal treatment of metals; the mechanical treatment of metals including casting; defects and failures in metals and alloys.

The following quotations from pp. 70, 249, 255, 329 are very interesting in themselves and give a fair idea of the general style of the book.

"Apart from the mere size of the crystals which result from gradual solidification, the rate of crystallization and the precise manner in which it occurs has a very important effect on the mechanical properties of the metal. This is due to an effect which occurs at the boundaries of the crystals forming the mass of the metal, and arises from the greater or less degree of mutual interpenetration of the dendritic arms or branches which shoot out from the centers of crystallization in the early stages of the process....The extent to which this interpenetration occurs depends upon both the rate and the mode of crystallization, and the strength of the metal and its power to resist external forces which tend to tear the crystals apart from one another will in turn depend upon the extent to which adjacent crystals are locked together by the mechanism of such interpenetration. Where there is much 'interlocking' the boundary surface of the adjacent crystals will not be straight and smooth, but serrated and indented, thus providing the metal with a much greater length of junction surface and with the additional strength which appears to reside in these junctions."

"Having freely availed ourselves of the conception of 'amorphous' metal, it may be well to state precisely what is understood in this connection by the term 'amorphous.' In accordance with Beilby's views and their recent development by the author and his collaborators, the amorphous condition is one in which the crystalline arrangement of the molecules is completely broken up, so that the molecules remain in a state of irregular arrangement similar to that *which is supposed to exist in the liquid state. In fact*, the 'amorphous phase' is regarded as being--from the point of view of the phase doctrine—identical with the liquid phase. Now extremely under-cooled liquids are well known in such substances as glass, vitreous silica, etc., and they are hard, brittle bodies devoid of plasticity and of crystalline structure. Amorphous metal is, therefore, to be regarded as being identical in nature with the liquid metal if that could be cooled down to the ordinary temperature without undergoing crystallization. It is admitted that such extreme under-cooling of metals has never been actually accomplished, and objections to the whole concept of amorphous metal have been based on that ground. These cannot be discussed here, but they have been fully dealt with by the author elsewhere. At the present moment it may well be claimed that the theory of an amorphous phase in metals, produced as the result of mechanical disruption of the crystalline arrangement of the molecules, holds the field as the best working hypothesis available. There are admittedly outstanding difficulties, but these the author regards as being inevitable in a theory whose wide generalizations cover a field which has as yet been but partially explored."

"While it cannot be claimed that all the intricate phenomena connected with the failure of metals under vibratory or alternating stresses have been fully and finally explained, the methods of Physical Metallurgy have so far elucidated the problem that a clear insight into the mechanism of failure under the simpler forms of alternating stress has been gained. The myth that metals 'become crystalline' under the influence of vibration has been finally dissipated by the demonstration of the manner in which the yielding of crystals by slip can lead to failure under alternating loads. Indeed microscopic study has shown very conclusively that, so far as iron or steel is concerned, no perceptible change of crystalline structure or arrangement ever occurs at the ordinary temperature. Quite recently, Garland has shown, by means of micro-sections of specimens of non-ferrous metal and alloys taken from ancient Egyptian tombs, that the metastable cored structures of cast solid solutions, as well as the distorted crystals produced by cold work, persist unchanged through periods of thousands of years. The author's examination of some specimens of ancient iron from Adam's Peak in Ceylon, and similar studies by Sir Robert Hadfield have shown that in pieces of iron probably over 4000 years old the structure is exactly the same as in iron that had been made yesterday. It is well, therefore, that the modern explanation of 'fatigue' phenomena rests on something much more secure than the unfounded supposition that vibration can cause change of crystalline structure in a metal so far removed from its softening temperature as iron or steel or even brass or bronze."

"The ancient iron of India and Ceylon is sometimes quoted as an example of practically incorrodible metal, but the permanence of the Delhi column and of the iron chains fastened, thousands of years ago, on the steep pilgrim's paths on Adam's Peak in Ceylon, must be due to some special cause, since samples of this iron, which have come into the author's hands, have rusted freely on the surfaces exposed by cutting them up. The inference is that these irons are not really incorrodible, but were originally covered with a really effective protective coating. Although a definite proof has not been given so far, it seems probable, from the author's observations, that this protective coating was simply a coating of cinder or slag derived from the crude manufacturing process employed. In any case it is evident that, even if the purest possible iron really proves to be incorrodible, its use would be limited by its softness and weakness as compared with the better grades of steel." *Wilder D. Bancroft*

Die Chemie der hydraulischen Bindemittel. *By Hans Kühl and Walter Knothe. 17 × 24 cm; pp. xvi + 347. Leipzig: S. Hirzel, 1915. Price: 14 marks, bound.*—Through the work of Rankin at the Geophysical Laboratory and of Klein and Phillips at the Bureau of Standards, the general facts as to the constitution and hydration of Portland cement are now pretty well established. If we worked with pure lime, silica and alumina, and if equilibrium were reached, Portland cement would be a mixture of tricalcium silicate, β-dicalcium silicate, and tricalcium aluminate. Since equilibrium is not reached, the mixture contains some free lime and some dicalcium aluminate. All of these are definite compounds with the possible exception of β-dicalcium silicate which apparently can vary slightly in composition. Magnesia can replace up to ten molecular percents of the lime in tricalcium aluminate and up to six molecular percents of the lime in tricalcium aluminate and up to six molecular percents of the lime in dicalcium silicate. It is probable that magnesia can also replace some of the lime in tricalcium silicate; but the limits, if any, are not known definitely. We do known, however, that magnesia may be present up to 7.5 percent (not molecular percentages) in Portland cement without any new phase appearing. Iron is probably present always as tricalcium ferrite, while sulphur occurs as calcium sulphate or sulpho-aluminate. Tricalcium aluminate sets rapidly to a hydrated tricalcium aluminate and dicalcium aluminate to hydrated tricalcium aluminate and free alumina. Tricalcium silicate sets to dicalcium silicate and lime, while dicalcium silicate changes direct to a hydrated salt. Pure dicalcium silicate hydrates extraordinarily slowly, but the rate is increased very much by the presence of aluminates, a fact for which we have no explanation as yet. It is not known what becomes of the magnesia during the setting of Portland cement.

Klein and Phillips say: "The hydration of cements is thus brought about by the formation of amorphous hydrated tricalcium aluminate with or without amorphous alumina, the aluminate later crystallizing. At the same time sulphoaluminate crystals are formed, and low-burned or finely ground lime is hydrated. The formation of the above compounds begins within a short time after the cement is gauged. The next compound to react is tricalcium silicate. Its hydration may begin within 24 hours and it is generally completed within 7 days. Between 7 and 28 days the amorphous aluminate commences to crystallize and β-orthosilicate begins to hydrate. Although the latter is the chief constituent of the American Portland cements, it is the least reactive compound. The early strength (24 hours) of cements is probably due to the hydration of free lime and the aluminates. The increase in strength between 24 hours and 7 days depends upon the hydration of tricalcium silicate, although the further hydration of aluminates may contribute somewhat. The increase between 7 and 28 days is due to the hydration of β-calcium orthosilicate, but here are encountered opposing forces, in the hydration of any high-burned free lime present and in the crystallization of the aluminate. It is to this hydration that is due the falling off in strength between 7 and 28 days of very high-burned, high-limed cements, whereas the decrease shown by the high alumina cements is due to the crystallization of the aluminate. Finally, the iron in the cement is resistive to hydration and does not form any definite crystalline hydration products, but occurs as a rust-like material."

The book by Kühl and Knothe was written too soon to include the work of Klein and Phillips or the final paper by Rankin; but it gives a very satisfactory account of our knowledge up to the beginning of 1914. The authors give various classifications of cements and then discuss the various raw materials. The second section is devoted to unsintered hydraulic cements. Under this head come hydraulic limes and Roman cements, this latter being the European term for what we call Rosendale cement or natural cements. The third and fourth sections deal with the theory and practice of sintered hydraulic cements, meaning Portland cement thereby. The fifth section is devoted to cements made out of latent hydraulic substances, meaning thereby pozzolan cements, cements from blast furnace slags, etc. The authors say, p. 307, that "making pure Portland cement out of blast furnace slag will pay only under exceptional conditions. The natural raw materials needed for making Portland cement are usually cheaper than the slag which takes the place of the clay." While this statement may be true, it is misleading so far as the United States is concerned because the U. S. Steel Corporation is making true Portland cement from slag more cheaply than anybody else can make it from cement rock. The pages on the granulation of slag are a little confusing. One might easily get the erroneous impression that air granulation is more important technically than water granulation.

Wilder D. Bancroft

The Metallurgy of Non-Ferrous Metals. *By William Gowland. 22 × 17 cm; pp. xxvii + 496. Philadelphia: J. B. Lippincott Company, 1914.*—The preface states that "an effort has been made to supply students and metallurgists with a concise treatise dealing with the principles on which the various processes which concern the non-ferrous metals are based, and the manner in which the processes are carried out in typical modern works.

"The general plan followed is to consider under the name of each metal (1) its physical and chemical properties; (2) the alloy of which it is the chief constituent; (3) the composition and applications of commercial brands, and the effects of substances which interfere with those applications; (4) the chief ores and the processes by which the metal is extracted from them or other sources, and refined or made suitable for industrial or other purposes; (5) the principles and conditions on which the success of these processes depend; (6) the furnace and appliances employed in the processes, and the chemical changes and reactions which occur in the operations; (7) examples of actual practice followed at the present time in important extraction works.

"The aim of the book is not only to help the student, but the author has also in view a wider circle than those merely who are going through a course of metallurgical training, and hopes that others who are actually engaged in practical work may find its pages worth consulting."

The book is the work of a man who combines sound knowledge of theory and a wide practical experience, and shows it, in that equal prominence is given to the chemical principles involved in any process, to the constructional details of the apparatus used, and to the rough shop tests by which the workmen control the operation.

Processes which have failed are mentioned only to show why they failed. The book is not a history of metallurgy, but is chiefly concerned with the practice of 1913 or later.

Detailed accounts of metallurgical practice all over the world are given, for instance, in the section on lead, the practice in Wales, Utah, New Jersey, Russia, Mexico, British Columbia, Greece, Spain, France, Germany, and New South Wales is discussed. In general the author makes it pretty clear what variation in conditions makes the method used the cheapest for that particular locality.

The headings of the sections are: refractory materials; roasting; fluxes and slags; copper; lead; gold; silver; platinum; mercury; zinc; cadmium; tin; nickel; cobalt; antimony; arsenic; bismuth; aluminum. There is a good index and many authorities are cited both in the body and the footnotes, although the references are not so full as in Hofman's recent "General Metallurgy." This is compensated for by the cosmopolitan nature of the book and by many paragraphs reading "In the author's experience" so-and-so is the case. If more of the professors who write our text and reference books had the practical experience in their particular line that Gowland has had in his, added to their theoretical knowledge, we would have more books of the same high grade as this, which is worthy to stand beside Hofman's on shelves within easy reach of the metallurgist's desk. That the book is a valuable reference work does not make it any the worse as a text-book. *H. W. Gillett*

REACTIONS BETWEEN POTASSIUM AMIDE AND CERTAIN SALTS OF CADMIUM, NICKEL AND CHROMIUM IN LIQUID AMMONIA SOLUTION[1]

BY GEORGE S. BOHART

CONTENTS

I. Introduction

1. The Ammonia System of Acids, Bases and Salts.—In two important papers,[2] Franklin has developed in detail an ammonia system of acids, bases and salts. He has called attention to the fact that the acid amides, the metallic amides and the metallic derivatives of the acid amides are formally related to ammonia as the familiar oxygen acids, bases and

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[1] The author's thesis presented to the Department of Chemistry of the Leland Stanford Junior University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Jour. Am. Chem. Soc., 27, 820 (1905); Am. Chem. Jour., 47, 285 (1912).

salts are related to water and he has shown that these substances actually exhibit in liquid ammonia the distinctive properties of acids, bases and salts respectively. Acid amides in liquid ammonia solution show an acid reaction toward phenolphthalein; they react with certain metals with the evolution of hydrogen and with metallic amides, imides and nitrides in a manner strictly analogous to the action of aqueous solutions of oxygen acids on metals, metallic hydroxides and oxides.

2. *Amphoteric Metallic Amides.*—A further analogy between the ammonia and water systems is found in the amphoteric behavior of certain metallic amides which recalls the familiar behavior of zinc, lead and aluminum hydroxides towards acids and strong bases. Fitzgerald[1] and Franklin[2] have shown that just as zinc hydroxide dissolves in aqueous solutions of potassium hydroxide to form potassium (aquo) zincate in accordance with the equation,

$$Zn(OH)_2 + 2KOH = Zn(OK)_2 + 2H_2O,$$

so zinc amide is converted into an ammonozincate of potassium by the action of a liquid ammonia solution of potassium amide on zinc amide as represented by the equation,

$$Zn(NH_2)_2 + 2KNH_2 = Zn(NHK)_2 + 2NH_3.$$

An ammonoplumbite of potassium[3] corresponding to the aquo plumbite of potassium has also been prepared.

It has been further found in this laboratory that potassium amide in liquid ammonia solution reacts with cuprous imide to form an ammonocuprite,[4] with thallium nitride to form an ammonothallite[5] and with magnesium amide to form an ammonomagnesate,[6] three compounds of the ammonia system whose aquo analogs are unknown.

3. *Object of this Investigation.*—The work here described

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[1] Jour. Am. Chem. Soc., 29, 660 (1907).
[2] Ibid., 29, 1274 (1907).
[3] Jour. Phys. Chem., 15, 509 (1911).
[4] Jour. Am. Chem. Soc., 34, 1501 (1912).
[5] Jour. Phys. Chem., 16, 682 (1912).
[6] Jour. Am. Chem. Soc., 35, 1455 (1913).

was undertaken for the purpose of studying the action of liquid ammonia solutions of potassium amide on certain salts of cadmium, nickel and chromium with the object in view of adding several new metallic amides, imides or nitrides to the limited number of such compounds already known, and to determine whether cadmium, nickel and chromium compounds similar to the ammonozincate mentioned above might be prepared.

II. Manipulation of Liquid Ammonia Solutions and Description of Apparatus Used

Since liquid ammonia has a low boiling point, special forms of apparatus must be used to control the high pressures which result at ordinary temperatures. A brief description of the apparatus and manipulation follows:

A reaction tube of the form shown in Fig. 1 is connected with a cylinder of liquid ammonia by means of a lead tube (*e*) and a sealing wax joint (*c*). The reaction tube is thoroughly dried by heating while a stream of ammonia gas passes through first one branch and then the other. While the gas is still flowing, (*a*) is corked and the required amount of potassium is inserted at (*b*) by cutting off portions of the potassium tube[1] previously prepared and calibrated. A small amount of platinum black is dried and added, after which the cork is transferred from (*a*) to (*b*) and the small tube is sealed off

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[1] In order to purify the potassium which is employed in these reactions a glass tube (*bd*), Fig. 2, about two centimeters in diameter is drawn down and welded to a long tube having a diameter which will permit its introduction into the reaction tube. The slender tube is fused shut at (*a*) and a loosely fitting glass plug is introduced at (*d*), nearly closing the opening. Pieces of potassium are removed from the oil in which they are kept, dried between pieces of absorption paper and dropped into the large tube. Enough is added to fill the slender tube when molten. A one-hole rubber stopper provided with a piece of glass tubing closes the opening at (*b*) and the apparatus is connected to a suction pump by means of heavy walled tubing. After a good vacuum has been produced the apparatus is heated from (*a*) to (*b*) until the potassium is molten. Air is allowed to enter at (*b*) whereby the pure liquid metal is forced into the slender tube, impurities having been caught by the plug at (*d*). The tube (*ad*) is removed and calibrated by weighing a measured length before and after dissolving the potassium in alcohol.

as illustrated at (*b*), Fig. 3. The gas pressure necessary to give the seal a rounded end of uniform thickness is obtained by momentarily closing the opening at (*a*) with the finger while the glass is soft. A slender glass tube containing the metallic salt which is to react with potassium amide is now

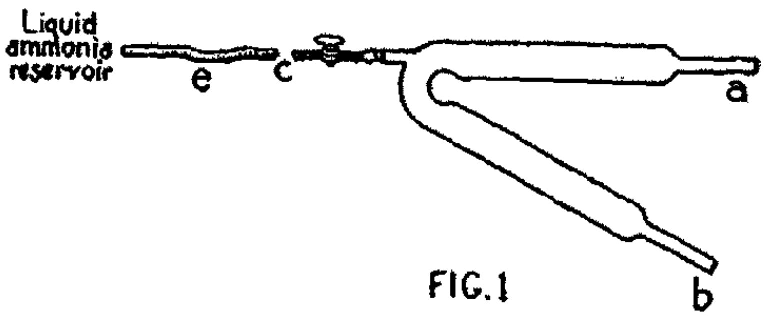

FIG. 1

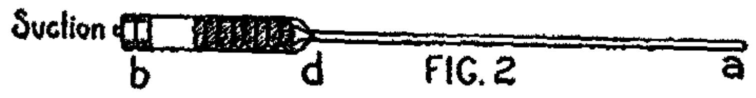

FIG. 2

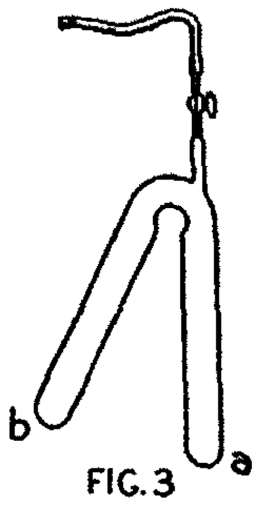

FIG. 3

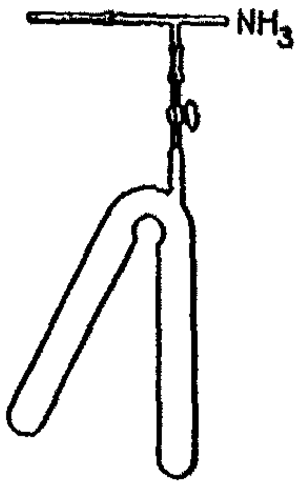

FIG. 4

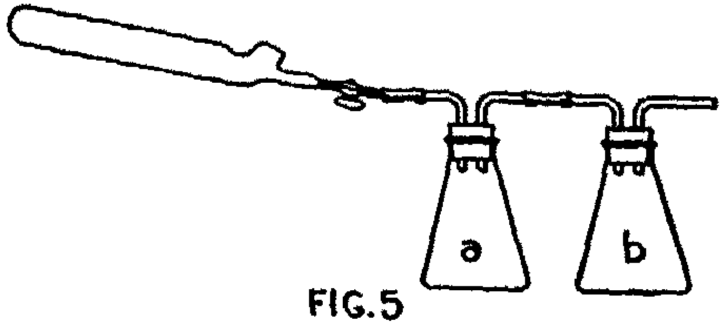

FIG. 5

introduced through (*a*) and its contents forced into the main apparatus with the aid of a fairly snugly fitting glass rod. The opening (*a*) is then corked at the same time as the key of the stopcock is removed. The leg (*a*) is sealed off and blown into shape by carefully placing a finger and thumb over the openings left by the removal of the stopper after which the latter is replaced.

By placing the reaction tube (Fig. 3) in ice water and opening the valve of the cylinder, ammonia distils over and condenses in both legs. When the liquid first comes in contact with the potassium a bright orange or fiery red color is produced which gives place to a deep blue solution with greater dilution. A rapid evolution of hydrogen gas occurs in accordance with the equation:

$$2K + 2NH_3 = 2KNH_2 + H_2$$

The platinum black greatly increases the speed of the reaction, reducing the time required for completion from weeks or months down to a half hour or less depending on the amount and efficiency of catalyzer used. When the reaction is complete the solution possesses a transparent, pale yellow appearance.

Upon pouring the potassium amide solution into the solution of the metallic salt, the action between the amide and the salt may be observed. If the product is relatively insoluble it may be obtained free from other compounds formed in the reaction by repeated washing with pure liquid ammonia. This is accomplished by placing the leg (*a*), Fig. 3, in ice water while (*b*) is immersed in tepid water. Pure ammonia distils over and after stirring and allowing the precipitate to subside the supernatant liquid is decanted back into (*b*). Three or four washings are sufficient for a crystalline product, but it is often necessary to repeat the operation fifteen to twenty times when a flocculent substance is being washed.

After the precipitate has been thoroughly washed in this manner the stopcock is opened slightly to allow the ammonia to slowly escape. When no more gas escapes the apparatus is connected to the ammonia reservoir by means of a "T" tube, Fig. 4, and a slow flow of gas is started to prevent any air finding its way into the reaction tube. The stopcock is now opened wide and the leg containing the washings is sealed off at its upper end. The other leg which contains the product is evacuated and weighed. By placing the nozzle of the stopcock beneath the surface of the solvent to be used and opening the stopper, liquid is drawn in. With the aid of the apparatus shown in Fig. 5 the solution of the compound is drawn into the flask (*a*). The reservoir (*b*) is employed for safety.

The solution is now removed to a calibrated flask and later divided into any desired number of aliquot parts, while the tube is washed first with alcohol, then with ether and finally evacuated and weighed. The difference between the two weighings of this tube is, of course, equal to the weight of the compound.

III. Action of Potassium Amide on Cadmium Salts

1. Potassium Ammonocadmiate, $Cd(NHK)_2.2NH_3$.—Considering the fact that cadmium hydroxide is not known to possess amphoteric properties it was somewhat of a surprise to find that a compound represented by the above formula, instead of the amide, imide or nitride, results from the treatment of a soluble salt of cadmium with an excess of potassium amide in liquid ammonia solution. The behavior of cadmium was found to follow that of zinc in this respect.

Cadmium iodide with ammonia of crystallization, $CdI_2.4NH_3$, is almost insoluble in liquid ammonia, but when crystals of this substance are brought into contact with an excess of potassium amide solution they are gradually replaced by a light, flocculent mass which subsides very slowly and incompletely. After washing this substance thoroughly to remove the soluble potassium iodide formed in the reaction, it is dissolved in dilute hydrochloric acid and removed from the tube in the manner described earlier in this paper.

In the preparation of Samples I, II and III, cadmium iodide was used. For preparing Sample IV potassium cyanocadmiate, on account of its ready solubility, was substituted for cadmium iodide. When treated with an excess of potassium amide, the double cyanide yields a white precipitate closely resembling that obtained with the use of cadmium iodide. All the preparations were heated to 50° *in vacuo* before removal from the preparation tube for analysis.

Analytical results:

I. One-fourth of the specimen which weighed 0.4070 g gave 0.0455 g Cd by electrolysis. One-half gave 0.0442 g N.

II. One-fourth of 0.2221 g of substance gave 0.0455 g $CdSO_4$; another fourth gave 0.0118 g N; and one-half gave 0.0769 g K_2SO_4.

III. One-half of 0.2978 g of substance gave 0.1230 g $CdSO_4$ and 0.1038 g K_2SO_4. One-fourth gave 0.0161 g N.

IV. One-half of 0.2841 g of substance gave 0.1193 g $CdSO_4$ and 0.0959 g K_2SO_4. One-half gave 0.0305 g N.

	Calculated for $Cd(NHK)_2.2NH_3$	Found			
		I	II	III	IV
Cd	44.1	44.7	44.2	44.5	45.2
N	22.0	21.7	21.3	21.6	21.5
K	30.7	—	31.1	31.3	30.3

The results of these analyses thus show the empirical formula of the compound to be $CdN_4H_8K_2$. The compound may be represented by the formulas: $Cd(NHK)_2.2NH_3$, $Cd(NH_2)_2.2KNH_2$, or, after Werner, $Cd(NH_2)_4K_2$. The reactions involved are represented by the equations:

$$CdI_2 + 4KNH_2 = Cd(NHK)_2.2NH_3 + 2KI$$

$$K_2Cd(CN)_4 + 4KNH_2 = Cd(NHK)_2.2NH_3 + 4KCN$$

Potassium ammonocadmiate has been obtained as a white, flocculent material which turns somewhat gray under the influence of light. It is insoluble in liquid ammonia and shows no tendency to assume a crystalline form as does potassium ammonozincate. When brought into contact with water it reacts with the generation of considerable heat and the formation of ammonia, potassium hydroxide and cadmium hydroxide as represented by the equation:

$$Cd(NHK)_2.2NH_3 + 4H_2O = Cd(OH)_2 + 2KOH + 4NH_3$$

2. *Cadmium Amide, $Cd(NH_2)_2$.*—When either cadmium sulfocyanate or potassium cyanocadmiate in solution in liquid

ammonia is treated with potassium amide in an amount not exceeding one equivalent, a white precipitate forms which settles rather rapidly. After prolonged washing by decantation it begins to disperse throughout the liquid in a colloidal condition. This tendency is probably due to the fact that the concentration of the electrolyte has been reduced almost to zero by the washing process.

Three of the specimens of cadmium amide analyzed were prepared from cadmium sulfocyanate. Sample IV was obtained by the action of potassium amide on potassium cyanocadmiate. Both of these cadmium salts are abundantly soluble in liquid ammonia. The preparations were heated *in vacuo* to 80° and then dissolved in dilute hydrochloric acid preparatory to analysis.

Analytical results:

I. One-fourth of 0.7520 g of substance gave 0.2728 g $CdSO_4$ and another fourth gave 0.0337 g N.

II. One-half of 0.1365 g gave 0.1004 g $CdSO_4$. The other half gave 0.0124 g N.

III. One-half of 0.1232 g of substance gave 0.0113 g N and the other half gave 0.4910 g Cd by electrolysis.

IV. One-half of 0.3536 g. gave 0.2549 g $CdSO_4$. The other half gave 0.0323 g N.

	Calculated for $Cd(NH_2)_2$	Found			
		I	II	III	IV
Cd	77.8	78.2	79.3	79.7	77.7
N	19.4	18.0	18.2	18.3	18.2

It, therefore, appears that cadmium amide is formed by the action of potassium amide on a solution of a salt of cadmium in accordance with reactions represented by the equations:

$$Cd(CN)_4K_2 + 2KNH_2 = Cd(NH_2)_2 + 4KCN$$
$$Cd(SCN)_2 + 2KNH_2 = Cd(NH_2)_2 + 2KSCN$$

The fact that nitrogen in the above samples runs distinctly low while cadmium shows a tendency to run high suggests that a small amount of cadmium imide or cadmium nitride may have been present in each specimen.

When the dry amide of cadmium is exposed to moist air it immediately assumes an orange color which gradually fades to the snow white of cadmium hydroxide. The yellow appearance may be due to the initial formation of cadmium oxide or possibly of a mixed base of the formula $HO—Cd—NH_2$. When pieces of cadmium amide come in contact with water they dance about on the surface of the liquid much as sodium does but without sufficient rise in temperature to produce incandescence. When heated suddenly to a high temperature, one sample exploded, coating the glass in the heated region with a mirror of metallic cadmium.

3. Cadmium Nitride, Cd_3N_2.[1]—When cadmium amide is heated to 180° in a vacuum it loses ammonia and is converted into cadmium nitride as shown by the following analyses:

I. One-half of 0.3041 g of substance gave 0.0118 g N and the other half gave 0.2549 g $CdSO_4$.

II. One-half of 0.1064 g of substance gave 0.0910 g $CdSO_4$. The other half gave 0.00437 g N.

	Calculated for Cd_3N_2	Found	
		I	II
Cd	92.3	90.4	92.2
N	7.7	7.8	8.2

Just as metallic hydroxides may lose water when heated to form oxides, so cadmium amide undergoes deammonation to form the nitride as represented by the equation:

$$3Cd(NH_2)_2 = Cd_3N_2 + 4NH_3$$

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[1] Frantz Fischer and Fritz Schröter [Ber. deutsch. chem. Ges., 43, 1465 (1910)] have prepared a black explosive substance, the qualitative analysis of which led them to believe they had cadmium nitride in their hands.

Cadmium nitride is a black, apparently amorphous substance which instantly assumes an orange color when exposed to moist air. The yellow color later gives place to white due to the formation of cadmium hydroxide. A small sample of the nitride exploded violently when it came in contact with water. Small fragments of the glass container picked up after the explosion were found to be covered on one side with a mirror of metallic cadmium.

IV. Action of Potassium Amide on Potassium Cyanonickelate

Attempts to prepare a pure ammono derivative of nickel by treating ammonated nickel iodide with potassium amide resulted in failure. The difficultly soluble, blue crystals of the nickel salt were changed to a red, granular mass but analyses showed the product to be a mixture of two or more compounds which could not be separated.

A search for a nickel compound which could be obtained in the anhydrous condition and which would be at the same time more soluble in liquid ammonia than nickel iodide, led to the discovery that potassium cyanonickelate could be employed. In order to obtain potassium cyanonickelate free from potassium carbonate, with which it is often contaminated, the following method was devised:

1. Preparation of Pure Potassium Cyanonickelate, $Ni(CN)_4K_2$.—Nickel sulfate is treated with enough potassium cyanide to form the double cyanide. The mixture of the cyanide and potassium sulfate in solution is then evaporated to dryness and the residue extracted with liquid ammonia in a vacuum jacketed beaker. Potassium sulfate and any potassium carbonate which may have been present in the potassium cyanide are entirely insoluble, whereas potassium cyanonickelate dissolves in about its own weight of the solvent. After filtering with the aid of a vacuum jacketed funnel and evaporating the ammonia from a Dewar beaker receiver, the salt is obtained pure as a light yellow, crystalline residue.

The following described compounds have been obtained as the result of treating potassium cyanonickelate in solution in liquid ammonia with potassium amide.

2. Compound No. 1. A Complex Product of the Empirical Formula $Ni_3N_2H_2K_4(CN)_6.8NH_3$ and its Deammonation Product, $Ni_3N_2H_2K_4(CN)_6$.—When the ammono base potassium amide is added to a large excess of potassium cyanonickelate, a brownish red solution results which after standing fifteen minutes to a half hour yields a crop of rather large, brownish red, prismatic crystals which have been found to have the composition represented by the empirical formula $Ni_3N_{10}H_{26}K_4(CN)_6$. The crystals readily lose ammonia and crumble to a light yellow powder having the composition represented by the formula $Ni_3N_2H_2K_4(CN)_6$.

In order to determine the amount of ammonia of crystallization thus liberated, each leg of the reaction tube previously described is placed in a bath of liquid ammonia and after connecting with the apparatus shown in Fig. 4 and opening the stopcock, the leg containing the washings is sealed off. While the leg containing the pure compound is still immersed in the ammonia bath the stopcock is connected to an air pump and ammonia is removed until the liquid phase has disappeared. At the temperature of an open bath of liquid ammonia the vapor tension of the compound $Ni_3N_{10}H_{26}K_4(CN)_6$ is almost zero. When the manometer shows that a constant low pressure has been reached the stopcock is closed and the tube is removed to a balance and weighed. It is then connected with the air pump and evacuated at 70°. The loss of weight represents the amount of ammonia of crystallization.

The analysis of the deammonated residue offered some difficulties at first but these were finally overcome by the following procedure: A silver nitrate solution acidified with nitric acid was introduced into the tube containing the sample, whereby the latter was decomposed according to the equation:

$$Ni_3N_2H_2K_4(CN)_6 + 6HNO_3 + 6AgNO_3 = 3Ni(NO_3)_2 + 2NH_4NO_3 + 4KNO_3 + 6AgCN$$

With the aid of the apparatus described in Fig. 5 the solution containing the silver cyanide in suspension was drawn into a small flask. The silver cyanide was filtered off, dried and weighed. The excess of silver was precipitated from the filtrate as the chloride and removed by filtration. In order to eliminate nitric acid this filtrate was treated with an excess of sulfuric acid and evaporated until sulfuric acid fumes began to appear. The solution was then diluted and divided into two equal portions. In one half nitrogen was determined; from the other half nickel was precipitated electrolytically and potassium determined from the residual solution as potassium sulfate. The same method was successfully applied in the analysis of the two nickel compounds, the description of which is given below.

In the following analytical data, Nos. III and IV were obtained from the analysis of the compound containing ammonia of crystallization, while I, II, V and VI represent analyses of the deammonated salt. The deammonated product was heated to about 70° *in vacuo* preparatory to analysis.

Analytical results:

I. The specimen which weighed 0.5930 g gave 0.0319 g N and 0.2017 g Ni.

II. The specimen weighed 0.3906 g and gave 0.4880 g Ag from the decomposition of AgCN. One-half of 0.3906 g gave 0.0664 g Ni.

III. Dried *in vacuo* at —40° the specimen weighed 1.0758 g. After heating to 70° the residue weighed 0.8522 g and gave 1.3280 g AgCN.

IV. Dried at —40°, the specimen weighed 0.6417 g. The deammonated residue weighed 0.5115 g and gave 0.0274 g N and 0.1743 g Ni.

V. The deammonated specimen weighed 0.5528 g and gave 0.8560 g AgCN. One-half of 0.5528 g gave 0.0938 g Ni and 0.1871 g K_2SO_4. The other half gave 0.0147 g N.

	Calculated for $Ni_3N_2H_2K_4(CN)_6$	Found				
		I	II	III	IV	V
Ni	33.9	34.0	34.0	—	34.1	33.9
N	5.4	5.4	—	—	5.4	5.3
K	30.1	—	—	—	—	30.4
CN	30.1	—	30.1	30.2	—	30.0
	Calculated for $8NH_3$					
NH_3	20.8	—	—	20.8	20.3	—

The analyzed preparations of this nickel compound were made up of rather large, brownish red, prismatic crystals of very uniform size and shape. The analytical results clearly indicate their purity. The crystalline substance of the formula $Ni_3N_2H_2K_4(CN)_6.8NH_3$ shows a very slight vapor tension at —40° but at ordinary temperature all of the ammonia of crystallization escapes leaving a straw yellow powder of the composition represented by the formula $Ni_3N_2H_2K_4(CN)_6$. When the yellow product is brought into contact with water it dissolves with surprising rapidity but without the evolution of a noticeable quantity of heat. When subjected to a temperature of 100° it begins to blacken and decompose. The crystalline compound is sufficiently soluble in liquid ammonia to give the solution a distinct yellow color.

While there can be no doubt of the existence of definite compounds of the empirical formulas, $Ni_3N_2H_2K_4(CN)_6.8NH_3$ and $Ni_3N_2H_2K_4(CN)_6$, the question of their constitution is a matter which has not been satisfactorily solved. Following are possible formulas:

$K_4Ni(CN)_6.6NH_3.2Ni(NH_2)_2$ and $K_4Ni(CN)_6.2NiNH$ or
$K_2(CN)_3Ni—NH—Ni—NH—Ni(CN)_3K_2.8NH_3$ and
$K_2(CN)_3Ni—NH—Ni—NH—Ni(CN)_3K_2$

3. Compound No. 2. A Mixed Cyanonickelate-Ammononickelate of Potassium, $K(CN)_2NiNHK$.—When potassium amide and potassium cyanonickelate in liquid ammonia solution are brought together in approximately equimolecular quantities a bright yellow, curdy precipitate instantly appears. It is necessary to wash this substance very rapidly, because if the amount of the nickel salt is too great the desired compound becomes contaminated with the compound described above, whereas if an excess of potassium amide is used the compound No. 3, described below, comes down with the product to be isolated. In spite of the greatest care, small amounts of these compounds did contaminate samples which were analyzed and the results are somewhat variable on that account. The substance was prepared for analysis by heating *in vacuo* to 80° and then treating in a manner described for the analysis of the above compound, No. 1.

Analytical results:

I. The specimen which weighed 0.3385 g gave 0.3468 g Ag from the decomposition of AgCN. One-half of the specimen gave 0.0107 g N and the other half gave 0.0472 g Ni.

II. The specimen weighed 0.1980 g and gave 0.2020 g Ag from AgCN. One-half gave 0.0268 g Ni and 0.0837 g K_2SO_4. The other half gave 0.00608 g N.

III. The specimen weighed 0.3130 g and gave 0.4135 g AgCN. One-half gave 0.0427 g Ni. One-fourth gave 0.0672 g K_2SO_4 and another fourth gave 0.00533 g N.

	Calculated for $NiNHK_2(CN)_2$	Found		
		I	II	III
Ni	28.8	27.9	27.1	27.3
N	6.8	6.3	6.1	6.8
K	38.4	—	38.0	38.6
CN	25.5	24.7	24.6	25.6

While the analytical data are not as concordant as might be desired there can be scarcely any doubt that the products analyzed were specimens of a compound having the empirical formula indicated. The constitution of the conpound seems fairly clear. It is potassium cyanonickelate which has, so to speak, been half converted into potassium ammononickelate as represented by the equation:

$$K(CN)_2Ni(CN)_2K + 2KNH_2 = K(CN)_2NiNHK + NH_3 + 2KCN$$

When first precipitated this compound has a bright, lemon-yellow color and presents a curdy appearance. It settles rather rapidly and after one or two washing crumbles to a finely divided granular material. When brought into contact with water it dissolves with mild sputtering and the evolution of a slight amount of heat.

4. Compound No. 3. A Complex Compound of the Empirical Formula $Ni_3N_{11}H_{22}K_7(CN)_2$.—When potassium cyanonickelate is treated with a large excess of potassium amide an emerald-green solution results which after a few minutes changes to a deep red color. At the end of an hour or so crystals begin to appear on the walls of the tube in which the reaction has taken place and after the lapse of about twelve hours the solution becomes almost colorless while a crop of red crystals adhere to the glass. After washing the crystals were treated for analysis in a manner described under Compound No. 1.

Since the analysis of this compound led to such an extraordinary formula it was considered advisable to determine carbon and hydrogen in two samples by combustion. The analyses given in III and IV were made by Mr. L. D. Elliott of this laboratory to whom the writer expresses his obligations. Previous to analysis the specimens of this compound were heated to 70° *in vacuo*.

Analytical results:

I. A specimen weighing 0.3750 g gave 0.1565 g AgCN. One-half of the specimen gave 0.0426 g N and the other half gave 0.0476 g Ni and 0.1684 g K_2SO_4.

II. A specimen weighing 0.4033 g gave 0.1281 g Ag from the decomposition of AgCN. One-half gave 0.0526 g Ni and 0.1803 g K_2SO_4. The other half gave 0.0468 g N.

III. A specimen weighing 0.0781 g gave 0.0107 g CO_2 and 0.0227 g H_2O by combustion.

IV. The specimen weighing 0.1605 g gave 0.0208 g CO_2 and 0.0454 g H_2O by combustion.

	Calculated for $Ni_3N_{11}H_{22}K_7(CN)_2$	Found			
		I	II	III	IV
Ni	25.9	25.4	26.1	—	—
N	22.7	22.8	23.1	—	—
K	40.4	40.3	40.2	—	—
CN	7.7	8.1	7.7	—	—
H	3.3	—	—	3.2	3.1
C	3.5	—	—	3.7	3.6

The above concordant analytical results together with the fact that the product was obtained in the form of beautiful crystals must be taken as conclusive proof that a definite compound of the empirical formula indicated has been obtained. The reaction involved in its formation is represented by the equation:

$$3Ni(CN)_4K_2 + 11KNH_2 = Ni_3N_{11}H_{22}K_7(CN)_2 + 10KCN$$

Not much can be done in the way of representing the constitution of the compound. Of a considerable number of more or less questionable formulas that may be written the formula $K(CN)_2NiNHK.NH_3.K_2NNiNKNiNK_2.6NH_3$, is perhaps the most satisfactory in that it represents the substance as a mixed cyanonickelate-ammononickelate, an equimolecular combination of compound No. 2 above[1] and potassium ammononickelate described below. It may also be represented by the formula $Ni(CN)_2.2Ni(NH_2)_2.7KNH_2$.

It was found impossible to determine ammonia of crystallization in this compound by the usual method of heating and evacuating, on account of the fact that no sharp line of

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[1] In view of the fact that all the compounds belonging to the group of which potassium ammonozincate is a typical representative, contain sufficient ammonia to permit their formulation either as salts with ammonia of crystallization or as molecular compounds of the amides of the two metals, it seems probable that a compound of the formula $K(CN)_2.NiNHK.NH_3$ would have been obtained had the preparation No. 2 been dried at low temperature.

division exists between the temperature at which pure ammonia comes off and a slightly higher temperature at which a mixture of ammonia and another undetermined gas escapes.

This compound appears as bright, red, skeleton crystals. Through a low power microscope they show evidence of homogeneity. When exposed to moist air they soon become coated with a green film which is probably nickel hydroxide. In contact with water the substance sputters vigorously evolving considerable heat.

In connection with the three nickel compounds just described, it is interesting to note the steady decrease in the amount of the cyanide radical as the content of potassium amide increases.

Compound No. I. $2KCN.2Ni(CN)_2.Ni(NHK)_2$.
Compound No. II. $2KCN.Ni(CN)_2.Ni(NHK)_2$.
Compound No. III. $Ni(CN)_2.2Ni(NHK)_2.3KHN_2.4NH_3$.

V. Action of Potassium Amide on Nickel Sulfocyanate

The remarkable results obtained by the action of potassium amide on potassium cyanonickelate led to a search for a soluble nickel salt free from cyanogen in order to avoid the complications encountered in the work above. Finding in ammonated nickel sulfocyanate $Ni(SCN)_2.4NH_3$, a readily soluble salt and one which may be easily prepared free from water, it was used in the experiments herewith described.

1. Ammonated Nickel Sulfocyanate.—A specimen of a compound which was thought to be tetra-ammonated nickel sulfocyanate, $Ni(SCN)_2.4NH_3$,[1] was observed to be different from that described by Meizendorff. Upon investigation it was found to have the composition represented by the formula $Ni(SCN)_2.3NH_3$. A further search led to the discovery of three additional ammonates of nickel thiocyanate; one having two, another five and a half, and a third, eight and a half molecules of ammonia.

2. Nickel Sulfocyanate with Four Molecules of Ammonia, $Ni(SCN)_2.4NH_3$.—Preparation: If a hot saturated solution

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[1] Meizendorff: Pogg. Ann., 56, 63 (1842).

of nickel sulfate is treated with an equivalent amount of ammonium sulfocyanate and enough ammonium hydroxide solution to produce a strong odor of ammonia, the color of the solution changes from green to blue, and upon cooling a crop of crystals of the compound $Ni(SCN)_2.4NH_3$ is deposited.

Nearly all of the nickel sulfocyanate from the mother liquor may be recovered by evaporating to dryness and extracting with a small amount of concentrated ammonium hydroxide solution. The success of this separation depends upon the fact that nickel sulfocyanate is much more soluble in concentrated ammonium hydroxide solution than is ammonium sulfate.

If a strong ammonium hydroxide solution of nickel sulfocyanate is exposed to the air until the excess of ammonia has escaped, most of the solute is deposited. This is to be expected since nickel sulfocyanate is much more soluble in liquid ammonia than in water.

Axial ratio: $a : b : c = 1.398 : 1 : 0.687$. $\beta = 75° 41'$

	Angle	No. measured	Measured	Calculated[1]
mm	$(110 : 1\bar{1}0)$	19	107° 7′	107° 7′
mm	$(110 : \bar{1}10)$	20	72° 53′	—
pp	$(111 : 1\bar{1}1)$	14	57° 30′	—
pp	$(111 : \bar{1}1\bar{1})$	9	122° 39′	122° 40′
mp	$(110 : 111)$	7	45° 28′	45° 20′
my	$(\bar{1}10 : \bar{2}01)$	4	68° 41′	69° 7′
my	$(110 : \bar{2}01)$	4	111° 3′	110° 53′
ma	$(110 : 100)$	15	53° 32′	53° 33′
cp	$(001 : 111)$	7	35° 39′	36° 12′
mc	$(\bar{1}10 : 001)$	7	98° 36′	98° 28′
bp	$(010 : 111)$	2	62° 25′	62° 20′
ay	$(\bar{1}00 : \bar{2}01)$	7	52° 47′	53° 7′
cy	$(001 : \bar{2}01)$	10	51° 32′	51° 12′
ap	$(100 : 111)$	7	57° 42′	57° 46′
ac	$(100 : 001)$	6	75° 40′	75° 41′
ac	$(\bar{1}00 : 001)$	7	104° 19′	—

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[1] Dull faces resulting from the instability of ammoniated nickel sulfocyanate in moist air was responsible for the lack of closer agreement between the measured and calculated values for the angles.

Crystals suitable for measurement on the reflection goniometer were obtained by making a saturated solution in a liquid made up of one part of concentrated ammonium hydroxide solution to four parts of water and exposing to the air for twelve hours.

Crystallography:[1] Crystals of this compound belong to the monoclinic system. Prismatic class. A_2.P.(C).

List of forms: *m*(110), *p*(111), *y*(201), *a*(100), *c*(001), *b*(010). The faces shown in Fig. 6 are those which are found on the typical crystal. Faces *a*(100) and *b*(010) are usually either very narrow or missing. Physical properties: Color, sapphire-blue. Luster, vitreous. Cleavage, perfect parallel to *m*(110) and *y*($\bar{2}$01). Solubility, slightly soluble in an aqueous solution of ammonium sulfocyanate but decomposed by pure water. This behavior may be explained by the equation:

$$Ni(SCN)_2 + 2NH_4OH \rightleftharpoons Ni(OH)_2 + 2NH_4SCN$$

The solubility in liquid ammonia is very great. In concentrated ammonium hydroxide solution about 60 g dissolve in 100 cc at 18°. Stability: The crystals are unaltered by dry air but rapidly lose their luster and turn green in moist air.

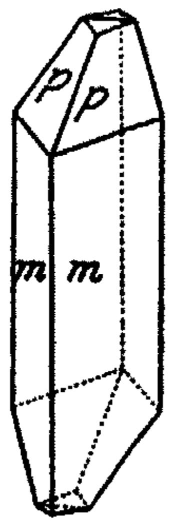

FIG. 6
$Ni(SCN)_2 \cdot 4NH_3$

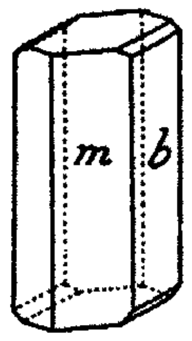

FIG. 7
$Ni(SCN)_2 \cdot 3NH_3$

3. Nickel Sulfocyanate with Three Molecules of Ammonia,

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[1] The crystallography given in this paper was done at the suggestion and under the direction of Professor A. F. Rogers of the Leland Stanford Junior University.

$Ni(SCN)_2.3NH_3$.—Preparation: If a saturated solution of the above described compound, $Ni(SCN)_2.4NH_3$, containing a small amount of ammonium sulfocyanate is exposed to the air for a few hours, crystals having a deeper blue color begin to appear and grow at the expense of the lighter blue compound if the latter is present. Analysis showed the deeper blue compound to be a substance represented by the formula $Ni(SCN)_2.3NH_3$.[1]

In the absence of ammonium sulfocyanate, nickel sulfocyanate with three molecules of ammonia does not form. This behavior results from a reaction expressed by the equation:

$$Ni(SCN)_2 + 2NH_4OH \rightleftharpoons Ni(OH)_2 + 2NH_4SCN$$

Crystallography: Crystals of this compound belong to the orthorhombic system. Bipyramidal class. $3A_2.3P.(C)$

Axial ratio: $a : b : c = 0.948 : 1 : 0.702$

Angle		No. measured	Measured	Calculated
bm	(010 : 110)	37	46° 31′	—
be	(010 : 011)	14	54° 55′	55° 11′
mm	(110 : $1\bar{1}0$)	23	86° 57′	86° 58′
ce	(001 : 011)	20	34° 49′	34° 46′
ma	(110 : 100)	2	43° 22′	43° 29′
cp	(001 : 111)	5	45° 16′	45° 14′
mp	(110 : 111)	5	44° 46′	—
mz	(110 : 114)	1	75° 10′	75° 49′

List of forms: *a*(100), *b*(010), *c*(001), *e*(011), *m*(110), *p*(111), *z*(114). The faces shown in Fig. 7 are those which are found on the typical crystal. Forms *p*(111) and *a*(100) are of comparatively rare occurrence and *z*(114) was found on one crystal only.

Physical properties: Color, deep blue. Luster, vitreous. Cleavage, absent. Solubility and stability, similar to nickel sulfocyanate with four molecules of ammonia.

Analytical results:

I. A specimen weighing 0.2329 g gave 0.4824 g $BaSO_4$ and 0.0526 g NH_3.

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[1] Ber. deutsch. chem. Ges., 41, 3178 (1908).

II. A specimen weighing 0.1892 g gave 0.3915 g $BaSO_4$ and 0.0424 g NH_3.

	Calculated for $Ni(SCN)_2.3NH_3$	Found	
		I	II
SCN	51.4	51.5	51.5
NH_3	22.6	22.6	22.5

4. *Nickel Sulfocyanate with Two Molecules of Ammonia,* $Ni(SCN)_2.2NH_3$.—Preparation: When an aqueous solution of nickel sulfocyanate in which a considerable amount of ammonium sulfocyanate has been dissolved is left exposed to the air for a few weeks, a compound having the composition represented by the formula $Ni(SCN)_2.2NH_3$ is formed. The crystals obtained were not suitable for measurement on the reflection goniometer.

Physical properties: Color, greenish blue. Luster, vitreous. Solubility and stability, similar to tetra-ammoniated nickel sulfocyanate.

Analytical results:

I. A specimen weighing 0.2246 g gave 0.5003 g $BaSO_4$ and 0.0364 g NH_3.

II. The specimen weighed 0.2214 g and gave 0.4949 g $BaSO_4$ and 0.0358 g NH_3.

	Calculated for $Ni(SCN)_2.2NH_3$	Found	
		I	II
SCN	55.5	55.5	55.6
NH_3	16.3	16.2	16.2

5. *Nickel Sulfocyanate with Five and a Half Molecules of Ammonia,* $Ni(SCN)_2.5^1/_2NH_3$.—Preparation: If a concentrated ammonium hydroxide solution is saturated with nickel sulfocyanate at about 20° after which the temperature is lowered a few degrees, a crop of large, beautiful, tabular

crystals appear. On account of their efflorescent nature these crystals were not measured on the reflection goniometer.

Physical properties: Color, blue with a violet tone. Luster, vitreous. Solubility, similar to tetra-ammoniated nickel sulfocyanate. Stability, when removed from the mother liquor and exposed to moist air, crystals of this compound instantly lose their luster and begin to lose ammonia.

Analytical results:[1]

I. A specimen weighing 0.2064 g gave 0.0174 g NH_3 and 0.3580 g $BaSO_4$.

II. A specimen weighing 0.2715 g gave 0.0940 g NH_3 and 0.4715 g $BaSO_4$.

III. A specimen weighing 0.1586 g gave 0.0551 g NH_3 and 0.2751 g $BaSO_4$.

IV. A specimen weighing 0.1946 g gave 0.0679 g NH_3.

	Calculated for $Ni(SCN)_2.5^1/_2NH_3$	Found			
		I	II	III	IV
SCN	43.3	43.2	43.1	43.2	—
NH_3	34.9	34.6	34.6	34.8	34.9

6. Nickel Sulfocyanate with Eight and a Half Molecules of Ammonia, $Ni(SCN)_2.8^1/_2NH_3$.—Preparation: When a tube containing a liquid ammonia solution of nickel sulfocyanate is immersed in an open bath of liquid ammonia, and ammonia

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[1] Working at 0° with a specimen of nickel sulfocyanate weighing in the neighborhood of 0.037 g, Walter Peters [Ber. deutsch. chem. Ges., 41, 3178 (1908)] obtained results which led him to believe that he had a compound with the composition represented by the formula $Ni(SCN)_2.6NH_3$.

With the hope of obtaining the same compound, a sample of nickel sulfocyanate weighing 0.1640 g was dissolved in liquid ammonia and the tube containing the solution was connected to a suction pump where it was evacuated at 0°. After the pressure had steadily fallen from 21 cm (the vapor tension of the compound $Ni(SCN)_2.8^1/_2NH_3$ at 0°) to nearly zero, the specimen was found to weigh 0.2539 g. The formula of the compound calculated from these results would be $Ni(SCN)_2.5.6NH_3$, which agrees closely with the formula of the compound having five and a half molecules of ammonia. In spite of careful observation the pressure in the manometer gave no indication of the existence of an ammoniated nickel sulfocyanate having six molecules of ammonia.

is removed from the solution until the liquid phase has disappeared, a crystalline residue is obtained.

Physical properties: Color, similar to the compound having five and a half molecules of ammonia. Stability, at −40° the vapor tension is about 7.5 cm. At laboratory temperature the compound rapidly loses ammonia and goes over to the modification having five and a half molecules of ammonia.

Analytical results:

A specimen of $Ni(SCN)_2.5^1/_2NH_3$ weighing 0.2520 g was dissolved in liquid ammonia and the tube containing the solution was placed in an open ammonia bath and connected to a suction pump. Ammonia was removed until the pressure became constant at about 7.5 cm, after which the tube with its contents were weighed. This entire procedure was repeated three times.

Calculated wt. for $Ni(SCN)_2.8^1/_2NH_3$	Found		
	I	II	III
0.2999 g	0.2991 g	0.2990 g	0.2986 g

7. *Potassium Ammonickelate*, $Ni_2N_3K_5.6NH_3$.—When the ammonia-soluble nickel sulfocyanate is treated with a large excess of potassium amide a deep red solution is formed from which a red, crystalline product is slowly deposited. After a few hours the liquid becomes nearly colorless. The crop of crystals may be readily freed from soluble impurities by four or five washings with pure liquid ammonia. For analysis the crystals were heated *in vacuo* to 50° and dissolved in sulfuric acid.

Analytical results:

I. One-half of 0.4967 g of the compound gave 0.0633 g Ni and the other half gave 0.0673 g N.

II. One-half of 0.5684 g of substance gave 0.0724 g Ni and 0.2730 g K_2SO_4. The other half gave 0.0808 g N.

III. One-half of 0.3253 g sample gave 0.0425 g Ni and 0.1558 g K_2SO_4. The other half gave 0.0449 g N.

	Calculated for $Ni_2N_9H_{18}K_5$	Found		
		I	II	III
Ni	25.7	25.5	25.5	26.1
N	27.6	27.0	28.4	27.7
K	42.8	—	43.1	42.9

The compound, to which either of the formulas $K_2N—Ni—NK—Ni—NK_2.6NH_3$ or $2Ni(NH_2)_2.5KNH_2$ may be given, is obviously a member of the same group of compounds to which potassium ammonocadmiate, described above, belongs. The reaction whereby potassium ammononickelate is formed may be represented by the equation:

$$2Ni(SCN)_2 + 9KNH_2 = Ni_2N_9H_{18}K_5 + 4KSCN$$

This compound is obtained in the form of rather small, red crystals resembling those of $Ni_3N_{11}H_{22}K_7(CN)_2$ in general appearance. It is sufficiently soluble in liquid ammonia to give the solution a pale red color. When brought into contact with water it reacts vigorously with the evolution of considerable heat.

8. Nickel Amide, $Ni(NH_2)_2$.—With a solution of potassium amide nickel sulfocyanate in excess yields a red, flocculent precipitate. In order to ensure the purity of this substance it must be thoroughly washed. The analyses of the two following samples were made after heating *in vacuo* to 40° and dissolving in dilute sulfuric acid:

I. One-half of 0.2242 g of substance gave 0.0730 g Ni and the other half gave 0.0335 g N.

II. One-half of 0.1613 g gave 0.0522 g Ni and the other half gave 0.0250 g N.

	Calculated for $Ni(NH_2)_2$	Found	
		I	II
Ni	64.7	65.1	64.7
N	30.9	29.9	31.0

The formation of nickel amide is expressed by the equation:

$$Ni(SCN)_2 + 2KNH_2 = Ni(NH_2)_2 + 2KSCN$$

It is obtained as an insoluble, flocculent, terra-cotta red substance which settles rather rapidly in liquid ammonia. After long continued washing it shows a tendency to go over into the colloidal condition. It reacts rather mildly with water, forming nickel hydroxide and free ammonia.

9. Nickel Nitride, Ni_3N_2.—When nickel amide is heated to about 120° *in vacuo* a slow evolution of ammonia occurs. Unfortunately, however, a secondary reaction takes place to a certain extent whereby free nitrogen is liberated. In the analysis of Samples I and II given below it will be seen that nickel runs high while nitrogen runs low. The nitrogen given off in the above-mentioned secondary reaction was measured in Sample III.

I. One-half of 0.1572 g of substance gave 0.0693 g Ni. The other half gave 0.00701 g N.

II. One-half of 0.1682 g gave 0.1981 g $NiSO_4$. The other half gave 0.00837 g N.

III. One-half of 0.0864 g gave 0.00646 g N. The other half gave 0.047 g NiO. The nitrogen gas collected in an eudiometer measured 3.75 cc over water at 23° and 760 mm.

	Calculated for Ni_3N_2	Found		
		I	II	III
Ni	86.3	88.2	89.2	85.5
N	13.7	8.9	10.0	14.9

The reactions whereby nickel nitride is formed from the amide is analogous to the formation of nickel oxide from nickel hydroxide and is represented by the equation:

$$3Ni(NH_2)_2 = Ni_3N_2 + 4NH_3$$

Nickel nitride is a black, apparently amorphous substance which reacts with water very slowly if at all. It dissolves slowly in dilute acids producing ammonium and nickel salts of the acid used.

$$Ni_3N_2 + 8HCl = 3NiCl_2 + 2NH_4Cl.$$

At about 120° it slowly decomposes into its constituent elements.

VI. Action of Potassium Amide on Ammonium Chromium Sulfocyanate, $NH_4Cr(SCN)_4.2NH_3$

Since the double ammonium chromium sulfocyanate is very soluble in liquid ammonia an attempt was made to determine the effect of potassium amide on its solution. Small additions of the ammono base cause the separation of a dense, wine-red, gelatinous substance. With the addition of further quantities of potassium amide the deep red color of the original solution is completely discharged and a beautiful salmon pink, flocculent precipitate appears. If now a slightly greater amount of potassium amide is added, the flocculent material takes on a dull purple color. With a large excess of the base the flocculent precipitate dissolves, forming a wine-red solution which later yields a crop of small crystals of the same color. A microscopic examination of these crystals indicate the presence of two different compounds. Several analyses showed this material to be composed of ammono chromites. Notwithstanding numerous attempts it has also been found impossible to prepare either of the flocculent precipitates mentioned above in a pure condition.

VII. Summary

When treated with potassium amide in liquid ammonia solution, cadmium sulfocyanate and potassium cyanocadmiate yield either cadmium amide, $Cd(NH_2)_2$, or potassium ammonocadmiate, $Cd(NHK)_2.2NH_3$, depending upon whether the cadmium salt or the ammono base is in excess. When cadmium amide is heated above 180° it is converted into the nitride.

Potassium cyanonickelate yields three distinct compounds when treated with potassium amide. With the salt in large excess, a brownish red, slightly soluble, crystalline substance is obtained having the formula $Ni_3N_2H_2K_4(CN)_6.8NH_3$. At ordinary temperature and pressure the eight molecules of ammonia escape, leaving a straw-yellow powder, of the composition represented by the formula $Ni_3N_2H_2K_4(CN)_6$.

When approximately equivalent amounts of potassium cyanonickelate and potassium amide are brought together, a lemon-yellow, curdy precipitate is formed. After a few washings with liquid ammonia this substance crumbles to a heavy powder having the composition $K(CN)_2—Ni—NHK$.

If a large excess of potassium amide is used the lemon-yellow product first formed dissolves, forming a deep red solution which upon standing twelve hours or so yields a crop of deep red crystals having the composition $Ni_3N_{11}H_{22}K_7(CN)_2$.

By varying the concentration of ammonia in ammonium hydroxide solutions of nickel sulfocyanate, the following crystalline modifications of ammoniated nickel sulfocyanate may be prepared: $Ni(SCN)_2.2NH_3$; $3NH_3$; $4NH_3$; $5^1/_2NH_3$. A fifth modification having eight and a half molecules of ammonia $Ni(SCN)_2.8^1/_2NH_3$ may be prepared by removing the liquid phase from a liquid ammonia solution of nickel sulfocyanate while the temperature is kept at about —40°.

A liquid ammonia solution of nickel sulfocyanate gives a precipitate of nickel amide $Ni(NH_2)_2$ when treated with an equivalent amount of potassium amide. Nickel amide is soluble in an excess of potassium amide, however, producing a deep red solution, from which a compound having the formula $Ni_2N_3K_5.6NH_3$ crystallizes out. If heated above 120° nickel amide is converted to the nitride.

When ammonium chromium sulfocyanate, $NH_4Cr(SCN)_4.2NH_3$ is treated with varying amounts of potassium amide, several different products appear. On account of the difficulty of getting any one of them in a pure condition they have not been isolated.

This work was done in the chemical laboratory of the Leland Stanford Junior University at the suggestion and under the direction of Professor E. C. Franklin.

Stanford University
California
April 1, 1914

ELECTRODEPOSITION OF NICKEL

BY C. W. BENNETT, C. C. ROSE AND L. G. TINKLER

In the discussion of the electrodeposition of nickel,[1] it was shown that the apparently mysterious results obtained by Calhane and Gammage[2] could be explained satisfactorily on the basis of the electrochemical series. In a solution of nickel ammonium sulphate, there are present hydrogen, nickel, and ammonium ions. Of these the hydrogen ions are liberated most easily. When the electrolysis is started for the deposition of nickel, hydrogen ions, being present, are liberated first, and the efficiency of nickel deposition is, therefore, low. If the electrolyte and cathode be stationary, there is an impoverishment of hydrogen with a subsequent deposition of nickel with an efficiency which depends upon the impoverishment of hydrogen or upon the rate of bringing up of hydrogen ions to the cathode. This rate of bringing up hydrogen ions to the cathode may be effected in two ways: First, the electrolyte or the cathode may be rapidly moved and, therefore, diffusion aided. Second, the concentration of hydrogen ions may be increased, and, therefore, the rate of bringing up hydrogen ions increased, because more are present to be brought up.

In the previous work on the deposition of nickel, the latter condition was studied, the concentration of hydrogen ions was changed by adding ammonium hydroxide to the solution, tending to make it alkaline. Under these conditions it was found that starting with straight nickel ammonium sulphate and measuring the efficiency every fifteen minutes, the efficiency of deposition began at about 87 percent and increased to the fairly definite maximum represented by about 96 percent. The conditions of such electrolysis were stationary cathode and stationary electrolyte. When varying quantities

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[1] Jour. Phys. Chem., 18, 373 (1914); Trans. Am. Electrochem. Soc., 25, 335 (1914).

[2] Jour. Am. Chem. Soc., 29, 1268 (1907).

of ammonium hydroxide were added to the solution, the efficiency began higher and reached finally a higher state.

The results obtained by Calhane and Gammage referred to above showed that the efficiency of nickel deposition with the rotating cathode was much lower than with a stationary one, and the efficiency decreased as the speed of rotation of the cathode increases.

In the previous work it was shown that the surface film at the cathode could be disturbed by stirring the solution as well as by rotating the cathode, and experiments were given to show that the efficiency of deposition is less the more rapidly the solution is agitated.

With reference to the rotating cathode, with which this investigation is interested, the same methods have been used for changing the concentration of hydrogen ions as were used in the previous work.

If small quantities of ammonium hydroxide be added to the solution with a rotating cathode, the efficiency should be affected in a way analogous to that with a stationary cathode. In other words, it may be expected that the addition of ammonium hydroxide would tend to raise the efficiency of deposition on the rotating cathode as well as on the stationary one, *i. e.*, the efficiency should start higher and approach the same point or perhaps reach a higher one. Experiments were accordingly made with stationary and rotating cathodes with varying amounts of ammonium hydroxide. 1 cc, 5 cc, and 10 cc of 1 : 10 ammonium hydroxide were added to 120 cc of the nickel ammonium sulphate solution. This, the same as in the previous work contained 8 grams of nickel ammonium sulphate with one gram of nickel chloride per 100 cc of water. The anodes were all electrolytic nickel containing 0.14 percent iron.

The current density was approximately 1.25 to 1.50 amperes per square decimeter.

The results of one set of experiments are shown in the curves of Fig. 1 and Fig. 2. Curve A, Fig. 1, represents a series of efficiency measurements taken every thirty minutes with a cathode rotating 1000 revolutions per minute. This cell had 1 cc of 1 : 10 ammonium hydroxide. Curve B shows a cell with a stationary cathode run under the same conditions in series with the first one. Curve C and D, Fig. 2, show, respectively, curves for the rotating and stationary

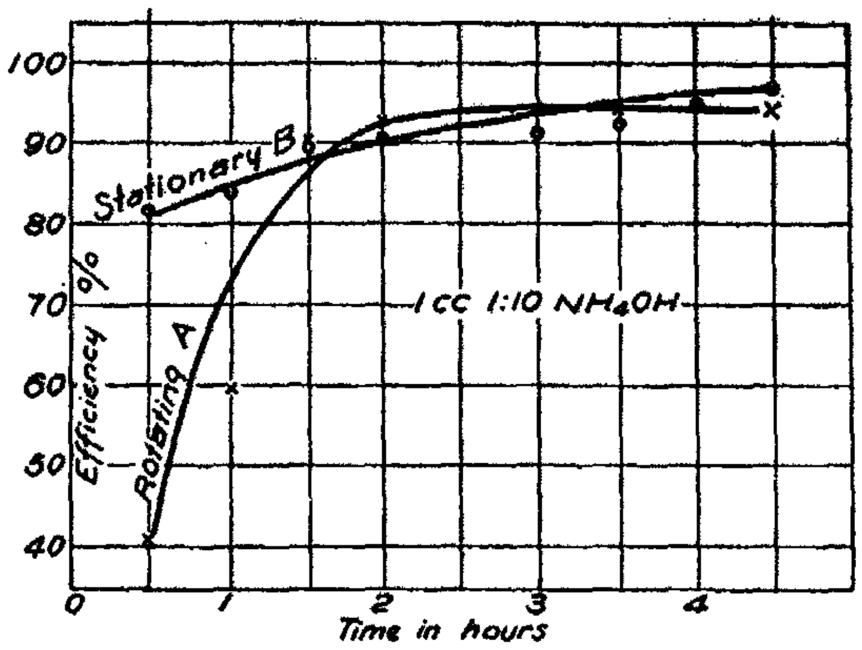

Fig. 1

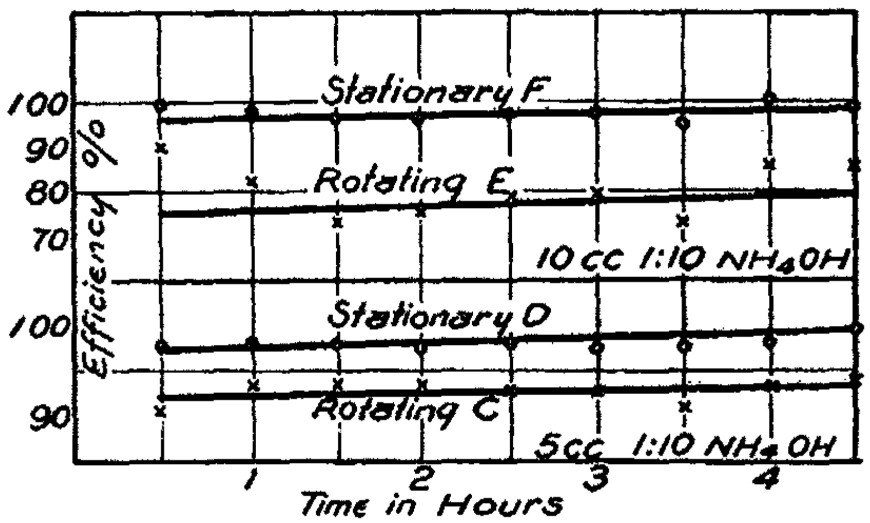

Fig. 2

electrodes with 5 cc of 1 : 10 ammonium hydroxide. Curves E and F show, respectively, rotating and stationary electrodes with 10 cc of 1 : 10 ammonium hydroxide. From these curves it is evident that if the solution is of the proper alkalinity, the efficiency begins high and is maintained at fairly high value when the cathode is rotated. This is best shown in Curve C.

Having shown that it is possible to increase the efficiency by decreasing the concentration of hydrogen ions, it is only a step theoretically to the extreme condition, where the concentration of hydrogen ions is practically zero. If nickel could be deposited from a strongly alkaline solution or from a solution of nickel in a strong base, the hydrogen ion concentration in this solution would be practically zero. Being practically zero, the agitation of the solution would practically not affect the electrolysis in so far as the hydrogen is concerned. If a solution could be obtained, which had a high concentration of hydrogen ions, agitation of the solution should practically not affect the efficiency. If, on the other hand, the ion concentration is low, agitation of the solution or rotation of the cathode should increase the efficiency over that obtained with a stationary electrode. We are, therefore, in a position to say that a solution of nickel in a strong base will yield nickel upon electrolysis with the same efficiency or a higher one if the electrode be rotated. In other words, the conditions will be just reversed from those obtained from the nickel ammonium sulphate solution.

A number of solutions were tried before a satisfactory one was obtained. A solution of nickel cyanide was finally used, the solution containing approximately 5 percent nickel cyanide and 7 percent potassium cyanide. The experiments were made with a stationary electrode and a rotating electrode in series with a copper coulometer. The runs lasted for one hour and the current density was 5 amperes per square decimeter. The solution, which was red at the start, became dark red in the case of the stationary electrode, and nickel hydroxide or cyanide precipitated. In the case of the rotating cathode, the solution changed from a red to a lemon-yellow and yielded less of the green precipitate than the stationary one. The efficiency of deposition from this solution is very low and has been found by Watts as 0.05 percent. This is due to the very low concentration of nickel ions in the solution. It would accordingly be expected that rotation of the cathode would increase the efficiency over that of the stationary electrode.

The results obtained are tabulated in the following table:

R. P. M.	Efficiency rotating	Efficiency stationary
500	0.13	0.033
500	0.13	0.048
1000	0.41	0.022
1000	0.58	0.000
2000	1.65	0.057

These values are shown in the curves in Fig. 3. The efficiency increases with increased rotation according to the prediction, and the efficiency of the rotating cathode is higher than that for the stationary.

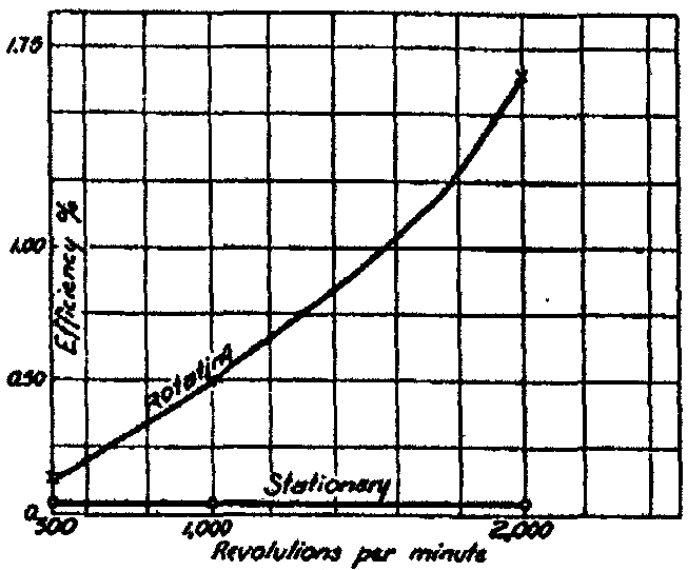

Fig. 3

In conclusion it may be said, that in the nickel ammonium sulphate solution the efficiency of the deposition of nickel on the rotating cathode, as well as the stationary one, may be changed by changing the concentration of hydrogen ions. When the concentration of hydrogen ions is practically zero, as in the case of a strongly alkaline solution, nickel is deposited more easily than the other ions, so that the lower efficiency would be occasioned by impoverishment of nickel. The rotation of the electrode prevents this impoverishment, and, therefore, increases the efficiency, while in the case of solutions where hydrogen ions are precipitated, the rotation of the cathode tends to prevent hydrogen ion impoverishment and, therefore, tends to decreases the efficiency.

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HYDROUS CHROMIC OXIDE. II

BY C. F. NAGEL, JR.

In the preceding paper[1] it was pointed out that Fischer and Herz[2] consider that hydrous chromic oxide is peptonized and not dissolved by caustic alkali. They base this conclusion on dialysis experiments and on conductivity measurements. At the suggestion of Professor Bancroft it was decided to supplement their work by other experiments. Freshly precipitated hydrous chromic oxide was treated with an excess of caustic potash to prevent jelling and was set away in glass-stoppered bottles. At the end of three weeks quite a large amount of green precipitate had formed, but the liquid was still green. On further standing, the amount of precipitate increased while the green color of the liquid became correspondingly less intense. At the end of two months the liquid was only faintly yellowish green, the bulk of the chromium oxide having precipitated. It is probable that practically all the chromium oxide would precipitate in time; but the experiment was stopped at this point for academic reasons. Experiments were also made on ultra-filtration.[3] Collodion filters were prepared by pouring 20 cc collodion solution on a clean surface of mercury in a flat dish. The films thus formed were allowed to dry until all smell of ether had disappeared, but not so long that the odor of alcohol had vanished. When in this state the films can easily be lifted out with the fingers and can then be allowed to dry subsequently in the air to whatever hardness is desired, the films being more impermeable the harder they are.[4] The films were placed in a regular Bechhold apparatus and distilled water run through to show how the filter was working. With hydrous chromic oxide and excess of caustic potash the liquid comes through the filter colorless, all the

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[1] Nagel: Jour. Phys. Chem., 19, 352 (1915).

[2] Zeit. anorg. Chem., 31, 352 (1902).

[3] Bechhold: Zeit. phys. Chem., 60, 257 (1907); 64, 328 (1908).

[4] I am indebted to Professor Briggs for much assistance in preparing these films.

chromium being left behind on the filter. While there may be some adsorption of the chromic oxide by the filter itself, this is of no importance because so much liquid was run through the filter that the chromic oxide was left in mass on the top of the filter and could be scraped off of it.

When hydrous chromic oxide is heated with a chromic chloride solution, some of the chromic oxide seems to go into solution forming what is often called a basic chloride. When this apparent solution is passed through an ultra-filter, the chromic oxide is removed. The solution comes through green, of course, because the filter does not remove the dissolved chromic chloride. A so-called basic chromic chloride solution, therefore, contains hydrous chromic oxide peptonized, but not dissolved, by chromic chloride. There is no evidence that any appreciable amount of basic salt is formed.

I had hoped to be able to shake out peptonized chromic oxide with benzene but this proved impossible in alkaline solutions. When precipitated chromic oxide is shaken with water and benzene, it goes into the dineric interface but addition of caustic alkali causes it to precipitate. This seems to be a general phenomenon, because zinc sulphide was precipitated from the dineric interface of kerosene and water by addition of alkali. This is in line with the experiments of Wilson[1] and of Twomey[2] showing that alkali is adsorbed at the surface separating organic liquids from water.

The general results of this paper are as follows:

1. Using a collodion ultra-filter it is possible to filter out the hydrous chromic oxide peptonized by caustic alkali.
2. On long standing nearly all of the peptonized chromic oxide precipitates from a caustic alkali solution.
3. Chromic chloride solutions peptonize hydrous chromic oxide. No appreciable amount of basic chloride is formed.
4. It is not possible to shake out hydrous chromic oxide from an alkaline solution either with benzene or kerosene.

Cornell University

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[1] Jour. Chem. Soc., 1, 174 (1848).

[2] Jour. Phys. Chem., 19, 360 (1915).

THEORIES OF THE LATENT IMAGE AND REVERSAL

BY E. P. WIGHTMAN

Of all the topics of photographic chemistry which have caused the greatest amount of investigation and discussion that of the nature of the latent image is preëminent. Yet, in spite of the vast quantity of experimental work which has been done, especially in the last ten or twelve years, and in spite of the volumes which have been written, the statement made in Roscoe Schorlemmer's *Treatise on Chemistry*, "that the exact change in the sensitive salt is as yet not understood," is as true to-day as it would have been fifty years ago. It should not be said that we are not any nearer a solution of the problem, because we would not, if we could, discredit the excellent work of Lüppo-Cramer, of von Hübl, of R. Luther, of K. Sichling, of Reinders, of Renwick, of Bancroft, Matthews, Mees, and many others.

For convenience the theories which have been set forth may all be classified in three groups, one attributing the change to a chemical change, another attributing it to a physical change, and the third to a mixture of physical and chemical changes, or rather, to a physical-chemical change.

The Chemical Theories of the Latent Image.[1]—Schelle,[2] in 1777, pointed out the loss of chlorine from silver chloride on exposure to light. He treated the darkened residue with ammonia and found that black flakes of silver remained behind.

"The notion that the darkened residue was a subchloride with the composition Ag_2Cl, was first suggested by Fischer in 1814, and reiterated by Wetzlar in 1834." It was reasoned in those early days that there must be either a subchloride or metallic silver formed. But they argued that the latter could not take place very well because the normal chloride will darken in the presence of nitric acid and apparently no

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[1] NOTE.—In the early history of the theory I have made free use of Meldola's Chemistry of Photography.

[2] Von der Luft und dem Feuer: Leipzig (1784), p. 64.

silver is dissolved. This happens, too—although the darkening is not quite so pronounced—even in a fairly concentrated acid.

Meldola states that "one strong argument formerly used in favor of a subchloride was Wöhler's supposed suboxide of silver, Ag_4O, obtained in 1839 by reducing silver citrate in a current of hydrogen at 100° C. But investigations in 1887 and 1888 by Muthmann,[1] by Friedheim,[2] and by Bailey and Fowler[3] appear to render the existence of the oxide improbable thereby making statements about the subchloride equally doubtful,"[4]

Meldola points out also that small amounts of moisture may influence photodecomposition because, "according to Abney, dry silver chloride sealed up in a Sprengel vacuum does not darken when exposed to light for months."[5]

Certain solvents such as sodium hyposulphite, potassium cyanide and ammonia are known to dissolve normal silver chloride. The darkened chloride, however, leaves a residue of silver. It might be assumed that such reactions as the following take place:

$$\begin{aligned} Ag_2Cl + Na_2S_2O_3 &= AgNaS_2O_3 + NaCl + Ag \\ Ag_2Cl + 2KCN &= AgK(CN)_2 + KCl + Ag \\ Ag_2Cl + 2NH_4OH &= AgNH_4(OH)_2 + NH_4Cl + Ag \end{aligned}$$

But this is merely an assumption for which we have no proof. It is similar to the argument of Riche that after exposure for a year and a half the reduced salt has the composition Ag_3Cl_2. He first assumes the existence of the salt, and then attributes the loss of chlorine to its formation.

What if we reason from analogy? Mercury, copper, and thorium form lower chlorides. Are their lower chlorides analogous to the subchloride of silver, as some have argued?

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[1] Ber. deutsch. chem. Ges., 20, 983 (1887).

[2] Ibid., 20, 2554 (1887); 21, 307 (1888). See also Pillitz: Zeit. anal. Chem., 21, 27, 496 (1882); Newberry: Am Chem. Jour., 8, 196 (1886); Pfordten: Ber. deutsch. chem. Ges., 20, 1458, 3375 (1887); 21, 2288 (1888).

[3] Jour. Chem. Soc. Trans., 51, 416 (1887).

[4] Bibra: Ber. deutsch. chem. Ges., 8, 741 (1875).

[5] Abney: "Recent Advances in Photography," p. 19 (1882).

Are they not more nearly similar to the normal chloride of silver? The lower chlorides of mercury, copper, and thorium are insoluble; they are not darkened, but are white, or nearly so, similar to silver chloride, $AgCl$. Moreover, mercurous chloride is "redissolvable by light, not to a subchloride, but to mercuric chloride." Besides, "these lower chlorides are definite chemical salts easily prepared by chemical methods, which cannot be claimed for the supposed subchloride of silver."

While there are still some chemists who hold to the subchloride theory, it has been practically abandoned since before Meldola's time (1890). Holleman and Cooper's textbook of Inorganic Chemistry (3rd edition, 1910, p. 362) states that "a subbromide of the composition Ag_2Br is formed by the action of light, and not metallic silver, because dilute nitric acid does not destroy the latent image. Moreover, not all the silver bromide is decomposed, but an equilibrium is established.

$$2AgBr \rightleftarrows Ag_2Br + Br$$

which is displaced farther to the right the stronger the illumination." A number of other such statements might be cited from text-books which have not been recently revised on this subject.

Eder,[1] in 1905, modified the theory to this extent. He suggested that there might be a series of subbromides, depending upon the length of exposure. Trivelli[2] holds that the phenomena of solarization, that is, double, or negative and positive image, cannot be accounted for on the assumption of only one compound, no matter what its composition. He gets around the difficulty by supposing four compounds having the composition Ag_8Br_7, Ag_8Br_6, Ag_8Br_5, Ag_8Br_4. There seems to be no grounds for such, however.

"That oxygen was essential to the darkening of the chloride was first announced by Robert Hunt,"[3] in 1854. Powdered silver chloride was placed in one end of a bent tube,

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[1] Brit. Jour. Phot., 52, 950, 968 (1905).

[2] Cf. Lüppo-Cramer: Das latente Bild., 23 (1911).

[3] "Researches on Light," 2nd Ed., p. 80 (1854).

the other end of which was held under water. "As the chloride darkened, the tube was thoroughly shaken in order to be sure that as much as possible of the chloride was exposed." The water rose in the other end of the tube.[1] Of course, this is not conclusive, because an oxide of chlorine might have been formed which is soluble in water. That an oxychloride of the composition Ag_4OCl_2 was formed was the explanation of the phenomenon given by W. R. Hodgkinson. Meldola was one of those who thought the solution of the problem might be in the direction of the oxychloride as a reduction product though he did not commit himself to any definite statement as to the exact nature of the change.

Baker[2] showed that not only is chlorine lost when the chloride blackens but apparently oxygen is at the same time absorbed, an oxychloride of the formula Ag_2ClO being the result. The amount is extremely small even for a large quantity of chloride when exposed for a long time. Abney and Baker both showed that pure, dry silver chloride does not blacken when exposed to light in a vacuum tube, in perfectly dry oxygen, or under carbon tetrachloride in the absence of oxygen.

Sonstadt states that hydrogen peroxide is always formed when light acts on silver chloride. He finds that if silver chloride is sealed up in a tube and blackened by exposure to light, a reversion to the white chloride takes place if the tube is kept in the dark. On the other hand, if the products of decomposition—those that are volatile—are removed by having calcium chloride and ammonia in another part of the tube containing the silver chloride no bleaching of the blackened compound takes place.

So much for the older and practically discarded theories. Now what have modern research and reasoning to say? "While Luther's[3] earlier work pointed to the formation of a

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[1] Cf., "The Art of Photography" (English translation) by Halleur, p. 76 (1854).

[2] Jour. Chem. Soc., 61, 728 (1892). Cf. Abney: "Treatise on Photography," 5th Ed., p. 24; also Hunt: "Researches on Light," 2nd Ed., p. 98.

[3] Heyer: Jour. Phys. Chem., 15, 557, 560 (1911).

subchloride or bromide, as the case might be, the later work from his laboratory has shown their non-existence. In his résumé of arguments for and against certain theories,[1] he thinks the problem may never be solved, because passage from chemical combination to mixtures and absorbed substances is of the most gradual kind."

Yet, we still have the argument of Perley[2] that since the action of light can be reproduced by suitable reducing agents, the latent image cannot be a modification of silver bromide but must be a reduction product. According to Bancroft[3] it cannot consist of metallic silver, "because the image does not show the reaction of metallic silver, because it does not show the electrical potential of metallic silver, and, moreover, the hypothesis can not be reconciled with the facts of solarization." He also discards the modification of the silver bromide and the subbromide views. What he does claim is that "the latent image is a phase of variable composition, presumably due to adsorption of silver by silver bromide, and that it is identical with photo-halides except as to color." He points out from the work of Lüppo-Cramer that the latent image which gives rise to a negative under normal development consists of silver bromide with an excess of about 0.002 to 0.1 percent silver.

The view of Bancroft which has just been stated, namely, that the latent image is a phase of variable composition with silver as the end-point, is the view first suggested by Carey Lea[4] in 1887, and later brought into prominence by Lüppo-Cramer. It was also adopted by Reinders[5] as the result of his most recent experiments. The silver, they say, probably exists in the colloidal state, which would explain the color phenomena.

In this connection Lüppo-Cramer[6] has boiled colloidal

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[1] Phot. Rundschau, 24, 221 (1910); Brit. Jour. Phot., 57, 651 (1910).

[2] Jour. Phys. Chem., 14, 689 (1910).

[3] Ibid., 17, 93–153 (1913).

[4] Am. Jour. Sci., (3) 33, 349 (1887).

[5] Zeit. phys. Chem., 77, 213, 256, 677 (1911).

[6] Zeit. Kolloidchemie, 8, 42 (1911); Phot. Korr., 48, 188 (1911).

silver with silk, wool, cotton, etc., and obtained colors which seem to confirm the formation of adsorptive combination of the photo-halides with colloidal silver, the color depending upon the size of the adsorbed colloidal particles.

C. E. K. Mees[1] points out that "Abegg considered the latent image to consist of a nucleus of silver forming a solid solution in silver bromide." He did not state whether or not the silver was supposed to be in the colloidal state.

K. Sichling,[2] by means of measurements of potential, and electrical determinations of solubility, shows that photo-chlorides are single phase systems—solid solutions of amorphous silver. He also showed that silver chloride and colloidal silver possess continuous miscibility.

Reinders[3] prepared crystallized photo-halides colored with colloidal silver and discusses the subhalide as opposed to the silver adsorption theory, and concludes that photo-halides are normal salts, colored by small amounts of colloidal silver. The color and other phenomena depends upon the size and distribution of the colloidal particles.

Hurter and Driffield[4] made certain energy calculations which Bancroft says lose their force when it is assumed that an almost infinitesimal change in the composition of the silver bromide grain is sufficient to make development possible. There seems to be no reason, also, he says, why all the silver bromide, instead of that part affected by the light, should be developable, although the argument has been attacked by Chapman, Jones,[5] by Namias,[6] and by others.

With reference to the extremely small quantity of silver bromide affected by light on a photographic plate, Meldola says that the character of the photo-decomposition products of the latent image on the plate are the same as in the case of the darkened silver bromide as ordinarily precipitated, differing

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[1] Jour. Frank. Inst., 179, 141 (1915).

[2] Zeit. phys. Chem., 77, 1 (1911); Phot. Korr., 48, 33 (1911).

[3] Zeit. phys. Chem., 77, 213, 356 (1911).

[4] Jour. Phys. Chem., 15, 365 (1911).

[5] Sci. and Prac. of Phot., 374, 387 (1902).

[6] Phot. Korr., 43, 155 (1905).

only in degree and not in kind. "The amount of silver bromide acted upon is so small as to be infinitesimal, the transverse section having a diameter hardly more than the molecules themselves. As to the color, that of such a thin layer could hardly be seen, besides, only the chloride is strongly colored."

Mention only can be made of other more or less important work on the chemical theories, by Wöhler,[1] Mees and Wratten,[2] Wöhler and Rodewald,[3] Baur,[4] Lüppo-Cramer,[5] and others.

Physical Theories Concerning the Latent Image.—These are few in number. It was found by Dewar that gelatine emulsions of silver bromide remained sensitive to light—though to a smaller extent to be sure—even at −252.5° C, at which temperature nearly all chemical actions proceed *very* slowly. This gave rise to the view that no chemical action is brought about on the photographic plate, but that the molecules of silver bromide are altered so as to make them more sensitive to light. So far as we could learn he did not say what the change was, nor whether it was accompanied by some sort of reduction.

It is hardly possible that the change is similar to that produced in "ripening" the sensitive emulsion, because it is likely that the amount of light acting in a normal exposure would be too small to bring about such a change—*i. e.*, a molecular or allotropic change, as stated by R. J. Wallace.[6]

"It is very generally understood that silver bromide ($2AgBr$) is the chief substance employed in the making of gelatine dry plates, but that silver bromide exists in several different allotropic forms has long been known—the first, formed by the admixture of the gelatine and bromide and silver salts, is of slow sensitiveness, but in the process of ripening passes gradually through several modifications, finally ending in a state which is capable of reduction by a developer without

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[1] Österr. Chem. Ztg., 14, 268 (1911).

[2] Brit. Jour. Phot., 55, 831 (1908).

[3] Zeit. anorg. Chem., 61, 54 (1909).

[4] Zeit. phys. Chem., 77, 58 (1911).

[5] Phot. Rundschau, 24, 226 (1910).

[6] Astrophys. Jour., (2) 20, 114 (1904).

the previous action of light, *viz.*, the blue allotrope of silver bromide (blue to transmitted light). If the ripening of the emulsion be stopped prior to the formation of this last form the result is still another allotrope, which is green by transmitted light, and of high sensitiveness."

Another theory, that of Renwick,[1] and known as the "explosion or pulverization theory" is based on an observation by Scheffer that the silver bromide grain on exposure violently throws off part of itself. It ruptures the surrounding gelatine, which, according to Renwick, encloses the bromide in a tangled meshwork. Where the bromide grains are surrounded by gelatine, the developer does not penetrate to any extent, but where the explosion has opened up a channel of relatively large size giving access to the developer it does attack the bromide.

That there is a certain amount of pulverization seems to be confirmed by an experiment made by Lüppo-Cramer,[2] in which a silver mirror is exposed to iodine vapors, becoming coated with a film of potassium iodide. The sensitive plate thus formed, or part of it at least, is exposed to the light for ten to fifteen minutes, and when brushed with cotton, silver iodide powder is removed from only the exposed portion.

It was J. C. Bose[3] who said, "With reference to photographic action, various facts are known which cannot be explained from purely chemical considerations. It will be shown that when a substance is molecularly strained, its chemical activity is modified in consequence of a physical strain. The acted and unacted portions will, therefore, be unequally attacked by developer. In the case of a compound the strain produced may cause a modification which renders it susceptible to decomposition by the action of a reducing agent. The observed evolution of chlorine when moist silver chloride is

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[1] Brit. Jour. Phot., **58**, 48 (1911).

[2] Phot. Korr., **47**, 226 (1910).

[3] Phot. Jour. Trars., June, 1902; see also Proc. Roy. Soc., 1899; Ibid., 1900; Ibid., 1902; Report, B. A., 1900 (Electrician); Travaux du Cong. Intern. de Phys., Paris, 1900; Friday Evening Discourse, Royal Inst., May, 1901; "Response in the Living and Non-living," J. C. Bose, Longmans, Green & Co. (1902).

exposed to the long continued action of intense light is often adduced in support of the chemical nature of photographic action. This extreme case of dissociation cannot, however, be regarded as representative of the action of light in the formation of latent images. In ordinary photograhic action we have nearly the effect of a moderate stress producing the corresponding strain (with concomitant variations of chemical activity, and not the disruptive effect of a breaking stress)."[1]

These remarks by Bose furnish the introduction to a very interesting paper on the subject of what he calls the "molecular strain theory." It would not be worth while to take up the subject, as he treats it, in detail, but it would be well, no doubt, to give the following conclusions with which he sums up his paper.

"It is thus seen:

"(1) That molecular strain is produced by the action of light.

"(2) That both in the artificial and real retinae, the molecular strain produced by light gives rise to similar electric impulses.

"(3) That as the physico-chemical properties of a substance are changed by strain, it is possible to develop the latent image, through the difference in the following properties between the exposed and unexposed portion, produced by light: (*a*) difference in adhesive power, *e. g.*, development of daguerreotype by mercury vapor; (*b*) difference in chemical stability, *e. g.*, development by reducing agents.

"(4) That molecular strain may not only be produced by visible or invisible radiation, but also by (*a*) electric, and (*b*) mechanical stress. Latent images produced by such means may be developed, *e. g.*, inductoscripts, development by pressure marks.

"(5) That nearly all substances are sensitive to radiation, but the effect cannot in all cases be rendered visible, (*a*) owing to want of suitable chemical developers; (*b*) owing

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[1] Cf. above R. J. Wallace (Loc. cit.) and preceding paragraph.

to quick self-recovery. The effect may be rendered more or less permanent by overstrain or by 'arrestors.'

"(6) That the molecular effect due to radiation can be demonstrated by the conductivity or E. M. F. variation method.

"(7) That the latent period of overcoming inertia corresponds to the photographic induction period.

"(8) That the relapse of image is due to self recovery.

"(9) That owing to the tendency toward self-recovery, the radiation effect does not solely depend on the total quantity of light, but depends also on the time rate of illumination. Hence, the photographic effects of intermittent and continuous illuminations are not the same.

"(10) That the continuous action of radiation produces recurrent reversals."

This molecular strain theory of Bose is interesting, but does not go far enough. It could be stated, probably a little more effectively in other words, as the theory of the change in internal equilibrium forces of the molecules due to the influence of light. We know that with change of molecular structure (such as white to red phosphorous, orthorhombic to monoclinic sulphur, etc., as cited by Bose) there is an accompanying loss or gain of intrinsic energy of the molecules, observable as heat given off or heat absorbed, respectively. This change of internal energy which is also accompanied by change of chemical activity does not necessarily mean a strain, or, in other words, a lack of internal equilibrium, it merely means that the chemical potential of the substance in question has been lowered or raised as the case may be, with respect to other chemical substances not so easily affected by light.

Even this modification of Bose's idea is not sufficient to explain all the facts; we are forced to go farther.

Physico-Chemical Theories of the Latent Image.—It is well known from Hertz and others that light has the power to cause a discharge of negative electrification from the surface of many bodies. Joly[1] considers that light causes an elec-

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[1] Nature, 72, 308 (1905).

tronization of silver bromide, since the silver haloids are known to be photo-electric. An interesting thing about it is that they are photo-electric in the descending order, bromide, chloride, and iodide, the same order as their photo-sensitiveness.

Moreover, an image capable of development is also formed by cathode rays or electronic discharges from radium. Joly thinks, therefore, that the latent image is made up of atoms or molecules electronized by the action of light, and that it is upon these that the developer acts.

In a recent paper, by C. E. K. Mees,[1] this theory is upheld as to the initial action of light. "An objection to all these theories," says Mees, referring to those which have to do with reduction either to subbromide or to silver, that is, the chemical theories, "is that the energy available during exposure is not sufficient to produce an appreciable amount either of metallic silver or silver subbromide from normal silver bromide. This was first pointed out by Hurter, who, from consideration of the amount of energy which was liberated in the burning of a candle, came to the conclusion that the available energy was not one percent of that necessary to reduce to silver subbromide the silver grains (he evidently means, "the silver bromide grains") which eventually proved to be developable."

Mees gives the following calculations made by Dr. P. G. Nutting for a high speed plate:

"Consider the exposure to light which is sufficient, after full development, to produce a deposit of unit density; that is, one which will transmit one-tenth of the incident light. A deposit which has this density contains ten milligrams of metallic silver per square decimeter, or one-tenth of a milligram per square centimeter, which represents roughly 10^{19} moles of silver, or 10^7 grains 3 μ in diameter. Now, the energy of the amount of violet light required to give an exposure necessary to make an emulsion film developable to this density,

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[1] Jour. Frank. Inst., 179, 146 (1915).

is of the order of 10^{-7} ergs per square centimeter. Therefore, each grain (which contains on the average, 10^{12} moles) receives 10^{-14} ergs to make it developable. We know that in order to detach one electron from a mole, 5×10^{-14} ergs are required in the separate moles of a gas...... Clearly, then, the energy incident on a grain during exposure may be sufficient to affect only one mole in the grain, and the latent image, may be composed of grains in each of which, on the average, only one mole has lost an electron by the action of light."

Beyond the initial stages of the action of light Mees thinks the changes taking place are more likely purely chemical, since, considering the facts from the chemical standpoint, he is able to explain with greater satisfaction the phenomenon of reversal. He is not in sympathy with Allen's[1] purely physical explanation on the basis of the electronic discharge. But more of this presently.

It has been said, with truth, that no theory of the action of light on the photographic film can be considered satisfactory until it explains the phenomenon known as *reversal* or *solarization*.

What is reversal? It is just this: with short exposure the latent image develops a negative, with longer exposure, a positive. How can this be explained on the basis of the theories which we have studied?

As late as 1912, Bancroft[2] states that "discussions up to the present on solarization have been merely qualitative. Lüppo-Cramer[3] has obtained data making silver bromide emulsions containing known amounts of colloidal silver adsorbed by the silver bromide." With 0.002 percent silver in the bromide emulsion there was a distinct fogging on development. "With increasing amounts of silver the rate of blackening increased and the sensitiveness to light also increased to a maximum at about 0.1 percent silver, the latter

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[1] H. S. Allen: "Photoelectricity," Longmans, Green & Co. (1913).

[2] Eighth Int. Congr. of Applied Chem., 20, 51 (1912); Jour. Phys. Chem., 17, 93-153 (1913).

[3] Phot. Korr., 46, 526 (1909).

being about twenty-five times as sensitive as one containing 0.4 percent silver. From 0.002 to 0.01 percent we are dealing with the first negative. Somewhere beyond 0.1 percent silver we have the first positive." Stating it in other words, Bancroft says, "The latent image which gives rise to a negative under normal development consists of silver bromide with an excess of about 0.002 to 0.1 percent colloidal silver"—adsorbed or in solid solution in the bromide. The reversed negative or positive image contains an excess of about 0.4 percent silver.

In another paper published by the 8th International Congress of Applied Chemistry, Bancroft drew the following conclusions as to a further reversal:

"(1) If a second positive exists, it requires a very long exposure even with a very bright light.

"(2) In many cases a false first positive or false mongrel may be obtained.

"(3) Since the emulsion on an ordinary plate is never homogeneous one really observes a combination solarization curve.

"(4) The inhomogeneity of the emulsion may easily account for the false positive or false mongrel.

"(5) With long exposures we find great differences between different boxes of the same make of plates and we even find some differences between plates in the same box."

In the light of Mees' paper,[1] one can obtain a clearer idea of the whole process. He points out that if we plot a curve of the density (that is, of a fully developed plate) against a logarithmic scale of exposure—density increases with exposure to a maximum, as shown in the figure,[2] then decreases to a minimum and increases again to another maximum, and so on, each time the maximum point being smaller than the one preceding, the minimum points representing the positives. Such change of image and of density is known as reversal.

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[1] Jour. Frank. Inst., 179, 141 (1915).

[2] This curve is not drawn to scale, but is merely an approximation somewhat similar to that given by Mees: Jour. Frank. Inst., 179, 146 (1915).

To return to his explanation of this phenomenon, Mees says that "under the continual influence of light (*i. e.*, after the initial exposure, which he accepts as photo-electric) the silver bromide is broken up into metallic silver and bromine, as it is well known to do, the bromine given off from a much over-exposed plate being easily smelt.[1] Now, bromine actually attacks exposed silver bromide, preventing it from being developed, so that it would seem likely that grains which have been completely decomposed by light simply suffered photo-electric change to the latent image. The gain in density observed with still more extended exposure may be ascribed to the actual production of metallic silver by long continued action of light, and indeed, such reduced silver can be shown to exist by fixing the exposed but undeveloped plate."

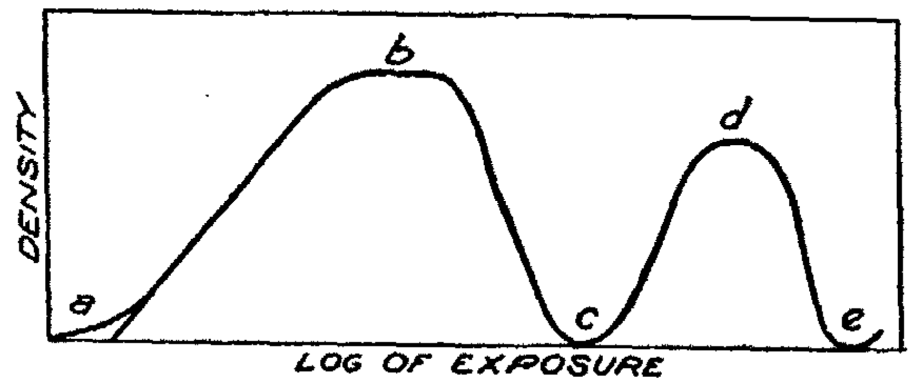

Fig. 1

(*a*) Period of underexposure.
(*b*) Maximum density of first negative.
(*c*) Maximum brightness of first positive.
(*d*) Maximum density of second negative.
(*e*) Maximum brightness of second positive.

Going back to Meldola's time, we find that he says,[2] "We must look upon the sensitive plate—say gelatino-bromide—as a film of silver bromide imbedded in a bromine-absorbing substance (gelatine) and bathed on its surface by atmospheric oxygen. When exposed to light the vehicle (*i. e.*, gelatine, which may be considered as a sensitizer) becomes brominated up to a certain degree of saturation; complex bromo-derivatives, or additive compounds, or oxidation

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[1] Note—The writer doubts this.

[2] Meldola: "Chem. of Photog.," p. 225.

products are formed, and these at length begin to react with the reduction product aided by the external oxygen. The process may be regarded as analogous to the destruction of the latent image by the haloid hydracids, and indeed it is not improbable that some hydrobromic acid is actually formed by the bromination of the gelatine, and takes part in the process of reversal......It is obvious that a highly sensitive plate would halogenize its sensitizer more rapidly than a less sensitive plate; *that is why solarization occurs more readily in the most sensitive processes.*"

The main difference between Meldola's idea and that of Mees (leaving out the initial photo-electric effect) lies in the rôle played by oxygen, yet the former admits that the phenomenon of reversal is still existent in the absence of oxygen.[1]

According to Mees' idea, the most important distinction between the production of a normal negative image and a reversed or positive image lies in the fact that in the first case we have simply a photo-electric effect, or driving off by light of one electron from each grain of the silver bromide, while in the latter case actual decomposition of the silver bromide particles takes place until the negative action of bromine, which is set free in the neighborhood of the grains, is sufficiently great to prevent the developer from attacking those grains. At the same time the grains which were less acted upon by the light are open to attack by the developer, thus producing, a positive, by reversing the image.

The above energy calculation of Nutting, which Mees cites, is, however, a little ambiguous. He says that there are approximately 10^{19} moles of silver per square centimeter of the emulsion, corresponding to 10^{7} grains 3μ in diameter. He assumes, evidently, that the silver grains have the same size as the bromide particles from which they are derived, and that these are of the maximum size and are all uniform. If his "10^{7} grains 3μ in diameter" refers to the silver bromide grains, then, after development instead of 10^{12} moles of silver per grain there would be 0.5×10^{12} moles of silver. More-

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[1] See Abney's "Treatise on Photog.," 5th Ed., p. 309.

over, Mees assumes that it takes five hundred times more energy to drive off an electron from a mole of a gas than that which will split off an electron from a mole of silver; however, it may be considered as a fairly reasonable assumption.

Let us calculate the approximate amount of energy necessary to decompose one molecule in each grain of silver bromide and see how it compares with the energy as calculated by Mees necessary to split off an electron from that molecule. We have the reaction

$$Ag + Br \rightleftarrows AgBr + 22700 \text{ calories.}$$

For each gram-mole of silver formed, therefore, 45,400 calories are required to decompose its equivalence of silver bromide and for 0.1 milligram of silver 0.042 calories or 1.76×10^6 ergs are necessary. Dividing this by 10^{19} moles in 0.1 milligram, gives 1.76×10^{-13} ergs per mole. In other words, about seventeen and a half times as much violet light would be necessary to decompose a mole of silver bromide as to split off an electron from it.

If, instead of employing the exposure suggested by Mees for his hypothetical experiment we should begin to over-expose the plate, then as we increase the exposure there is no reason to suppose that a greater number of moles in each grain of silver bromide would not throw off electrons. Soon those moles which have been exposed the longest would begin to decompose. Mees does not give the time of exposure upon which his calculations were based, but supposing it were as small as 0.001 of a second, and that only one mole in each grain could be acted on for each instant of exposure (this is obvious from the above consideration) it would require about sixty-six years to drive off one electron each from the 10^{12} moles of bromide in one grain of the latter. To completely *decompose* all the moles each grain contains would require about seventeen and a half times this long, or over one thousand years. Even though these figures may not come within a hundred percent, even within a thousand percent of being correct, we can see why silver bromide when exposed to the light even for a comparatively long time apparently does not all decompose.

Of course, with the whole spectrum (including the ultraviolet light) the time for decomposition would be much shortened, and still further so since many grains are smaller than 3μ.

Allen's view of reversal,[1] as stated by Mees,[2] is that "electrons are expelled and become attached to the surrounding gelatine moles; external stimulus, such as radiations of longer wave length, enable the electrons to enter again into combination with the atoms from which they are liberated, due to electrostatic forces between oppositely charged particles. If recombination is not assisted, the electrostatic field increases under the influence of light, and self-neutralization takes place as suggested by Joly."

Assembling all these ideas, we might say that when the light begins to act, electrons are driven off from one mole after another until the point is reached when sufficient light has acted to start decomposition of the bromide. As the negative electrons are expelled from the bromide particles, the latter become charged positively. On decomposition, the bromine being likewise expelled, or split off (and possibly absorbed, as Meldola said, by the surrounding gelatine) leaves the residue of silver, which may be considered as dissolved (as a solid solution) in the surrounding bromide particle, charged positively. This may account for the latent image not being destroyed, or greatly affected, when it is formed, on exposure of the sensitive film in the presence of nitric acid. It should be noted that this idea does not necessarily imply the initial formation of colloidal silver, in fact, the colloidal state could not be reached until a sufficient number of molecules of the electrically charged silver had been formed to produce a colloidal particle, which, according to Ostwald's classification[3] has a diameter not exceeding 100 $\mu\mu$ and is not smaller than 1 $\mu\mu$.

As the particles become more and more decomposed by

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[1] A. H. Allen: "Photoelectricity," Longmans, Green & Co. (1913).

[2] Loc. cit.

[3] Wo. Ostwald: Grundriss der allgemeinen Chemie, 548 (1909); also von Weimarn and Wo. Ostwald, Zeit. Kolloidchemie, 3, 26 (1908).

the light we might consider three things as happening. First, the positive electrification of the silver bromide becomes greater and greater in consequence of more and more electrons being expelled, and this would sooner or later result in a self-neutralization of the electrostatic forces, as explained by Allen. Secondly, the gelatine immediately surrounding the bromide particle would become saturated with bromine and this would then tend to be given off as the gas, thus leaving a residue of silver behind—this would only happen on very long exposure, of course. Finally, since all molecules possess the property of rapid motion, some, if not all of the charged silver particles resulting from decomposition might find their way to the surrounding gelatine, and combine with it. This, too, would help to explain the lack of action of nitric acid above spoken of.

When the plate is developed an image will result provided the exposure has not been less than enough to produce the electronic discharge, or provided it has not been given an exposure just equal to that which will produce self-neutralization. Just over this exposure electronization may set in again, but wherever sufficient free bromine is in the vicinity of the particles of silver bromide the action of the developer may be prevented as explained by Mees.

It has been pointed out to me recently that the presence of gelatine or other material surrounding the grain is not necessary in order to produce a picture. This seems perfectly obvious, the old daguerreotype process being a sufficient proof of it. Our theories of the nature of the photographic change must, therefore, be independent of the presence of the gelatine on the plate, however much that presence may assist the process.

The author of the present paper is about to undertake some experimental work on reversal and this paper may be considered as a preliminary introduction to the work.

Chemical Laboratory
Washington University
St. Louis, Mo.
April, 1915

ON THE REACTIONS OF BOTH THE IONS AND THE MOLECULES OF ACIDS, BASES AND SALTS

THE REACTION OF SODIUM ETHYLATE WITH ETHYL BROMIDE AND ETHYL IODIDE IN ABSOLUTE ETHYL ALCOHOL AT 25°

BY E. K. MARSHALL, JR. AND S. F. ACREE

[Twentieth Communication on Catalysis][1]

In March, 1905,[2] Brunel and Acree began to measure the conductivities of urazoles and their salts and the velocities of their reactions with alkyl halides, to learn whether both the urazole ions and the nonionized urazole salts are active. Up to that time chemists had generally believed that the ions are the only portions of electrolytes which show any considerable activity. The contribution from our laboratory, therefore, was in calling the attention of chemists to the *proof of the large activity* of *nonionized electrolytes*, to which Kahlenberg,[3] especially, and also Michael[4] and Armstrong, had so often and ably directed their efforts. The work of Blanksma,[5] and later of Johnson and Acree[6] in 1907, on the rearrangement of acetylchloraminobenzene ($CH_3CONClC_6H_5$) in the presence of hydrochloric acid was interpreted by Johnson and Acree as a decomposition of the *nonionized salt*, $CH_3CONHCl_2C_6H_5$, the cation, $CH_3CO\overset{+}{N}HClC_6H_5$, seeming to enter into the reaction to a very small extent only, if at all. We gave the

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[1] For the earlier papers see Am. Chem. Jour., **49**, 474 (1913). Jour. Chem. Soc., **105**, 2582 (1914). This work was finished in 1910–1911 and withheld from publication till this chapter could be more nearly completed. As Dr. Marshall has withdrawn from the investigation on account of other duties it seems wise to present the experimental evidence without further delay. We are indebted to the Carnegie Institution of Washington for aid in this work.—S. F. Acree.

[2] Am. Chem. Jour., **43**, 505 (1910).

[3] Jour. Phys. Chem., **5**, 339 (1901); **6**, 1 (1902).

[4] Am. Chem. Jour., **43**, 322 (1910).

[5] Rec. trav. chim. Pays-Bas, **21**, 366 (1902); **22**, 290 (1903).

[6] Am. Chem. Jour., **37**, 410; **38**, 266 (1907); **41**, 461 (1909).

equation $dx/dt = K_{trans} \times \alpha(A - x)^2$ for the ionic reaction,[1] as Arrhenius, Ostwald, Walker, Stieglitz, Bredig, Goldschmidt, Lapworth and others had done before, and then gave the equation $dx/dt = K'_{trans} (1 - \alpha)(A - x)^2$ for the activity of the "undissociated acid, base or salt,"[2] the first time this latter equation was ever used for the large[3] activity of a *nonionized electrolyte.*

In May, 1908, Rogers and Nirdlinger[4] completed their work on the action of ethyl iodide on sodium 1-phenyl-3-thiourazole in absolute alcohol at 25°, which showed beyond question that *the ethyl iodide reacts with the urazole anion with a velocity* $K_i = 0.43$ *and also with the nonionized sodium urazole with a velocity* $K_m = 0.17$. The same work was repeated recently, under somewhat better conditions, by Dr. J. Chandler, who finds nearly the same values, $K_i = 0.46$ and $K_m = 0.16$. Dr. S. K. Loy, in 1909, and Dr. H. C. Robertson, Jr., in 1910, did work with alkyl halides and sodium ethylate and sodium phenolate,[5] respectively, which showed clearly that the ethylate and phenolate ions react side by side with the *nonionized* sodium ethylate and sodium phenolate.

Since 1908 our efforts have been to apply our theory to as many cases as possible involving *interreactions* or *metatheses,* such as $C_2H_5ONa + IC_2H_5 \longrightarrow (C_2H_5)_2O + NaI$, and *purely catalytic changes,* such as $C_2H_5ONa + CH_3C:N + C_2H_5OH \rightleftarrows C_2H_5ONa + CH_3C(:NH)OC_2H_5$, and *intramolecular rearrangements,* such as

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[1] Shadinger and Acree: Am. Chem. Jour., **39**, 227 (1908).

[2] Ibid., **39**, 228 (1908).

[3] Stieglitz (Jour. Am. Chem. Soc., **35**, 1774(1913)) states that he looked upon the decomposition of free imidoesters as the slow change of a nonionized electrolyte. Although our theory had already appeared (Am. Chem. Jour. **37**, 410; **38**, 258 (1907)) Stieglitz overlooked the possibility that the "salt effect" discussed by him in his papers of 1908 could be due to the *nonionized* imidoester salts and has only recently used our equations to reinterpret his results in the light of this theory that both the ions and the molecules of imidoester salts can be hydrolyzed (Jour. Am. Chem. Soc., **34**, 1687, 1688, 1689, 1690, 1694 (1912))

[4] Am. Chem. Jour., **43**, 519 (1910); **49**, 116 (1913).

[5] Ibid., **43**, 519 (1910); **49**, 474 (1913).

$$CH_3CONClC_6H_5 + \overset{+}{H} + \overset{-}{Cl} \rightleftarrows CH_3CONHCl_2C_6H_5 \longrightarrow$$
$$CH_3CONHC_6H_4Cl + \overset{+}{H} + \overset{-}{Cl}.$$

These three, together with oxidation and reduction, are the most important classes of reactions. Since we have found our theory to hold in about thirty cases worked out by us *in both concentrated (N/1 to N/32) and ideal (N/32 to N/2048) solutions* and in our reinterpretation[1] of the work of Arrhenius, Ostwald, Koelichen, Tubandt, van Dam, Bredig, Goldschmidt, Stieglitz, Holmberg, Senter, Walker, Conrad and his coworkers, Segaller, Bruyn, Lulof, Steger, and others, on organic reactions, and in certain inorganic reactions, and especially as Arrhenius,[2] Goldschmidt,[3] Bredig,[4] Biddle,[5] Stieglitz,[6] Holmberg,[7] Dawson,[8] Kilpi,[9] Worley[10] and others are now beginning to use this theory, we are now bringing out the details of our work. We wish to emphasize[11] that we realize that we must later correct the data for certain "abnormal salt effects" when we study more fully other possible side reactions, and the physical factors, such as viscosity, solvation, ionic velocities, electronic phenomena, and the reaction velocities in very dilute solutions in all cases.

The present communication deals with the study of the reaction between ethyl bromide and sodium ethylate and ethyl iodide and sodium ethylate, in absolute ethyl alcohol at 25°. The experimental methods used have been described in some detail in former papers.[12] The ionization was measured by

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[1] Am. Chem. Jour., **48**, 352 (1912); **49**, 345, 369 (1913).

[2] Arrhenius and Taylor: Memoirs of the Nobel Institute, Vol. 2, Nos. 34, 35, 37.

[3] Zeit. Elektrochemie. **15**, 6 (1909); Zeit. phys. Chem., **70**, 627 (1910).

[4] Zeit. Electrochemie, **18**, 535, 543 (1912); Zeit. phys. Chem., **85**, 129, 170, 211 (1913).

[5] Jour. Am. Chem. Soc., **36**, 99 (1914) and earlier papers.

[6] Jour. Am. Chem. Soc., **34**, 1687, 1688, 1689, 1690, 1694 (1912); **35**, 1774 (1913).

[7] Zeit. phys. Chem., **84**, 451, 468, 469 (1913).

[8] Jour. Chem. Soc., **103**, 2135 (1913).

[9] Zeit. phys. Chem., **86**, 427, 644, 740 (1913).

[10] Phil. Mag., (5) **27**, 459 (1915).

[11] Am. Chem. Jour., **49**, 485 (1913) and earlier papers.

[12] Am. Chem. Jour., **49**, 116, 127, 369, 486 (1913) and earlier papers.

Dr. H. C. Robertson, Jr., to whom we are greatly indebted for this and other valuable aid.

The data presented here harmonize with the idea that the alkyl halide reacts with both the ethylate ion and the nonionized sodium ethylate according to the equation $K_N = K_i\alpha + K_m(1 - \alpha)$, developed in the earlier papers.[1] The values $K_i = 0.00576$ and $K_m = 0.00233$ found by us for ethyl bromide and sodium ethylate at 25° agree closely with $K_i = 0.00557$ and $K_m = 0.00232$ observed by Dr. Julia Peachy Harrison in a repetition of this work, and the same is seen in the tables on page 606 to hold for the work on ethyl iodide and sodium ethylate.

The best confirmation of our theory, however, comes from the study of the reactions of ethyl bromide (and also methyl iodide and ethyl iodide) with potassium ethylate and lithium ethylate. If our theory is correct we should find the same[2] value for the *activity* of the *ethylate ion*, whether it comes from sodium, potassium or lithium ethylate. But the *nonionized* sodium, potassium and lithium ethylates are *different substances* and could, therefore, react with *different velocities* with ethyl bromide. The confirmation of our theory lies in the fact that Dr. Harrison and Dr. Shrader, in work on ethyl bromide and potassium and lithium ethylates, have actually found practically the same values for K_i, but *different* values for K_m, which are shown in the following table:

	K_i	K_m
Dr. Marshall: sodium ethylate and ethyl bromide	0.00576	0.00233
Dr. Harrison: the same	0.00543	0.00237
Dr. Harrison: potassium ethylate and ethyl bromide	0.00539	0.00296
Dr. Shrader: lithium ethylate and ethyl bromide	0.00574	0.00157

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[1] Am. Chem. Jour., 37, 410; 38, 258 (1907); 43, 519 (1910); 48, 352 (1912); 49, 477 (1913).

[2] See Ibid., 39, 229 (1908); 43, 507, 519 (1910); 48, 352 (1912) and later papers.

Our work on sodium ethylate and ethyl iodide at 25° in the second section of the experimental portion gives the values $K_i = 0.0120$ and $K_m = 0.00427$ found in Table XIV. These agree very well with the data $K_i = 0.0122$ and $K_m = 0.00402$ obtained by Dr. Shrader in his repetition of this work. In confirmation of this theory Dr. Shrader and Dr. Harrison have found that potassium and lithium ethylates and ethyl iodide give practically the same values for K_i but different values for K_m shown in the following table:

	K_i	K_m
Dr. Marshall: sodium ethylate and ethyl iodide	0.0120	0.00427
Dr. Shrader: the same	0.0122	0.00402
Dr. Harrison: potassium ethylate and ethyl iodide	0.0122	0.00457
Dr. Shrader: lithium ethylate and ethyl iodide	0.0121	0.00304

In later articles giving our work on the reactions of methyl iodide, ethyl iodide and ethyl bromide with sodium, potassium, and lithium ethylates and phenolates we shall show that each alkyl halide gives practically the same value for its K_i, whatever the ethylate or phenolate used, but that the nonionized ethylates and phenolates react with different velocities with the same alkyl halide, in conformity with our theory.

The best evidence for our theory comes, not from the above work in *concentrated solutions*, but from the investigations of Dr. E. K. Marshall,[1] Dr. Julia P. Harrison,[2] and Dr. C. N. Myers[3] on the purely catalytic action of *dilute solutions* ($N/32$ to $N/2048$) of sodium, potassium and lithium ethylates on the reversible addition of ethyl alcohol to nitriles,

$$RC{:}N + HOC_2H_5 + NaOC_2H_5 \rightleftarrows RC({:}NH)OC_2H_5 + NaOC_2H_5.$$

Dr. Myers' investigations on *p*-bromobenzonitrile show beyond question that *both* the ethylate ions and the nonionized ethylates

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[1] Am. Chem. Jour., 49, 127 (1913).

[2] Ibid., 49, 369 (1913).

[3] Ibid., 49, 122, 132, 485 (1913).

must be considered *active* even in the *ideal* or *dilute* solutions. In accordance with the theory he obtains the *same* value for K_i for the ethylate ion common to all three ethylates, but different values for the activity, K_m, of the three nonionized ethylates. Sodium ethylate gave the values $K_i = 0.161$ and $K_m = 0.158$, potassium ethylate gave $K_i = 0.163$ and $K_m = 0.144$, while lithium ethylate gave $K_i = 0.159$ and $K_m = 0.093$. Dr. Marshall and Dr. Harrison found the values $K_i = 0.1172$ and $K_m = 0.0976$, and $K_i = 0.344$ and $K_m = 0.228$ in their work on the action of sodium ethylate on benzimidoethylester and acetimidoethylester, respectively.

Salt Catalysis

Arrhenius called the deviation from the purely ionic reaction a "salt catalysis." This same idea has been used since by Euler[1] and by Stieglitz,[2] both of whom believed that this change in velocity in reactions involving water is due to a change in the ionization of the water. We have shown in another article[3] that though his ideas have much for praise, Stieglitz's own very fine work shows that his reaction velocities do not increase with rise in temperature anywhere nearly as much as the increase in the ionization of the water demands.

In our theory of salt catalysis we broke away[4] entirely from the purely ionic reaction of chemical activity and began to investigate whether the so-called "salt catalysis" may not be due in part or in whole to the activity of the nonionized electrolytes. We proved experimentally that the added salt or other electrolyte may have a "normal salt effect" arising from the changes in ionization conforming to the Arrhenius theory of isohydric solutions, and may also have an extra specific "abnormal salt effect" not yet understood. This theory has been

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[1] Zeit. phys. Chem., **32**, 348 (1900); Ber. deutsch. chem. Ges., **39**, 2726 (1906).

[2] Am. Chem. Jour., **39**, 29, 166, 402, 437, 586, 719 (1908); Jour. Am. Chem. Soc., **32**, 221 (1910); **34**, 1687 (1912); **35**, 1774 (1913).

[3] Am. Chem. Jour., **41**, 466–483 (1909); **48**, 369–372 (1912).

[4] *Ibid.*, **38**, 273 (1907); **39**, 230 (1908); **48**, 356 (1912) and later papers.

recently accepted and used generously by Arrhenius[1] and Stieglitz.[2] It should be suggested that the "abnormal salt effects" perhaps involve electronic transfers through portions of the electrolyte not directly concerned in the reaction. In this connection we wish to emphasize especially that the addition of neutral salts in our own and the reactions studied by others seems to keep the reaction velocities much more constant, especially toward the end of the reaction. These facts will be discussed later in great detail.

That there may be a small "abnormal salt catalysis" in the present data can be seen from the following: Suppose that there is a small negative salt catalysis proportional to the total concentration of sodium ethylate, or sodium bromide formed, irrespective of the ionization, the factor being 8 percent per gram molecule. The equation $K_N = [K_i\alpha + K_m(1 - \alpha)][1 - 0.08\,C_{salt}]$ then gives us the *true values* for $K_i\alpha + K_m(1 - \alpha) = K'_N$ found in Table XVI instead of those in Table XI. From these new values of K'_N we find the values for K_i and K_m given in Table XVI, namely $K_i = 0.00540$ and $K_m = 0.00260$, respectively. These differ only slightly from those found by Dr. Harrison for potassium ethylate and by Dr. Shrader for lithium ethylate and the differences may then be considered close to the experimental errors.

In the work on sodium ethylate and ethyl iodide at 25° in the second section of the experimental portion we give in Tables XVII and XVIII the data that would be obtained for K_i and K_m if the sodium ethylate, or sodium iodide formed, can exert a *positive* "abnormal salt effect" of 8 percent per gram molecule of total salt, ionized or nonionized. It is seen in Table XVIII that K_i and K_m are changed from 0.0120 and 0.00427, found in Table XIV, to 0.0132 and 0.00372, respectively. This positive "abnormal salt catalysis" of 8 percent per gram molecule therefore *lowers* the K_i about 9 percent

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[1] Arrhenius and Taylor: Memoirs of the Nobel Institute, Vol. 2, Nos. 34, 35, 37.

[2] Jour. Am. Chem. Soc., 34, 1687, 1688, 1689, 1690, 1694 (1912); 35, 1774 (1913).

and *raises* the K_m about 14 percent. These values are much larger than the experimental errors of the work. This shows us that a small "abnormal salt catalysis" may be involved in all the values of K_i and K_m calculated by the above methods, even though we secure excellent agreement among the values for K_i from the sodium, potassium and lithium ethylates. We are, therefore, justified in concluding that the "abnormal salt effect," *whether small or large,* is about the same for all three of these ethylates. We cannot determine the exact magnitude until our work in the dilute solutions is completed, but the work of Dr. B. Marion Brown on the influence of sodium iodide on the reaction of methyl iodide with sodium ethylate at 25° seems to show conclusively that both the sodium iodide and sodium ethylate have a measurable influence on the reactions of the ethylate ions and nonionized sodium ethylate. In order to secure the data necessary for a final solution of this problem of "abnormal salt catalysis" much more work is needed.

Experimental

The reactions of sodium ethylate with the alkyl halides have been studied by several investigators, most notably Hecht,[1] Conrad and Brückner, and Conrad[2] and Brückner. That these workers did not consider these reactions as even ionic, much less both ionic and molecular in the sense that we use in our theory, is shown by their statement:[3] "Da dieses Gesetz für die Elektrolyte allgemeine Gültigkeit besitzt, so war es von Interesse zu untersuchen, ob dasselbe auch auf *nichtleitende* (Italics ours!) Körper, wie Alkylhaloide und Metallalkylate, ausgedehnt werden darf." Furthermore, Conrad and his workers apparently never made any conductivity measurements with the ethylates in alcoholic solutions, which Bruyn and Tijmstra[4] and also Dr. H. C. Robertson, Jr., have found to be comparatively strong electrolytes. These

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[1] Zeit. phys. Chem., 3, 450; 4, 274 (1889); 5, 289 (1890).

[2] Ibid., 4, 631 (1889); 7, 274, 283 (1891).

[3] Ibid., 5, 289 (1890).

[4] Ibid., 49, 345 (1909).

investigators showed that the velocity of the reaction increases with dilution,[1] they measured the increase in reaction velocity with the rise in temperature, and they proved that the formula $K_N - K_i = a \log V$, or more generally $K'_N - K_N = a \log (V'/V)$ in which K'_N and K_N represent $V'K_{V'}$ and VK_V, as used in our former articles, gives very close agreement between their found and calculated reaction velocities. This equation took no account of the changes in ionization and we[2] have now found that it holds because the equation $a = \frac{K'_N - K_N}{\log (V'/V)} = \frac{(K_i - K_m)(\alpha' - \alpha)}{\log (V'/V)}$ can be derived from a comparison of our equation $K_N = K_i\alpha + K_m(1 - \alpha)$ with theirs. The dilution formula, $\frac{\alpha' - \alpha}{\log (V'/V)} = K$, derived from these equations has been found to hold fairly closely for all of our concentrated solutions of strong and weak electrolytes in alcohol and we shall attempt to extend this to all other known data on ionization.

The experimental methods described in previous papers have been used, with modifications, in the present studies. The reaction was followed by titrating the ethylate with acid, the values given for A and x representing the number of cc of $N/1$, $N/2$, $N/4$, etc., acid required to neutralize 20 cc or 40 cc portions in the presence of methyl orange. The unit of time, t, is the minute. When the values of K_V, $K_{V'}$, $K_{V''}$ are multiplied by V, V′, V″, etc., we obtain K_N, K'_N, K''_N, etc., the reaction velocities of normal solutions having the ionizations corresponding to the concentrations $1/V$, $1/V'$, $1/V''$, etc. A comparison of the simultaneous equations $K_N = K_i\alpha + K_m(1 - \alpha)$, $K'_N = K_i\alpha' + K_m(1 - \alpha')$, $K''_N = K_i\alpha'' + K_m(1 - \alpha'')$ which are solved by the use of the equa-

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[1] Ibid., 5, 289 (1890). Dr. J. H. Shrader [Jour. Chem. Soc., 105, 2582 (1914)] and Dr. W. A. Taylor have reinterpreted their excellent data by the use of our theory and shown that both the ethylate ions and nonionized sodium ethylate seem to be active.

[2] Shrader and Acree: Jour. Chem. Soc., 105, 2582 (1914). Dr. W. A. Taylor will soon publish his results along this line.

tions $K_i = \frac{K'_N(1-\alpha) - K_N(1-\alpha')}{\alpha' - \alpha}$ and $K_m = \frac{K_N\alpha' - K'_N\alpha}{\alpha' - \alpha}$, gives us the values of K_i and K_m, as illustrated in Table XIII of both sections. Those values of K_i and K_m with asterisks involve smaller errors in $\alpha' - \alpha$, but the average of these is practically the same as the average of all the values of K_i and K_m, as can be seen in Table XIII of both sections. K_i and K_m represent the velocities of the reaction of a gram equivalent of ethylate ions, and of nonionized sodium ethylate, respectively, with a gram molecule of the alkyl halide in one liter. When the average values of K_i and K_m are substituted in the equation $K_N = K_i\alpha + K_m(1 - \alpha)$ we obtain the theoretical reaction velocity, "K_N Calculated," which is compared with "K_N Found" in order to give the experimental "Error in Percent" shown in Table XIV of both sections. The percent of reaction due to ions and that due to molecules are given in Table XV of both sections. The values of α are taken from[1] a former article.

The addition of considerable quantities of ether and sodium iodide to some of the reaction mixtures shows that the small amounts of these substances formed during the time periods measured have no great effect on the reaction velocities, as is also shown in the next communication on this subject.

Sodium Ethylate and Ethyl Bromide at 25° C

TABLE I

N Sodium Ethylate and *N* Ethyl Bromide

A = 10.00

t	x	K_V
[30	0.819	0.00297]
60	1.486	0.00291
90	2.064	0.00289
110	2.413	0.00289
130	2.703	0.00289
	Mean =	0.00290
	K_N =	0.00290

TABLE II

N Sodium Ethylate and *N* Ethyl Bromide

A = 10.00

t	x	K_V
60	1.459	0.00284
90	2.056	0.00287
120	2.557	0.00286
150	3.003	0.00286
170	3.260	0.00285
	Mean =	0.00286
	K_N =	0.00286

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[1] Jour. Phys. Chem., 19, 407 (1915).

TABLE III

0.5 *N* Sodium Ethylate and 0.5 *N* Ethyl Bromide

A = 10.00

t	x	K_V
30	0.452	0.00157
50	0.724	0.00154
70	0.980	0.00155
100	1.342	0.00155
130	1.690	0.00156
160	1.990	0.00155
[1180	6.366	0.00149]

Mean = 0.00155

K_N = 0.00310

TABLE IV

0.5 *N* Sodium Ethylate and 0.5 *N* Ethyl Bromide

A = 10.00

t	x	K_V
50	0.738	0.00159
80	1.112	0.00156
110	1.444	0.00154
140	1.800	0.00157
170	2.090	0.00155

Mean = 0.00156

K_N = 0.00312

TABLE V

0.25 *N* Sodium Ethylate and 0.5 *N* Ethyl Bromide

A = 10.00 B = 20.00

t	x	K_V
[20	0.296	0.000756]
50	0.808	0.000858
80	1.216	0.000836
110	1.612	0.000842
170	2.360	0.000843
1260	7.760	0.000796

Mean = 0.000845

K_N = 0.00338

TABLE VI

0.25 *N* Sodium Ethylate and *N* Ethyl Bromide

A = 10.00 B = 40.00

t	x	K_V
[20	0.62	0.000806]
40	1.26	0.000854
60	1.82	0.000856
80	2.33	0.000854
100	2.77	0.000843

Mean = 0.000852

K_N = 0.00340

Table VII

0.125 *N* Sodium Ethylate and *N* Ethyl Bromide

A = 10.00 B = 80.00

t	*x*	K_V
50	1.68	0.000465
80	2.52	0.000461
100	3.03	0.000461
120	3.53	0.000463
140	3.96	0.000463
[275	6.12	0.000452]

Mean = 0.000463

K_N = 0.00370

Table VIII

0.125 *N* Sodium Ethylate and *N* Ethyl Bromide

A = 10.00 B = 80.00

t	*x*	K_V
60	1.98	0.000465
82	2.61	0.000466
100	3.05	0.000463
120	3.51	0.000461
140	3.95	0.000461
160	4.34	0.000458

Mean = 0.000462

K_N = 0.00370

Table IX

0.0625 *N* Sodium Ethylate and 0.5 *N* Ethyl Bromide

A = 20.00 B = 160.00

t	*x*	K_V
50	1.86	0.000244
80	2.92	0.000249
110	3.92	0.000251
130	4.50	0.000249
150	5.12	0.000249

Mean = 0.000248

K_N = 0.00397

Table X

0.0625 *N* Sodium Ethylate and 0.5 *N* Ethyl Bromide

A = 20.00 B = 160.00

t	*x*	K_V
60	2.20	0.000244
80	2.88	0.000244
100	3.61	0.000251
130	4.51	0.000249
150	5.13	0.000250

Mean = 0.000247

K_N = 0.00395

TABLE XI—K_N FOUND FOR SODIUM ETHYLATE AND ETHYL BROMIDE AT 25°

Conc. $NaOC_2H_5$ V	K_N	K_N (Average)
1	0.00290 0.00286	0.00288
2	0.00310 0.00312	0.00311
4	0.00338 0.00340	0.00339
8	0.00370 0.00370	0.00370
16	0.00397 0.00395	0.00396

TABLE XII—IONIZATION OF SODIUM ETHYLATE AT 25°

V	α	$1-\alpha$
1	0.148	0.852
2	0.234	0.766
4	0.312	0.688
8	0.393	0.607
16	0.481	0.519
32	0.577	0.423
40	0.605	0.395

TABLE XIII—K_i AND K_m FOUND FOR SODIUM ETHYLATE AND ETHYL BROMIDE AT 25°

	K_i	K_m
V = 1:V = 2	0.00527	0.00248
V = 1:V = 4	0.00533	0.00242
V = 1:V = 8	0.00573*	0.00238*
V = 1:V = 16	0.00567*	0.00240*
V = 2:V = 4	0.00586	0.00228
V = 2:V = 8	0.00595*	0.00224*
V = 2:V = 16	0.00575*	0.00230*
V = 4:V = 8	0.00602	0.00220
V = 4:V = 16	0.00571*	0.00235*
V = 8:V = 16	0.00550	0.00253
Mean,	0.00570	0.00236
Mean,[1]	0.00576	0.00233

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[1] The average of all values with stars.

Table XIV—K_N Calculated and Found for Sodium Ethylate and Ethyl Bromide at 25°

V	K_N found	K_N calculated		Variation in percent from K_N found	
		$K_i = 0.00570$ $K_m = 0.00236$	$K_i = 0.00576$ $K_m = 0.00233$	(1)	(2)
1	0.00288	0.00285	0.00284	—1.0	—1.3
2	0.00311	0.00314	0.00313	+1.0	+0.6
4	0.00339	0.00340	0.00340	+0.3	+0.3
8	0.00370	0.00367	0.00368	—0.8	—0.5
16	0.00396	0.00396	0.00398	0.0	+0.5

Table XV—Percent of Reaction Due to Ions and to Molecules

Concentration of $NaOC_2H_5$ V	Percent of reaction due to αK_i	Percent of reaction due to $(1 - \alpha)K_m$
1	30.0	70.0
2	43.1	56.9
4	52.9	47.1
8	61.5	38.5
16	69.6	30.4

Table XVI—K_N for Sodium Ethylate and Ethyl Bromide at 25°, Corrected for a Negative Salt Catalysis of 8 Percent per Gram Molecule of Sodium Ethylate

V	α	$1 - \alpha$	K_N calculated	K_N corrected for salt catalysis
1	0.148	0.852	0.00284	0.00307
2	0.234	0.766	0.00313	0.00326
4	0.312	0.688	0.00340	0.00347
8	0.393	0.607	0.00368	0.00372
16	0.481	0.519	0.00398	0.00400

TABLE XVII—K_i AND K_m FOUND FOR SODIUM ETHYLATE AND ETHYL BROMIDE AT 25°, CORRECTED FOR A NEGATIVE SALT CATALYSIS OF 8 PERCENT PER GRAM MOLECULE OF SODIUM ETHYLATE

	K_i	K_m
V = 1 : V = 2	0.00495	0.00274
V = 1 : V = 4	0.00515	0.00271
V = 1 : V = 8	0.00533	0.00268
V = 1 : V = 16	0.00545	0.00266
V = 2 : V = 4	0.00532	0.00263
V = 2 : V = 8	0.00534	0.00259
V = 2 : V = 16	0.00555	0.00256
V = 4 : V = 8	0.00559	0.00251
V = 4 : V = 16	0.00563	0.00249
V = 8 : V = 16	0.00565	0.00247
	Av., 0.00540	0.00260

Sodium Ethylate and Ethyl Iodide at 25° C

TABLE I

N Sodium Ethylate and *N* Ethyl Iodide

A = 10.03

t	*x*	K_V
20	1.003	0.0055
30	1.452	0.0056
40	1.830	0.0055
50	2.168	0.0055
60	2.370	0.0052

Mean = 0.00546
K_N = 0.00546

TABLE II

N Sodium Ethylate and *N* Ethyl Iodide

A = 10.03

t	*x*	K_V
20	1.042	0.0058
30	1.424	0.0055
40	1.787	0.0054
50	2.134	0.0054
60	2.455	0.0054

Mean = 0.00543
K_N = 0.00543

TABLE III

0.5 *N* Sodium Ethylate and 0.5 *N* Ethyl Iodide

A = 9.99

t	*x*	K_V
30	0.83	0.00305
40	1.09	0.00306
50	1.32	0.00305
60	1.53	0.00302
70	1.73	0.00300

Mean = 0.00304
K_N = 0.00608

TABLE IV

0.5 *N* Sodium Ethylate and 0.5 *N* Ethyl Iodide

A = 9.98

t	*x*	K_V
20	0.58	0.00307
30	0.84	0.00306
40	1.09	0.00306
50	1.33	0.00306
60	1.55	0.00305

Mean = 0.00306
K_N = 0.00612

TABLE V

0.25 *N* Sodium Ethylate and 0.5 *N* Ethyl Iodide

A = 10.02 B = 20.04

t	*x*	K_V
40	1.24	0.00171
50	1.52	0.00171
60	1.76	0.00169
70	2.02	0.00169
80	2.25	0.00169

Mean = 0.00170
K_N = 0.00680

TABLE VI

0.25 *N* Sodium Ethylate and 0.5 *N* Ethyl Iodide

A = 10.00 B = 20.00

t	*x*	K_V
20	0.64	0.00168
40	1.25	0.00170
60	1.77	0.00170
80	2.21	0.00166
100	2.68	0.00168

Mean = 0.00168
K_N = 0.00672

TABLE VII

0.125 *N* Sodium Ethylate and 0.5 *N* Ethyl Iodide

A = 10.00 B = 40.00

t	*x*	K_V
40	1.30	0.000881
60	1.94	0.000918
80	2.50	0.000928
100	3.01	0.000932
120	3.34	0.000886

Mean = 0.00091
K_N = 0.00728

TABLE VIII

0.125 *N* Sodium Ethylate and 0.5 *N* Ethyl Iodide

A = 10.00 B = 40.00

t	*x*	K_V
40	1.34	0.000911
60	1.97	0.000937
80	2.50	0.000928
100	2.98	0.000921
120	3.46	0.000928

Mean = 0.000925
K_N = 0.00740

TABLE IX

0.0625 *N* Sodium Ethylate and 0.25 *N* Ethyl Iodide

A = 20.00 B = 80.00

t	*x*	K_V
40	1.58	0.000518
60	2.34	0.000525
80	2.96	0.000509
100	3.60	0.000506
120	4.20	0.000504

Mean = 0.000507
K_N = 0.00811

TABLE X

0.0625 *N* Sodium Ethylate and 0.25 *N* Ethyl Iodide

A = 20.08 B = 80.32

t	*x*	K_V
40	1.55	0.000506
60	2.27	0.000506
80	2.94	0.000502
100	3.52	0.000493
120	4.22	0.000503

Mean = 0.000502
K_N = 0.00803

TABLE XI

0.0625 *N* Sodium Ethylate and 0.25 *N* Ethyl Iodide

A = 20.00 B = 80.00

t	*x*	K_V
60	2.27	0.000509
80	2.95	0.000508
100	3.57	0.000502
120	4.23	0.000509
190	6.14	0.000502

Mean = 0.000506
K_N = 0.00809

TABLE XII—K_N FOUND FOR SODIUM ETHYLATE AND ETHYL IODIDE AT 25°

Conc. $NaOC_2H_5$ V	K_N	K_N Average
1	0.00546 0.00543	0.00545
2	0.00608 0.00612	0.00610
4	0.00680 0.00672	0.00676
8	0.00728 0.00740	0.00734
16	0.00811 0.00803 0.00809	0.00808

TABLE XIII—K_i AND K_m FOUND FOR SODIUM ETHYLATE AND ETHYL IODIDE AT 25°

	K_i	K_m
V = 1:V = 2	0.0119*	0.00411*
V = 1:V = 4	0.0123*	0.00427*
V = 1:V = 8	0.0128*	0.00460*
V = 1:V = 16	0.0110*	0.00383*
V = 2:V = 4	0.0126	0.00412
V = 2:V = 8	0.0121*	0.00427*
V = 2:V = 16	0.0122*	0.00422*
V = 4:V = 8	0.0117*	0.00452*
V = 4:V = 16	0.0121*	0.00432*
V = 8:V = 16	0.0108	0.00403
Mean	0.01195	0.00423
Mean[1]	0.0120	0.00427

TABLE XIV—K_N CALCULATED AND FOUND FOR SODIUM ETHYLATE AND ETHYL IODIDE AT 25°

V	K_N found	K_N calculated		Error in percent	
		K_i = 0.01190 K_m = 0.00423 *a*	K_i = 0.01200 K_m = 0.00427 *b*	*a*	*b*
1	0.00545	0.00537	0.00541	+1.5	+0.8
2	0.00610	0.00602	0.00608	+1.3	+0.3
4	0.00676	0.00662	0.00668	+2.1	+1.2
8	0.00734	0.00724	0.00731	+1.3	+0.4
16	0.00808	0.00792	0.00798	+2.0	+1.2

TABLE XV—PERCENT OF REACTION DUE TO IONS AND TO MOLECULES

Concentration of $NaOC_2H_5$ V	Percent of reaction due to αK_i	Percent of reaction due to $(1-\alpha)K_m$
1	32.8	67.2
2	42.0	57.9
4	56.0	44.0
8	64.5	35.5
16	72.3	27.7

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[1] The mean of all values with stars.

TABLE XVI—K_N FOR SODIUM ETHYLATE AND ETHYL IODIDE AT 25°, CORRECTED FOR A POSITIVE SALT CATALYSIS OF 8 PERCENT PER GRAM MOLECULE OF SODIUM ETHYLATE

V	α	$1-\alpha$	K_N calculated	K_N corrected for salt catalysis
1	0.148	0.852	0.00541	0.00498
2	0.234	0.766	0.00608	0.00584
4	0.312	0.688	0.00668	0.00655
8	0.393	0.607	0.00781	0.00773
16	0.481	0.519	0.00798	0.00794

TABLE XVII—K_i AND K_m FOUND FOR SODIUM ETHYLATE AND ETHYL IODIDE AT 25°, CORRECTED FOR A POSITIVE SALT CATALYSIS OF 8 PERCENT PER GRAM MOLECULE OF SODIUM ETHYLATE

	K_i	K_m
V = 1:V = 2	0.0135	0.00350
V = 1:V = 4	0.0131	0.00356
V = 1:V = 8	0.0145	0.00322
V = 1:V = 16	0.0126	0.00353
V = 2:V = 4	0.0129	0.00372
V = 2:V = 8	0.0150	0.00305
V = 2:V = 16	0.0124	0.00385
V = 4:V = 8	0.0166	0.00201
V = 4:V = 16	0.0122	0.00398
V = 8:V = 16	0.0092	0.00679
	Av., 0.0132	0.00372

Conclusions

1. In this article we have shown that the theory that the ions are the only chemically active portions of the electrolytes is only partly correct, and that much of the earlier work on which this theory was based was interpreted unfortunately. We have, therefore, proposed the hypothesis that both the ions and nonionized forms of acids, bases and salts may undergo transformation with comparable velocities. These reactions may be influenced by so-called "salt effects" and other physical factors which we are investigating further.

2. A list of tables is given in which we present the velocities of the reactions of sodium ethylate with ethyl bromide and

with ethyl iodide at 25° in absolute ethyl alcohol, the concentrations varying from $N/1$ to $N/16$.

3. The proper numerical data have been substituted in the general formula $K_N = K_i\alpha + K_m(1 - \alpha)$, and the series of simultaneous equations so obtained solved. Constant values are obtained for K_i and K_m, which represent the velocity of transformation of unit concentrations of ethylate ions, nonionized sodium ethylate and alkyl halide. We have interpreted this fact as evidence that both the ethylate ions and the nonionized sodium ethylate react with the nonionized alkyl halide, although we wish to point out that there may be still other side reactions or "abnormal salt effects" involved which we do not yet understand.

4. If this theory is correct the same values should be obtained for K_i, the velocity of transformation of unit concentrations of the ethylate ions and a given alkyl halide, whether the source of the ethylate ions be the sodium, potassium, lithium or other salt. The work reported here and other studies by Dr. Julia P. Harrison and Dr. J. H. Shrader, which were given in the table on page 593 and will be presented in later articles, show that the same alkyl halide actually does give practically the same value for K_i for sodium, potassium and lithium ethylates.

5. The effect on K_i and K_m of a positive or negative salt catalysis of 8 percent per gram molecule of the electrolyte was calculated in order to see the extent of the errors involved in these constants.

6. We are investigating the peculiarities, or abnormalities, of the concentrated solutions (absolute alcohol) as rapidly as possible by attempting to measure their physical properties, especially the fluidities of the solutions by Bingham's methods, the effect of added salts on the reaction velocities and physical properties, and the probable extent of solvation (alcoholation) of the reacting constituents by Washburn's methods. These *physical factors* and the *electronic phenomena* probably play a rôle having far greater significance than we can possibly understand with our present knowledge.

Johns Hopkins University

NEW BOOKS

Oedema and Nephritis. *By Martin H. Fischer. 2nd Ed. 16 × 23 cm; pp. x + 695. New York: John Wiley and Sons, 1915. Price: $5.00.*—This is practically a new and enlarged edition of the author's two books on Oedema (15, 414) and Nephritis (16, 424, 620). The subject is treated under the following headings: the argument; absorption and secretion in individual cells and tissues; oedema; absorption and secretion in the complex organism; the colloid-chemical theory of water absorption, and some problems in biology, physiology, and pathology; nephritis; glaucoma.

When discussing the possible existence of semi-permeable membranes in living cells, p. 156, the author says: "But aside from these physicochemical facts which stand so immovably against any belief which sees in living cells a replica of the artificial osmotic cells of our laboratories, biological considerations make the whole conception impossible. To have the laws of osmotic pressure tenable for living cells we must have semi-permeable membranes about them. Only as this is the case can changes in osmotic pressure become available for the movement of water into and out of the cells. If now, for the sake of argument, we grant this assumption, then no dissolved substances can get into or out of the cells. Such a conception of the cell is impossible, for how under such circumstances could it get its necessary food, or how could it rid itself of its various metabolic products? Both processes are absolutely indispensable for the continuation of life. To get around the difficulty various observers have made these osmotic membranes permeable to some or many dissolved substances. But the moment we grant this, then the dissolved substances can diffuse from regions of higher to regions of lower concentration, and so differences in osmotic pressure are equalized and no forces remain available for the movement of water. The adherents to the view that "osmotic" membranes exist about cells can take their choice, they can either utilize their conception to make water move or they can make their membranes permeable and so have dissolved substances move, but they cannot have both. Yet for life to go on in the cell both processes must be able to go on interruptedly."

The author makes a good point here, though exception might be taken to some of the details. For years the reviewer has pointed out in his lectures that it was easy to see how osmotic pressure can raise the sap in a tree provided one has the tree; but that is not easy to see how one can carry through the lower cells the salts necessary to give the upper cells the osmotic pressure which we assign to them. It is possible to assume that the sap rises between the cells; but then the osmotic pressure is superfluous. It is also possible to assume that the cell walls are permeable to two sets of salts which react and form a salt which does not pass through the membrane. This has never been shown to be the case and until it is shown to be so, Fischer's view is unquestionably the most plausible one. The reviewer would have liked to have seen a paragraph to the effect that semi-permeable membranes are colloidal and that we are, therefore, dealing with selective, negative adsorption.

On p. 71, the author says: "Were we at this point to sum up our conception of the structure of protoplasm as thus far developed, we could liken it fairly accurately to a mass of protein intimately mixed with more or less fat-like material (the fats and lipoids), the whole being under physiological conditions immersed in a liquid (pond water in the case of an ameba, or lymph and blood in the case of our body cells) from which the protein-fat mixture soaks up a certain amount of water as well as a certain amount of the various dissolved substances found in the water. The water absorption is governed by the state of the (hydrophilic) emulsion colloids. The absorption of dissolved substances is a matter of equilibrium between the concentration of those found in the medium outside of the cell and that of the same substances found in the cell itself. We have indicated how solubility characteristics, phenomena of adsorption, and chemical combination influence the point at which equilibrium is reached. This simple picture of the cell furnishes to our minds an adequate conception of its main structure."

When discussing transudation, the author says, p. 242: "The accumulation of fluid in the serous cavities and in the so-called tissue spaces in oedematous states represents the separation of a dilute liquid protein colloid from the more solid, heavily hydrated ones making up the oedematous tissues themselves. It is the analogue of syneresis as observable in hydrated colloids. As degree of hydration and the time element are of importance in determining the amount of fluid that is thus squeezed off from laboratory colloids, so also do the high hydration characteristic of oedema and the time element, as determined by the chronicity of the agencies leading to the oedema, play important parts in the development of its accompanying transudations."

In the subdivision on the absorption of water by spermatozoa, epithelial cells, and white blood corpuscles, p. 356, the author says: "In the attempt to establish the validity of the laws of osmotic pressure for certain physiological and pathological manifestations of water absorption, biologists have been particularly eager to work with material which on experiment was found to approximate most closely the behavior demanded by theory. It is for this reason that certain plant cells and the red blood corpuscles have been the subject of more exhaustive study, so far as their behavior toward water absorption is concerned, than any other cells. The reason why just these cells should have approximated obedience to the laws of osmotic pressure more perfectly than most others that have been studied may appear later. But even these chosen cells show such great exceptions to the behavior demanded by theory that it is impossible to escape the experimentally well-grounded conclusion that most, if not all, cells do not follow the laws of osmotic pressure. The attempts that have been made to harmonize the observed behavior of various cells with that demanded on the theory that cells represent osmotic systems are ingenious, but we can scarcely believe sufficiently supported by experiment to be convincing. For the most part the explanations given are complicated, which constitutes in itself a threatening feature when the explanation of any natural phenomenon is hazarded. What strikes one as particularly encouraging about the colloid idea of water absorption is its simplicity, and the breadth of water absorption phenomena to which it may be applied without apparent experimental or theoretical objection.

"In a preceding part of this book we tried to show how the absorption of water by the cells of muscle, the eye, the central nervous system, the kidney, and the liver is essentially a function of their colloid state. What was said regarding these cells is also true regarding spermatozoa, white blood corpuscles, and the epithelial cells of the bronchi, intestine, bladder, and esophagus. We need not enter into the detailed experimental findings on this subject which may be found in H. J. Hamburger's excellent work. We again encounter no difficulty in explaining the experimentally observed facts when we call to mind the effect of acids, alkalies, salts, and these in mixture upon the swelling of (hydrophilic) protein colloids. All the cells mentioned swell if placed in distilled water. This fact, which has always been interpreted as due to differences in osmotic pressure, is really to be explained by remembering that, under the conditions prevailing in these experiments, the cells produce acids which increase the capacity of their colloids for holding water. A second factor is found in the diffusion of at least some salts out of the cell, for the higher the concentration of the neutral salts in a colloid, the less does it swell."

It is quite likely that the author's enthusiasm has given him a slightly distorted perspective. It is quite likely that he has erred occasionally in statement of facts, as in regard to the molecular weights of colloids, p. 40. It seems to be certain, however, that his general point of view is sound and that he is opening up a very fruitful field. It is only by taking into account the phenomena of colloid chemistry that one can hope to make permanent progress along physiological lines. The author is to be congratulated on the excellent work that he is doing. *Wilder D. Bancroft*

Genetic Theory of Reality. *By James Mark Baldwin. 22 × 15 cm; pp. xvii + 335. New York: G. P. Putnam's Sons, 1915. Price: $2.00.*—This book forms the author's fourth contribution to genetic logic and contains his doctrine of Pancalism, or, as he calls it, his contribution to the theory of reality.

The problem of interpretation, or the reaching of objective meaning of things, is first treated. In individual interpretation, practical and emotional interest determines the character of one's decision, and these decisions pass through prelogical, logical and immediate stages, giving intuitive, perceptive, discursive and over-discursive moods.

In racial and social interpretation there is a tendency to force the individual to follow generally accepted customs. An extension of such interpretation can, therefore, never cause development. This can only come when some individual breaks away from conventional methods of looking at things. These values are then worked back into the social fabric and development is occasioned. Religious interpretation, being both logical and teleological, forms a connecting link between the actual and the ideal. In the development of these types of interpretation, the growth of imagination is of great importance and comes with the process of mediation.

In further development from the mediate back to immediacy the interpretation by philosophers has led to mysticism, dogmatism, etc. The author, therefore, proposes to consider reality from the standpoint of aesthetic experience. The author's theory of reality may be stated thus: Reality exists because the summation of aesthetic experience, interpretation, and interest points to this existence as an ideal apart from one's self. According to this, a consideration of aesthetic beauty is looked upon as all important, all-inclusive, and universal. Art and beauty must, therefore, be considered as self-sufficient, unrelated, and all-inclusive.

The author has developed this theory practically entirely from the immediate or intuitive standpoint. "We realize the real in achieving and enjoying the beautiful." Take the question of music, for instance. The sound is perceived, but there would be no sound unless the human ear were present. There would be vibration but no sound, hence we cannot ascribe reality to sound separate from, or without consideration, of the human ear. The author's postulate of non-relativity is not warranted. The theory is, therefore, a statement of belief only. Making experience the criterion of reality reminds one of the classical proof of immortality from simplicity. It is wholly unwarranted.

The author's style and diction in this book is of such a nature that it is hard reading. For that reason it will probably not be widely read.

C. W. Bennett

Handbuch der Mineralchemie. *By C. Doelter. Vol. III: Parts III-V. 18 × 25 cm; pp. 160 (each part). Dresden: Theodor Steinkopff, 1914. Price: 6.50 marks (each part).*—In these numbers are taken up the phosphates of magnesium, calcium, manganese, iron, copper, zinc, lead, and alumina; the double aluminum or iron phosphates; the arsenates and antimoniates.

In spite of the fact that blue, green, yellow, and red apatites are known, p. 344, we are very far from a knowledge of what the coloring matter is. Doelter does not accept the view of Wöhler that the color is due to an organic substance, nor the view of Pupke that the color is due to manganese.

On p. 359 is pointed out that large deposits of phosphorites occur in the ocean wherever a cold current meets a warm current. The sudden temperature change kills both the warm-water and the cold-water fauna, the bodies sinking to the bottom. In some places the bed of the ocean is covered six feet deep with bones of fishes and other sea creatures. One large deposit occurs on the Agulhas Bank off the Cape of Good Hope where a warm equatorial current coming down between the island of Mozambique and the mainland meets the cold antarctic current.

There is an interesting account of the preparation and properties of Thomas slag, p. 370; and another on the treatment of the monazite sands, p. 567. The various modifications of arsenic and of antimony are discussed in detail, pp. 601, 754; so are the inter-relations of the arsenic oxides, p. 619. There is apparently some work still to be done on the crystalline modifications of antimony oxide, senarmontite and valentinite, p. 762. According to Henglein, who writes this portion of the book, the two oxides precipitate together from melts and solutions, while the direct change of one into the other has not been observed when neither fusion nor solution took place. Of course, this is merely a proof of careless work, but it is another one of the innumerable details which somebody must straighten out.

Wilder D. Bancroft

De la Pirotechnia. *By Vannoccio Biringuccio. Edited by Aldo Mieli. 13 × 21 cm; pp. lxxvi + 198. Bari: Società Tipografica Editrice Barese, 1914. Price: 3 francs.*—This is the first of a series of scientific and philosophic classics which the enterprising publishers are going to bring out. Biringuccio was born in 1480. He travelled much in Italy and Germany studying metallurgical processes. He was exiled several times from Siena and died in Rome in 1539. Biringuccio does not use the word "Pirotechnia" to denote fireworks but rather to include all arts requiring the use of fire. The present volume includes only the first volume and part of the second volume of Biringuccio's ten volume treatise. This first instalment contains the chapters on the ores of gold, silver, copper, lead, tin, iron, mercury, sulphur, and antimony; and those on the preparation of iron and brass. In those days zinc itself was not known and brass was obtained direct from mixed ores of copper and zinc. Biringuccio was a contemporary of Paracelsus and his book is essentially a scientific treatise, one of the earliest to which this name could apply. We are, therefore, grateful to the publishers for making this truly classic work available to us. *Wilder D. Bancroft*

Molecular Association. *By W. E. S. Turner. 22 × 15 cm; pp. viii + 170. New York: Longmans, Green and Co., 1915. Price: $1.40 net.*—The headings of the chapters are: introductory; the molecular complexity of dissolved substances; the influence of the solvent; molecular complexity in the liquid state; surface tension methods of determining molecular complexity in the liquid state; molecular complexity in the liquid state—some other methods and a review; the molecular complexity of water and the theory of dynamic allotropy; the selection and use of molecular formulae; molecular association and physical properties; molecular association and chemical combination.

The compilation has been made somewhat uncritically. On p. 30 the author tabulates a molecular weight of over 5000 for ferric hydroxide based on freezing-point measurements of colloidal ferric oxide solutions. On p. 45 it is stated explicitly that the theoretical osmotic pressure of a dilute aqueous solution will change if the degree of polymerization of the water is changed by the addition of the solute, in spite of the fact that theory and experiment show that the molecular weight of the solvent as vapor is what counts and not the molecular weight of the solvent as liquid. *Wilder D. Bancroft*

Food Industries. *By H. T. Vulté and S. B. Vanderbilt. 16 × 22 cm; pp. iv + 309. Easton: The Chemical Publishing Co., 1914.* The subject is treated under the headings: food principles; water; the king of cereals—old milling processes; modern milling and mill products; cereals; breakfast foods and coffee substitutes; utilization of flour—bread making; leavening agents; starch and allied industries; the sugar industry; alcoholic beverages; fats; animal foods; the packing house; milk; milk products; preservation of foods; the canning industry; tea, coffee and cocoa; spices and condiments.

In regard to the cost of living, the authors say, p. 3: "Foods may be roughly divided into permanent and perishable material. Among the permanent foods, the cost has decreased, as sugar and flour. The great advance in prices of our food material is found entirely in the perishable foods. Such material is now often brought from a long distance, thus adding cost of freight and many times the cost of preservation during transportation. The many hands through which food material must pass also increases the cost."

There is an interesting paragraph on p. 190 as to the reasons for cooking meat. "In great contrast to the carbohydrate group, protein does not become more digestible on cooking. In fact, meat fiber subjected to high temperature or prolonged heating becomes toughened and more difficult of digestion. It is obvious, therefore, that we must look for other reasons for the almost universal custom of cooking meat. Sterilization is the reason usually given, but this is only true to a limited extent. As meat is not a good conductor of heat, the interior of large portions, such as roasts, frequently does not reach the temperature when all pathogenic bacteria are killed. Neither can we hope that harmful ptomaines will be affected if by any chance such compounds have been developed. Our real reason for cooking is probably the development of desirable flavors, largely due to the extractive creatin, which yields creatinin on heating. This is important as it is now a well known fact, that we do not derive as much benefit from food that we do not relish." There is a curious lack of perspective about this. The authors seem to have forgotten that meat was cooked thousands of years before anybody knew anything about digestibility, sterilization, or ptomaines.

On p. 104 we read that "in the world's food products made from wheat, macaroni has occupied an important place in the diet of several nations. The Japanese claim to be the original manufacturers but whether this be true or not, the Europeans first heard of it from the Chinese who had been using it for a long period. Although the Germans were the European discoverers of macaroni, it was the Italians who early learned to appreciate its virtues and to adopt it as a national food. By the fourteenth century, Italy was the only European nation that understood its preparation, and for nearly four hundred years she held the secret of the method of manufacture." *Wilder D. Bancroft*

Foundations of Chemistry. *By Arthur A. Blanchard and Frank B. Wade. 14 × 19 cm; pp. 446. New York: American Book Co., 1914. Price: $1.25.*— In the preface the authors say: "Formerly, the study of the classics occupied a very prominent position in educational training, and many of the ablest men of our times owe their efficiency largely to the excellence of the mental discipline thus acquired. The essential mental training can, however, be furnished in the study of subjects that possess vital interest and present day usefulness, provided these subjects are as well taught as were the classics. A tendency is now evident to depart from the study of the classics and to substitute therefor a multitude of vocational and informational subjects. It is extremely likely that this type of study will not only fail to prove as practically useful as its advocates hope, but that it will fail to impart that sturdy independence of thinking—that ability to apply what has previously been gained—which is so essential to success in all walks of life, and which can be imparted in large measure by a thorough study of the underlying principles of science in their applications to well-selected cases.

"With the ideal in mind of teaching the scientific method of thought while considering the facts and principles of chemistry, the authors have striven to write a book, the intelligent study of which will develop both the power of the pupil to think originally and his appreciation of the relation between the subject matter of chemistry and his daily life. In illustrating the principles of chemistry, very many important industrial processes and applications to daily life have been chosen, but the greatest effort has been made to keep the idea uppermost that the principles concerned are of universal application, whereas the individual processes are transient and of relatively less importance to the general student of chemistry."

It is a good programme and such paragraphs as those on the kindling point, p. 45, are instances of the book at its best. *Wilder D. Bancroft*

Das Lebensmittelgewerbe. *By K. von Buchka: Vol. I, Parts I and II, pp. 48, each part: 18 × 25 cm. Leipzig: Akademische Verlagsgesellschaft m. b. H., 1913. Price: 2 marks per part.*—This hand-book deals with foods and beverages from all points of view; but with special reference to the legal restrictions which have been found necessary and to the reasons for them. The volume opens with a chapter on human nourishment by Dr. Kreutz of Strassburg, after which comes an introductory section by Professor von Buchka of Berlin. The first special chapter deals with foods and drinks containing alkaloids. This is to include sections on coffee and coffee substitutes; tea; cocoa and chocolate; tobacco. Only the opening pages of the section on coffee and coffee substitutes are included in the second number. The book is an interesting one and deals with a field which has never been covered in the same way. *Wilder D. Bancroft*

A Manual of Oils, Resins, and Paints. *By Harry Ingle. Vol. I. 14 × 20 cm; pp. 129. Philadelphia: J. B. Lippincott Co., 1915. Price: $1.25.*—The manual is to consist of three volumes, each one complete in itself and sold separately. The first volume deals with analysis and valuation, the subject being treated under the headings: introduction to the chemistry of the oils, gums, etc.; physical tests; chemical tests; qualitative tests for oils; the classification of oils; the systematic examination of oils, fats, and waxes; technological analysis. *Wilder D. Bancroft*

Données numériques de Spectroscopie. *By L. Brüninghaus. 22 × 28 cm; pp. viii + 73. Chicago: University of Chicago Press, 1914. Price: 10 francs.*—This is a reprint of a portion of Volume III of the Annual International Tables (19, 251). It contains the data for 1912 on emission spectra, absorption spectra, and the Zeeman effect. There is a preface by H. Deslandres. The publication of the reprint has been made possible by the co-operation of the French Department of Public Instruction. *Wilder D. Bancroft*

Données numériques de l'electricité, magnétisme et électrochemie. *By P. Dutoit, W. C. McC. Lewis and A. Mahlke. 22 × 28 cm; pp. ix + 159. Chicago: University of Chicago Press, 1914. Price: 10 francs.*—This is a reprint of a portion of Volume III of the Annual International Tables (19, 251). The collection and publication of the data have been made possible by the co-operation of the French Department of Commerce, Industry, and Posts, of the Society of Civil Engineers (Paris) and of the International Society of Electricians (Paris). There is a preface by Maurcie LeBlanc, president of the International electrotechnical commission, in which he points out that only a few years ago an electrician would have laughed at the thought of being interested in data on the viscosity of rubber or on the action of light on selenium. *Wilder D. Bancroft*

Données numériques de radioactivité. *By J. Saphores and F. Bourion. 22 × 28 cm; pp. viii + 12. Chicago: University of Chicago Press, 1914. Price: 2.50 francs.*—This is a reprint of a portion of Volume III of the Annual International Tables (19, 251), and is published with assistance from the Institute of Radioactivity of the University of Paris. The subheads are: atomistics, electronics and ionization, radioactivity, atmospheric electricity, atomic weights. *Wilder D. Bancroft*

Données numériques de cristallographie et de minéralogie *By L. J. Spencer. 22 × 28 cm; pp. iii + 21. Chicago: University of Chicago Press, 1914. Price: 4 francs.*—This is a reprint of a portion of Volume III of the Annual International Tables (19, 251). Funds have been furnished by the German Mineralogical Society, the New York Academy of Sciences, the French Mineralogical Sceiety, the Imperial Russian Mineralogical Society, the Mineralogical Society, the Vienna Mineralogical Society. In the preface M. A. Lacroix says that "all who are interested in minerals and in the science of crystals will find here precious new data on: chemical composition; crystallographic properties (especially the enumeration of recently discovered forms); optical, thermal, and electrical properties, hardness, density, and specific heats; temperatures of fusion, decomposition, transformation, etc.; minerals occurring in nature and also innumerable organic or inorganic compounds prepared in the laboratory." *Wilder D. Bancroft*

Données numériques de biologie. *By Emile F. Terroine. 22 × 28 cm; pp. xi + 20. Chicago: University of Chicago Press, 1914. Price: 4 francs.*—This is a reprint of a portion of Volume III of the Annual International Tables (19, 251). The subdivisions are: biometrics, biological physical chemistry, biochemistry, microbiology, pharmacodynamics, physiology. *W. D. B.*

Art de l'ingénieur et métallurgie. *By S. L. Archbutt, G. Fieck, W. Hinrichsen, E. Nusbaumer and A. Portevin. 22 × 28 cm; pp. viii + 92. Chicago: University of Chicago Press, 1914. Price: 10 francs.*—This is a reprint of a portion of Volume III of the Annual International Tables (19, 251). It is published with assistance from the French Department of Public Works, the Committee of French Ironmasters, the Franco-Belgium Group of the International Association for Testing Materials, the Iron and Steel Institute, the French Society of Civil Engineers, the Eastern Section of the Industrial Society (Nancy). Under engineering the subheads are: mechanical constants of materials of construction, textiles, etc.; thermal constants of refractories and combustibles. Under metallurgy the subheads are: various technical data on metals and alloys; mechanical constants. *Wilder D. Bancroft*

THE PASSIVIFICATION OF IRON BY NITRIC ACID[1]

BY S. W. YOUNG AND ELTON MARION HOGG

Introduction

The passive state of certain metals may be induced by methods which resolve themselves into two general subdivisions: Passivity produced by strong nitric acid and other oxidizing agents, and that produced by anodic or cathodic polarization. The experimental work described in the present paper is confined to a study of the passivification of iron by nitric acid. This limitation was imposed upon the research in view of the fact that of all the former work done, that with nitric acid seemed to be less understood and there appeared to be some points of attack on this particular phase of the problem which might result in the clarification of our knowledge of the entire subject.

Historical

In the historical discussion in this paper both general methods of passivification will be briefly discussed and a general statement of the principal theories will be made.

The study of the passivity of iron has engaged the attention of scientific investigators for nearly one hundred years and yet our knowledge of the subject is still very limited. The recent activity in this field, recorded in the late symposiums before the British Faraday Society,[2] indicates that our information on the subject has, in the past, been greatly circumscribed. Many new methods of attack are described which are distinct departures from those of the earlier students, and many new and important facts have been discovered. To explain these facts many theories are put forward which, in most cases, are merely modifications of older ones, so that

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[1] Presented by Elton M. Hogg to the Faculty of Chemistry of Stanford University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, May, 1915.

[2] Met. Chem. Eng., 11, 12, 679 (1914).

for present purposes an outline of the three most prominent theories will be sufficient.

Theories of Passivity

1. The Oxide Film Theory of Faraday.[1]—According to this theory the surface of the iron is either oxidized or the superficial particles of the metal are in such relation to the oxygen of the electrolyte as to be equivalent to oxidation. The formation of a layer of oxide is supposed to cause passivity by mechanically hindering the metallic ions from entering the solution. To this theory Hittorf raises the objection that no oxide could be found which would display the necessary properties. The destruction of passivity by elevation of temperature is also hard to explain by this means. Finkelstein states that if an oxide is formed it must conduct electricity like the metal itself. LeBlanc raised the objection that the reflecting power of the surface in the active and passive conditions is the same; hence, if a film is present, it must be of less than molecular thickness.

2. The Valency Theory of Kruger-Finkelstein[2] *and Muller.*[3]—According to this theory passivity is due to the change of the metal to a nobler modification. This change of state depends somewhat upon temperature. Otherwise the electrochemical behavior of the metal depends on the relative oxidation and reduction potentials of the electrolyte.

3. The Reaction Velocity Theory of LeBlanc.[4]—In its general form this theory states that passivity is due to the slow rate of change at the anode. The passive metal sends out ions into the solution very lowly; that is, the reaction

$$\mathrm{Fe} + {}^{\cdot\cdot} = \mathrm{Fe}^{\cdot\cdot}$$

proceeds very slowly because the ionization of the metal is associated with chemical changes, and, when these changes are slow, passivity occurs. Several hypotheses have been

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[1] Phil. Mag., (3) 9, 57 (1836).

[2] Zeit. phys. Chem., 39, 104 (1902).

[3] Ibid., 48, 577 (1904).

[4] Zeit. Elektrochem., 6, 472 (1900); 11, 9 (1905).

advanced regarding the mechanism of the reaction and the following are of importance:

a. The Oxygen Charge Hypothesis of Fredenhagen[1] *and Muthmann and Frauenberger.*[2]—The cause of passivity is sought in the slow rate of reaction between the anode and the oxygen liberated there, with the result that the anode becomes charged with the gas, or that a metal-oxygen alloy is formed. Grave objects to this hypothesis because it does not explain the fact that iron may be passive in alkalies and when heated in nitrogen.

b. The Anion Discharge Hypothesis.[3]—By this theory the main change at the anode is not the formation of metallic ions, but the discharge of anions. The electrode, when active, is supposed to contain hydrogen and the discharged anion reacts with and removes the hydrogen. The slowness of this reaction allows oxygen to accumulate on the metal rendering it passive.

c. The Hydrogen Activation Hypothesis of Foerster[4] *and Schmidt.*[5]—According to this hypothesis the normal condition of iron is assumed to be passive and it becomes active under the influence of a catalyst. The reaction

$$\mathrm{Fe} + {}^{\cdot\cdot} = \mathrm{Fe}^{\cdot\cdot}$$

is reversible and is a retarded reaction in both directions. If this is true, the formation of a film may be considered the consequence, and not the cause, of passivity. The cause of passivity is taken as the absence or the removal of hydrogen and the deposition of oxide follows as a result of the inactivity of the metal. Foerster claims that hydrogen or an alloy of hydrogen and iron is the catalyst; but Grave and Schmidt favor the view that hydrogen ions are responsible for the change.

d. The Retarded Hydration Hypothesis of LeBlanc.[6]—According to this view the active iron sends out ions into the

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[1] Zeit. phys. Chem., **43**, 1 (1903); **63**, 1 (1908).

[2] Sitzungber. bayr. Akad., **34**, 201 (1904).

[3] Chem. News, **108**, 249, 259, 271, 283 (1913).

[4] Abhandlungen der Bunsen Gesellschaft, 2 (1909).

[5] Zeit. phys. Chem., **77**, 513 (1911).

[6] Lehrbuch der Elektrochemie, 5th Ed., p. 285.

electrolyte and with metals tending to become passive, these ions combine slowly with the water

ion + water = ion hydrate.

The concentration of free ions at the electrode becomes great and finally the potential difference between the electrode and electrolyte becomes so great that the discharge of anions and development of oxygen begins. This view is based on the observation of Grave that when the ion concentration is sufficiently large, polarization begins at both anode and cathode. LeBlanc considers that the hydration and dehydration of ions under certain circumstances may be a very slow process.

To all of the above theories objections may be raised, many of them seemingly valid, and, on the other hand, the observed phenomena seem in many respects to fit one theory as well as another.

Definition

Up to the present time no single definition of passivity has been accepted by the many investigators who have busied themselves with this problem. In the present work the passivity of iron is taken to mean *that state of the metal in which it is not attacked immediately by dilute nitric acid.* Normally nitric acid of specific gravity 1.250 will instantly and vigorously attack iron and finally dissolve it; but if the metal is first treated with acid of densities from 1.590 to 1.260 the attack is delayed for some time, frequently as long as seventy-two hours and even longer in some cases. During this period of inactivity the metal remains bright and no apparent action occurs.

Preliminary Work

A number of simple hand experiments were performed to determine, if possible, whether there was a measurable effect of the following factors on the passivity reaction:

1. Varying concentrations of nitric acid.
2. Different grades of iron.
3. Presence of iron salts.
4. Contact with platinum and zinc wire.

5. Electrolytes other than nitric acid.
6. Varying periods of time in passivifying acid.

The work, while giving many important facts, yielded results so inconsistent that we decided to pass directly to a set of carefully controlled reaction velocity experiments.

On the basis of information derived from the preliminary experiments, certain lines of investigation naturally suggested themselves as likely to give fruitful results. After careful consideration, it seemed important to first investigate the rate at which iron is dissolved by nitric acid in varying concentrations and at various temperatures. It was hoped that the results of such investigations might throw some light on the character of the reaction in general, and show whether the development of passivity was gradual, or whether there was a definite state which might be looked upon as a passive state, and also whether this state was influenced by temperature.

Velocity of the Reaction between Iron and Nitric Acid

The metal used was "Merck's Pure Iron Wire," in the form of pieces two inches long (5.08 cm) and bent horse-shoe in shape so as to be readily hung from a glass hook. The density of the wire was 7.850 and each sample weighed about 180 mg.

The acids were made up from "Baker's C. P. Nitric Acid, sp. gr. 1.42" and triple distilled water, the last distillation being with potassium permanganate and potassium hydroxide. In all, sixteen strengths of acid were prepared with the following concentrations:

Table 1[1]

Sp. gr.	Grams HNO_3 in 100 cc	Sp. gr.	Grams HNO_3 in 100 cc
1.025	4.7150	1.240	47 4796
1.050	9.4395	1.250	49.7750
1.075	14.1362	1.260	52.0884
1.100	18.8210	1.270	54.4449
1.200	38.8320	1.275	55.6610
1.210	40.9222	1.285	58.0563
1.220	43.0416	1.300	61.7370
1.230	45.8210	1.400	91.4200

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[1] Physico-Chemical Tables, John Castell-Evans, Vol. 2, 839–842 (1911).

The apparatus, shown in Fig. 1, consisted of a constant temperature bath with its stirring apparatus, constant level attachment apparatus for stirring the acid in the test tubes, and thus preventing the accumulation of gas bubbles on the surface of the iron, and an attachment for holding four test tubes in the bath. In the figure, *a* indicates a covering of wool packing, *b* is a large battery jar, *c* is the stirring apparatus for the bath, *d* is the constant level attachment, *e* is the thermometer, *f* is a pulley which operates the stirring apparatus for the acid in the test tubes, *g* is a glass rod which is attached to the pulley *f* and holding the iron sample in a hook at the lower end, *h* is a glass tube serving as a guide for *g* and entering the top of the test tube through a perforated cork stopper, *i* is a Jena glass test tube containing the acid and the iron sample, *j* is the motor which operates the stirring apparatus in the bath and raises and lowers the iron sample twenty times a minute, and *k* shows the shape and position of the iron.

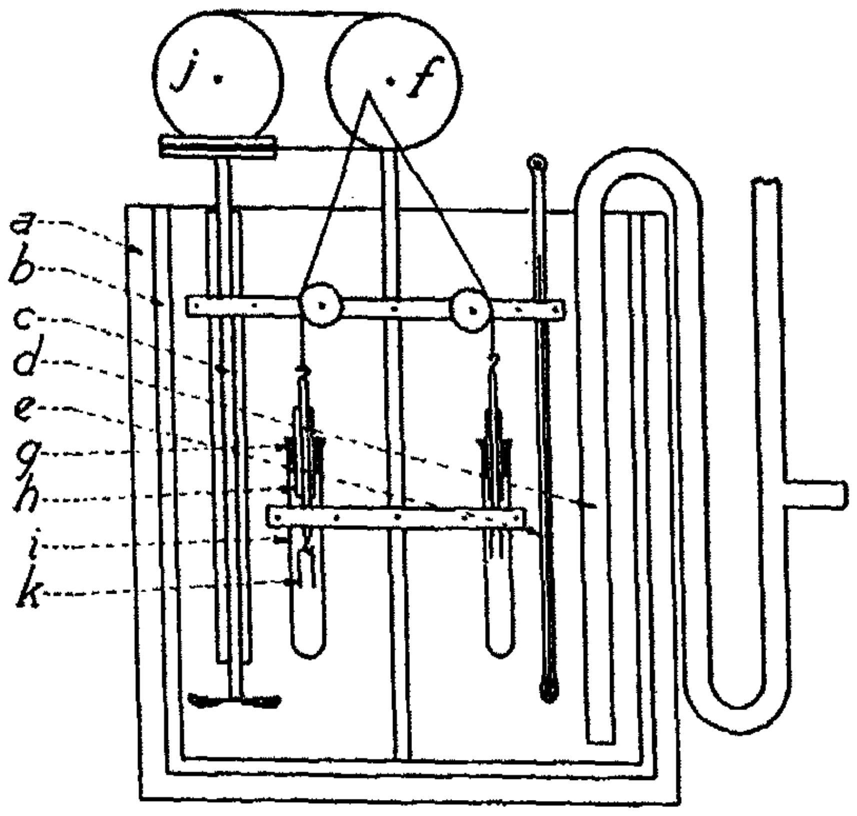

Fig. 1

The method consisted in taking weighed samples of iron wire and allowing twenty-five cubic centimeters of nitric acid of known concentration to act on them at a given temperature for periods of fifteen, thirty, forty-five, and sixty minutes, respectively. The samples were removed at the end of each period, washed, dried and reweighed. The loss of weight was taken as a measure of the amount of reaction. All samples were run in duplicate so that for each and every period of time, for every concentration of acid used, and for every given temperature, two observations were possible.

Reaction Velocity Equations

The reactions between iron and nitric acid are at present not well understood. Some investigators claim that with concentrated acid there is no action on the iron; others state that the strong acid causes the evolution of nitrogen peroxide, while dilute acid gives nitric oxide. Mellor[1] is of the opinion that "with dilute nitric acid, hydrogen is not evolved; but the acid is reduced to ammonia'......With hot nitric acid ferrous nitrate and nitrogen oxides are formed." Gmelin-Kraut[2] states that in strong nitric acid some peroxide of nitrogen is formed, while nitric oxide passes off from the action with dilute acids, and in intermediate concentrations mixtures of these oxides are evolved. It is, therefore, a difficult matter to choose any one equation to represent the reaction in question. Since, however, stronger acids act relatively slowly, the main reaction to be considered is that brought about by weaker acids, namely that which produces nitric oxide instead of the peroxide.

The equation, assuming ferric nitrate to be the iron salt produced, is

$$Fe + 4\,HNO_3 = Fe(NO_3)_3 + 2\,H_2O + NO.$$

If ferrous nitrate were formed instead of the ferric salt, the tendency would be to produce variations in the velocity constant in the opposite direction from those found, which only confirms the more strongly the conclusions to be drawn later.

The formation of nitrogen peroxide along with nitric oxide would influence the variations in the same sense as those

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[1] Mellor: "Modern Inorganic Chemistry," 485 (1912).

[2] Handbuch der anorganischen Chemie, Band 1, Abteilung 1.

found, thus tending to somewhat discount the conclusions. But evidence to be given will show that this fact may be ignored, because, as will be proven, the reaction stops going at any easily measurable rate when nitrogen peroxide is present. For these reasons the equation has been assumed to be sufficiently correct for its purpose.

According to the equation, 56 grams of iron react with 252 grams of nitric acid, and 1 gram of iron is dissolved by $4\frac{1}{2}$ grams of the acid.

The generally accepted Reaction Velocity Equation for a heterogeneous system, of which only one concentration is variable[1] (in this case the acid), is

$$\frac{dx}{d\theta} = K.S.(A - x),$$

where $dx/d\theta$ is the rate of solution, K the reaction velocity constant, S the surface exposed, and $(A - x)$ the concentration of the acid. For our purposes, dx measures the amount, in grams, of iron dissolved in the time $d\theta$, and, since, each gram of iron dissolved uses up $4\frac{1}{2}$ grams of nitric acid, the x in the right-hand member of the equation must be multiplied by $4\frac{1}{2}$. The equation then becomes

$$\frac{dx}{d\theta} = K.S.(A - 4\tfrac{1}{2}x).$$

On transformation and integration this equation becomes

$$\frac{dx}{(A - 4\frac{1}{2}x)} = K.S.d\theta,$$

and

$$ln\, A - ln\, (A - 4\tfrac{1}{2}x) = K.S.\theta.$$

Then, obtaining the value for K, we have

$$K = \frac{1}{\theta . S} . ln \frac{A}{(A - 4\frac{1}{2}x)}.$$

To obtain an equation for the surface, it is only necessary to make use of the following equation:

$$S^2 = 4\pi^2 l^2 \frac{m}{\pi l d},$$

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[1] On account of the great tendency to simplification in reaction rates, it is assumed that the reaction is proportional to the concentration of the acid, and not to its fourth or other power.

where l is the length of the wire, m its mass, d its density, and π has its usual value. Solving for S, we have

$$S^2 = \frac{4\,\pi l m}{d},$$

and

$$S = \sqrt{\frac{4\,\pi l m}{d}}.$$

Substituting this value in the Reaction Velocity Equation, we have

$$K = \frac{1}{\theta . \sqrt{\frac{4\,\pi l m}{d}}} . \ln \frac{A}{(A - 4^1/_2 x)},$$

in which A and x are measured in grams of nitric acid and not in gram equivalents. Thus K represents the number of grams of iron dissolved in one minute from one square centimeter of surface under the given conditions and m is the average mass of the sample, *i. e.*,

$$m = \frac{m_0 + m_1}{2},$$

where m_0 is the original mass and m_1 the mass at time θ. Under these conditions

$$\sqrt{\frac{4\,\pi l m}{d}}$$

represents the average surface.

Experimental Results

The first series of observations was made at 0° C, and the value of the reaction velocity constant calculated for each sample of iron taken. The results showed a distinct decrease of the value of the constant for increasing concentrations of acid, while with the stronger acids there was also a decrease with increasing time. Observations were also made at 10° C. and 20° C. Complete tables giving concentration, time, and temperature would be too large to present in full so we have chosen four representative ones, Table 2 gives a full summary of the reaction velocity constants obtained in the whole series of experiments. As it became evident, after a a time, that data beyond certain limits of concentration would be superfluous, we frequently omitted such observations.

TABLE 2
Values of K
T = 0° C
θ = time in min.

Sp. gr. of acids	15	30	45	60
1.025	0.00574	0.00661	0.00655	0.00680
	0.00645	0.00685	—	0.00583
1.050	0.00431	0.00479	0.00442	0.00439
	0.00466	—	0.00466	0.00450
1.075	0.00368	0.00373	0.00366	0.00364
	0.00411	0.00407	0.00424	0.00390
1.100	0.00387	0.00305	0.00327	0.00321
	0.00389	0.00338	0.00322	0.00324
1.200	0.00157	0.00134	0.00151	0.00129
	0.00152	0.00133	0.00149	0.00129
1.250	0.000825	0.000736	0.000834	0.000814
	0.000862	0.000797	0.000792	0.000843
1.260	0.000254	0.000129	0.0000877	0.0000554
	0.000229	0.000123	0.0000946	0.0000815
1.270	0.0001036	0.0000539	0.0000414	0.0000320
	0.0000889	0.0000584	0.0000389	0.0000253
1.275	0.0000561	0.0000372	0.0000238	0.0000160
	0.0000994	0.0000280	0.0000256	0.0000228
1.300	0.0000463	0.0000156	0.0000104	0.00000777
	0.0000285	0.0000126	0.0000104	0.00000782
1.400	0.00000273	0.00000137	0.00000091	0.00000068
	0.00000274	0.00000137	0.00000091	0.00000068

TABLE 2a[1]
Values of K
T = 10° C
θ = time in min.

Sp. gr. of acids	15	30	45	60
1.100	0.00623	0.00569	Entire sample of iron dissolved in specified time	
	0.00677	0.00611		
1.200	0.00402	0.00332		
	0.00366	0.00292		
1.210	0.00396	0.00314		
	0.00402	—		
1.220	0.00401	0.00300		
	0.00367	0.00301		
1.230	0.002585	0.000615	0.000331	0.000484
	0.000814	0.000751	0.000338	0.000277
1.240	0.000398	0.000193	0.000113	0.0001322
	0.000384	0.000200	0.000124	0.0000785
1.250	0.000256	0.000130	0.0000887	0.0000607
	0.000266	0.000128	0.0000867	0.0000649
1.260	0.000176	0.0000885	0.0000630	0.0000468
	0.000171	0.0001081	0.0000587	0.0000439
1.275	0.0000880	0.0000439	0.0000291	0.0000220
	0.0000880	0.0000436	0.0000250	0.0000219
1.300	0.0000437	0.0000218	0.0000146	0.00001097
	0.0000438	0.0000191	0.0000146	0.00000958
1.400	0.00000273	0.00000136	0.00000089	0.00000068
	0.00000272	0.00000136	0.00000091	0.00000068

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[1] With acids (sp. gr. 1.025–1.075) the entire sample of iron dissolved inside of 15 min. and with acids (sp. gr. 1.100–1.240) inside of 30 min.

TABLE 2*b*[1]
Values of K
T = 20° C
θ = time in min.

Sp. gr. of acids	15	30	45	60
1.250	0.000251	0.000131	0.0000741	0.0000584
	0.000278	0.000128	0.0001000	0.0000685
1.260	0.000171	0.0000888	0.0000538	0.0000429
	0.000172	0 0000885	0.0000537	0.0000401
1.275	0.0000936	0.0000441	0.0000294	0.0000221
	0.0000883	0.0000442	0.0000313	0.0000220
1.285	0.0000828	0.0000443	0.0000276	0.0000220
	0.0000828	0.0000495	0.0000240	0.0000207
1.300	0.0000382	—	0.0000128	0.00000964
	—	0.0000192	0.0000164	0.00000273
1.400	0.00000545	0.00000137	0.00000181	0.00000068
	0.00000272	0.00000136	0.00000091	0.00000068

In Tables 3, 4, 5 and 6 appear the complete data for concentrations of acid corresponding to densities 1.050, 1.250, 1.260 and 1.400, respectively, the measurements being for 0° C. These tables are chosen because they present typical forms of conduct, and some considerable discussion of them will be given, from which, it is hoped, the significance of the results in Table 2 will become quite clear.

TABLE 3
Sp. Gr. = 1.050
T = 0° C
A = 2.360

θ	x	m	K
15	0.0376	0.1632	0.00431
	0.0403	0.1606	0.00466
30	0.0758	0.1454	0.00479
	—	—	—
45	0.0973	0.1310	0.00442
	0.1024	0.1320	0.00466
60	0.1212	0.1223	0.00439
	0.1232	0.1204	0.00450

TABLE 4
Sp. Gr. = 1.250
T = 0° C
A = 12.444

θ	x	m	K
15	0.0395	0.1643	0.000825
	0.0408	0.1610	0.000862
30	0.0668	0.1489	0.000736
	0.0723	0.1488	0.000797
45	0.1052	0.1305	0.000835
	0.1009	0.1325	0.000792
60	0.1294	0.1179	0.000814
	0.1326	0.1164	0.000843

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[1] With acids (sp. gr. 1.025–1.240) the entire sample of iron dissolved inside of 15 min.

TABLE 5

Sp. Gr. = 1.260

T = 0° C

A = 13.022

θ	x	m	K
15	0.0137	0.1767	0.000254
	0.0124	0.1767	0.000229
30	0.0139	0.1776	0.000129
	0.0134	0.1760	0.000123
45	0.0140	0.1705	0.000088
	0.0153	0.1756	0.000095[1]
60	0.0117	0.1733	0.000055[1]
	0.0176	0.1741	0.000081

TABLE 6

Sp. Gr. = 1.400

T = 0° C

A = 22.855

θ	x	m	K
15	0.0001	0.1827	0.00000273
	0.0001	0.1822	0.00000274
30	0.0003	0.1827	0.00000137
	0.0003	0.1809	0.00000137
45	0.0002	0.1834	0.00000091
	0.0003	0.1842	0.00000091
60	0.0003	0.1837	0.00000068
	0.0001	0.1813	0.00000068

From an inspection of Table 3, it is seen that since the value of K remains practically constant throughout, the loss of iron in the varying concentrations of acid is in exact agreement with the mass action theory of reaction velocity in heterogeneous systems on the basis of the equation assumed, and from this fact we may conclude that there is no inhibition to reaction, and, hence, no tendency towards the development of passivity as time goes on.

In Table 4 there is a similar agreement in the time-concentration relation, but the value of the constant is about one-fifth that of the corresponding value in the preceding table. This means that in the stronger acid there is a marked decrease in the rate of reaction. Notwithstanding this, however, 1.250 acid does not develop a passivity which increases with the time of action.

Table 5 gives data which show the first evidence of the gradual development of the passive state. The value of the constant for the fifteen-minute period is about one-third that of the corresponding value in Table 4; and for the thirty-, forty-five and sixty-minute periods in the same concentration of acid these values become still smaller. The attack on the iron is practically limited to the first fifteen minutes of reaction, as is shown by the values of x, which, with slight varia-

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[1] Probable error.

tions, are practically constant after that time. Thus, at the end of the thirty-minute period, the inhibiting force reaches its maximum value, and the attack of the acid is practically stopped. At 0° C the passive point or what we will hereafter call the "passive break," occurs somewhere between acid concentrations of 1.250 and 1.260.

The passive break is shown in the Curve 1*a*, Plate I, where the acid concentrations, expressed in grams of nitric acid in twenty-five cubic centimeters of solution, are abscissae and the values of K × 10^6 are ordinates. The curve is plotted from values of K obtained at 0° C, for sixty-minute periods, using data for all concentrations of acid in Table 1. The acid concentration, 12.444, corresponds to HNO_3 (1.250). The curve is made up of three parts, one (BC) showing the gradual decrease of the velocity constant with increasing concentrations, the second (BA) showing the very rapid drop of the velocity constant to a very small value, and OA showing the very slow decrease of the constant in passivifying acids. 1*b* shows the same curve except that the value of K is multiplied by 10^7 instead of 10^6. In these curves identical letters refer to identical points. The latter curve is introduced to show that the drop in the velocity constant is a gradual, although a very rapid one, in the portion BA.

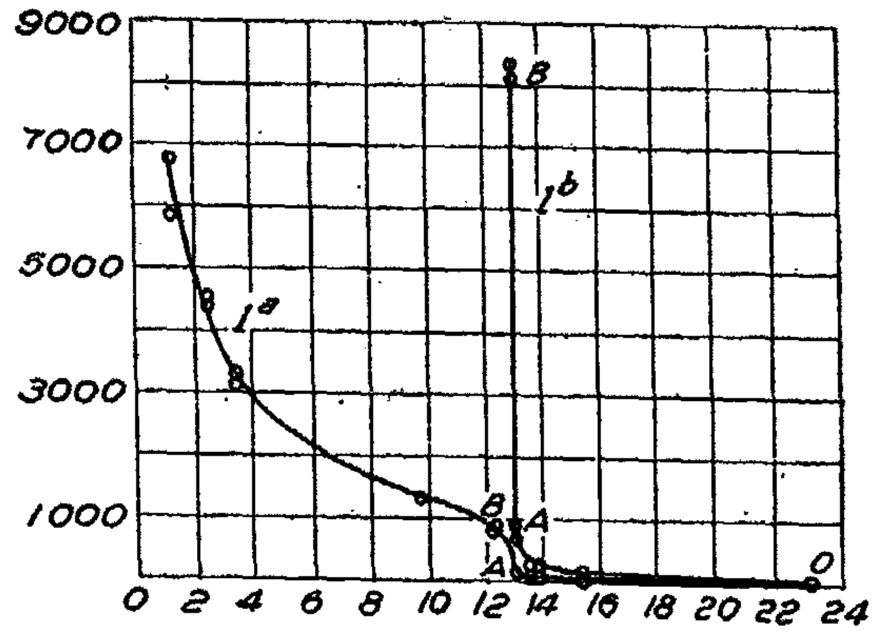

Plate I[1]

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[1] Abscissae are grams HNO_3 per 25 cc.

The portions of the curves represented by AB show the passive break. This point has the characteristic that acids having greater concentrations will induce passivity, passivity always being considered as a somewhat variable quantity, whereas those acids having lower concentrations will activify. Even so, it is to be seen that neither passivity nor activity are perfectly definite states. All passive iron even in passivifying acids is still undergoing some solution. In acids more dilute than those corresponding to the passive break, iron is slowly and imperfectly activified, while in the still lower concentrations this is accomplished more rapidly and completely.

Table 5 gives the results for acid of density 1.400, the highest concentration used in the experiments. The value of the constant has suffered a very marked decrease, and there is, nevertheless, as the table shows, a very slow rate of solution. The 1.400 acid is, therefore, a strongly passivifying acid.

The results indicated by the data in these tables is confirmed and amplified by the results given in the complete summary of all results, namely Table 2, and the complete data for the curves 1*a* and 1*b* in Plate I were taken from this table.

It is to be noted that in some cases, namely in those experiments carried on with acids of high passivifying power, the whole measurable amount of reaction was over in the first fifteen minutes. In such cases, of course, the decrease of the values of K with increasing time is without particular significance.

From the results given above, we must conclude that an increase of concentration of nitric acid inhibits the rate of solution of iron very greatly even at concentrations which are not sufficient to produce visually complete passivity. In concentrations of acid just below the passive break, that is, from 1.200 to 1.25, it is also evident that the degree of inhibition increases very materially with the time of action. In no case was the development of the inhibition complete at the end of one hour, although in some cases the sample of iron had completely dissolved at that time. When the density of the acid used reaches 1.260, there occurs a break in the reaction velocity. The values of K fall off at a far more rapid rate than in more dilute acids, although even here the drop is not abrupt. Rather the values of K decrease at a measurable pace to the very small values corresponding to visually complete passivity. Visually complete passivity is not perfect passivity, but merely a very slow rate of reaction.

Rate of Solution of Iron in Passivifying Acids

In order to be positively sure that there was solution of iron in passivifying acids, and to obtain some data on the solution rate, the following experiments were devised: Weighed samples of iron and ten cubic centimeters of nitric acid (1.300) were placed in Jena test tubes and the tops of the tubes drawn out to a capillary to prevent evaporation. Duplicate sets were prepared to allow of observations over a period of twelve weeks. At the end of the periods specified in the table the samples were removed from the acid, washed, dried, and reweighed. The data appear in Table 7. The entire experiment was repeated with nitric acid (1.400) and Table 8 gives the results so obtained.

TABLE 7
Sp. Gr. = 1.300
A = 6.174

θ in weeks	x	m	K
1	0.0043	0.1820	0.00279
	0.0043	0.1813	0.00255
2	0.0062	0.1786	0.00187
	0.0060	0.1808	0.00181
3	0.0086	0.1792	0.00174
	0.0088	0.1804	0.00179
5	0.0150	0.1751	0.00183
	0.0143	0.1751	0.00174
6	0.0187	0.1752	0.00191
	0.0177	0.1729	0.00183
8	0.0258	0.1694	0.00201
	0.0259	0.1690	0.00204
10	0.0347	0.1668	0.00220
	0.0340	0.1651	0.00218
12	0.0413	0.1618	0.00222
	0.0427	0.1614	0.00230

TABLE 8
Sp. Gr. = 1.400
A = 9.142

θ in wks.	x	m	K
1	0.0043	0.1793	0.00166
	0.0040	0.1790	0.00157
2	0.0077	0.1778	0.00158
	0.0079	0.1796	0.00161
3	0.0123	0.1748	0.00168
	0.0115	0.1748	0.00159
5	0.0209	0.1719	0.00176
	0.0197	0.1726	0.00165
6	0.0244	0.1678	0.00173
	0.0243	0.1712	0.00170
8	0.0356	0.1619	0.00196
	0.0367	0.1651	0.00196
10	0.0452	0.1584	0.00197
	0.0454	0.1601	0.00197
12	0.0544	0.1544	0.00202
	0.0547	0.1540	0.00203

From these tables it is evident that there is a continuous rate of solution of iron even in passivifying acids. The results further show that while the absolute amounts of solution (values of x) is noticeably greater in the stronger than in the less strong acid, nevertheless, this increase is not sufficiently great to make up for the theoretical effect (as demanded by the mass action law) of the increased concentration of the acid used. This accounts for the fact that while in the stronger acid the values of x are larger, the values of K are smaller. This points, of course, to an increased inhibiting effect with increasing concentrations, even with these extremely strong acids.

The Time-Temperature-Concentration Function

From the data given in Table 2, a number of cross compilations might be made. In Plate II are shown the values of $K \times 10^6$ plotted against the time for five concentrations of acid at 0°, 10° and 20° C. Each individual curve shows the decrease in the velocity constant with increasing time. With decreasing concentrations of acid the curves assume a

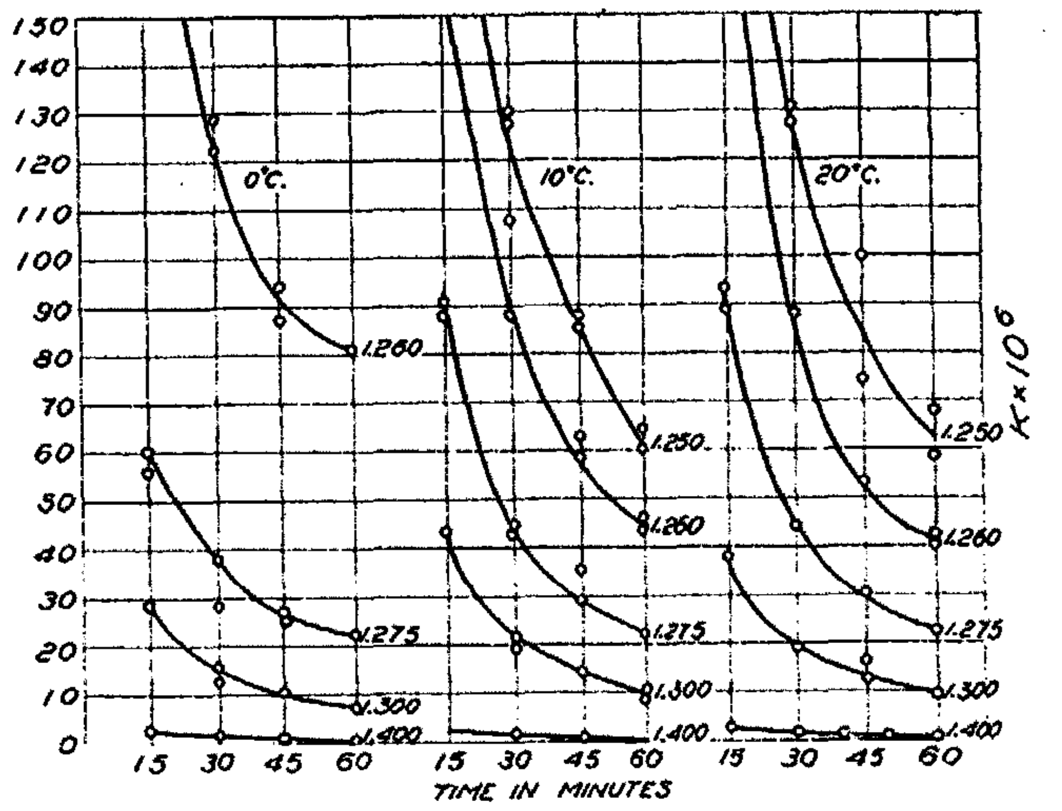

Plate II

steeper slope, showing a rapid falling off in the value of the constant in partially passivifying acids. It will be seen that, in the case of acids of higher concentrations, namely, 1.400, 1.300, and 1.275, the values of the constant for the sixty-minute periods are nearly the same at all temperatures, while for the shorter periods the value increases as we pass from 0° to 10° C, and then remains constant or decreases slightly from 10° to 20° C. With 1.250 acid at 0° C, the value of the constant is so large as to be entirely off the plate. Some of the points for the duplicates show considerable variation, but when we consider that the amounts of iron dissolved are extremely small, they are no greater than is to be expected. The facts, which are brought out above, seem to indicate a much slower development of passivity at 0° C than occurs at 10° and 20° C, and we have the curious phenomenon, between 0° and 10° C, of a reaction with a negative temperature coefficient. Thus, 1.250 acid shows no development of passsivity at 0° C. At 10° C the constants are smaller from the start, and rapidly decrease with time. (Compare values for 0° and 10° C in Plate II.) In the summary possible explanations of these phenomena will be given. (See Summary *B*, 8.)

The Temperature Function of the Passive Break Concentration

It has been previously pointed out that at a given temperature there is a fairly definite concentration of acid, above which the reaction rate diminishes rapidly. This point in concentration we have called the "passive break." At different temperatures this passive break occurs at different concentrations. The following data show this. The values for 0°, 10° and 20° C are taken from Table 2, while that for 100° C is taken from an experiment to be described later.

Passive break density	1.260	1.230	1.250	1.300
Temperature	0°	10°	20°	100°

Thus the passive break concentrations decrease from 0° to 10° C, and thereafter increase.

Miscellaneous Experiments

In view of the fact that a better understanding of some of the phenomena of passivity was obtained from the preceding investigation, it was considered advisable to repeat certain of the preliminary experiments, not only as checks, but also with the hope that new phases of the problem would present themselves.

Different Samples of Iron.—Although many investigators claim that impurities do not influence the passivity reaction, it was found to be nevertheless true that different grades of metal gave different results. In the case of "Stubb's Drill Rod," nitric acid 1.300 failed to passivify. This was also true in a few cases with "Bessemer Steel Rod." "Merck's Pure Iron Wire," however, gave better results, and acid of specific gravity 1.300 produced passivity in every case. In all of the following experiments Merck's wire was used exclusively.

Reaction at Higher Temperatures.—It was found that the amounts of iron dissolved were approximately the same in acid of density 1.300 at all temperatures used in the reaction velocity experiments. With a view of obtaining data at a still higher temperature, the following experiment was made at the boiling point of the acid. Nitric acid (1.300) was heated to its boiling point (about 115.3° C) and the sample of iron dropped into the hot acid. Violent continuous action occurred for some time, after which the iron became partially passive, a slow evolution of nitrogen peroxide persisting. The acid was allowed to cool slowly and the tube was jarred at frequent intervals.

TABLE 9

Boiling point of acid	Visible action from boiling point to	Temperature at which jarring produced no further action
115.0° C	101.0° C	84.0° C
115.5°	99.0°	80.0°
115.3°	100.0°	83.0°

This jarring always produced temporary action for a few seconds. As the tube cooled, a point was always reached at which jarring would not produce this temporary activity. Table 9 gives the results of the experiment. While there is a great probability that there is considerable solution of iron at temperatures below 100° C, we may conclude that the passive state is fairly stable under these conditions, and that the passive break will occur somewhere about 100° C for acid of this strength. No explanation of the fact that jarring produces temporary activity can be offered at this time.

Effect of Time of Immersion.—A sample of iron was immersed in ten cubic centimeters of nitric acid (1.400) for five seconds and then quickly transferred to ten cubic centimeters of 1.050 acid until active, after which it was returned to the first acid for five seconds. This procedure was repeated until the iron remained passive in the dilute acid for a period of at least ten minutes, the same portions of the acids being used. Sets were also run for immersion periods of fifteen, thirty, and sixty seconds in the 1.400 acid and the results are recorded in Table 10.

TABLE 10

	θ = 5 sec.			θ = 15 sec.		
N	θ'			θ'		
	1	2	3	1	2	3
1	4	2	4	8	7	9
2	10	12	20	12	17	10
3	18	44	64	26	18	19
4	53	60	86	26	17	15
5		10 min.	—	37	21	30
6	—	—	—	93	42	29
7	—	—	—	—	63	70
8	—	—	—	—	10 min.	—
9	—	—	—	—	—	—
10	—	—	—	—	—	—
11	—	—	—	—	—	—

	θ = 30 sec.			θ = 60 sec.		
N	θ'			θ'		
	1	2	3	1	2	3
1	6	12	6	15	14	13
2	14	18	10	17	20	19
3	17	17	19	14	16	29
4	10	17	15	15	18	35
5	18	14	18	18	17	46
6	19	26	27	23	21	50
7	24	35	54	21	22	45
8	44	37	23	23	20	55
9	—	10 min.	—	30	30	—
10	—	—	—	53	33	—
11	—	—	—	46	45	—
					10 min.	

θ is the time of immersion in 1.400 acid, θ' is the time in seconds required to destroy passivity in 1.050 acid, and N is the number of immersions. The results are taken from a complete series of observations on ten independent samples for each immersion period. Of these, the results for three samples only are reported here.

Despite the slight disagreement in some instances, the experiment clearly shows that the time of immersion in passivifying acids has a marked influence on the degree of passivity. For shorter periods of immersion there is a decrease in the number of trials necessary to retain passivity for ten minutes, while the longer passivifying immersions give at the outset a longer persistence of passivity in the activifying acid. For these phenomena, we have no explanation at present.

Experiments with the Same Portions and also with Fresh Portions of Acids.—It was thought to be interesting to find if the time of activation after passivification was varied by the number of immersions in the same portions and also in fresh portions of both activifying and passivifying acids. The following experiments were carried out under laboratory conditions. The method of procedure was the same as that employed in the preceding experiment, one minute passivifying immersions being used. The work was divided into five parts and five samples of iron were used for each part.

(*a*) Sample of iron passivified in same portion of 1.400 acid and activified in same portion of 1.050 acid.

(*b*) Sample of iron passivified in same portion of 1.400 acid and activified in fresh portions of 1.050 acid.

(*c*) Sample of iron passivified in fresh portions of 1.400 acid and activified in same portion of 1.050 acid.

(*d*) Sample of iron passivified in fresh portions of 1.400 acid and activified in fresh portions of 1.050 acid.

(*e*) A fresh sample of iron passivified and activified in the acids already used in part (*a*).

The results are given in Table 11.

TABLE 11

θ = one minute
θ' = time in seconds of persistence of passivity in 1.050 acid
N = number of immersions

N	Values of θ'										
	(*a*)		(*b*)		(*c*)		(*d*)		(*e*)		
1	15	14	8	9	16	8	15	8	11	11	12
2	17	20	14	15	19	13	17	15	18	—	—
3	14	16	19	19	16	15	18	18	10 min.		
4	15	18	21	21	18	17	17	19			
5	18	17	24	22	18	20	15	18			
6	23	21	25	26	15	20	19	21			
7	21	22	28	30	16	27	18	20			
8	23	20	32	36	23	30	20	24			
9	30	30	33	37	27	39	25	26			
10	53	33	45	39	29	42	23	29			
11	10 min.		35	52	41	—	29	39			
12			51	50	10 min.		31	40			
13			67	57			40	39			
14			78	64			38	48			
15			79	78			48	55			
16			88	93			61	73			
17			102	96			70	68			
18			106	102			69	84			
			Not passive				Not passive				

These data show that the difference in effect produced by using the same portion or fresh portions of the passivifying acid is very slight, while in the case of the fresh portions of the activifying acid the iron was not made passive for a period of ten minutes even after eighteen immersions, while with used portions, a far less number of immersions accomplished this.

The results shown in part (*e*) are most striking. Such results as these may be duplicated at will. In fact, where only two duplicate experiments are given in each part, five were actually performed. The interesting point is that activifying acids, even as dilute as 1.050, sooner or later lose their activifying power when repeatedly used for this purpose, while fresh acids will always activify. An explanation for this will be given later. (See Summary *B*, 3.)

Influence of Different Strengths of Nitric Acid on Passivity.—The experiments were carried out under laboratory conditions. The samples of iron were subjected to the action of different concentrations of acids which were known to passivify and then transferred to acids which would activify. The time of immersion was sixty seconds in the case of the passivifying acids. Table 12 gives the data taken from five separate determinations in each case.

From the table it appears that with decreasing concentrations of passivifying acids the persistence of passivity in the same activifying acid always increases. In the case of passivifying acids of the densities 1.260 and 1.270, it would seem that, by use, these acids became diluted to a strength below that required to produce passivity, although up to this time the persistence of passivity was greater than with stronger acids. A possible explanation of the above phenomenon will be offered in the summary. (See Summary *B*, 9.) It will also be noticed that the more dilute the activifying acid, the less persistent the passivity.

Effect of Contact with Platinum and Zinc.—A piece of platinum wire was wound around the iron sample and the usual procedure followed. The results given in Table 13 are

TABLE 12

Activifying acids	Passivifying acids				
	1.400	1.300	1.275	1.270	1.260
	θ' = time in seconds				
1.250	10 min.	10 min.	10 min.	10 min.	10 min.
1.200	10 min.	10 min.	10 min.	10 min.	10 min.
1.100	8 9 18 18 10 min.	15 15 19 23 36 39 10 min.	17 18 43 44 10 min.		
1.050	15 14 17 20 14 16 15 18 18 17 23 21 21 22 23 20 30 30 53 33 46 45 10 min.	15 18 26 30 36 40 52 59 75 93 109 116 10 min.	25 28 51 35 100 97 135 147 189 204 10 min.	39 36 69 66 160 138 196 231 Fails to make passive	56 75 153 145 Fails to make passive

for sixty-second immersion periods in 1.400 acid and θ' is the time in seconds in 1.050 acid.

TABLE 13

θ' = time in seconds	
64	157
128	138
72 hours	

While no explanation of the effect of platinum on the passive state can be given at this time, the results show that the nobler metal exerts an inhibiting effect on the activification of iron in dilute nitric acid, a fact previously noted by both Faraday and Schoenbein. A peculiar phenomenon was noticed in connection with the effect of platinum. The nobler metal was wound around the middle of the iron sample and the couple placed in acid in which the iron alone would have remained active. It became passive. If one end of the iron wire was now touched with zinc, that end only became active and remained so as long as the zinc was in contact. In some instances after removing the zinc, the end formerly passive became active for a moment and as it became passive again the opposite end became active. The alternations often occurred four or five times before the entire wire became passive. No explanation of this phenomenon is offered at this time. Zinc always activified the iron immediately by contact in dilute acids in which it would have otherwise remained passive for some time.

The Influence of Iron Salts.—In order to ascertain the influence of iron salts on passivity, the following experiment was performed: Samples of iron, previously weighed, were placed in ten cubic centimeters of nitric acid (1.300), together with one cubic centimeter of ferric nitrate solution containing 0.0653 grams of iron and 0.5304 gram of nitric acid in each cubic centimeter. The density of the ferric nitrate solution used was 1.4459. The tops of the test-tubes containing the samples were drawn out to capillaries. After a specified time had elapsed the tubes were opened, the iron removed, washed, dried and reweighed.

TABLE 14

$A = 6.704$

θ	x	m	K
1	0.0052	0.1813	0.00280
	0.0062	0.1804	0.00338
2	0.0079	0.1792	0.00220
	0.0079	0.1760	0.00222
3	0.0110	0.1759	0.00209
	0.0126	0.1776	0.00236
5	0.0208	0.1710	0.00239
	0.0199	0.1753	0.00226
6	0.0260	0.1716	0.00247
	0.0239	0.1697	0.00231

The values of K were calculated and the data appear in Table 14, where θ is in weeks, x is loss in grams, A is the acid concentration in grams of nitric acid in each ten cubic centimeters, and K is the reaction velocity constant, which measures the amount of iron dissolved from one square centimeter of surface in one week under laboratory conditions. At the time of starting the experiment it was noticed that there was a rapid initial action for a few seconds which accounts for the seemingly large amount of iron dissolved in the first week. The table shows a slight decrease in the amount of iron dissolved as compared with Table 7 where there was not an excess of iron. However, this is not so great as to be very significant and we may conclude that the presence of iron salts has little or no effect on the passivity reaction.

The Influence of Nitrites.—To determine the influence of nitrites on the passivity reaction, a solution of sodium nitrite was prepared containing fifty grams of the salt in five hundred cubic centimeters of solution. Three-hundredths of a cubic centimeter of the solution was added to ten cubic centimeters of nitric acid (1.400) and this combination was used as the passivifying agent. The persistence of passivity was determined as usual in 1.050 acid. The results appear in Table 15.

TABLE 15

N	θ' in seconds		N	θ' in seconds	
1	13	10	6	28	44
2	18	16	7	37	47
3	20	25	8	37	57
4	21	29	9	10 min.	
5	23	35			

These results are but little different from those obtained without the addition of nitrites. The experiment was repeated, adding the nitrite solution to the activifying acid instead of the 1.400 acid. The influence of nitrites on the reaction is very evident when added to the activifying acid, in which case the iron remained passive for more than seventy-two hours in every case.

Experiments with Nitrogen Peroxide and Iron.—Our attention was called to the fact that those strengths of nitric acid, which were capable of passivifying iron, gave off, on standing, reddish brown fumes of the higher nitrogen oxides while activifying acids are water-white, and it seemed possible that this gas might be a factor in the passivity reaction. To obtain some data on this point and also to find whether a measurable amount of this gas was occluded, the following experiment was carried out: Nitrogen peroxide was generated by the action of concentrated nitric acid on copper, the gas dried over phosphoric anhydride, and liquefied at atmospheric pressure in a bulb cooled with a freezing mixture. The liquid so obtained furnished the gas used in the experiment. It was soon noticed that when much of the gas escaped into the room, files and other iron instruments became passive. Iron samples passivified in the dry gas remained for many hours in dilute nitric acid without any inclination toward activification. Since the metallic surface remained bright and also since exposure to the air had little effect, we were led to suspect that there was a possibility that the metal occluded much of the gas and formed something of the nature of a nitrogen peroxide-iron alloy, or in some other way entered into reaction with the iron. Following this idea an apparatus of the design shown in Fig. 2 was prepared. The bulb *b* was filled with "Merck's Pure Iron Wire for Standardization" and the entire apparatus thoroughly dried by desiccation over phosphoric anhydride and aeration with pure, dry air. The apparatus was then connected with a supply of nitrogen peroxide and a stream of the gas allowed to flow through the tube for one hour. The gas was displaced by dry air for the same length of time and the following data gathered:

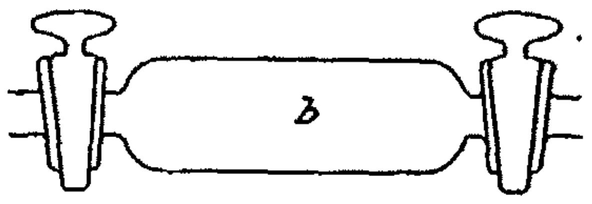

Fig. 2

Weight of tube, iron and nitrogen peroxide	71.2900 grams
Weight of tube and iron	71.2674 grams
Weight of nitrogen peroxide occluded	0.0226 grams
Weight of tube and iron	71.2674 grams
Weight of tube	66.6001 grams
Weight of iron	4.6673 grams
Weight of nitrogen peroxide occluded by one gram of iron = 0.0226/4.6673 =	0.00484 grams

Immediately after the dry iron was removed from the tube, and exposed to air (the atmosphere was moist) small liquid globules appeared on its surface, which proved to be strongly acid. It was undoubtedly either nitric acid or a mixture of this with nitrous acid. This point will be further investigated.

These results lead us to suspect that passivity is due, not to nitric acid itself, but to nitrogen peroxide, or at least to oxides of nitrogen higher than nitric oxide. Whether the active agent is nitrogen peroxide or possibly nitrous acid is virtually impossible to determine, because nitrous acid always breaks down readily yielding the oxide and peroxide of nitrogen, and the peroxide on dissolving in water always yields nitrous acid. Thus, in all cases, in aqueous solution, nitrous acid, nitrogen peroxide and nitric oxide presumably exist together.

It is perfectly possible that both nitrous acid and nitrogen peroxide may be passivifying agents. That nitric oxide is not will be shown in the following experiment.

Experiment with Nitric Oxide and Iron.—Nitric oxide was prepared by passing the gases from the reaction of dilute nitric acid on copper through a freezing mixture and then through water, thus removing the peroxide. The gas so obtained had no effect on iron as far as passivification was concerned.

History of the Effect of Nitrogen Peroxide on Iron

It is of interest in this connection to note that there are at least four instances, in former work on the subject of passivity, where nitrogen peroxide was noted by investigators.

Schoenbein[1] found that when the temperature of nitric acid (1.36) was raised to 70° C, a gas was given off which he called the "deutroxide of nitrogen," and that up to this point the iron remained inactive.

Herschel[2] noticed that after nitric acid (1.399) was repeatedly used for passivification, it became unfit for use. He ascribes the reason, "because it was impregnated with nitrous gas."

Varenne[3] found that when passive iron was made active *in vacuo*, there was an evolution of an orange-colored gas which he believed to be the "peroxide of nitrogen."

Grave[4] found that iron heated in nitrogen up to white heat was passive and also that ionized nitrogen was a good passivifying agent. These phenomena are quite referable to traces of oxygen which under these conditions might yield some nitrogen peroxide.

From a consideration of any of these four statements, it seems strange that the possibility of passivification in nitrogen peroxide directly has never occurred to investigators long before this time, since it appears to be the next logical step in each of the above instances.

Summary

A. The results of an extensive set of velocity determinations of the reaction between iron and nitric acid are given. These were carried out with acids of densities ranging from 1.025 to 1.400, by small intervals, and the measurements were duplicated for three different temperatures, namely, 0°, 10° and 20° C. Isolated observations at higher temperatures are also given. From these results are drawn the following conclusions, the reference data being taken from results at 0° C. As these results do not differ very materially from those at 10° or 20° C, the conclusions are generally applicable to all results.

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[1] Phil. Mag., (3) 9, 259 (1836).

[2] Ibid., (3) 11, 329 (1836)

[3] Ibid., (5) 9, 76 (1836).

[4] *Loc. cit.*

1. The value of the velocity constant for the solution of iron by nitric acid decreases with increasing concentration of acid throughout the whole range investigated.

2. This decrease in rate is not uniform, but shows a rapid, though not vertical drop in the velocity constant at the concentration corresponding to a density of 1.260.

3. In all concentrations of acid of 1.260 or greater, the value of the velocity constant shows a decrease with the time in a given experiment. That is, the rate of solution of iron is most rapid at the start and falls off as the reaction continues. This is to be interpreted as a gradual development of passivity, increasing as the reaction proceeds.

4. The concentration 1.260 is thus characterized by two things: first, it is the point, in concentration of acid, at which progressive passivification begins; second, it is the point at which the rapid drop in the reaction rate takes place. For want of a better term, we have called this point the "passive break."

5. The passive break is not independent of the temperature, but seems to fall somewhat from 0° to 10° C, thereafter to rise to 20° C and even to 100° C, as shown by a few experiments.

6. Passivifying acids, no matter how concentrated, bring about a slow but steady solution of iron.

B. Passivification by Nitrogen Peroxide.—It is shown that a degree of passivity, far greater than any produced by the strongest nitric acid, is brought about by exposing iron to dry nitrogen peroxide gas. Nitric oxide is without effect. This fact explains many of the phenomena of passivification which we, as well as others, have observed.

1. Passivifying acids are more or less yellow or red, *i. e.*, contain some of the higher oxides of nitrogen,[1] while those acids which activify, in general, remain water-white.

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[1] On account of the reversibility of the reaction, $N_2O_3 = NO_2 + NO$, in aqueous solution, it is impossible to state with certainty whether the nitrogen peroxide or the nitrous acid is the passivifying agent, or whether both perform this function. All statements that are made here concerning the effects of nitrogen peroxide must, thus, be considered subject to this reservation.

2. The great preponderance of opinion in the literature is to the effect that acids of low concentrations yield nitric oxide alone, while those of higher concentration yield some nitrogen peroxide also. Our results would make it seem probable that those acids which passivify are such as yield nitrogen peroxide in sufficient amounts, while activifying acids are those of such dilution as do not yield sufficient amounts of this substance. We have not, as yet, been able to investigate this point any further.

3. Activifying acids (even quite dilute ones such as 1.050) lose their activifying power when repeatedly used. This is presumably due to the accumulation of dissolved nitrogen peroxide (or nitrous acid) as a result of such use.

4. Experiments, which we have performed and which are too simple to need description, showed that acids in which iron is ordinarily active, rapidly produce passivity when small quantities of nitrogen peroxide are bubbled through near to the iron which is being attacked.

5. A similar effect is produced by the addition of nitrites.

6. When iron is passivified in nitrogen peroxide, a considerable, easily weighable, amount of the peroxide is absorbed by the iron. On exposure to moist air, the absorbed peroxide combines with the moisture and is converted into drops of a strongly acid liquid, presumably nitric acid, probably mixed with nitrous.

7. While we have, as yet, been unable to determine the minimum concentration of nitrogen peroxide capable of producing noticeable passivity, it seems likely that but little is necessary, since all iron and steel articles in a room in which a little of the gas is allowed to escape, assume a very considerable degree of passivity. The observation of Grave (loc. cit.) that iron which is exposed to the silent discharge in tubes evacuated from nitrogen, is probably to be explained as due to the formation of some nitrogen peroxide in the tube.

8. Schoenbein[1] records that when a bar of iron is only partially immersed in a passivifying acid, the unimmersed

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[1] Phil. Mag., (3) 9, 53 (1836).

portion also becomes passive. We have found that this is wholly due to exposure to the higher oxides of nitrogen (nitric anhydride, N_2O_5 passivifies as well as nitrogen peroxide[1]). If the unimmersed portions are protected from contact with the vapors and gases evolved, they do not become passive, as we have determined experimentally.

9. It has been pointed out that while nitric acid of density 1.250 shows markedly the phenomenon of the development of passivity with time at 10° and 20° C, it does not show this at 0° C. In the light of the foregoing discussion, the probable explanation is that such acid develops nitrogen peroxide at 10° C, but does not do so at 0° C.

10. Another curious fact brought out in the body of this paper is that the more dilute the passivifying acid the greater is the persistence of the passivity produced when it is brought into the activifying acid. No very positive explanation of this fact seems possible without further investigation. It may be, however, that, owing to the more gradual development of the passive state in the weaker acids, time is offered for a deeper penetration of the iron by the gas, or by whatever condition constitutes the passive state.

C. The best conception of the passive state, as induced by nitric acid, which we are able to formulate, as a result of our investigations, is somewhat as follows:

1. The passive state is not a definite one. There may be an indefinitely great number of degrees of passivity, taking the rate of solution of iron as a measure of the degree of passivity.

2. The passive state seems to be the result of an equilibrium between iron and nitrogen peroxide. Iron is capable of absorbing nitrogen peroxide from any solution in which it is being produced, and the rate of reaction is thereby inhibited. The degree of inhibition will, therefore, be determined by the concentration of the nitrogen peroxide which the reaction itself is capable of maintaining. In strong acid this concentration is great, and in weak acids it is small, or perhaps zero. Thus, when a piece of iron, which has adjusted its rate of solution to a strong passivifying acid, is

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[1] R. Weber: Jour. prakt. Chem., (2) 6, 342 (1873).

brought into a more dilute one, it is charged with a higher concentration of nitrogen peroxide than can be maintained in the more dilute acid, and a new adjustment takes place, whereby the iron slowly gives off some of its store of inhibiting peroxide. This results in an increased rate of solution, which is what is usually called "activification." The slow development of activity in such cases is thus explained, as is also the fact that the "lag" in activification is less the more dilute the activifying acid.

3. Since iron passivified by dry nitrogen peroxide gas is much more persistently passive in activifying acids than that which is passivified in nitric acid, it would seem probable that the amount of nitrogen peroxide absorbed by iron, from even very concentrated nitric acid, is relatively quite small.

4. What has been called the "passive break" in the concentration of nitric acid is, from our point of view, to be looked upon as that concentration at which the reaction begins to develop relatively large amounts of nitrogen peroxide. At concentrations below the passive break, it would seem probable that nitrogen peroxide in decreasing amounts is still being developed, since the values for the velocity constants continue to increase with dilution, although, as has been pointed out, it is difficult to say how much of this effect is due to increased electrolytic dissociation of the acid. We have not, as yet, been able to investigate this point any further, but hope to do so at some future time.

5. As to why nitrogen peroxide should produce passivity, or as to what the ultimate mechanism of the process is, we do not feel that we can say much. Whether passive iron is a solid solution of nitrogen peroxide in iron, or whether the result of the action of the peroxide on the iron is the reversible production of some highly oxidized condition of iron, are questions which we do not feel competent to discuss. We may state, however, that we have observed nothing which seems to indicate the existence of anything like a true gas film in any case.

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May, 1915

MOLECULAR ATTRACTION. XII

BY J. E. MILLS

In a recent article by the author in This Journal,[1] attention was called to the possibility of diagraming the internal pressure produced by molecular attractive forces as a negative pressure. Several well known equations were studied and new relationships between these equations were pointed out. The facts and forces operating to produce these relations, were not, and are not yet, fully understood. But it seems worth while to point out other relations as they are recognized, in order to simplify the problem as much as possible to successive workers in this field.

In order to avoid a rather useless repetition, figures, references, explanations of symbols, etc., used in the previous article are not here reprinted.

1. In the previous article it was shown that the negative pressure at the critical temperature and volume could be found in four ways, namely:

$$1. \qquad \frac{dP}{dT}T_c - P_c = \frac{31414\mu'}{3V_c^{1/3}} = \frac{\mathfrak{C}RT_c}{V_c} = a.$$

For isopentane the values obtained were respectively 161,800 = 159,500 = 157,700 = 159,924, giving as the most probable negative pressure the average value 159,731. If to this negative pressure the actually observed vapor pressure 25,005 is added, a total critical pressure of 184,736 is obtained. Now if the theoretical vapor pressure for isopentane at the critical temperature and pressure is calculated from the equation,

$$2. \qquad P = \frac{62392\,T}{mV}\text{, millimeters of mercury,}$$

the value obtained is 93,427. Now since 2 × 93,427 = 186,854 it will be seen that the total external and internal pressure at the critical temperature is equal, within the limit of ex-

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[1] Jour. Phys. Chem., 19, 257 (1915).

perimental error, to two times the theoretical vapor pressure for the substance under the same conditions, if the substance was a perfect gas. Similar results are obtained for other non-associated substances. Why such a relationship exists is not yet clear to the writer.

2. We have pointed out repeatedly since 1905 when the fact was deduced by the author as a consequence of an equation given by Crompton that at the critical termperature,

$$3. \qquad \frac{dP}{dT} = \frac{2R}{V_c},$$

that is to say, at the critical temperature the rate of change of the pressure with the temperature is just twice what it is for a perfect gas under the same conditions. Since it now appears from the section above, that at the critical temperature the total positive and negative pressure is also just twice what it is for a perfect gas, it is possible to write,

$$4. \qquad \frac{dP}{\pi} = \frac{dT}{T},$$

where π is used to represent the sum of the external and internal pressure, that is the total pressure.

3. A similar equation to the one just given seems also to hold under many other conditions. From the usual equation for a perfect gas $PV = RT$, it is easy to deduce the relationship at constant volume,

$$5. \qquad \frac{dP}{P} = \frac{dT}{T}.$$

Moreover, the equation of Ramsay and Young deduced for constant volume and nearly true for both liquids and gases,

$$6. \qquad P = \frac{dP}{dT}T - a,$$

can be thrown into the form,

$$7. \qquad \frac{dP}{P + a} = \frac{dT}{T}.$$

As shown in the article of which this paper is a continuation a is to be regarded as representing the negative internal pressure. Hence, $P + a$ represents the total pressure π and it is clear that the relationship, $\frac{dP}{\pi} = \frac{dT}{T}$, is at least very approximately true at constant volume over a very wide range of volume, pressure and temperature.

But the equation seems also applicable, with a suitably modified interpretation, under circumstances where a constant volume is not maintained. Thus in the Clausius-Clapeyron thermodynamical equation,

$$8. \qquad L = \frac{dP}{dT}T(V - v),$$

L being the heat absorbed (rejected) during the change in volume is equal to $\int Pdv$ and, hence, $\frac{dP}{dT}T$ must represent the *average total pressure* during the given change in volume. This interpretation is enforced in the previous article. Therefore, allowing the former symbols to apply to these changed average conditions, the relation $\frac{dP}{dT}T = \pi$ or $\frac{dP}{\pi} = \frac{dT}{T}$, is again true. In fact, if the thermodynamical Equation 8 is combined with the equation given by the author,

$$9. \qquad \lambda = \mu'(\sqrt[3]{d} - \sqrt[3]{D}) \text{ Calories,}$$

the relationship under discussion can be made much more specific. For we then get,

$$10. \qquad \frac{dP}{dT}T - P = \frac{31414\,\mu'(\sqrt[3]{d} - \sqrt[3]{D})}{V - v},$$

whence

$$11. \qquad \frac{dP}{P + \frac{31414\,\mu'(\sqrt[3]{d} - \sqrt[3]{D})}{V - v}} = \frac{dT}{T}.$$

As shown in the previous paper, $\frac{31414\,\mu'(\sqrt[3]{d} - \sqrt[3]{D})}{V - v}$ is the mathematical average of the ordinates of the internal pressure curve between the limits V and v. Moreover, Equation 11 has already been proved true. At the critical temperature it reduces to,

$$12. \qquad \frac{dP}{P_c + \frac{31414\,\mu'}{3V_c^{4/3}}} = \frac{dT}{T_c},$$

giving the relationship discussed in Paragraph 2, more specifically, for isopentane.

Dieterici's equation, $\lambda = \mathrm{CRT} \ln \frac{\mathrm{V}}{v}$, would give similarly

$$13. \qquad \frac{d\mathrm{P}}{\mathrm{P} + \dfrac{\mathrm{CRT} \ln \frac{\mathrm{V}}{v}}{\mathrm{V} - v}} = \frac{d\mathrm{T}}{\mathrm{T}}.$$

As a matter of fact, the relationship,

$$14. \qquad \frac{d\mathrm{P}}{\text{Total pressure}} = \frac{d\mathrm{T}}{\mathrm{T}},$$

is so persistently true over such a wide range of conditions as to suggest very forcibly that perhaps the relation expresses a universal law. Moreover, since both the temperature and the pressure are functions of the velocity of the molecules a general consideration of the meaning of Equation 14 rather strengthens the hope that it does contain a universal truth.

Equation 6, and hence Equation 7, are not exactly true, and other objections to accepting Equation 14 as a universal law will appear to the critic familiar with the field here studied. After considerable consideration of the question I am inclined to the belief that Equation 14 does represent a very fundamental truth, and that properly interpreted it may prove to be a universal and exact law applying to changes at constant volume and to phase change equilibria. For that reason I have suggested it here. Probably the pressure of the numerator should be taken also as referring to the total pressure.

I am a believer in thermodynamical formulae, but I have never been able to understand, and I have sought to understand, how such a relationship as the Clausius-Clapeyron Equation 8 can be applied to fusion, vaporization, and other phase change phenomena. Some explanations ignore infinitesimals of the first order at will, though usually this is done in a non-mathematical sort of way to lessen the crime. Some apply the perfect gas, reversible cycle, reasoning without troubling much as to how the reasoning happens to be applicable. Others are at great pains to explain that there really is a reversible process in phase change phenomena, because the process really can be reversed by infinitesimal changes, etc., etc. As a matter of fact the various arguments are made to give correct equations but I have always thought that this might be due to some undiscovered relationship. If Equation 14 is true of phase change equilibrium conditions extensive explanations of reversible cycles will not be required.

4. In the previous article the negative pressure due to molecular attraction was expressed by the equation,

15. $p = \frac{31414\mu'}{3V^{4/3}}$. Writing the equation $pv^{4/3} = 10471\mu'$,

and comparing with the equation for an adiabatic of a perfect gas, $PV^{\gamma} =$ constant, their similarity is noted. The so-called intrinsic energy of the adiabatic given by the equation,

16. $$\text{Work}_{\infty} = \frac{C}{\gamma - 1} \cdot \frac{1}{V^{\gamma - 1}} = \frac{10471\mu'}{(4/3 - 1)31414} \cdot \frac{1}{V^{4/3 - 1}} = \mu'\sqrt[3]{d},$$

corresponds with the energy given out by the molecules on coming together from an infinite distance apart to volume V, as derived in previous papers. In a perfect gas, pressure is caused by a given amount of kinetic energy, E_K, according to the equation,

17. $$P = \frac{2 \times 31414E_K}{3V},$$

while from Equation 15, the internal pressure, caused by a given amount of energy derived from molecular attractive forces following the inverse square law, is given by the equation,

18. $$p = \frac{31414\mu'\sqrt[3]{d}}{3V}.$$

The same amount of energy produces twice the pressure in Equation 17 that it does in Equation 18. There is no error here, mathematical or otherwise. Since the pressure is produced by the operation of different laws the same amount of energy corresponds to twice the pressure in one case as in the other. Since there is always present in a substance both temperature energy and energy derived from attractive forces it is important to recognize the above fact. It suggests a new meaning for the relationship pointed out some years ago[1]

$$19.\quad C = \frac{\mu'^{3}\sqrt{d_c}}{3RT_c} = \frac{\text{energy necessary to overcome molecular attraction}}{2 \times \text{kinetic energy of molecules}},$$

C is the important constant of Dieterici's equation,

$$20.\qquad \lambda = CRT \ln \frac{V}{v}.$$

Transforming Equation 19 from terms of energy to pressure, it will be seen that C should equal the ratio of the internal negative pressure at the critical temperature to the theoretical critical pressure. This is, as a matter of fact, true, for taking isopentane, and using values given, $C = \frac{159{,}731}{93427} = 1.710$. The actually observed average value of C for isopentane is 1.688. For the 26 normal non-associated substances measured by Dr. Young and his co-workers the average difference between the value of C calculated as above and the observed average value of C was 2.6 percent. The greatest divergence was 4.5 percent. The relation,

$$21.\quad C = \frac{\text{Internal negative pressure at critical temperature}}{\text{Theoretical critical pressure}},$$

is, therefore, certainly very nearly true. I do not understand the cause of the relationship.

5. It has been shown[2] that,

$$22.\qquad C = 2 - \frac{D_c}{d_c}$$

where D_c = theoretical, and d_c = actual, density at the critical temperature. This relation could now be expressed as follows for the critical conditions,

$$23.\quad \frac{\text{Negative pressure}}{\text{Theoretical pressure}} + \frac{\text{Observed pressure}}{\text{Theoretical pressure}} = 2,$$

which reduces to the relation already given in Section 1,

$$\frac{\text{Total pressure}}{\text{Theoretical pressure}} = 2.$$

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[1] Jour. Am. Chem. Soc., 31, 1117 (1909).
[2] Ibid., 31, 1121 (1909).

6. The causes operating to produce the relations cited in this article, and in the previous article, are not fully understood and no extended discussion of the causes will be undertaken here. It is, however, not out of place to point out some additional facts that should be borne in mind when seeking an explanation of the relations derived.

First. The total heat added to a monatomic element such as aluminium, copper, silver, lead, from the absolute zero to the molten condition, is approximately not quite three times the energy necessary to effect the temperature change if the elements behaved as perfect gases. In other words, the entropy of these monatomic elements in the molten condition at their melting points is roughly a constant, and is for many of these elements from 8 to 8.5 per gram molecular weight.

Second. The indications are that from the melting point to the boiling point of the liquid element the specific heat will be from 2 to 3 times as great as for the element in the condition of a perfect gas. Consequently at the boiling point of a monatomic element it is certain that there is, in many cases at least, a very large amount of energy in the liquid element that cannot be accounted for as molecular energy of translational motion (temperature energy).

Third. Estimates based on thermodynamical relations indicate that the specific heat at constant volume of a liquid or solid element is not greatly different from the specific heat at constant pressure of the same element. Hence no very large proportion of the excess energy of the liquid indicated above is *directly* due to the change in volume of the element under the action of the molecular attractive force. The idea of molecular attractive force proposed in the present series of papers leads to the same conclusion.

Fourth. While the experimental data on more complex compounds is not sufficient, nor sufficiently understood, to enable the above remarks to be extended with certainty so as to include them, yet probably everything that we do know indicates, that in a general way at least, the same conclusion should be applicable to these compounds.

Fifth. In a previous paper[1] the author proved that *the energy given out by any two bodies originally at rest at an infinite distance apart in forming any stable configuration under the action of gravitational attraction, is equal to the kinetic energy which they retain and is, for either body, inversely proportional to the mean distance from their common center of mass.* This proposition is a necessary consequence of the law of gravitational attraction and of the laws of motion. The proof rests entirely upon well known, universally accepted, dynamical principles.

It is possible to extend the proposition to a system of n particles as follows:

Newtonian mechanics depends upon the truth of the principle that "If two or more forces act on a body, each produces its own change of momentum in its own direction independently of the others." It has been shown that two particles coming from an infinite distance apart to a distance s and forming a stable system under the action of gravitational attraction retain exactly as much energy as they give out. Now making use of the fundamental principle above stated, it is obvious, that when n particles come together to form a stable system, that we can consider the action of any one of these n particles upon any other particle of the system independently of the $n^2 - n - 1$ actions of the other particles upon these two particles and upon each other. But the result of the action of any two particles upon each other is that the *energy lost = energy retained,* and when the mutual action of every particle has been determined we will have $n^2 - n$ similar equations. Since in every equation the energy lost = energy retained, the total energy lost by the system must be equal to the total energy retained by the system and we can state that,

The amount of energy retained by a system of n particles in forming a stable system under the action of the gravitational

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[1] Phil. Mag., (6) 22, 84 (1911).

law of force is equal to the amount of energy given out by these particles in coming together from an infinite distance apart.

There seems to be no escape from this conclusion. For the individual particles of a stable system are in dynamic stable equilibrium and it is clearly possible to separate the tangle of individual forces into their components, and these components act independently and must be in equilibrium in accord with the analysis that has been made.

Sixth. A similar result must follow if the molecular law of force, $f = -\frac{\mu m}{s^2}$, is substituted for the gravitational law of force. This result can be obtained by paralleling the previous argument in its entirety. Or it can be seen to follow directly. For the result that, the energy lost by the system = the energy retained by the system, is true independently of the absolute value of the masses of the particles and of the absolute value of the attractive forces.

Seventh. The above arguments take no account of the temperature energy. It is interesting to note the actual relations that exist for one gram of isopentane at the critical temperature. $\mu'\sqrt[3]{d_c} = 65.01$ calories, surrendered in coming to the critical density, and the same amount of energy should be retained by the liquid isopentane according to the above argument. The kinetic translational energy for isopentane at the critical temperature $E_K = 19.04$ calories. If this energy is additional energy, the total retained energy of the liquid would be 84.05 calories. As a matter of fact only one-half of the temperature energy also, seems to be retained, making the total energy retained 74.53 calories. This amount of energy substituted in Equation 10 of the previous article gives a total pressure of 182,900 millimeters of mercury, which is to be compared with the value 184,736 given in Section 1 of this paper.

However, it must be noticed that there is no *experimental* evidence to indicate that $\mu'\sqrt[3]{d_c} = 65.01$ calories, and the extrapolation may not be justified. Also I frankly do not understand the relation between the temperature energy (translational molecular motion) and the retained attractive energy (orbital motion) of the molecules. The relation given just above holds true for other substances, and I point it out only for what it is worth as a *possible explanation* of the pressures obtained at the critical temperature.

Summary

1. The persistent exact, or very approximate truth, under many circumstances, of the relation, $\frac{dP}{P} = \frac{dT}{T}$, suggests that the relation may always be true for constant volume and for phase change equilibrium conditions. P refers to the total pressure, *i. e.*, to the numerical sum of the external and the internal pressure.

2. The relationship of several deductions previously made is discussed.

3. The following relation is derived: The amount of energy retained by a system of *n* particles forming a stable system under the action of the molecular attractive force is equal to the amount of energy given out by these particles in coming into the system from an infinite distance apart. Temperature affects this relation in a manner not yet understood.

University of South Carolina
May 8, 1915

NOTES UPON THE POTENTIALS OF CALOMEL AND HYDROGEN ELECTRODES

BY N. EDWARD LOOMIS

Because of recent references in chemical literature to two articles published a few years ago by Loomis and Acree[1] it has seemed advisable to recalculate certain of their results in the light of subsequent work.

Loomis and Acree adopted the value 0.339 volt for the potential of the electrode

0.1 KCl-HgCl-Hg

at 25° C. Subsequently, Auerbach[2] reviewed the literature in this field and decided that 0.337 volt was the most probable value for the potential of this electrode. In a recent article Lewis and Randall[3] conclude from a careful review of previous work and from unpublished results of their own that the electromotive force of the combination

H_2-0.1 *N* HCl-0.1 *N* KCl-HgCl-Hg

is 0.3990 after correction has been made for the contact potential of the system. If we assume with Lewis that solutions of hydrochloric acid are dissociated to the same extent as solutions of potassium chloride at the same dilution, the degree of dissociation of 0.1 *N* HCl is 86 percent and the potential of the decinormal hydrochloric acid hydrogen electrode is 0.0629. From this we readily calculate the potential of the decinormal calomel electrode to be

$$0.3990 - 0.0629 = 0.3361 \text{ volt}$$

This result is given added weight by the fact that unpublished experimental work by Sebastian in Lewis' laboratory upon the electromotive force of the system

H_2-0.1 *N* HCl-HgCl-Hg

yields the same figure, 0.3990 volt. This is just the result which we should expect if decinormal hydrochloric acid is

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[1] Am. Chem. Jour., 46, 585, 621 (1911).

[2] Zeit. Elektrochemie, 18, 13 (1912).

[3] Jour. Am. Chem. Soc., 36, 1974 (1914).

dissociated to the same extent as decinormal potassium chloride. On the other hand both Loomis and Acree and Myers and Acree[1] obtained a voltage of 0.4000 for the above system, indicating a value of 0.3371 for the potential of the calomel electrode.

It is seen that all of the recent work points to a lower value for the potential of the decinormal calomel electrode than that which Loomis and Acree adopted for their calculations. This value probably lies between 0.336 and 0.337 volt. It should be emphasized that before the electromotive force method can be applied to the study of chemical problems with any great degree of accuracy it is absolutely necessary that the potential of the calomel electrode or that of the decinormal hydrochloric acid hydrogen electrode be known more exactly than it is at present and that an accurate method for measuring or calculating contact potentials be developed. In the subsequent part of this article the hydrogen electrode experiments of Loomis and Acree are recalculated by using 0.336 as the potential of the decinormal calomel electrode.

In the study of the hydrolysis of aniline hydrochloride the ratio $\frac{\text{H}' \text{ conc.} \times 100}{\text{Total salt}}$ was found to be 2.07 and 2.93 for sixteenth and thirty-second normal solutions respectively. When 0.336 volt is used for the potential of the calomel electrode these values become 1.84 and 2.60 respectively. Assuming again that hydrochloric acid is dissociated to the same extent as corresponding solutions of potassium chloride we have the following degrees of ionization:[2]

$N/16\ N$ HCl = 89.7%.

$N/32\ N$ HCl = 92.6%.

1.84/0.897 = 2.05% for the degree of hydrolysis of $N/16$ aniline hydrochloride.

2.60/0.926 = 2.81% for the degree of hydrolysis of $N/32$ aniline hydrochloride.

From these values we may calculate the ratio of K_w/K_b.[3]
For V = 16,

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[1] Am. Chem. Jour., 50, 396 (1913).

[2] These dissociation figures are calculated from the conductivity data of Jones and West at 25° C. See Landolt and Börnstein, p. 1112.

[3] See p. 629 of original article.

$$K_w/K_b = \frac{(0.0184)^2}{(1 - 0.0205) \times 0.844 \times 16} = 2.62 \times 10^{-5}$$

For V = 32,

$$K_w/K_b = \frac{(0.0260)^2}{(1 - 0.0281) \times 0.866 \times 32} = 2.51 \times 10^{-5}$$

Average value of K_w/K_b $= 2.57 \times 10^{-5}$
Tizard's value[1] $= 2.42 \times 10^{-5}$
Bredig's value[2] $= 2.4 \times 10^{-5}$
Average value with 0.339 $= 3.37 \times 10^{-5}$

Experiments were also carried out upon the degree of ionization of 0.25 *N* acetic acid. Assuming that saturated potassium chloride solution entirely annuls the contact potential the dissociation is found to be 0.99 percent when 0.339 is used for the potential of the calomel cell and 0.88 percent when 0.336 is used. The latter figure agrees much better with 0.89 percent calculated from the conductivity data of White and Jones.[3] There would also be a change in the degree of dissociation of acetic acid in the presence of neutral salts but since the relative values would change but slightly from those given in the original article these have not been recalculated.

The experiments with both aniline hydrochloride and acetic acid show that the electromotive force method gives results in closer concordance with other methods when 0.336 is adopted for the potential of the decinormal calomel electrode than when a higher value is used.

While speaking of the experiments upon acetic acid opportunity will be taken to answer a rather misleading comment recently made by McBain and Coleman.[4] They say, P. 1525, "Loomis and Acree have applied the electromotive force method to the case of acetic acid with and without the addition of potassium chloride. They obtain diametrically opposite results in each concentration of salt, depending upon whether they assumed that ammonium nitrate or potassium chloride

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[1] Jour. Chem. Soc., 98, 2492 (1910).
[2] Zeit. phys. Chem., 13, 289 (1894).
[3] Am. Chem. Jour., 44, 159 (1910).
[4] Jour. Chem. Soc., 105, 1517 (1914).

in saturated solution, had removed the diffusion potential; thus 2.06 *N* KCl either lowers the dissociation of acetic acid to 54.5 percent or increases it to 176 percent." The actual figures were 0.797 percent for the degree of dissociation when ammonium nitrate was used and 1.30 percent when potassium chloride was used to annul the contact potential. In the first case the ionization appears to be repressed to 73.2 percent of its original value; in the second case increased to 132.7 percent of its original value. McBain and Coleman neglected to state or, perhaps, failed to realize that our experiments were carried out for the express purpose of determining the relative value of potassium chloride, ammonium nitrate, calcium acetate, potassium iodide, and potassium bromide for eliminating contact potential; we showed conclusively that potassium chloride is the most effective and that consequently much more weight is to be given to that series of measurements in which potassium chloride is used.[1]

The author also wishes to call attention to an error which appeared in the original article of Loomis and Acree. In the original dissertation corrections for barometric pressure were omitted because such corrections were in most cases within the limits of experimental error. Before the publication of the work, however, it was decided to include these corrections and the published calculations were made by Myers and Acree. Because their work covering a narrow range gave

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[1] This question of "salt catalysis" or the effect of salts on the activity of ions in electromotive force measurements, conductivities, and reaction velocities was discussed by Loomis and Acree (Dissertation, P. 52) and in many papers by Acree (Am. Chem. Jour., 44, 159 and later) and is the subject of a number of investigations in Acree's laboratory. Our ideas should not have been misunderstood by McBain and Coleman and have recently been fully confirmed by the work of Poma (Zeit. phys. Chem., 88, 671). It should also be pointed out in discussing Lewis' paper (see especially Jour. Am. Chem. Soc., 36, 1978) that Acree (Am. Chem. Jour., 41, 475; 48, 369, etc.) has already discussed the relation of the work of Lewis and of Lorenz and Böhi on the potential of the hydrogen electrode in solutions of potassium hydroxide and hydrochloric acid to the ionization of water, and its bearing on the question whether water causes hydrolytic metatheses through its ions or its molecules, or both.

(Signed) S. F. ACREE.

more consistent results and because of other facts connected with the hydrogen electrode which they will publish later, they used the equation

$$e = \frac{R.T}{F} \log p$$

for their calculations instead of the thermodynamic equation

$$e = \frac{R.T}{2F} \log p$$

in which e represents the desired correction, P the barometric pressure in atmospheres, and R, T and F have their usual significance. The work of Czepinski,[1] Haber,[2] and Lewis[3] over a much wider range has sufficiently proved the correctness of the second equation.[4] As a result all barometric corrections appearing in the papers of Loomis and Acree and of Myers and Acree are probably just twice too great. This makes a maximum error in some individual cases of 0.0001 volt but it should be noted that because of the nearly normal average barometric pressure in Baltimore the average value for the comparison of the hydrogen and calomel electrodes (see P. 610 of the original article) is not affected by this change.

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[1] Zeit. anorg. Chem., 30, 1 (1902).

[2] Ibid., 51, 289 (1906).

[3] Jour. Am. Chem. Soc., 33, 305 (1911); 36, 1974 (1914).

[4] See also Walpole: Jour. Chem. Soc., 105, 2523 (1914).

THE ADSORPTION OF POTASSIUM AND PHOSPHATE IONS BY TYPICAL SOILS OF THE CONNECTICUT VALLEY

BY ROBERT H. BOGUE

It has been known for a long time that soils possessed the power of taking up or adsorbing certain salts from a solution, and a large amount of work has confirmed the fact that soils show a selective power of adsorption towards the different ions in the solution.[1] Thus in general the positive ion is adsorbed to a greater extent than the negative, consequently leaving the soil solution in the acidic condition. This was formerly explained as a simple metathetical reaction—the bases of the soil and of the solution interchanging, or as the hydrogen of the complex organic acids known as humic acids being replaced by the base of the salt in the solution. That there is more or less interchange among the bases is easily shown by analysis to be true, but it has been repeatedly proven that the base liberated by the soil is usually not nearly equivalent to the base adsorbed from the solution.[2] Although the acidity of the resulting soil solution may be explained by the former hypothesis as being due to the formation of an acid or an acid salt, yet it entirely fails to explain the latter fact of non-equivalent metathesis.

Moreover, soil is not the only substance which shows the power of selective adsorption. Cameron[3] has shown that metallic silver may be separated from a solution of silver nitrate by the selective adsorption of charcoal; and moist cotton entirely free from soluble acid will redden blue litmus paper left in contact with it for some time. Linder and

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[1] Way: Jour. Roy. Agric. Soc. of Eng., 1850, 313-79; Eichorn: Landwirtschafilches Central-Blatt., 2, 169 (1858); Biedermann and Rautlenberg: Jour. Landwirtschaft, New Series, 7, 49 (1862); Armsby: Am. Jour. Sci., (3) 14, 75 (1877).

[2] See references above.

[3] "The Soil Solution," p. 66.

Picton[1] and also Whitney and Ober[2] have shown that when barium chlorid is used to precipitate arsenic trisulfid from colloidal solution, small amounts of barium are adsorbed, leaving in the solution a corresponding amount of free hydrochloric acid. These phenomena may be explained by attributing to the substances enumerated a special selective adsorbing power for the base in question, and Harris[3] points out that the action of soils in the presence of soluble salts may be explained in the same way. Harris further points out the probability of this explanation from the action of electrolytes in general on colloids, for Linder and Picton[4] have shown that the coagulation of negatively charged colloids is accompanied by the adsorption of the positively charged ion, and Coehn[5] has shown that the colloids of the soil will in general be charged negatively since their dielectric constant, being solids, is less than that of water.

Thus the theory of selective adsorption has been steadily gaining ground, and in 1906 Schreiner and Failyer[6] undertook a special study of several type soils with the intent of noting the effect of continued application of phosphate and potassium salt solutions, and subsequently of continued leaching, on the concentration of these salts in the soil solution. As a result they substantiated the theory developed by Schloesing, which is in brief, that the concentration of soluble salts in the free soil moisture is largely dependent on the adsorptive powers of the individual soils. The minerals of the soil yield, and apparently continue to yield, a solution whose concentration approaches equilibrium between the solution and the solid, but as true equilibrium probably never exists there must be other factors entering in to affect this state, as the area of soil directly exposed to the soil moisture during a limited period of time would pro-

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[1] Jour. Chem. Soc., 67, 63 (1895).
[2] Jour. Am. Chem. Soc., 23, 842 (1901).
[3] Jour. Phys. Chem., 18, 355 (1914).
[4] Jour. Chem. Soc., 67, 63 (1895).
[5] Wied. Ann., 64, 217 (1898).
[6] Bur. of Soils, Bull. 32 (1906).

duce a disturbance in the equilibrium. But the concentration of salts in the soil solution tends to remain practically constant for any given soil. Thus for example if the concentration of potassium in the soil moisture should be lessened by the leaching of heavy rains, or the taking up of potassium by the plants, or by any other cause, this concentration would quickly be reestablished by the soil giving up of its adsorbed potassium until the constant was again reached. Or if, on the other hand, the concentration of potassium in the soil solution should be increased, as by the application of a soluble fertilizer, or by evaporation of the soil moisture, the constant would be restored by the adsorption of the excess potassium by the soil.

As the results of Schreiner and Failyer show a very marked difference between the adsorptive capacities of the different type soils used in their experiments, and inasmuch as "type soils" are not definite compounds, that is, a soil described as a fine sand from Maryland might be quite different from and have very different adsorptive capacities from a soil of the same description from Massachusetts, it was thought expedient to examine four of the most characteristic soils of the Connecticut Valley in order to determine their respective adsorptive capacities for potassium and phosphate ions, and to plot the adsorption and leaching curves for each type.

The soils studied in this investigation were a Windsor sand, a Podunk fine sandy loam, a Connecticut Meadow silt loam, and a Suffield clay.

The Windsor sand was obtained about a half mile north of Mount Orient on the Pelham Road. It is described[1] as consisting of six to ten inches of light yellow or brown, coarse sand, resting on yellowish, coarse sand and fine gravel, slightly loamy. Its origin is considered to be a shallow lake deposit. There are two types of this sand: a light, loose form and a

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[1] Soil Survey of the Connecticut Valley, Field Operations, Bur. of Soils (1903).

heavier type which is more of a sandy loam. The former was the one studied.

The Podunk fine sandy loam was obtained about a mile west of the Massachusetts Agricultural College, and is described[1] as consisting of twelve inches of friable, dark brown, sandy loam, underlain with a yellow or brownish, fine, sandy loam. The material composing this soil originated by deposition in deeper lake waters, but has been largely reworked and redeposited by later stream action.

The Connecticut Meadow silt loam was obtained about a half mile west of North Amherst, on Meadow Street, and is described[2], as consisting of a dark silt loam in the upper twelve inches. This is underlain by a heavier dark grayish to yellow or brown silt loam. The material consists of the finest grades of sand and silt that have been reworked and deposited by the streams along which it flows. In the process of reworking and deposition large amounts of organic matter have been incorporated with the sand and silt.

The Suffield clay was obtained about one and a half miles west of Amherst Centre on Amity Street. It is described[3] as consisting of four to eight inches of heavy, dark-drab clay loam resting on a heavy, tenacious, gray-drab clay, which extends to a depth of twenty and in some instances seventy-five feet. It is of deep lake origin, and while appearing very heavy and tenacious, it is largely composed of silt, probably of the finer grades.

The apparatus used in these experiments was essentially that used in the laboratory of the Bureau of Soils on similar investigations.[4] The soil was placed within a nickel plated tube twelve inches long by one and a quarter inches inside diameter. A section of a Pasteur Chamberland filter was inserted at the lower end, the porous filter projecting about

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[1] Soil Survey of the Connecticut Valley, Field Operations, Bur. of Soils (1903).

[2] Ibid.

[3] Ibid.

[4] Schreiner and Failyer: U. S. Bur. of Soils, Bull. 32, 11 (1906).

one and a half centimeters above the rubber stopper, which held it in position. The upper part of the filter was plugged with a solid rubber stopper, while the lower end was fitted with a one hole stopper with a glass tube, through which the solution percolated. The upper end of the nickel tube was fitted with a two-hole stopper provided with two glass tubes. One of these was several feet in length, the length being determined by the pressure necessary to force the liquid through the filter at the desired rate, *i. e.*, 50 cc in 24 hours. This tube was connected by a syphon to a flask containing the solution to be passed through the filter. The shorter of the glass tubes was provided with a short piece of rubber tubing and a pinch cock, and served to let the air out of the tube when starting the experiment.

The samples of soil were weighed out, mixed with distilled water to form a thin paste and this poured into the nickel tube. The tube was then connected with the rest of the apparatus, the syphon started, and a small Erlenmeyer flask provided to catch the percolate. By lengthening or shortening the height of the water column, and by the use of screw pinch cocks in the rubber connections, the desired rate of flow was obtained. The apparatus is shown in Fig. 1.

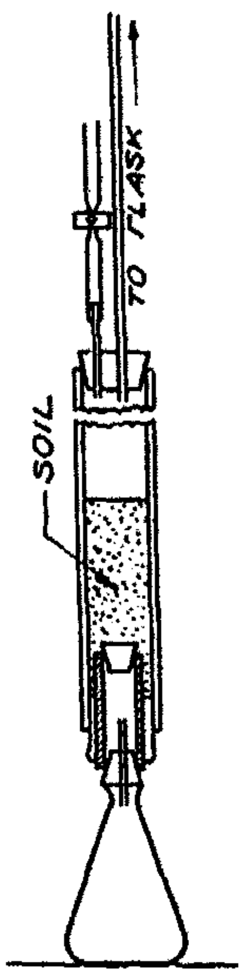

Fig. 1

Before a comprehensive study of the adsorption of soluble salts by the soil can be made, it is necessary to know how the salt in question, which the soil already contains, will be affected by the continued leaching with water. And it is also necessary in order to make a just comparison of the adsorption capacities of the various soils to have them all brought to a state of practical equilibrium, as regards their potassium and phosphate content, before beginning the adsorption experiments.

The tubes were therefore charged with 100 grams of the soil, and pure, distilled water allowed to run through them at the rate of 50 cubic centimeters in 24 hours. The percolate was collected in fractions, and the potassium and phosphate content determined in each fraction. The method used in the determination of potassium was that described by Cameron and Failyer,[1] which is based on the red color produced by the addition of an excess of potassium iodide to a solution of a platinic salt, as described by Morrell.[2] "The method consists in precipitating the potassium as chlorplatinate, after removing ammonia by ignition, and washing this with alcohol in a manner similar to that followed in the usual gravimetric procedure. The chlorplatinate is dissolved in water, and the addition of potassium iodide develops the color above mentioned. The solution is then compared with a standard solution of potassium chlorplatinate in which the color has been similarly developed."

The method used in the determination of phosphate was that described by Schreiner and Brown.[3] "It consists in converting the phosphate into magnesium ammonium phosphate, as is done in the usual gravimetric procedure, all silica, as well as other salts, and to a large extent also, soluble organic matter, being removed by washing with ammonia water. The magnesium ammonium phosphate is dissolved in nitric acid and determined by means of the yellow color produced by the addition of ammonium molybdate, comparing with a standard phosphate solution in which the color is similarly developed."

On testing out for the accuracy of these methods, a difference of three parts per million could usually be detected if the concentration in the sample was not greater than 200 parts per million. A higher concentration, however, especially in the case of potassium, rendered the results somewhat less accurate.

The results for the removal of potassium from the soils

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[1] Jour. Am. Chem. Soc., 23, 1063 (1903).
[2] Ibid., 2, 145 (1880).
[3] Ibid., 26, 1463 (1904).

are given in Tables I, II, III and IV. In the first column is given the number of cubic centimeters in each individual fraction of percolate analyzed. In the second is given the total number of cubic centimeters that have passed through the filter. The third column shows the concentration of

TABLE I

Removal of Potassium from a Sandy Soil

Volume of sol. in sample cc	Total volume of solution cc	Potassium in sample p.p.m. of sol.	Potassium in sample p.p.m. of soil	Total potassium extd. p.p.m. of soil
55	55	10	5	5
45	100	7	3	8
86	186	6	5	13
86	272	6	5	18
119	391	3	4	22
129	520	4	5	27
134	654	4	5	32
186	840	3	6	38
166	1006	2	3	41
252	1258	3	8	49
332	1590	1	3	52
522	2112	2	10	62
1888	4000	1	18	80

TABLE II

Removal of Potassium from a Sandy Loam

Volume of sol. in sample cc	Total volume of solution cc	Potassium in sample p.p.m. of sol.	Potassium in sample p.p.m. of soil	Total potassium extd. p.p.m. of soil
50	50	28	14	14
54	104	20	11	25
108	212	16	17	42
78	290	17	13	55
127	417	12	15	70
111	528	9	10	80
142	670	8	11	91
220	890	6	13	104
240	1130	6	14	118
350	1480	4	14	132
854	2334	2	17	149
709	3043	4	28	177
957	4000	3	29	206

potassium in each of the fractions taken, expressed in parts per million of percolate. The fourth column expresses the amount of potassium extracted from the soil in each fraction, expressed in parts per million of soil, and the fifth column shows the total potassium extracted from the soil.

TABLE III

Removal of Potassium from a Silt Loam

Volume of sol. in sample cc	Total volume of solution cc	Potassium in sample p.p.m. of sol.	Potassium in sample p.p.m. of soil	Total potassium extd. p.p.m. of soil.
35	35	30	10	10
61	96	28	17	27
75	171	24	18	45
121	292	19	23	68
121	413	18	22	90
147	560	14	21	111
128	688	10	13	124
154	842	9	14	138
238	1080	4	9	147
167	1247	5	8	155
238	1485	4	9	164
1343	2828	3	40	204
1172	4000	4	47	251

TABLE IV

Removal of Potassium from a Clay Soil

Volume of sol. in sample cc	Total volume of solution cc	Potassium in sample p.p.m. of sol.	Potassium in sample p.p.m. of soil	Total potassium extd. p.p.m. of soil
48	48	20	10	10
67	115	17	11	21
116	231	14	16	37
124	355	14	17	54
93	448	9	8	62
139	587	6	8	70
98	685	7	7	77
114	799	4	5	82
164	963	4	7	89
215	1178	5	11	100
249	1427	3	7	107
1206	2633	4	48	155
1367	4000	3	40	195

It will be noticed that the percolate from the sandy soil is very quickly brought down to a concentration which is practically constant, while in each of the other cases much more of the distilled water has to pass through before this constant is reached. The fact of there being a higher concentration of the potassium in the first few fractions is interesting. The assumption that this is due to readily soluble potash salts in the soil which are quickly leached out does not seem tenable in view of the adsorptive powers of the soils as will be shown later. The probable explanation of this higher concentration at the start lies in the fact that the soils were air dried before the leaching process was begun, and it has been demonstrated by Whitney and Cameron[1] and later by King[2] that oven- and air-dried soils would yield a larger quantity of soluble salts to water than would the same soils in the moist condition.

The results for the removal of phosphates from the four soils are given in Tables V, VI, VII and VIII. The main noticeable difference between the removal of the potassium and of the phosphate is that in the latter case the percolates from three of the four soils investigated increased somewhat in their phosphate content during the first part of the flow, whereas with the potassium the concentration in the percolate diminished regularly from the first. The same general tendency exists however as with the potassium, *i. e.*, a fairly rapid diminution in the phosphate concentration to a certain point where it is maintained nearly constant.

After prolonging the preliminary leaching until four liters of water had passed through the soil, the tubes were allowed to drain completely, and these same soils were then treated in the same manner as before, one set with a solution of potassium chlorid and the other set with a solution of monocalcium phosphate, $CaH_4(PO_4)_2$. These solutions were made up to a strength of 200 parts per million of potassium (K), and of phosphate (PO_4), respectively, and were prepared by

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[1] Bur. of Soils, Bull. 22, 42 (1903).

[2] Ibid., 26, 55 (1905).

TABLE V

Removal of Phosphate from a Sandy Soil

Volume of sol. in sample cc	Total volume of solution cc	Phosphate in sample p.p.m. of sol.	Phosphate in sample p.p.m. of soil	Total phosphate extd. p.p.m. of soil
52	52	12	6	6
50	102	10	5	11
55	157	9	5	16
54	211	8	4	20
82	293	7	6	26
104	397	5	5	31
116	513	5	6	37
115	628	4	5	42
113	741	4	4	46
119	860	5	6	52
138	998	4	5	57
117	1115	3	4	61.
420	1535	4	17	78
607	2142	3	18	96
945	3087	2	19	115
913	4000	3	27	142

TABLE VI

Removal of Phosphate from a Sandy Loam

Volume of sol. in sample cc	Total volume of solution cc	Phosphate in sample p.p.m. of sol.	Phosphate in sample p.p.m. of soil	Total phosphate extd. p.p.m. of soil
44	44	9	4	4
47	91	13	6	10
60	151	16	9	19
65	216	21	14	33
65	281	18	12	45
92	373	15	14	59
113	486	12	13	72
106	592	9	9	81
121	713	8	10	91
123	836	6	7	98
126	962	6	7	105
129	1091	6	8	113
392	1483	5	19	132
578	2061	5	29	161
1079	3140	4	43	204
860	4000	4	34	238

TABLE VII

Removal of Phosphate from a Silt Loam

Volume of sol. in sample cc	Total volume of solution cc	Phosphate in sample p.p.m. of sol.	Phosphate in sample p.p.m. of soil	Total phosphate extd. p.p.m. of soil
56	56	15	8	8
51	107	17	9	17
44	151	18	8	25
49	200	16	8	33
74	274	14	10	43
81	355	11	9	52
103	458	10	10	62
111	569	8	9	71
113	682	7	8	79
101	783	6	6	85
121	904	4	5	90
164	1068	6	10	100
422	1490	5	21	121
477	1967	4	19	140
1035	3002	4	41	181
998	4000	4	40	221

TABLE VIII

Removal of Phosphate from a Clay Soil

Volume of sol. in sample cc	Total volume of solution cc	Phosphate in sample p.p.m. of sol.	Phosphate in sample p.p.m. of soil	Total phosphate extd. p.p.m. of soil
54	54	24	13	13
57	111	25	14	27
57	168	25	14	41
64	232	24	15	56
57	289	23	13	69
76	365	19	14	83
116	481	15	17	100
109	590	12	13	113
106	696	9	10	123
118	814	8	9	132
117	931	7	8	140
139	1070	6	8	148
443	1513	7	31	178
598	2111	6	36	214
1006	3117	6	60	274
883	4000	6	53	327

diluting a stock solution which had previously been standardized by gravimetric analysis.

The results obtained in the adsorption of potassium are given in Tables IX, X, XI and XII. The first three columns are as in the leaching tables, *i. e.*, 1st, the volume of percolate in the individual fraction; 2nd, the total volume of percolate which has passed through the soil when any given fraction is taken; and 3rd, the concentration of potassium in the fraction of percolate taken. The 4th column represents the amount of potassium adsorbed from the solution expressed in parts per million of solution, and is obtained by subtracting the concentration of the potassium in the solution, 3rd column, from 200, the concentration of the solution flowing through. The 5th column represents the amount of potassium adsorbed by the soil, expressed in parts per million of soil. The last column shows the total amount of potassium adsorbed, expressed in parts per million of soil, when any given fraction is taken.

TABLE IX

Adsorption of Potassium by a Sandy Soil

Volume of sol. in sample cc	Total vol. of solution cc	Potassium in sample p.p.m. of sol.	Potassium adsorbed p.p.m. of sol.	Potassium adsorbed p.p.m. of soil	Total potassium adsorbed p.p.m. of soil
43	43	3	197	85	85
46	89	14	186	86	171
38	127	26	174	66	237
64	191	78	122	78	315
106	297	151	49	52	367
117	414	179	21	24	391
116	530	188	12	14	405
92	622	192	8	7	412
95	717	193	7	7	419
89	806	190	10	9	428
101	907	194	6	6	434
86	993	193	7	6	440
94	1087	198	2	2	442
255	1342	197	2	8	450
296	1638	199	1	3	453
364	2002	198	2	7	460

TABLE X

Adsorption of Potassium by a Sandy Loam

Volume of sol. in sample cc	Total vol. solution cc	Potassium in sample p.p.m. of sol.	Potassium adsorbed p.p.m. of sol.	Potassium adsorbed p.p.m. of soil	Total potassium adsorbed p.p.m. of soil
56	56	6	194	108	108
51	107	12	188	97	205
50	157	25	175	87	292
57	214	39	161	92	384
53	267	70	130	69	453
107	374	129	71	76	529
124	498	161	39	48	577
108	605	175	25	27	604
106	712	183	17	18	622
197	809	189	11	21	643
102	911	190	10	10	653
108	1019	195	5	5	658
105	1124	193	7	7	665
310	1434	198	2	6	671
287	1721	196	4	11	682
334	2055	198	2	6	688

TABLE XI

Adsorption of Potassium by a Silt Loam

Volume of sol. in sample cc	Total vol. solution cc	Potassium in sample p.p.m. of sol.	Potassium adsorbed p.p.m. of sol.	Potassium adsorbed p.p.m. of soil	Total potassium adsorbed p.p.m. of soil
51	51	4	196	100	100
53	104	10	190	100	200
44	148	18	182	80	280
63	211	29	171	108	388
59	270	44	156	92	480
98	368	69	131	128	608
119	487	107	93	111	719
106	593	150	50	53	772
113	706	164	36	41	813
109	815	179	21	23	836
123	938	187	13	16	852
117	1055	192	8	9	861
107	1162	195	5	5	866
288	1450	193	7	20	886
318	1768	195	5	16	902
292	2060	197	3	9	911

Table XII
Adsorption of Potassium by a Clay Soil

Volume of sol. in sample cc	Total vol. solution cc	Potassium in sample p.p.m. of sol.	Potassium adsorbed p.p.m. of sol.	Potassium adsorbed p.p.m. of soil	Total potassium adsorbed p.p.m. of soil
35	35	4	196	68	68
51	86	6	194	99	167
41	127	7	193	79	246
61	188	11	189	115	361
77	265	20	180	138	499
105	370	45	155	163	662
121	491	74	126	152	814
116	607	111	89	103	917
105	712	141	59	62	979
97	809	158	42	41	1020
107	916	172	28	30	1050
106	1022	184	16	17	1067
169	1191	187	13	23	1090
291	1482	191	9	26	1116
309	1791	193	7	28	1144
357	2148	191	9	32	1176

It will be seen that the concentration of potassium in the percolate increases very rapidly from the start, but, however, with different degrees of rapidity for each soil, the percolates from the sandy soil increasing the most rapidly, the sandy loam next, the silt loam next, and the clay soil the slowest. This emphasizes two points: 1st, that the sandy soil reaches its state of saturation with respect to its potassium content in the shortest length of time, the clay soil taking the longest time to reach this condition; and 2nd, that the total adsorptive capacity of the sandy soil is the lowest of the four soils, while that of the clay soil is the greatest, the clay soil adsorbing 1176 parts of potassium as against 460 parts for the sandy soil, 688 parts for the sandy loam, and 911 parts for the silt loam, on the passage of nearly equal amounts of potassium chlorid solution.

The adsorption of phosphates is shown in Tables XIII, XIV, XV and XVI.

The most striking difference noted between these figures and those for the adsorption of potassium is that the adsorption of phosphate takes place very much slower. In fact, the clay soil is still adsorbing phosphate when nearly five liters of the solution have passed through it, while in the case of the potassium, one liter was nearly sufficient to saturate the same soil. The same general relationship holds between the different soils with respect to the rate of adsorption, and the total amount of phosphate adsorbed, as with the potassium adsorption.

It seems somewhat peculiar that in both cases the soils continue to adsorb the ions in question, in very small amounts it is true, long after their approximate points of saturation have been reached, and in practically constant quantities for any given soil. It seems probable that this continued apparent adsorption is due to a metathetical reaction between

TABLE XIII

Adsorption of Phosphate by a Sandy Soil

Volume of sol. in sample cc	Total vol. solution cc	Phosphate in sample p.p.m. of sol.	Phosphate adsorbed p.p.m. of sol.	Phosphate adsorbed p.p.m. of soil	Total phosphate adsorbed p.p.m. of soil
56	56	8	192	107	107
48	104	15	185	89	196
59	163	22	178	105	301
65	228	41	159	103	404
108	336	80	120	130	534
135	471	105	95	128	662
117	588	132	68	80	742
104	692	133	67	70	812
133	825	170	30	40	852
112	937	168	32	36	888
115	1052	175	25	29	917
126	1178	181	19	24	941
117	1295	186	14	16	957
266	1561	194	6	16	973
323	1884	190	10	32	1005
283	2167	195	5	14	1019
1013	3180	197	3	30	1049
580	3760	196	4	23	1072
995	4755	198	2	20	1092

TABLE XIV

Adsorption of Phosphate by a Sandy Loam

Volume of sol. in sample cc	Total vol. solution cc	Phosphate in sample p.p.m. of sol.	Phosphate adsorbed p.p.m. of sol.	Phosphate adsorbed p.p.m. of soil	Total phosphate adsorbed p.p.m. of soil
47	47	5	195	92	92
53	100	5	195	103	195
56	156	11	189	106	301
73	229	16	184	134	435
69	298	19	181	125	560
119	417	32	168	200	760
114	531	45	155	177	937
127	658	55	145	184	1121
131	789	71	129	169	1290
102	891	88	112	114	1404
126	1017	100	100	126	1530
149	1166	121	79	118	1648
104	1270	135	65	67	1715
226	1496	148	52	117	1832
321	1817	165	35	112	1944
268	2085	172	28	75	2019
918	3003	186	14	128	2147
882	3885	190	10	88	2235
795	4680	192	8	71	2306

the potassium chlorid or the monocalcium phosphate and some of the mineral constituents of the soil, as for example:

$$NaAlSi_3O_8 + KCl = KAlSi_3O_8 + NaCl,$$

and

$$Ca_2Al_2Si_2O_8 + CaH_4(PO_4)_2 = H_4Al_2Si_2O_8 + Ca_3(PO_4)_2.$$

If this is the case it seems probable that as the experiments were carried out this apparent adsorption would continue indefinitely, or until all of the mineral matter of the soils that was capable of metathesis with the salts applied had undergone the reaction. Equilibrium could not be attained, inasmuch as the salt solutions entering are constantly percolating through and being replaced by fresh solution. This theory was not, however, worked out in any detail, but offers interesting material for further investigation.

After continuing the adsorption experiments for some time,

TABLE XV

Adsorption of Phosphate by a Silt Loam

Volume of sol. in sample cc	Total vol. of solution cc	Phosphate in sample p.p.m. of sol.	Phosphate adsorbed p.p.m. of sol.	Phoshate adsorbed p.p.m. of soil	Total phosphate adsorbed p.p.m. of soil
57	57	4	196	112	112
47	104	4	196	92	204
59	163	7	193	114	318
56	219	10	190	106	424
110	329	15	185	203	627
127	456	21	179	227	854
110	566	40	160	176	1030
118	684	43	157	185	1215
114	798	60	140	160	1375
114	912	72	128	146	1521
120	1032	79	121	145	1666
132	1164	91	109	144	1810
123	1287	102	98	120	1930
204	1491	120	80	163	2093
276	1767	134	66	182	2275
279	2046	152	48	134	2409
1002	3048	175	25	250	2659
725	3800	181	19	143	2802
896	4696	186	14	125	2927

the apparatus was again disconnected and allowed to thoroughly drain as previously. Distilled water was then allowed once more to run through the soils, at the same rate, and the rate and extent of the leaching out of the potassium and of the phosphate noted.

The results for the leaching out of the potassium from the four soils are given in Tables XVII, XVIII, XIX and XX. The columns are arranged as in the tables of the preliminary leaching.

The leaching takes place very rapidly at first, diminishing in rate as more water passes through, much the same as in the preliminary leaching. But it is at once noticed that the amount of potassium which is thus readily leached out is not nearly equivalent to the amount which had previously been adsorbed by the same soil. By extended leaching the dis-

Table XVI

Adsorption of Phosphate by a Clay Soil

Volume of sol. in sample cc	Total vol. of solution cc	Phosphate in sample p.p.m. of sol.	Phosphate adsorbed p.p.m. of sol.	Phosphate adsorbed p.p.m. of soil	Total phosphate adsorbed p.p.m. of soil
45	45	6	194	87	87
56	101	5	195	109	196
57	158	6	194	110	306
50	208	7	193	96	402
101	309	11	189	191	593
108	417	17	183	208	801
117	534	20	180	211	1012
116	650	27	173	201	1213
121	771	40	160	193	1406
122	893	46	154	188	1594
123	1016	51	149	183	1777
134	1150	52	148	198	1975
122	1272	65	135	165	2140
111	1383	75	125	139	2279
324	1707	97	103	334	2613
339	2046	115	85	288	2901
948	2994	148	52	493	3394
810	3804	168	32	259	3653
905	4709	178	22	199	3852

tilled water continues to take with it a small amount of potassium, but at a rate so slow that a very large amount of water would be required to extract all of the adsorbed potassium from the soil. The only explanation for this seems to be that the potassium which has been adsorbed has been converted into an insoluble compound which in turn goes back to the soluble form, but very slowly. This appears to be in accordance with the explanation previously given to account for the continued adsorption of the potassium and phosphate ions from the solution after the approximate point of saturation had been reached. The soil appears to be able to "take up" mineral salts in solution in two ways: 1st, by adsorption, as we commonly understand the term, wherein the soil merely saturates itself, like a sponge, with the salts, these being readily soluble, and as easily washed out as taken up; and 2nd, by

TABLE XVII

Removal of Adsorbed Potassium from a Sandy Soil

Volume of sol. in sample cc	Total volume of solution cc	Potassium in sample p.p.m. of sol.	Potassium in sample p.p.m. of soil	Total potassium extracted p.p.m. of soil
46	46	58	27	27
52	98	24	12	39
53	151	11	6	45
63	214	12	8	53
56	270	8	4	57
45	315	8	4	61
67	382	4	3	64
88	470	5	4	68
95	565	6	6	74
123	688	5	6	80
192	870	4	8	88
185	1055	5	9	97
465	1520	4	18	115
488	2008	3	15	130

TABLE XVIII

Removal of Adsorbed Potassium from a Sandy Loam

Volume of sol. in sample cc	Total volume of solution cc	Potassium in sample p.p.m. of sol.	Potassium in sample p.p.m. of soil	Total potassium extracted p.p.m. of soil
35	35	101	35	35
54	89	63	34	69
53	142	40	21	90
51	193	34	17	107
55	248	25	14	121
51	299	20	10	131
66	365	18	12	143
87	452	11	10	153
106	558	11	12	165
89	647	10	9	174
185	832	8	15	189
180	1012	9	16	205
468	1480	8	37	242
522	2002	8	42	284

TABLE XIX

Removal of Adsorbed Potassium from a Silt Loam

Volume of sol. in sample cc	Total volume of solution cc	Potassium in sample p.p.m. of sol.	Potassium in sample p.p.m. of soil	Total potassium extracted p.p.m. of soil
43	43	114	49	49
48	91	77	37	86
56	147	56	31	117
53	200	40	21	138
53	253	36	19	157
56	309	28	16	173
58	367	21	12	185
81	448	18	15	200
108	556	15	16	216
116	672	15	17	233
179	851	10	18	251
187	1038	11	21	272
408	1446	9	37	309
552	1998	9	50	359

TABLE XX

Removal of Adsorbed Potassium from a Clay Soil

Volume of sol. in sample cc	Total volume of solution cc	Potassium in sample p.p.m. of sol.	Potassium in sample p.p.m. of soil	Total potassium extracted p.p.m. of soil
51	51	137	70	70
41	92	103	42	112
46	138	90	41	153
53	191	63	33	186
61	252	57	35	221
63	315	42	26	247
71	386	38	27	274
80	466	28	22	296
112	578	25	29	325
106	684	21	22	347
188	872	19	36	383
188	1060	18	34	417
425	1485	14	60	477
545	2030	11	60	537

metathesis, wherein the mineral constituents of the soil interact with the salts in the solution producing insoluble compounds which are reconverted into the soluble salts just as slowly as the soluble salts were first transformed into insoluble compounds, and are thus not readily washed out.

The results for the leaching of the phosphates are expressed in Tables XXI, XXII, XXIII and XXIV.

Here the phosphate is leached out, as in the case of the potassium, quickly at first, but becoming less and less rapid as the process continues. The main difference to be noted, however, is the much slower rate with which this is accomplished, the soils requiring about five times as much water to bring the phosphate content down to a constant. This large amount of water corresponds closely to the amount of solution required to bring the phosphate content up to a constant, during the adsorption process. The total amount of phosphate extracted when this constant is finally reached is,

TABLE XXI

Removal of Adsorbed Phosphate from a Sandy Soil

Volume of sol. in sample cc	Total volume of solution cc	Phosphate in sample p.p.m. of sol.	Phosphate in sample p.p.m. of soil	Total phosphate extracted p.p.m. of soil
52	52	185	96	96
78	130	151	118	214
76	206	118	90	304
109	315	89	97	401
97	412	68	66	467
138	550	48	66	533
146	696	35	51	584
183	879	24	44	628
125	1004	20	25	653
236	1240	12	28	681
337	1577	9	30	711
171	1748	8	14	725
264	2012	8	21	746
604	2616	6	36	782
608	3224	3	18	800
784	4008	7	55	855
702	4710	6	42	897

TABLE XXII
Removal of Adsorbed Phosphate from a Sandy Loam

Volume of sol. in sample cc	Total volume of solution cc	Phosphate in sample p.p.m. of sol.	Phosphate in sample p.p.m. of soil	Total phosphate extracted p.p.m. of soil
48	48	180	86	86
59	107	161	95	181
96	203	139	133	314
108	311	117	126	440
97	408	95	92	532
108	516	81	87	619
155	671	66	102	721
179	850	51	91	812
144	994	39	56	868
228	1222	31	71	939
326	1548	19	62	1001
203	1751	12	24	1025
251	2002	11	28	1053
638	2640	8	51	1104
605	3245	8	48	1152
667	3912	6	40	1192
809	4721	7	57	1249

TABLE XXIII
Removal of Adsorbed Phosphate from a Silt Loam

Volume of sol. in sample cc	Total volume of solution cc	Phosphate in sample p.p.m. of sol.	Phosphate in sample p.p.m. of soil	Total phosphate extracted p.p.m. of soil
57	57	178	101	101
60	117	159	95	196
92	209	146	134	330
100	309	128	128	458
114	423	110	125	583
121	544	99	120	703
131	675	83	109	812
178	853	72	128	940
174	1027	63	110	1050
234	1261	47	110	1160
271	1532	32	87	1247
194	1726	28	54	1301
263	1989	18	47	1348
518	2507	15	78	1426
632	3139	18	114	1540
662	3791	10	66	1606
937	4728	9	84	1690

TABLE XXIV
Removal of Adsorbed Phosphate from a Clay Soil

Volume of sol. in sample cc	Total volume of solution cc	Phosphate in sample p.p.m. of sol.	Phosphate in sample p.p.m. of soil	Total phosphate extracted p.p.m. of soil
51	51	174	89	89
61	112	166	101	190
104	216	153	159	349
89	305	146	130	479
106	411	134	142	621
127	538	125	159	780
124	662	112	139	919
186	848	100	186	1105
185	1033	87	161	1266
210	1243	74	155	1421
285	1528	63	180	1601
233	1761	49	114	1715
309	2070	41	127	1842
519	2589	26	135	1977
603	3192	21	127	2104
708	3900	16	113	2217
878	4778	15	132	2349

however, far short of the amount of phosphate previously adsorbed, as was the case with the potassium.

These results may be expressed graphically, and in this form show, perhaps, the better advantage the similarities and differences which exist for the various soils, and under the different form of treatment.

In Fig. 2 are shown the solution curves for the preliminary leaching out of the potassium from the four soils under examination. The abscissas represent the liters of distilled water which have passed through the 100 grams of soil in the percolating tubes, and the ordinates show the concentration of potassium, expressed in parts per million, of the resulting solution. The curves are all smoothed curves.

In Fig. 3 are shown the soil curves for the preliminary leaching. That is, the ordinates, instead of representing the concentration of potassium in the solution, indicate the amount of potassium which has been extracted from the soil, expressed in parts per million of soil. The abscissas, as before, represent the liters of water that have passed through the soils.

These figures show very clearly that after about one and a half liters of water have passed through the soils the concentration of potassium in the percolate is practically constant, and also that the soils are losing potassium at a slow but constant rate.

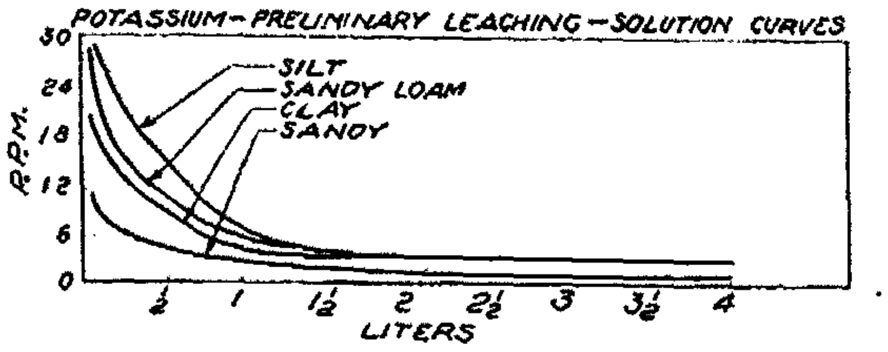

Fig. 2

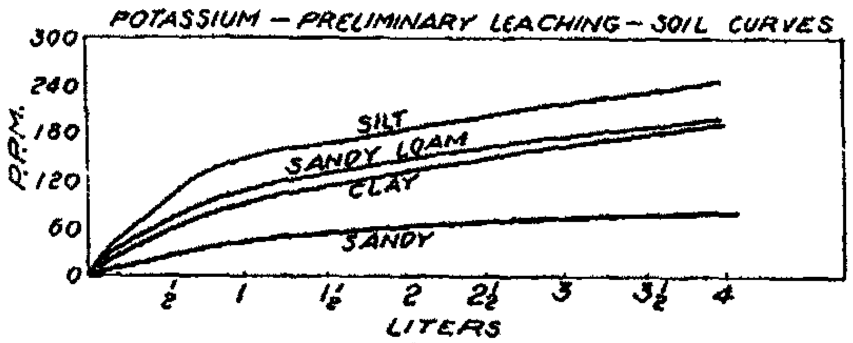

Fig. 3

In Fig. 4 are shown the soln. curves for the adsorption of potassium ions, and in Fig. 5 the soil curves for the same. The ordinates in Fig. 4 represent the concentration of the solution in parts per million of potassium ions, the upper boundary line indicating the original concentration of the solution before passing through the soil. In Fig. 5 the ordinates show the amount of potassium that has been adsorbed by the soils, expressed in parts per million of soil. The abscissas in both cases represent the liters of solution that have passed through.

Here again, after about a liter of solution has passed through the soils the concentration in the percolates is constant and the soils continue to adsorb the potassium at a slow but constant rate. The differences in the adsorptive capacity of the four soils are also very clearly brought out by these curves, the sandy soil being nearly saturated when only 400 parts per million have been adsorbed, while the clay soil does not approach the horizontal position until over a thousand parts have been adsorbed.

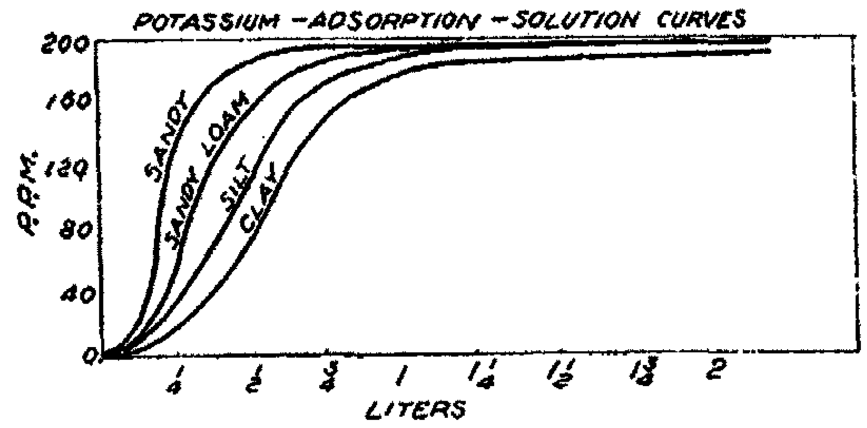

Fig. 4

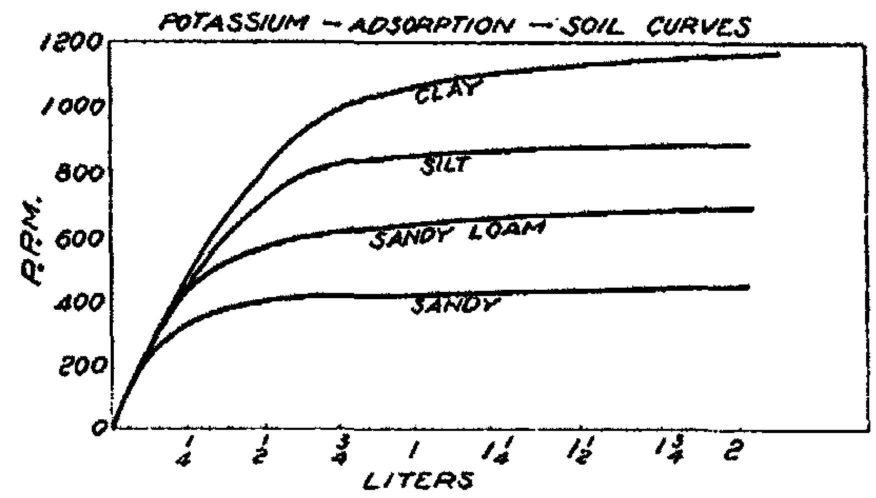

Fig. 5

In Figs. 6 and 7 are given the solution and soil curves for the final leaching out of the potassium. The ordinates in Fig. 6 show the concentration of potassium in the solution, while in Fig. 7 they represent the amount of potassium leached out of the soils. The abscissas show the liters of water which have passed through.

Instead of starting the leaching curves at the point represented by the end of the adsorption curves, *i. e.*, from a point representing the total amount of potassium adsorbed, they have been started uniformly from the same point, zero, the rise in the curves indicating the amount of potassium leached out. A more accurate comparison of the behavior of the different saturated soils, when treated similarly with distilled water, may be made by plotting them in this manner.

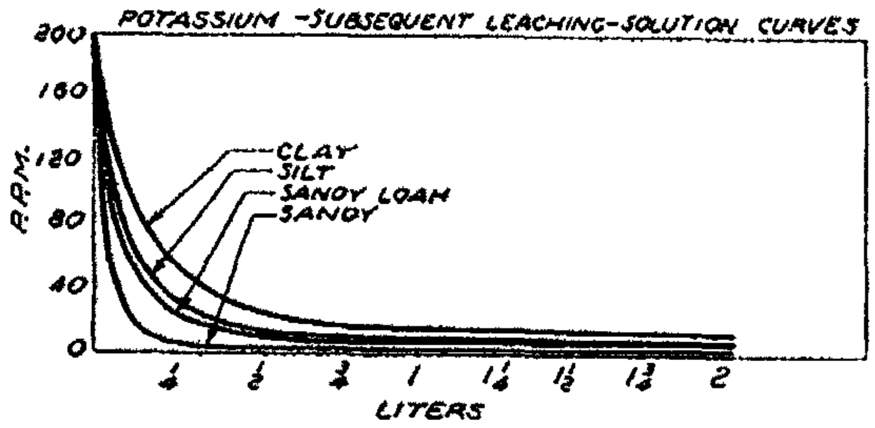

Fig. 6

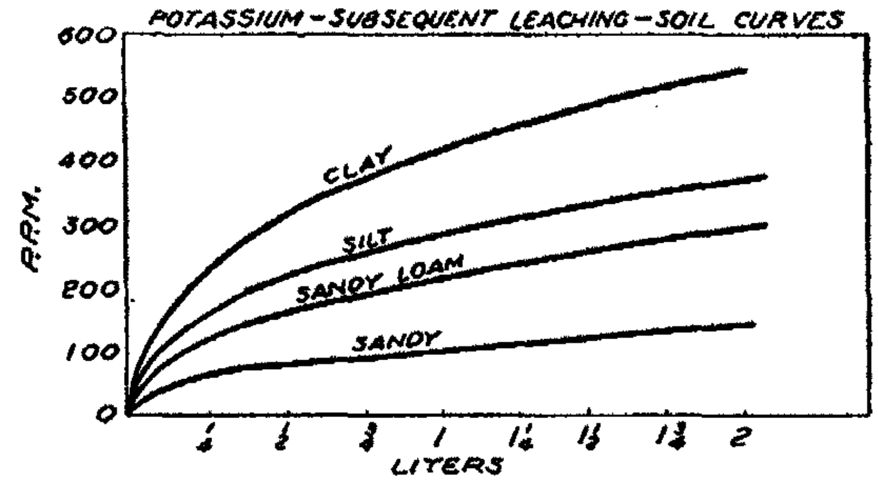

Fig. 7

It will be seen that a part of the potassium is very quickly removed on the passage of water through the soils, but that even by continued treatment with water only a fraction of the total amount of potassium adsorbed is removed, the parts per million of adsorbed potassium still remaining in the sandy soil after two liters of water have passed through it being 330, and that remaining in the clay soil being 639.

It will also be noticed taht the concentration of potassium in the percolate gets down very close to the constant attained in the original leaching, and that the soils attain a constant rate of loss, with reference to their potassium content, which is practically the same as the rate of loss in the original leaching. But the important point is that the soils still retain a large percentage of the potassium adsorbed by them, even after these constants are reached.

In Figs. 8 and 9 are shown the solution and soil curves for the preliminary leaching of the phosphate from the soils. The abscissas and ordinates represent in each case the same factors as in the corresponding plots with potassium, only, of course, phosphate is indicated instead of potassium.

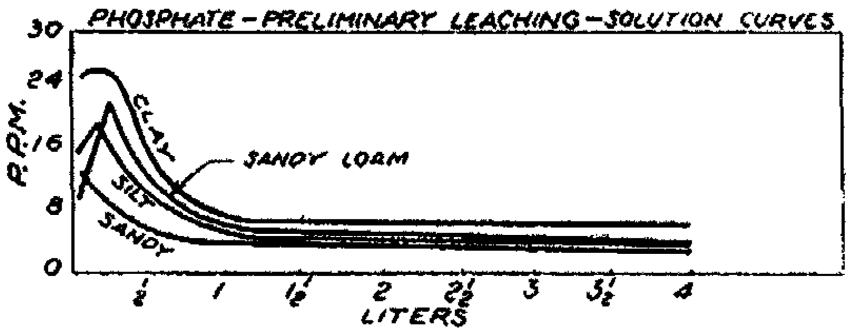

Fig. 8

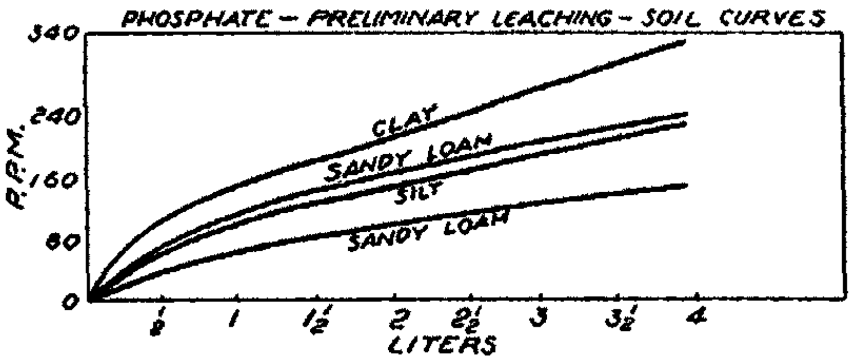

Fig. 9

The peculiar rise in phosphate concentration of the solutions from three of the soils is an apparent unconformity with the rest of the curve. The same general tendency exists, however, as in the potassium experiments, the percolate quickly falling to a constant concentration, and the soils attaining a slow but constant rate of loss in their phosphate content.

In Figs. 10 and 11 are shown the solution and soil curves for the adsorption of phosphate.

These curves differ markedly from the corresponding curves for potassium in the rate with which the soils become saturated, and also in the total amount adsorbed. Here the clay soil is still rapidly adsorbing phosphate when nearly five liters of solution have passed through it, while the same soil has reached its constant with respect to potassium when only about one liter has passed through. And when two liters of phosphate solution have passed through the clay soil it has adsorbed 2800 parts of phosphate, while when an equal amount of potassium solution has passed through the same soil, only 1150 parts of potassium have been adsorbed.

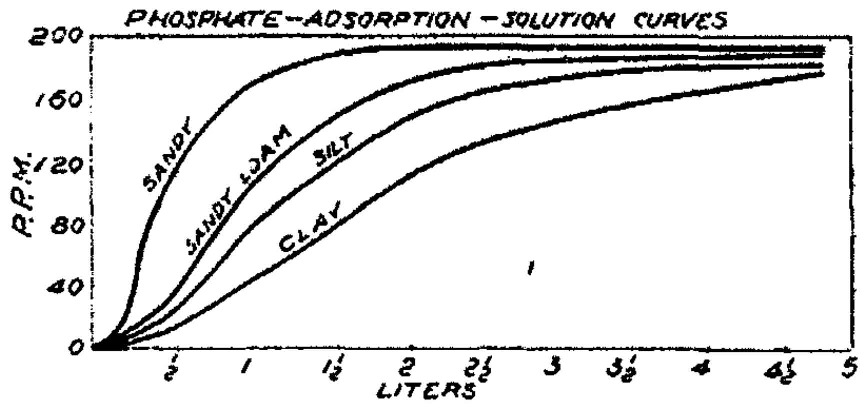

Fig. 10

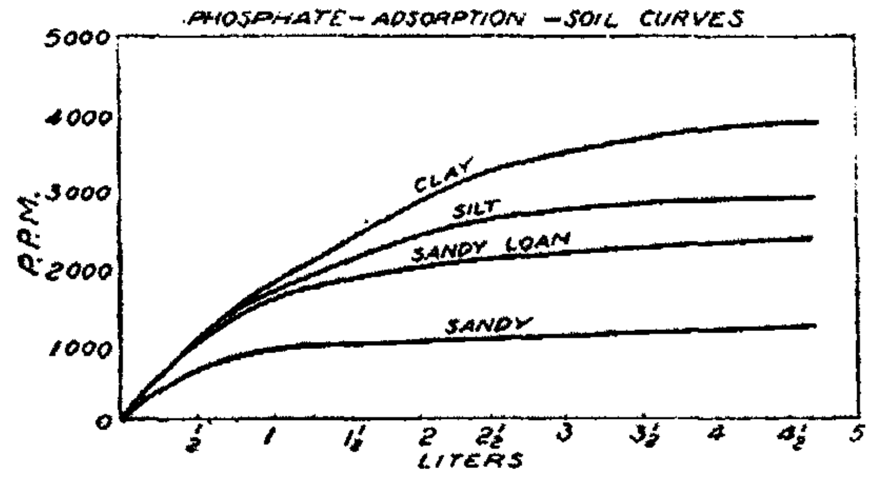

Fig. 11

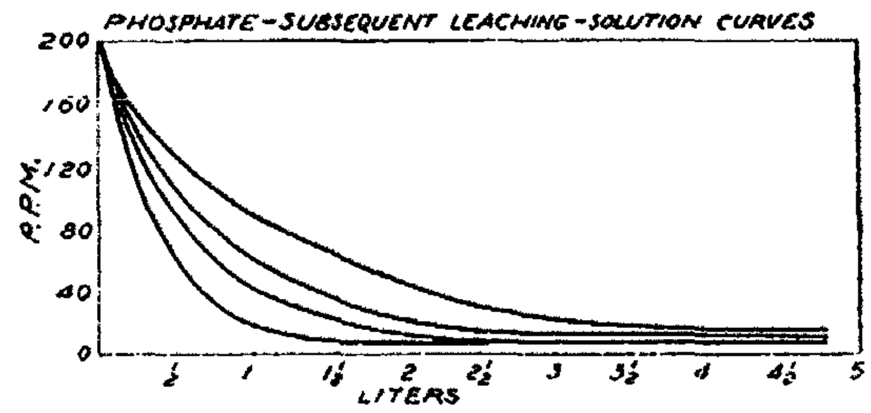

Fig. 12

In Figs. 12 and 13 are shown the solution and soil curves for the final leaching out of the phosphate.

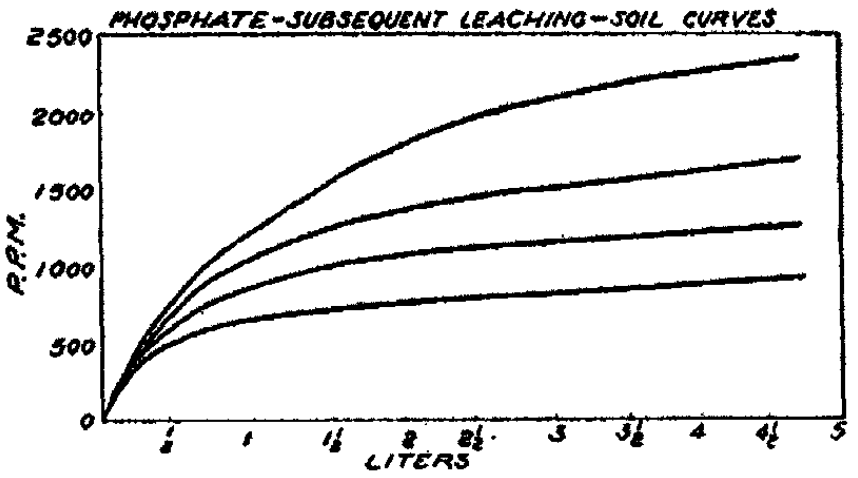

Fig. 13

Here, again, as in the adsorption of phosphate, the soils require a much larger amount of water to bring them down to a constant than was the case with the potassium. But like the potassium, only a part of the total phosphate adsorbed has been removed when this constant is finally reached.

Summary

The study of these four Connecticut Valley soils has accomplished two purposes: 1st, it has presented the data, summarized in the foregoing curves, of the rate and extent of the adsorption of potassium and phosphate ions by these four soils, together with the rate and extent to which these adsorbed ions are subsequently leached out; and 2nd, it has substantiated the results of Cameron, Schreiner, Failyer, Schloesing, and others, in the following points:

1. When soils are subjected to the leaching action of water, the concentration of potassium and phosphate ions in the soil extract approaches a constant, which appears to be fixed and definite for any given soil.

2. When soils are subjected to the action of soluble potassium and phosphate salts, the concentration of these salts in the soil extract is at first not materially increased, owing to the power of the soils to adsorb these salts, but as adsorption proceeds it becomes weaker, and a point is finally reached

where the amount of soluble salts extracted in the soil extract is nearly equivalent to the amount applied.

3. The concentration of the potassium and phosphate ions in the soil extract approaches a low constant, which appears to be fixed and definite for each soil, when only a part of the adsorbed ions has been removed by the leaching action of water.

4. The constants attained by the four soils by the leaching action of water are very nearly alike, which would seem to indicate that the concentration of the potassium and phosphate ions in the soil solutions of the various soils were practically the same, and not at all dependent on the amount of adsorbed potassium or phosphate they originally contained.

5. These results substantiate the theory that the concentration of salts in the soil solution is very largely dependent on the specific adsorptive capacity of the individual soil.

6. These results, furthermore, tend to disprove the theory that the composition of the soil moisture, hence the adsorptive capacity of the soil, is determined primarily by the chemical composition of the soil, but tend rather to prove this quality to be dependent on the mechanical texture of the individual soil.

Furthermore, inasmuch as these soils continue to adsorb small amounts of potassium and phosphate ions long after the approximate point of saturation has been reached; and as these soils continue to lose these potassium and phosphate ions in small amounts long after the soluble forms must have been entirely leached out; and as this latter point is reached long before all of the previously adsorbed potassium and phosphate ions have been leached out, it would appear that the soils were able to take up these ions from the solution in two distinct ways: 1st, by saturating itself with the ions, these undergoing no chemical change, and thus remaining readily soluble, and easily leached out; and 2nd, by interacting with the salts, producing insoluble compounds which are reconverted into soluble forms on the application of water, but very slowly. Thus on the application of a salt in solution the soil first rapidly adsorbs the various ions for which it has an attraction, and in proportion to the strength of this attraction, and then proceeds slowly to interact with the salts to produce insoluble compounds. On the application of water to this soil, the soluble adsorbed salts would be quickly leached out, and then the insoluble compounds would in turn be very slowly rendered soluble, by the reversion of the previous reactions, and ultimately they, too, would pass off in the solution.

Acknowledgment is due to Dr. Ernest Anderson for suggesting this investigation, and to Dr. Anderson and Professor Morse for advice and further suggestions before its completion.

Massachusetts Agricultural College
June, 1915

ELECTROCHEMICAL SYNTHESIS OF PHENYLHYDROXYLAMINE

BY F. M. FREDERIKSEN

Snowdon[1] has pointed out that the chemical and electrochemical methods of reducing nitrobenzene are by no means similar though, in general, they should be. At the suggestion of Professor Bancroft, I have made a few experiments to fill one gap in the case of phenylhydroxylamine. Bamberger[2] prepared phenylhydroxylamine chemically by heating nitrobenzene for a few minutes with zinc dust and water. The yield varies very much—from 0 to 57 percent of the theoretical. Bamberger calls attention to the fact that different samples of zinc dust give very different yields even though the content of metallic zinc be the same and even though all other conditions are kept the same. Thus, one sample of zinc dust gave aniline and no phenylhydroxylamine. Bamberger considers that these enormous differences may be due, in part, to the fact that one sample of zinc dust gives chiefly molecular and, therefore, inactive hydrogen. Another way of wording the same thing is to say that different impurities in the zinc affect the over-voltage differently. The best yield was obtained by adding ten grams of nitrobenzene to half a liter of boiling water, throwing in 75 g zinc dust (about 67 percent metallic zinc) all at once, boiling for three-quarters of an hour, cooling rapidly and saturating with sodium chloride. The phenylhydroxylamine was shaken out with ether, the ether distilled off, and the crystallized oil washed with ligroin. The yield was 57 percent of the theoretical. Other products are azoxybenzene, azobenzene, and aniline.

The question of yield is also discussed by Wohl[3] who had discovered the reaction independently of Bamberger. At first, nitrobenzene was heated for twenty minutes with

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[1] Jour. Phys. Chem., 15, 797 (1911).

[2] Ber. deutsch. chem. Ges., 27, 1348, 1548 (1894).

[3] Ibid., 27, 1432 (1894).

ten times its volume of water and an excess of zinc dust. With 50 percent of zinc dust a yield of about 12 percent phenylhydroxylamine was obtained. When three times the theoretical amount of zinc was taken, the yield increased to about 20 percent. It is not feasible to heat for a long period because azoxybenzene, azobenzene, and aniline are then formed.

It was found that salts like calcium chloride, magnesium chloride, and zinc chloride accelerate the reaction between zinc dust and nitrobenzene. According to Wohl, this is because they form insoluble salts with zinc hydroxide. To obtain the best yield, 250 cc 60 percent aqueous alcohol were heated in a flask with reverse cooler. To the flask were added 60 g nitrobenzene and then 6 g anhydrous calcium chloride, after which 75 g commercial zinc dust were added in the course of fifteen minutes. The contents of the flask were heated for about five minutes after the last of the zinc dust was added, and were then cooled and filtered. The alcohol was distilled rapidly from the filtrate until an oil layer appeared which solidified on cooling. About 70–75 percent of the theoretical yield of phenylhydroxylamine was obtained in this way.[1]

Wislicenus and Kaufmann[2] found that a 38 percent yield of phenylhydroxylamine could be obtained by reducing nitrobenzene in 90 percent alcohol with amalgamated aluminum. In a later paper, Wislicenus[3] points out that better results are obtained with an ether solution. Nitrobenzene is dissolved in at least ten times its volume of ether, freshly prepared amalgamated aluminum is added and then water, a little at a time. The flask is equipped with a reverse cooler and is placed in ice to prevent the ether from foaming too much. When one starts with 20–30 g nitrobenzene the yield of phenylhydroxylamine is said to be quantitative.

Bamberger and Knecht[4] obtained an 85 percent yield

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[1] Bamberger states that he has never been able to average more than 35% yield in this way and that the maximum observed was 50%; Ber. deutsch. chem. Ges., 29, 864 (1896).

[2] Ber. deutsch. chem. Ges., 28, 1326, 1983 (1895).

[3] Ibid., 29, 494 (1896).

[4] Ibid., 29, 863 (1896).

of phenylhydroxylamine (3.8 g) by dissolving 5 g nitrobenzene in 50 cc 90 percent alcohol, and adding first a solution of 12 g aluminum sulphate in 100 g water, and then 250 g of a 5 percent zinc amalgam. The mixture was shaken vigorously for two hours, the temperature being kept below 5°.

I repeated Wohl's work heating 250 cc 60 percent alcohol with 60 g nitrobenzene and 6 g $CaCl_2$ (ammonium chloride is just as good) on a water bath in a flask equipped with a return condenser. After bringing the solution just to boiling, 95 g zinc dust were added through an interval of fifteen minutes, the temperature of the water bath being regulated so that the liquid in the flask boiled gently while the reaction was taking place. Five minutes after all the zinc dust had been added, the reaction mixture was cooled, first with running water and then with ice. The mixture was filtered by suction and the zinc oxide washed with about 50 cc alcohol. The alcohol was boiled off until the temperature of the distilling vapor reached 86°, this being about the point at which the solution clouds, owing to the separation of an oil. When the solution is cooled in a freezing mixture, the phenylhydroxylamine separates in crystals contaminated with some azobenzene. The crystalline mass, colored a bright orange by the azobenzene, was filtered by suction and then washed with ligroin. The washing must be done with care because phenylhydroxylamine is somewhat soluble in ligroin. The azobenzene is removed practically completely, leaving the phenylhydroxylamine almost pure and white. The yields varied between 30 and 40 percent, which is in accord with the results of Bamberger.[1]

An attempt was now made to duplicate the reaction electrolytically by using zinc electrodes in an ammonium chloride solution. Of course a zinc anode is not essential theoretically, but it obviates the use of a diaphragm and cuts down the voltage considerably. Since it would be difficult to use electrodes having a surface equal to, say, 100 g zinc dust, the reaction must take longer. In order to prevent the decomposi-

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[1] Ber. deutsch. chem. Ges., 29, 864 (1896).

tion of the phenylhydroxylamine which would probably occur if the solution were kept heated a long time, it was deemed advisable to run at a low temperature.

The solution was placed in a 350 cc beaker and stirred during electrolysis by means of a spiral stirring rod run by a motor. After the reduction had gone on as long as desired, the solution was filtered through a Büchner by suction and the alcohol then distilled off as in the chemical reduction. On account of the smaller amounts of substance taken, the solution was not cooled and filtered but was saturated with sodium chloride and extracted with ether. The ethereal extract contained the phenylhydroxylamine and azobenzene with only a trace of salt or of ammonium chloride. The ether was driven off and the residue was crystallized from a small amount of benzene to which ligroin was added after solution and filtration. Phenylhydroxylamine is very soluble in hot benzene and only slightly soluble in cold benzene. Addition to the benzene of an approximately equal volume of ligroin cuts down the solubility still more. The azobenzene remains in solution.

Theoretically it requires 107.2 ampere hours (4 × 26.8) to reduce one molecular weight of nitrobenzene (123 g) to phenylhydroxylamine. Since nitrobenzene has a specific gravity of 1.2, 10 cc nitrobenzene is approximately 12 g and calls for 10.46 ampere hours, which should give 10.73 g phenylhydroxylamine.

The following results were obtained:

Run 1. 250 cc 60 percent alcohol, 12.5 g ammonium chloride, 10 cc nitrobenzene. Zinc electrodes. Cell packed in ice. Average temperature 12°. One ampere for 9.5 hours. No stirring for the first hour. Yield, 28 percent.

Run 2. 250 cc 60 percent alcohol, 10 g ammonium chloride, 5 cc nitrobenzene. Zinc electrodes. Cell cooled in running water. Average temperature 14°. 0.75 amperes for 6.7 hours. Yield, 21 percent.

Run 3. 250 cc 60 percent alcohol, 10 g ammonium chloride, 5 cc nitrobenzene. Zinc electrodes. Cell cooled in freezing mixture. Average temperature —5°. 0.75 amperes for 6.7 hours. Yield, 20 percent.

Run 4. 250 cc 60 percent alcohol, 10 g ammonium chloride, 5 cc nitrobenzene. Zinc electrodes. Cell cooled with running water. Average temperature 19°. 2 amperes for 2.67 hours. Yield, 29 percent.

Run 5. 250 cc 60 percent alcohol, 10 g ammonium chloride, 5 cc nitrobenzene. Zinc electrodes. Cell not cooled. Average temperature, 36°. 4.8 amperes for 1.11 hours. Yield, 22 percent.

These yields are all lower than those for the chemical reduction; but part of this difference is undoubtedly due to the fact that the losses are greater when 6 g nitrobenzene are used instead of 60 g in the same amount of solution. Also, we do not know what the reduction efficiency of the zinc dust is, though that could be determined; but we know that it is necessary to use more than the theoretical amount of zinc. The time at my disposal did not permit me to make runs to see what effect an excess of ampere hours would have.

It is possible to tell something about the results during the run. If much hydrogen is evolved at the cathode or if much zinc is precipitated there, the efficiency is necessarily low. A deep red color to the solution shows a considerable formation of azobenzene, an orange color a much less formation, and a light yellow color hardly any formation of azobenzene.

The general results of this paper are:

1. It is possible to reduce nitrobenzene to phenylhydroxylamine electrochemically without the use of a diaphragm by using a zinc anode.

2. The chemical process of reducing nitrobenzene to phenylhydroxylamine with zinc dust can be duplicated electrochemically.

3. The yield from the electrochemical process is less at present than the yield from the chemical process. Part of this difference is due to the fact that the percentage losses are larger the smaller the amount of nitrobenzene taken.

4. The efficiency of reduction and the conversion to azobenzene both decrease with falling temperatre. One has to strike a mean therefore between slight conversion to azobenzene but low reduction efficiency and high reduction efficiency with high conversion to azobenzene. The best results so far have been obtained at about room temperature.

I take this opportunity to express my appreciation of the active interest Professor Bancroft has taken in the progress of the work.

Cornell University

NEW BOOKS

Chemistry of Familiar Things. *By Samuel S. Sadtler. 15 × 22 cm; pp. xiii + 320. Philadelphia: J. B. Lippincott Co., 1915. Price: $1.75 net.*— In the preface the author says: "This book has been written because of a demand for an insight into chemistry by those whose training or whose reading has been directed in other channels. Chemistry has been regarded as a difficult and confusing study by beginners; yet they seem to grant that it must be a very absorbing and interesting pursuit to the chemist himself. If this be true it is only necessary for the chemist to present the subject with its natural attractions in a non-technical way. He may then both instruct and interest those who would like to extend their courses of reading to learn more about natural phenomena and to familiarize themselves with things in Nature and the Arts."

The headings of the chapters are: introduction; brief chemical outline; historical development of chemistry; the periodic system of elements; the chemistry and production of light; heat, combustion, and insulation; air, oxidation, and ventilation; water; alkalies and salts; metals; gold and silver; chemistry of the earth's evolution; soil and its conservation; food elements and food classes; individual foods; animal feeding; fermentation; chemistry of the body; soaps, solvents, and paints; paper and textiles; leather and rubber; siliceous substances and glass; a few important definitions.

This is a good programme and the task that the author has set himself is one that is very well worth doing. The gap between the chemist and the public is unfortunately very large. As the reviewer has said before, chemistry is taught at the colleges solely for the benefit of the people who intend to use it. It is essentially a professional subject. On the other hand it is a subject with which everybody deals continually without knowing it, and it ought to be one of the most popular of the general education courses. That it is not is the fault of the teacher of chemistry. We are therefore very grateful to anybody who contributes something which will help us to do what we ought to do. The author has done this to a certain extent and to that extent this book is a success. On the other hand it must be remembered that the author has set himself a very difficult task, one for which very few people are qualified. Tyndall and Huxley are, of course, the classical models. Robert Kennedy Duncan was successful in a distinctly meretricious way. There are no others, though some might include Cooke. The author's literary skill is not on a par with his ambition. His style is jerky, he writes down to his readers, and his attempts at humor are not always successful He is distinctly at his best when he quotes from Burroughs. This one illustration shows what is needed and how nearly impossible it will be to get it. It is very likely that the things will have to be done in two stages. After many chemists have tried their hands at the problem, somebody will work over their attempts into a real book. That the author has not hit the bulls-eye at the first shot is not to his discredit. He has not only seen the target —which is more than most chemists do—he has hit in the outer ring.

In a book covering so much ground there are necessarily some errors of detail. The following could profitably be corrected in the next edition. Woodruff was the man who developed the theory as to the pigmentation of the negroes,

p. 37. The striking characteristic of the Edison cell, p. 48, is its durability and not its lightness. It is distinctly misleading to say, p. 55, that "probably the little fires all over the body would be rather hot if the blood did not circulate by means of a pump designed for the purpose, the blood carrying off the heat as fast as formed." It is difficult to believe, p. 60, that the latent heat of vaporization of water was a wonderful provision of nature to enable us to boil meat. The reviewer would guarantee to secure a boiled dinner even if the latent heat of vaporization of water were negligible. The latent photographic image, p. 75, is not Ag_2Br. The author apparently believes, p. 169, that wells near the ocean contain fresh water because the soil adsorbs the salts. The water in these wells is rain water and does not come from the ocean at all. The water remains fresh because the flow is from the well to the ocean. If the level of the water in the well is kept permanently below mean low water mark, the water will become salt. It is scarcely accurate to say, p. 295, that Professor Harries, Sir William Ramsay, and others have succeeded in making rubber economically. Also the vulcanization of rubber does not give rise theoretically to hydrogen sulphide. The reviewer does not believe that the Romans ever made Portland cement, p. 311. A eutectic, p. 315, is not a solid solution. While these errors are not very important in themselves, it is desirable to eliminate them from a book of this sort.

Wilder D. Bancroft

La vie et la lumière. *By Raphael Dubois. 15 × 22 cm; pp. 338. Paris: Felix Alcan, 1914. Price: 6 francs.*—The first part deals with what the author calls biophotogenesis, the production of light by living organisms; the second part with the action of light on living organisms; and the third part with the physiological effects of X-rays, radium rays, Hertzian waves, and high frequency currents.

The power of emitting light is wide-spread and is to be found among vegetables, protozoa, coelenterates, echinoderms, worms, crustaceans, insects, mollusks, fishes, etc. Some idea of the extent of the literature on the subject may be obtained from the statement, p. 18, that in 1835 Ehrenberg referred to four hundred and thirty-six authors who dealt with self-luminous sea creatures only, while in 1887 de Kerville quotes the works of three hundred and twenty-six investigators who were dealing with self-luminous insects alone.

Though there are apparently some cases, p. 38, where oxygen is not essential, the author takes the ground quite definitely, p. 132, that in general the production of light by living organisms is a chemiluminescence involving oxidation. It is not clear in many cases what is the physiological value of the luminescence to the organism, though many hypotheses have been put forward, p 142.

In the section on the action of light on living organisms the author emphasizes the law of Grotthuss, p. 160, that only that light which is absorbed can produce chemical action but he makes no mention of depolarizers. There is quite an account of the bactericidal action of ultra-violet light. Very interesting also is the evidence that some of the photogenic organisms emit light of wave-lengths suitable to produce fluorescence. The author seems to think that this is identical with proving that these organisms emit ultra-violet light. The author is very bitter in his criticisms of Loeb's work on phototropism; but he does not seem to the reviewer to make out a good case.

On p. 233 the author describes the experiments of Hess, in which dyed grains were spread before a turkey. The turkey ate the red ones but did not touch the blue ones. From these and other experiments Hess concluded that birds are blind to blue and do not see the blue grains. If this were only true, it would open up all sorts of thrilling possibilities. It would only be necessary to develop blue strawberries and blue cherries to do away completely with the attacks of birds on these fruits. It would be wiser, however for the enthusiastic horticulturist to be very sure of these facts before starting to develop a blue strawberry. Dubois thinks that the birds are not blind to blue; but simply do not like the color. "It is not necessary to be a turkey to object to blue or violet food. The same instinctive repulsion exists in man, who does not like to drink out of glasses of these colors." The author goes rather too far here. It is a very abnormal man or boy who has an instinctive repulsion for blueberries and milk. In a little Dutch town the reviewer once saw a beautiful blue liqueur. He does not know the name of it; but the evidence was overwhelming that people drank it.

The section on the physiological action of radium, X-rays, etc., is short and does not contain anything which is especially new. *Wilder D. Bancroft*

Geschichte des Elektroeisens. *By Oswald Meyer. 16 × 24 cm; pp. viii + 187. Berlin: Julius Springer, 1914.*—The author is an ardent admirer of Borchers to whom he often refers as the great metallurgist. He, therefore, follows the lead of Borchers and distinguishes three periods in the development of the electric furnace for producing iron before the invention of Stassano's furnace which opens the fourth period. The fifth period runs from 1904 to 1909. It begins with the report of the Canadian Commission and ends in 1909 chiefly to enable the author to start the sixth period then when an electrical blast furnace was installed at Domnarvfet. By the end of 1913 nearly 250 electric furnaces for iron had been built or were in course of construction. The author gives a distinctly interesting list of all the installations so far as he has been able to learn about them.

There is nothing critical about the book. It is valuable chiefly as a compilation of data, representing a large amount of work on the part of the author. In many places the author states that steel from an electric furnace is much better than any other steel but one has to take this chiefly on the author's statement, which seems a pity. So far as the reviewer can judge it would be quite out of the question to try to determine from this book under what conditions it would be desirable to introduce an electric furnace, barring the very simple case of cheap water power and expensive coke. *Wilder D. Bancroft*

Chemical German. *By Francis C. Phillips. Second edition. 16 × 23 cm; pp. viii + 252. Easton: The Chemical Publishing Co., 1915. Price: $2.00.*—The first edition was reviewed less than two years ago (**18**, 82). The reviewer is glad to see that the edition was exhausted so promptly, and that a re-issue has become necessary. *Wilder D. Bancroft*

AN INTERPRETATION OF VAN DER WAALS' EQUATION FROM THE STANDPOINT OF VOLUME DETERMINED BY EQUILIBRIUM OF PRESSURES

BY W. V. METCALF

Van der Waals' equation is $(p + a/v^2)(v - b) = RT$, in which p represents the external pressure; a/v^2, according to the kinetic interpretation of the equation, represents the pressure which is due to the attraction between the molecules, and which acts with the external pressure to compress the mass; v represents the volume; b the correction in the ideal gas equation necessitated by the volume actually occupied by the molecules; T the absolute temperature; and R a quantity which is constant for a given mass of a given substance.

In spite of the fact that this equation is not quantitatively accurate, the fact that it predicts and interprets qualitatively the metastable conditions; the critical point; the minimum volume of pv in the case of gases, with the exceptional case of hydrogen; and other phenomena; makes it one of the important generalizations of science. Its most important achievement is its qualitative interpretation of the phenomena connected with the boiling points of a liquid at successively higher pressures until the critical point is reached, with its continuity between the liquid and the gaseous states. The equation is one of the third degree in v. Figure 1 shows the type of the curves obtained by plotting the equation for v as a function of T at successively higher constant pressures; Figure 2 the type obtained by plotting for v as a function of p at successively higher constant temperatures.

Each point on these curves represents a condition of equilibrium between the volume, the temperature, and the external pressure of a given mass of a given substance. Confining our attention to Figure 1, it is to be noted that the dotted line *bf* is not a part of van der Waals' curve. If we substitute *bf* for *bcdef*, then the curve *abfg* represents what happens when a liquid is heated to its boiling point, then boiled away at constant temperature, and the resulting vapor heated still further. There is a sharp distinction between what happens along this line *bf* and what is represented by the curve *bcdef*. There are two possible methods by which a given mass can pass from the liquid to the gaseous condition. One is a process of evaporation from a surface, and involves a discontinuous change in volume and in other physical properties. The other is a process of continuous expansion of the entire mass, and involves only a single phase and only continuous changes in properties. The two are wholly independent processes, although they may take place simultaneously. Van der Waals' equation has to do only with the latter,—the continuous expansion process. The distinction between these two processes has not always been kept as clearly in mind as it should have been.

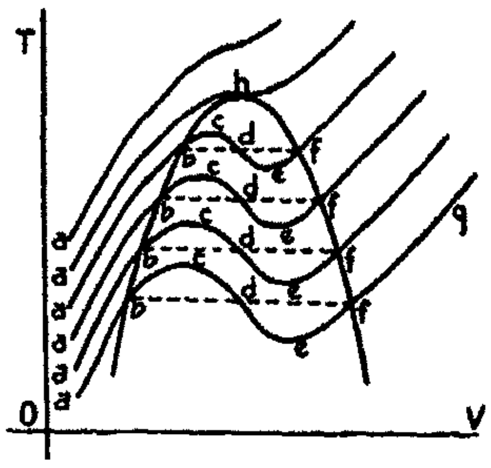

Fig. 1

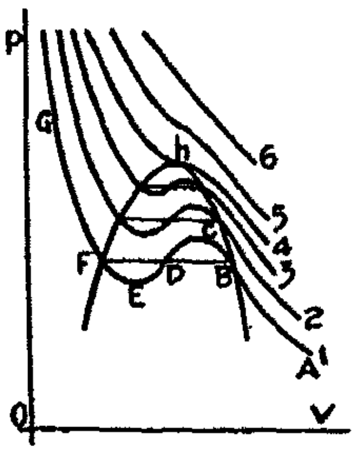

Fig. 2

On the curve *abcdefg*, *ab* represents the ordinary stable condition of the liquid; the ordinate of the line *bf* represents the boiling temperature; the parts *bc* and *ef* represent the so-called metastable conditions which are realized experimentally in a superheated liquid and a supercooled vapor; the part *ce* represents the unstable condition which has not been studied experimentally. A comparison of the successive curves of the figure, plotted for successively higher constant pressures, shows that as the pressure increases, the maximum and minimum points *c* and *e* approach each other horizontally and vertically, and finally, at a certain definite temperature, pressure and volume, represented by *h*, the two points coincide. Above this "critical point" no unstable condition can intervene between the liquid and the gaseous states.

Van der Waals' equation emphasizes the fact of the continuity of the liquid and the gaseous states, and, according to the kinetic interpretation of the equation, it makes it clear that in the liquid as well as in the gaseous state, the volume under given conditions is the result of an equilibrium between opposing pressures, some of which tend to decrease the volume and others to increase it. The equation may be written $p + \frac{a}{v^2} = \frac{RT}{v - b}$, in which p represents the external pressure, and a/v^2 the pressure due to cohesion between the molecules. This latter pressure the Germans call Binnendruck or Kohäsionsdruck. In English it is usually called internal pressure,—an ambiguous term unless distinguished as positive or negative. I will call it cohesive pressure. In the case of the more perfect gases it is ordinarily negligible. In ordinary liquids however we have reason to believe that it amounts to some thousands of atmospheres. The external and the cohesive pressures act together in tending to decrease the volume. If these were the only pressures tending to change the volume, there could be no volume equilibrium. There must be another pressure balanced against these two, which tends to increase the volume. The value of this third pressure is expressed in the equation by the term $RT/v - b$.[1] The kinetic theory explains this pressure as due to the total effect, per unit area, of the blows of the individual molecules. It is a function of the temperature and of the density. It is due to the elasticity and to the heat vibrations of the molecules. In the more perfect gases it is comparatively small,—practically equal to the external pressure. In liquids it is ordinarily very large,—approximately equal to the cohesive

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[1] The term $RT/v - b$ has the dimensions of pressure, since R has the dimensions of pv, $v - b$ expresses a volume, and T simply multiplies the term by an abstract number without changing its dimensions.

pressure. I will call it elastic pressure. The condition of constant volume then, in both states, is expressed by the equation: External Pressure + Cohesive Pressure =

Elastic Pressure, or $p + \frac{a}{v^2} = \frac{RT}{v - b}$.

It is not a new idea to look at these phenomena from the viewpoint that volume, in the case of liquids as well as of gases, is determined by an equilibrium of pressures. Harold Whiting[1] in 1884 published a somewhat elaborate mathematical paper, taking this equation as the starting point of his argument. Such an equilibrium, in the case of both liquids and gases, is really involved in the kinetic interpretation of van der Waals' equation, and it is more or less clearly implied in most of the thought on the subject.[1] It has not however been kept always so clearly in mind as to avoid all confusion of thought on the subject.

A second point is necessarily involved in the kinetic explanation of van der Waals' equation. Suppose we have a given mass of liquid in equilibrium, and we cause a minute rise in temperature by adding heat. This has no effect on the external pressure and probably none on the cohesive pressure, but it increases the kinetic energy of the molecules and thus increases the elastic pressure. This destroys the equilibrium by making the force tending to cause expansion greater than that tending to cause contraction, and an increase in volume results. As the volume increases, the average distance between the molecules increases. This does not affect the external pressure, but both the elastic and cohesive pressures are decreased. If these two pressures decreased by equal amounts for a given decrease in density,—that is, neglecting external pressure for the time being, if the density coefficients[2]

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[1] Proc. Am. Acad., 19, 353 (1884). See also Thomas Young, Phil. Trans. for 1805, p. 43, quoted by Mathews: Jour. Phys. Chem., 17, 491 (1913); also Lewis: Proc. Faraday Soc., 7, 94 (1911–12); Bridgman: Proc. Am. Acad., 49, 96 (1913).

[2] The term "density coefficient" of a pressure means, in this paper, $\frac{P_1 - P_2}{P_1(D_1 - D_2)}$ or $\frac{1}{P}\frac{dP}{dD}$. The term rate of change of a pressure with density means $\frac{dP}{dD}$. The first is the rate of change of the pressure relative to its own value; the second is its absolute rate of change.

of the two pressures were equal,—then the equilibrium could not be restored by expansion and the volume would go on increasing indefinitely. As a matter of fact the volume increases slightly and then comes to equilibrium again at the higher temperature. This must mean that the pressure tending to cause expansion decreases, as the density decreases, more rapidly than the pressure tending to cause contraction, —that is, when the two pressures are equal, that the density coefficient of the elastic pressure is greater than that of the cohesive pressure. The equilibrium is thus automatically restored by an increase in volume as soon as the disturbing cause ceases to act, and the condition is therefore stable. If the density coefficient of the cohesive pressure were greater than that of the elastic pressure, then any inequality of pressures would be increased, not decreased, by a change of volume, and equilibrium could not be restored by expansion or contraction. No stable equilibrium would be possible in this case. A necessary condition of stable equilibrium is that the pressure tending to cause expansion changes with density more rapidly than that tending to cause contraction.

One further point:—It seems to be true that in the case of all pure liquids the coefficient of expansion by heat increases as the temperature rises toward the boiling point.[1] There can be but one interpretation, from the standpoint of pressure equilibrium, for this increase in the coefficient of expansion. If the density coefficients of the two pressures were the same, external pressure neglected, then a slight rise in temperature would cause the mass to expand indefinitely,

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[1] The only exceptions known to the author are water, which we now believe to be a mixture of different kinds of molecules rather than a pure liquid, and several liquids under very high pressure which have been studied by Bridgman: Proc. Am. Acad., 49, 1 (1913–14) and Amagat: Ann. chim. phys., 11, 520 (1877). All of these exceptions are capable of explanation as due to complex phenomena of association and dissociation, although Bridgman suggests also a second explanation on the basis of the introduction into liquids at high pressures of an incipient form energy before the solid condition is reached. Either explanation would remove these cases from the category of normal pure liquids.

as explained above, and the coefficient of expansion would be infinite. On the other hand, if the density coefficient of the elastic pressure be very much greater than that of the cohesive pressure, then equilibrium is restored by a slight increase in volume and the coefficient of expansion is small. A small coefficient of expansion, then, means a large difference between the density coefficients of the two pressures, and *vice versa*. The fact, therefore, that the coefficient of expansion of a liquid increases as the temperature rises must mean that, while the density coefficient of the elastic pressure on the right side of the equation is greater than that of the total pressure on the left, the difference between the two density coefficients decreases with rise in temperature.

T. W. Richards[1] in a recent article calls attention to the fact that a small coefficient of expansion necessarily involves a large cohesive pressure. It is of interest to note that the converse of this, while probably always true, does not follow necessarily from the nature of the case. We might conceivably have a large cohesive pressure with a large coefficient of expansion. If we should have in equilibrium with each other two pressures whose rates of change with density were the same, then, however powerful the pressures, a slight force added to either would permanently destroy the equilibrium, and the coefficient of expansion would be infinite. The value of the coefficient of expansion depends ultimately not on the intensity of the pressures, but on the difference of their density coefficients. The same kind of statement applies to compressibility.

To sum up, we have three propositions derived as necessary consequences of the kinetic interpretation of van der Waals' equation: First, volume is determined by an equilibrium of opposing pressures. Second, in the case of a stable liquid the elastic pressure, which tends to increase the volume, increases with density more rapidly than does the cohesive pressure which tends to decrease the volume. Third, the difference between the density coefficients of these two pres-

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[1] Jour. Am. Chem. Soc., 36, 2425 (1914).

sures decreases as the density of a liquid decreases. The first of these propositions is not new. Attention has not been called to the last two, however, so far as I know, although they seem to be necessarily implied in the kinetic interpretation of van der Waals' equation.

These three propositions furnish a simple interpretation for the different parts of van der Waals' curve and the phenomena represented by them. Part *ab* represents the ordinary stable condition of the liquid, as explained above. The part *bc* represents the metastable condition,—the superheated liquid. If our propositions represent the real facts, then this is a true stable condition, so far as the continuous volume change is concerned. But the liquid is above its boiling point and therefore there is a strong tendency for evaporation to take place. In other words, the condition is stable in reference to the continuous volume change, but unstable in reference to the surface change. If we could exclude the possibility of evaporation, all portions of this part of the curve might be realized experimentally. It is the difficulty of preventing evaporation that makes it difficult to obtain and hold a liquid in this condition. This difficulty has been partially overcome in numerous cases, and we are fairly familiar with this metastable condition in the case of many liquids.

The equilibrium conception points also to the real significance of the maximum point *c* on the curve. Continuing to neglect external pressure, from *a* to *c* the condition is stable because the density coefficient of the elastic pressure is greater than that of the cohesive pressure, but as we have seen, the difference between the two coefficients is steadily decreasing. The point *c* represents the density at which the two coefficients become equal and the equilibrium therefore ceases to be stable. From *c* on, the *density coefficient* $\left(\frac{dP}{PdD}\right)$ of the cohesive pressure becomes increasing greater than that of the elastic pressure. From *c* to some point, as *d*, the *rate of change* $\left(\frac{dP}{dD}\right)$ of the cohesive pressure is also increasingly greater than that of the elastic pressure. But at the point *d* this latter change reverses, and from *d* on, the rate of the elastic pressure gains on that of the cohesive pressure, becoming equal to it again at *e*. From *a* to *d* the rate of change of the cohesive pressure gains on that of the elastic pressure, passing it at *c* where the two are momentarily equal. From *a* to *c* the rate of change of the elastic pressure is the greater. From *c* to *e* that of the cohesive pressure is the greater, this difference reaching a maximum at *d* and then decreasing to zero again at *e*. From *c* to *e*, then, the condition is unstable because the cohesive pressure changes with density more rapidly than the elastic pressure, and consequently the equilibrium, if once disturbed, cannot be restored by the resulting change of volume.[1] From *e* on, the rate of change of the elastic pressure is greater than that of the cohesive pressure. The condition is therefore stable so far as volume is concerned, but from *e* to *f* the condition is that of a vapor below its boiling point, and it is therefore unstable in reference to the surface change. Here again we have the metastable condition, which simply means a condition of stability in reference to the continuous volume change, but of instability in reference to the surface changes of evaporation and condensation.

Attention was called above to the fact that in the curves plotted for successively higher constant pressures, the maximum and minimum points *c* and *e* approach each other as the external pressure increases, and finally come together at *h*, the critical point. The reason for this is clear from the standpoint from which we are viewing the subject. The statement was made above that the maximum point *c* represents the density at which the density coefficients of the elastic and cohesive pressures became equal. This is not strictly true,

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[1] It is possible that the passage of a substance through an unstable condition similar to that from C to E along van der Waals' curve (Fig. 2) is realized in nature on the surface of dust particles that prevent the supersaturation of water vapor. It is possible that the cause of their action is the condensation of the vapor onto their surface by adsorption until the vapor reaches the condition represented by *c*. After this it would contract spontaneously and practically adiabatically to a liquid condition. The liquid phase would thus be introduced and prevent the supersaturation of the remaining vapor.

however, since we were rejecting for the time being the external pressure. This would be rigidly true only in the absence of external pressure, an impossible limiting case. The accurate statement is that *c*, the point at which the equilibrium changes from stable to unstable, represents the density at which the rate of change of the elastic pressure on one side of the equation equals the rate, not of the cohesive pressure alone, but of the sum of the cohesive and external pressures on the other side of the equation. At ordinary pressures these two statements are nearly equivalent, but as the external pressure increases it becomes an increasingly important term on the left side of the equation. The external pressure does not change with the density. The maximum point *c*, therefore, must correspond to a density coefficient of the cohesive pressure which is somewhat greater than that of the elastic pressure, in order to make the rate of change of the total pressure on the left equal to that of the pressure on the right, and this excess must increase with an increase in the external pressure. But this increase in the excess of the density coefficient of the cohesive pressure over that of the elastic pressure corresponds, as shown above, to a decrease in density,—that is, to a movement of the point *c* further to the right. As the external pressure increases, therefore, the maximum point *c*, at which the equilibrium changes from stable to unstable, moves toward the right. In an exactly similar way it can be shown that the minimum point *e* must move toward the left with increasing external pressure, and the two points therefore approach each other horizontally. It is easy to show that the vertical distance between them must also decrease and that they coincide at a certain definite value of the external pressure.

The interpretation that this concept gives to the critical point is of interest. As stated above, there is a certain maximum possible excess of the rate of change with density of the cohesive pressure over that of the elastic pressure. This occurs on the curve of the limiting case of external pressure equal to zero, and is a characteristic of each substance.

It occurs at the density represented by the point *d* on the curve,—approximately that of the critical point. The critical point is the point at which, in the equation

External Pressure + Cohesive Pressure = Elastic Pressure,

the cohesive pressure has become so small a proportion of the left side of the equation, and therefore of the elastic pressure on the right, that the maximum possible rate of change of the cohesive pressure is no longer great enough to make the rate of change of the total pressure on the left of the equation greater than that of the pressure on the right. Beyond this point there can be no unstable equilibrium, and the change from liquid to gaseous state must be a single-phase continuous process.

In a speech[1] made in 1910 in Stockholm, on the occasion of his receiving the Nobel Prize, van der Waals made the following statement in reference to the critical temperature: "Bei dieser Temperatur sind die köexistierenden Densitäten gleich gross. Das ist das einzige, was dieser Temperatur eine Bedeutung gibt, die in allen Beziehungen ihr nicht zukommt." If the above treatment of the critical point is correct, there is a property which characterizes this point which is more fundamental than the equality of densities, of which the equality of densities is merely a consequence.

T. W. Richards[2] has explained the peculiar sensitiveness to change of volume at the critical point as due to the fact that at this point the volume is determined simply by such an equilibrium of pressures as we are discussing. If our viewpoint is correct, such an equilibrium exists at all points of the curve, as recognized elsewhere by Richards, and the stability at any point depends not on the existence of such an equilibrium, but on the difference between the density coefficients of the different pressures involved. The sensitiveness to volume change at the critical point would be due, not to the fact that the volume is dependent on an equilibrium at this

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[1] Van der Waals: "Die Zustandsgleichung." p. 14 (1911).

[2] Jour. Am. Chem. Soc., 36, 632 (1914).

point, but to the fact that as the substance, in moving along the curve, passes through the critical point, it is momentarily in a condition in which the density coefficients on the two sides of the equation are equal and the coefficient of expansion is therefore momentarily infinite. In both directions along the curve from the point *h* the excess of the density coefficient on the right side of the equation over that on the left increases; the coefficient of expansion therefore decreases and the volume conditions become more stable.

We have so far confined our attention to the curves shown in Fig. 1. An entirely similar analysis applies to those shown in Fig. 2,—the pressure-volume curves plotted at successively higher constant temperatures.

It seems to be true, then, that the equilibrium conception under discussion furnishes a clear, qualitative interpretation of all parts of van der Waals' curves and the phenomena connected with them.

It helps also to give an insight into other problems,—into the mechanical explanation of osmotic pressure for example, and the mechanical explanation of why the vapor tension of a liquid is decreased by dissolving in it a non-volatile substance without change of temperature. Some have found difficulty in explaining this latter problem on the basis of the kinetic theory of solution.[1] The vapor tension of a liquid depends on the rate at which the molecules escape from its surface. Cohesion tends to hinder their escape. One might think therefore that the solute pressure, which acts against cohesion, should increase rather than decrease the vapor tension. A more careful analysis however makes the situation clear. The tendency of the molecules to escape depends on the kinetic energy of the molecules,—that is, on the temperature,—and also on the density of the liquid, exactly the factors on which the elastic pressure depends. When the solute is introduced, its gas pressure is added to the previous elastic pressure and the equilibrium is thus destroyed. The volume therefore increases until the expansion causes such a decrease in the

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[1] See Nernst: "Theoretische Chemie," 7th Ed., page 248.

elastic pressure that it, plus the solute pressure, is now equal to the cohesive pressure plus the external pressure. At this point the equilibrium is restored. The cohesive pressure has been decreased,[1] due to the decrease in density, but the decrease in the elastic pressure has exceeded that of the cohesive pressure by an amount equal to the solute pressure, in spite of the fact that the kinetic energy of the molecules has not changed. We should therefore expect a lowering of the vapor pressure proportional to the solute pressure,—proportional that is, in dilute solutions, to the concentration. The equilibrium conception therefore explains the phenomena both qualitatively and quantitatively. The decrease in vapor tension, if the thought of this paper is valid, is not contrary to the kinetic theory, but is what that theory would predict. The mechanical explanation therefore is as clear as the dynamic. No mere thermodynamic explanation of a phenomenon is a complete one. It needs to be supplemented by a clearing up of the mechanical situation.

If this explanation is the true one, it ought to be possible to increase the vapor tension of a solution until it equals that of the pure solvent, by applying to the solution what Ostwald calls a "Pressung," equal in amount to the solute pressure. According to Callender's[2] vaporization theory of osmosis, this is what really does take place at the semi-permeable membrane when the back pressure becomes

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[1] Jäger (Drude's Ann., 41, 854 (1913)) argues that because of variation from Dalton's law, the solute when added without change of volume adds more than its normal gas pressure to the elastic pressure of the liquid, but that where flow through a semi-permeable membrane is possible, this flow takes place in such a way as to automatically restore the equality between the elastic pressure of the solvent in the solution and that of the pure solvent without, thus leaving the total elastic pressure of the solution greater than that of the pure solvent by an amount just equal to the gas pressure of the solute. If Jäger is right, then the decrease in the cohesive pressure caused by expansion when a solute is dissolved in a liquid should be just equal to its increase due to variation of the elastic pressure from Dalton's law. The two should just balance, leaving the cohesive pressure of the solvent in the solution the same as that of the pure solvent.

[2] Nature, 81, 235 (1909). See also Battelli and Stefanini: Abs. Chem. Soc., 92, II, 233 (1907).

sufficient to stop the flow. Callender assumes that the pores of the membrane are filled with vapor instead of liquid, and that the osmotic flow is due to vaporization and condensation within the pores. If his assumption is correct, his theory offers a self-consistent and logical explanation of osmosis, in accordance with the kinetic theory of solution. But ordinarily, probably always, the membrane is wet by the solvent and the pores are filled with liquid rather than with vapor. In this case the kinetic theory offers an equally clear mechanical explanation of osmosis along the line of LeBlanc's suggestion.[1] In either case, the oft-repeated statement that the real mechanical cause of osmotic flow is still a mystery is not true. The kinetic theory offers as clear a qualitative explanation of osmotic pressure as it does of gas pressure, and the quantitative limitations are analogous in the two cases, although more complicated in the case of solutions.

Another point should be considered,—the question why a decrease in density should cause such curious changes in the relative rates of changes $\left(\frac{dP}{dD}\right)$ of the two internal pressures as is described above. As shown, it seems to follow from the kinetic interpretation of van der Waals' equation, that when along any curve the density of the mass is greater than a certain fixed value the rate of change of the cohesive pressure divided by that of the elastic pressure increases as density decreases; but that, at this particular density of the mass, the process reverses, and thereafter the value of this fraction decreases as density decreases. The reason for this is inherent in the nature of the equation,—in the relative importance in the equation of the quantities a/v^2 and b at different densities.

There has been much discussion as to whether the inaccuracy of van der Waals' equation is due to the variability of the quantity "*a*" or of the quantity "*b*" or of both. It seems now to be fairly established that "*b*" is variable. Van der Waals' latest thought[2] is that "*a*" also is variable in all cases.

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[1] "Lehrbuch der Elektrochemie," 3rd Ed., p. 40.

[2] Van der Waals: Loc. cit., pp. 14–17.

His hypothesis is that as a substance approaches the liquid from the gaseous state, association always takes place, and that this causes a decrease in the cohesive pressure and results in less compression than is called for by the equation. The theory of the compressibility of the molecule and of the atom has an interesting bearing on this point. In the light of the evidence presented by Richards and others, and in the light of our present views as to the complexity of the atom as well as of the molecule, it seems difficult to doubt that both the molecule and the atom are compressible and that they therefore have volume elasticity as well as form elasticity. Richards believes that as a vapor is cooled the molecules approach each other until, somewhere in the region of condensation, they come into continual contact with each other; and that as the liquid is cooled still further the molecules become more and more compressed. If this is true it introduces a new element into the situation not taken into account in the kinetic demonstration of van der Waals' equation,—namely, the volume elasticity of the molecules and perhaps also of the atoms. The elastic pressure due to this cause could not be identical with that due to heat vibrations, since it would exist in the absence of heat vibrations. Bridgman[1] has given us a most interesting discussion of this kind of elastic pressure. This pressure would be introduced gradually as the density of the vapor or the gas is increased toward the boiling point or the critical point. The phenomena produced would be qualitatively the same as the experimental variations from van der Waals' equation. The same lessening of the full compression called for by the equation would be produced either by a lessening of the cohesive pressure through association or by an increase in the elastic pressure due to molecular compression. Van der Waals' hypothesis, however, makes "a" variable in all substances, while the molecular compression hypothesis leaves it still reasonable to suppose that in normal liquids "a" is constant and therefore that the cohesive pressure is a function of the density only, varying

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[1] Bridgman: Loc. cit., p. 105 and following.

inversely as the square of the volume, as called for by van der Waals' equation.

The presentation of the thought of this paper is a purely qualitative one. In order to give the thought its full value the density coefficients of the cohesive and the elastic pressures, and their changes with density, would have to be expressed in terms of the first and second derivatives of the pressures with respect to density, and the relation between these and compressibility, coefficient of expansion, and other physical properties would have to be expressed mathematically and tested experimentally. It may prove possible, also, to work back by integration to the values of the two internal pressures, and to determine the laws of their variation. The question may be raised whether there would be advantage in substituting a new equation of state, expressed in terms that can not at present be measured with any accuracy, in place of the older one expressed in easily measurable quantities. The answer is that there is no suggestion of replacing van der Waals' equation, but only of supplementing it. The advantage of the new standpoint is that it is an attempt to deal directly with the forces themselves, which are the real causes of the phenomena in question. However the quantitative side may work out, the fact that the three fundamental propositions of this paper seem to be necessarily involved in the kinetic theory would seem to make it legitimate and of value to use them qualitatively, in order to visualize the phenomena involved, and in order to check up other thought on the subject.

Oberlin, O.

THE RELATIVE AFFINITY OF METALS IN NON-AQUEOUS SOLUTIONS AND THEIR REACTIVITY IN INSULATING MEDIA

PART I

BY JNANENDRA CHANDRA GHOSH

Gates[1] investigated the replacement of metals in non-aqueous solutions of various organic salts of copper, the replacement being indicated by the brassy nature of the metal. The non-aqueous solutions of simple inorganic salts whose mode of ionization in water is exactly known have not received much attention. In the present paper, an account of the experiments mostly carried out with several simple salts will be given.

The allied subject of chemical reactivity in non-aqueous solvents has been extensively investigated by Kahlenberg[2] and his pupils. They have arrived at the conclusion that instantaneous chemical reaction is possible even in the best insulators and the hypothesis that chemical reaction is entirely due to ions is not rigidly true. Our conception of a reaction between a metal and a salt is entirely ionic, and it appeared interesting to determine how the electrical resistance of the solutions affects the displacement.

Experimental Method

To obtain trustworthy results, it is absolutely necessary that the purest substances obtainable should be used. The work was restricted only to the following solvents: benzene, toluene, nitrobenzene, aniline, chloroform, amyl alcohol, amyl acetate and ethyl acetate, and to the following metals: mercury, copper, lead, iron, tin, nickel, zinc and magnesium. The samples taken were in most cases Merck's extra pure reagents, and in several cases procured from Kahlbaum. The solvents used were then further purified with the greatest precaution in the laboratory. Perfectly pure and anhydrous

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[1] Jour. Phys. Chem., 15, 97–146 (1911).

[2] Ibid., 6, 6, 447 (1902); 9, 641 (1905).

salts were taken and mixed with the solvent. Whether any salt has passed into solution was determined in each case by analyzing a portion of the clear liquid above the salt. Glass tubes closed at one end and constricted at the other were washed thoroughly clean and kept in an air-bath having a temperature of 150° C for several hours. They were then cooled in the desiccator. Carefully cleansed, chemically pure, metal pieces were then put inside the tubes, and the solution poured into them as soon as it was prepared. The constriction was then quickly drawn out by means of the blowpipe and the tubes thus sealed were watched from time to time to see whether any reaction was taking place. The reaction was allowed to take place at room temperature, which was 21° C on the average. The tubes were broken open after several days, and both the metal and the solution were subjected to thorough chemical analysis. The deposit on the metals was often found to consist of both adherent and non-adherent layers. The non-adherent layer was separated from the metal by washing and boiling with distilled water, and then carefully analyzed.

Measurement of Specific Resistance

It is essential to measure the specific resistance of the solutions to be investigated, to determine whether the reactions are really ionic or not. The Kohlrausch method of determining conductivity could not be well applied for the measurement of extremely high resistance. The following well-known method was therefore adopted: A battery was connected to a high resistance galvanometer and a megohm in series, and the deflection of the galvanometer, x, was measured. The megohm was then put out of circuit, the conductivity cell substituted instead, and the deflection, y, determined. The resistance $= \frac{x}{y}$ megohm. If y is not of the same order of magnitude as x, the galvanometer is used with a shunt of known resistance and we have the resistance of the cell $\frac{S}{S+R} \cdot \frac{x}{y}$, where S is the resistance of the shunt and R the galvanometer resistance. The Kohlrausch method was always employed when the resistance of the solutions was rather low. Before use, the electrodes and the cell were perfectly dried in the desiccator. The specific resistance of some of the solvents are quite remarkable. Indeed some proved to be the best insulators. Thus benzene, toluene, aniline, nitrobenzene, chloroform, each had a specific resistance exceeding 500 million ohms, the limit of the sensitiveness of the instruments employed. The specific resistances of the solutions were generally found to be less than that of the solvent.

Experiments with $FeCl_3$ as Solute

Pure, anhydrous ferric chloride was prepared in the laboratory. It is easy to determine whether $FeCl_3$ has passed into solution, because of the reddish brown color which it imparts to the liquid. The results are given in Table I. The solution was analyzed by evaporating it to dryness and then proceeding in the usual way.

Table I

(a)

$FeCl_3$ in benzene. Time of exposure, 36 days. Specific resistance of solution—more than 500 million ohms

I Metal	II Analysis of metal	III Analysis of solution	IV Remarks
1. Mg	Gray adherent deposit containing iron	Colorless, contain considerable amount of Mg	Replacement
2. Zinc	Gray adherent deposit containing iron	Greenish, contain zinc	Replacement
3. Lead	Adherent black deposit containing iron	Clear and colorless, contain no lead	Replacement
4. Tin	Nonadherent gray deposit containing iron	Clear and colorless	Reduction certain
5. Copper	Adherent deposit of copper salt	Pale red, no copper	Reduction
6. Mercury	Clear and bright	Opaque with white granules of Hg_2Cl_2	Reduction

(*b*)

$FeCl_3$ in toluene
Time of exposure, 31 days
Specific resistance = 7500 million ohms

Metal	Observation
1. Mg	Replacement
2. Zinc	Replacement
3. Lead	Replacement
4. Tin	Replacement probable
5. Copper	Reduction
6. Mercury	Reduction

(*c*)

$FeCl_3$ in aniline
Time of exposure, 35 days
Specific resistance = 0.25 million ohms

Metal	Observation
1. Mg	Replacement
2. Zinc	Replacement
3. Lead	Replacement
4. Tin	Replacement
5. Copper	Replacement
6. Mercury	No reaction

(*d*)

$FeCl_3$ in nitrobenzene
Time of exposure, 34 days
Specific resistance = 5100 ohms

Metal	Observation
1. Mg	Replacement
2. Zinc	Replacement
3. Lead	Replacement
4. Tin	Replacement
5. Copper	Reduction
6. Mercury	Reduction

(*e*)

$FeCl_3$ in chloroform
Time of exposure, 26 days
Specific resistance = 2 million ohms

Metal	Observation
1. Mg	Replacement
2. Zinc	Replacement
3. Lead	Replacement
4. Tin	Replacement
5. Copper	Reduction

(*f*)

$FeCl_3$ in ethyl acetate
Time of exposure, 25 days
Specific resistance = 6000 ohms

Metal	Observation
1. Mg	Replacement
2. Zinc	Replacement
3. Tin	Replacement
4. Copper	Reduction

(*g*)

$FeCl_3$ in amyl acetate
Time of exposure, 30 days
Specific resistance = 21000 ohms

Metal	Observation
1. Mg	Replacement
2. Zinc	Replacement
3. Tin	Replacement
4. Copper	Reduction
5. Hg	Reduction

(*h*)

$FeCl_3$ in amyl alcohol
Time of exposure, 31 days

Metal	Observation
1. Mg	Replacement
2. Zinc	Replacement
3. Tin	Replacement
4. Copper	Replacement probable
5. Mercury	Reduction

From the above table (I) it will be noticed that in all the solvents used, magnesium, zinc and lead replace iron; tin replaces iron in the majority of cases; copper in aniline and probably in amyl alcohol solutions. Mercury can only reduce ferric salt to the ferrous state. It is peculiar that in aniline solution mercury has no action on ferric chloride. On examining the specific resistances of the different solutions, it will be observed that they vary from 4000 ohms in the case of amyl alcohol to upwards of 500 million ohms in the case of benzene, toluene, etc. It is remarkable, however, that the velocity of reduction of the ferric salts in the several solutions does not bear any proportion to the electrical resistances of the respective solutions. The $FeCl_3$ content of the majority of the solutions was approximately the same, as also the surface of each metal exposed to the various solutions. It was found, however, that the time taken for the complete reduction by a metal, of $FeCl_3$ in various solvents, as indicated by the complete decoloration of the solution, was not widely different.

Experiments with $HgCl_2$ as Solute

Pure $HgCl_2$ was recrystallized and dried carefully. Arctowski,[1] Sulc,[2] etc., have determined the solubility of $HgCl_2$ in various solvents. The experiments were performed in the same way as in the case of $FeCl_3$. Here, however, it is easy to determine whether the mercury salt has been replaced, from the shining appearance of the amalgamated metals.

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[1] Zeit. anorg. Chem., 6, 267 (1894).

[2] Ibid., 25, 401 (1900).

TABLE II

(*a*)

$HgCl_2$ in benzene. Time of exposure, 31 days
Specific resistance > 500 million ohms

Metal	Analysis of metal	Analysis of solution	Remarks
1. Mg	Amalgamated	Opalescent with granules of Hg_2Cl_2	Replacement
2. Zinc	Amalgamated, deposit of Hg_2Cl_2	Opaque with Hg_2Cl_2	Replacement
3. Iron	No change	Opaque with Hg_2Cl_2	Reduction
4. Lead	Amalgamated	Opaque with Hg_2Cl_2	Replacement
5. Copper	White on washing deposit of Hg_2Cl_2	Clear and colorless, contain no copper	Replacement

(*b*)

$HgCl_2$ in toluene
Time of exposure, 33 days
Specific resistance > 7500 million ohms

Metal	Observation
1. Mg	Replacement
2. Zinc	Replacement
3. Iron	Reduction
4. Lead	Replacement
5. Copper	Replacement

(*c*)

$HgCl_2$ in nitrobenzene
Time of exposure, 32 days
Specific resistance > 0.95 ohms

Metal	Observation
1. Mg	Replacement
2. Zinc	Replacement
3. Iron	Reduction
4. Lead	Replacement
5. Copper	Replacement

(*d*)

$HgCl_2$ in chloroform
Time of exposure, 32 days
Specific resistance > 500 million ohms

Metal	Observation
1. Mg	Replacement
2. Zinc	Replacement
3. Iron	Reduction
4. Lead	Reaction very slight
5. Copper	Replacement

(*e*)

$HgCl_2$ in ethyl acetate
Time of exposure, 28 days
Specific resistance = 45000 ohms

Metal	Observation
1. Mg	Replacement
2. Zinc	Replacement
3. Iron	Free globules of Hg, replacement
4. Lead	Reduction
5. Copper	Replacement

(*f*)

$HgCl_2$ in amyl acetate
Time of exposure, 27 days
Specific resistance = 10 million ohms

Metal	Observation
1. Mg	Replacement
2. Zinc	Replacement
3. Iron	Replacement
4. Lead	Reduction certain
5. Copper	Replacement

(*g*)

$HgCl_2$ in amyl alcohol
Time of exposure, 25 days
Specific resistance = 7.7 million ohms

Metal	Observation
1. Mg	Replacement
2. Zinc	Replacement
3. Iron	Replacement
4. Lead	Replacement
5. Copper	Replacement

(*h*)

$HgCl_2$ in aniline
Time of exposure, 30 days
Specific resistance = 1.5 million ohms

Metal	Observation
1. Mg	Replacement
2. Zinc	Replacement
3. Iron	Reduction
4. Copper	Replacement

It will be seen from Table II that magnesium, zinc and copper replace mercury in all cases. Iron replaces mercury only in ethyl acetate, amyl acetate and amyl alcohol solutions. It is peculiar that in chloroform solution lead seems to have no action on $HgCl_2$; otherwise the reduction of $HgCl_2$ to Hg_2Cl_2 is evident in all cases. It will be seen that the electrical resistance in benzene, toluene and chloroform solution is very great; here the reaction does not also proceed vigorously. The electrical resistance in aniline, nitrobenzene, ethyl acetate, amyl acetate and amyl alcohol is of the same order. The reduction to mercurous chloride in the last three solvents is quite vigorous, as judged by the appearance of milkiness. When magnesium is the reacting metal, milkiness appears almost instantaneously in them. In aniline and nitrobenzene solution, the reduction is much slower. Copper in aniline solution seems to be very reactive. That copper replaces iron in aniline solution has been noticed before.

Experiments with $Hg(CN)_2$ as Solute

It was thought interesting to determine whether the behavior of $Hg(CN)_2$ solutions is analogous to $HgCl_2$ solutions. Any difference in the behavior of the two might be set down as due to the influence of the negative radical of the salt. In aqueous solutions, both the salts are characterized by their remarkably small dissociation.

TABLE III

(a

$Hg(CN)_2$ in nitrobenzene. Time of exposure, 30 days
Specific resistance = 1.5 million ohms

Metal	Analysis of metal	Analysis of solution	Remarks
1. Mg	Clean and bright	No trace of Mg	No reaction
2. Zinc	Clean and bright	Zinc absent	No reaction
3. Iron	Clean and bright	Contain considerable iron	Replacement
4. Lead	Clean and bright	Lead absent	No reaction
5. Copper	White	Clear, greenish, contain copper	Replacement

(b)

$Hg(CN)_2$ in aniline
Time of exposure, 33 days
Specific resistance = 4.9 million ohms

Metal	Observation
1. Mg	No reaction
2. Zinc	No reaction
3. Iron	No reaction
4. Lead	No reaction
5. Copper	Replacement

(c)

$Hg(CN)_2$ in amyl alcohol
Time of exposure, 30 days
Specific resistance = 0.75 million ohms

Metal	Observation
1. Mg	Replacement, free globules of Hg
2. Zinc	No reaction
3. Iron	Replacement
4. Lead	Replacement
5. Copper	Replacement

(*d*)
$Hg(CN)_2$ in ethyl acetate
Time of exposure, 28 days
Specific resistance = 3 million ohms

Metal	Observation
1. Mg	No reaction
2. Zinc	No reaction
3. Iron	No reaction
4. Lead	Replacement
5. Copper	Replacement

(*e*)
$Hg(CN)_2$ in amyl acetate
Time of exposure, 38 days
Specific resistance = 20 million ohms

Metal	Observation
1. Mg	No reaction
2. Zinc	No reaction
3. Lead	No reaction
4. Iron	No reaction
5. Copper	Replacement

The remarkable difference between the behavior of $HgCl_2$ and $Hg(CN)_2$ solutions is apparent from the preceding table (III). The specific resistance of a $Hg(CN)_2$ solution is of the same order as that of the corresponding $HgCl_2$ solution. The extraordinary inertness of $Hg(CN)_2$ solutions could not therefore be attributed to poor conductivity. The base metals magnesium and zinc are rather conspicuous by their inactivity, magnesium only displacing Hg in amyl alcohol solution, zinc in none. On the other hand copper, which is the most electropositive of the group, was found to be uniformly active. Iron replaced mercury in nitrobenzene and amyl alcohol, while lead replaced it in amyl alcohol and ethyl acetate solution. In this connection it is interesting to notice that copper in aqueous solutions of KCN appears to be baser than zinc.

Replacement of Mercury Salts by Silver in Non-Aqueous Solutions

It is well known that the electrolytic solution pressures of Ag and Hg, in aqueous solution, are quite close to each other. To determine whether this relationship holds in other solvents, clean pieces of silver foil were allowed to act upon solutions of $HgCl_2$ and HgI_2 in ether, ethyl acetate, glycerine, carbon tetrachloride, chloroform, benzene, toluene and carbon disulphide. The solvents were purified with extreme care, *e. g.*, ether was twice distilled over sodium, ethyl acetate several times over fused $CaCl_2$, etc. In all the cases Hg was found to have amalgamated with Ag. In several cases, *e. g.*, in ethyl acetate, ether, glycerine, the silver foil became dull and grayish instantaneously. It is remarkable that in all the solvents used Ag and Hg retain the same order in replacement series as in water.

Experiments with CdI_2 as Solute

Pure CdI_2 was recrystallized and dried very carefully. The experiments were carried on as in the previous cases.

From Table IV it will be seen that magnesium replaced cadmium in all the solutions tried, whereas zinc could replace cadmium in none. It is peculiar that cadmium is replaced by iron in aniline, chloroform and amyl alcohol solutions, and by copper in aniline, chloroform, amyl alcohol and amyl

TABLE IV

(*a*)

CdI_2 in aniline. Time of exposure, 36 days
Specific resistance of solution = 1.35 million ohms

Metal	Analysis of metal	Analysis of solution	Remarks
1. Mg	Clean and bright	Contain considerable Mg	Replacement
2. Zinc	Clean and bright	Zinc absent	No reaction
3. Iron	Clean and bright	Contain iron	Replacement
4. Copper	Clean and bright	Contain considerable copper	Replacement
5. Hg	No reaction	....	No reaction

(*b*)

CdI_2 in chloroform
Time of exposure, 33 days
Specific resistance > 500 million ohms

Metal	Observation
1. Mg	Replacement
2. Zinc	No reaction
3. Iron	Replacement
4. Copper	Replacement
5. Mercury	No reaction

(*c*)

CdI_2 in amyl alcohol
Time of exposure, 34 days
Specific resistance = 1.5 million ohms

Metal	Observation
1. Mg	Replacement
2. Zinc	Replacement
3. Iron	Replacement
4. Lead	No reaction
5. Copper	Replacement
6. Mercury	No reaction

(*d*) CdI_2 in amyl acetate Time of exposure, 25 days Specific resistance = 0.35 million ohms		(*e*) CdI_2 in ethyl acetate Time of exposure, 34 days Specific resistance = 0.25 million ohms	
Metal	Observation	Metal	Observation
1. Mg	Replacement	1. Mg	Replacement
2. Zinc	No reaction	2. Zinc	No reaction
3. Iron	No reaction	3. Tin	No reaction
4. Lead	Replacement	4. Lead	Replacement
5. Copper	Replacement	5. Copper	No reaction

acetate solutions. In aqueous solutions copper is far nobler than cadmium. The very high resistance of chloroform solutions did not, as in previous cases, prevent the replacement of salts by metals.

Experiments with Lead Oleate as Solute

No suitable inorganic salt of lead could be found which is soluble in a large number of organic solvents. An organic salt of lead was used in the experiments. Pure lead oleate from Merck was carefully heated in the air bath until the whole melted. The sample should not be allowed to char. Whether any lead has passed into solution was determined by evaporating the solution, dissolving the residue in nitric acid and then examining the solution for lead.

TABLE V

(*a*)

Lead oleate in aniline. Time of exposure, 33 days

Metal	Analysis of metal	Analysis of solution	Remarks
1. Mg	Bright and clean	Slight Mg present	Replacement probable
2. Zinc	Black deposit, contain lead	Contain considerable zinc	Replacement
3. Iron	Clean	Brownish, contain iron	Replacement
4. Copper	Black deposit, contain lead	Copper present	Replacement.
5. Mercury	Clean and bright	Mercury absent	No reaction

(*b*)

Lead oleate in benzene
Time of exposure, 39 days
Specific resistance = 420 million ohms

Metal	Observation
1. Mg	Replacement
2. Zinc	Replacement
3. Iron	No reaction
4. Copper	Replacement

(*c*)

Lead oleate in toluene
Time of exposure, 34 days
Specific resistance = 330 million ohms

Metal	Observation
1. Mg	Replacement
2. Zinc	Replacement
3. Iron	Replacement probable
4. Copper	Replacement

(*d*)

Lead oleate in chloroform
Time of exposure, 34 days
Specific resistance > 500 million ohms

Metal	Observation
1. Mg	Replacement
2. Zinc	Replacement
3. Iron	No reaction
4. Copper	Replacement
5. Mercury	No reaction

(*e*)

Lead oleate in nitrobenzene
Time of exposure, 37 days
Specific resistance = 140 million ohms

Metal	Observation
1. Mg	Replacement
1. Zinc	Replacement
3. Iron	No reaction
4. Copper	Replacement
5. Mercury	No reaction

(*f*)

Lead oleate in amyl alcohol
Time of exposure, 29 days

Metal	Observation
1. Mg	Replacement
2. Zinc	Replacement
3. Iron	Replacement
4. Copper	Replacement
5. Mercury	No reaction

(*g*)

Lead oleate in ethyl acetate
Time of exposure, 33 days
Specific resistance = 2.1 million ohms

Metal	Observation
1. Mg	Replacement
2. Zinc	Replacement
3. Iron	No reaction
4. Tin	No reaction
5. Copper	Replacement

It will be noticed from Table V that magnesium and zinc replaces lead in all the solvents used. The behavior is therefore the same as in aqueous solutions. The replacement by copper of the lead salt in all the non-aqueous solutions is, however, quite interesting, for copper is nobler than lead in aqueous solutions. Iron could not replace lead in benzene, chloroform, nitrobenzene and ethyl acetate solution, and mercury could replace it in none. Here, too, the velocity of replacement cannot be connected in any way with the electrical resistance of the solution.

Conclusion and Summary

It thus becomes evident that the arrangements of the metals according to their relative basicity in the various solvents do not coincide with one another or with the electrochemical series. Below are given tables of the electrochemical series and the number of solvents in which a salt is replaced by a metal:

Electrochemical series		No. of solvents out of a total of 8 in which $FeCl_3$ is replaced by the respective metal.	
	Normal potential		
1. Mg	1.55	—	
2. Zn	0.76	—	
3. Fe	0.43	Mg	8
4. Cd	0.40	Zn	8
5. Pb	0.12	Pb	8
6. Tin	0.10	Tin	6
7. Cu	0.34	Cu	2
8. Hg	0.86	Hg	0

No. of solvents out of 5 in which CdI_2 is replaced by the respective metal		No. of solvents out of 7 in which lead oleate is replaced by a metal		No. of solvents out of 8 in which $HgCl_2$ is replaced by a metal	
Mg	5	Mg	7	Mg	8
Zn	0	Zn	7	Zn	8
Fe	3	Iron	4	Fe	3
Cu	4	Cu	7	Pb	
		Hg	0	Cu	8

No. of solvents out of 5 in which $Hg(CN)_2$ is replaced by a metal	
Mg	1
Zn	0
Iron	2
Lead	2
Cu	5

It is thus clear that the replacement series is not at all a "characteristic of the metal but is dependent upon the mutual relationship of the metals, the acid radicals, and the solvent present in any given combination."

It has been shown that replacement of one metal by another is possible even in the best insulators. The velocity of reaction in a solution having a resistance upwards of 500 million ohms is indeed slow, but never nil. The change in velocity when we pass from one solvent to another is also not comparable to the change in electrical resistance.

My best thanks are due to Professors Ray and Bhaduré.

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THE DIELECTRIC CONSTANTS OF SOME COMPOUNDS OF VANADIUM[1]

BY ALBERT G. LOOMIS AND HERMAN SCHLUNDT

We have continued the measurements of dielectric constants in this laboratory by determining the dielectric capacities of some compounds of vanadium that are liquid at ordinary temperatures. The tetrachloride, VCl_4, the oxychloride, $VOCl_3$, and the oxybromide, $VOBr_3$, were prepared and their dielectric constants measured at several temperatures.

Measurements.—The measurements were conducted with the standard apparatus of Drude-Schmidt used in former investigations.[2] Since the compounds studied react readily with water vapor the rectified samples were measured in sealed cells of the type used by Schaefer and Schlundt for liquid hydrogen chloride.[3] Some of the compounds are, moreover, somewhat sensitive to light and are unstable,—the oxybromide, $VOBr_3$, decomposes gradually *in vacuo* in the dark at room temperatures. Hence the measurements were conducted with freshly prepared samples. Several determinations were made with different samples of each compound in cells whose dielectric capacity differed somewhat.

The cells were calibrated with the standard solutions of acetone and benzene recommended by Drude. At least four points were determined in obtaining the calibration curves by plotting scale readings against dielectric constants. Each scale reading plotted represents the average of ten settings for resonance—five by each of us. To guard against errors that may be introduced by accidental displacements of the plates of the cells or by slight changes in the spark gap and other parts of the apparatus the cells were recalibrated after

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[1] Abstract of a thesis submitted in the Graduate School of the University of Missouri by Albert G. Loomis in partial fulfillment of the requirements for the degree of Master of Arts, June, 1915.

[2] Jour. Phys. Chem., 11, 699 (1907); 13, 669 (1909).

[3] Ibid., 13, 671 (1909).

each series of measurements of one of the vanadium compounds.

Preparation of Compounds.—The samples of vanadium oxychloride, $VOCl_3$, were prepared by the method of Roscoe:[1] Dry chlorine is passed over a heated mixture of vanadium trioxide and sugar charcoal and the distillate caught in an atmosphere of carbon dioxide. We followed the details of Roscoe's method given by Prandtl and Bleyer[2] for the preparation of pure vanadium oxychloride from which the atomic weight of vanadium was determined. The vanadium oxide used was prepared from iron vanadate containing about thirty percent of vanadic acid, V_2O_5, kindly furnished by the National Radium Institute through the courtesy of Mr. R. B. Moore, in charge of the radium investigations U. S. Bureau of Mines, Denver, Colorado. The vanadic oxide was extracted from this material in the following manner: The powdered iron vanadate was decomposed by hydrochloric and nitric acids. The nitric acid was added to oxidize the iron to the ferric condition, and also vanadium trioxide to vanadium pentoxide. The excess acid was evaporated off, the residue taken into solution with water and boiled for half an hour with an excess of sodium carbonate. The iron, calcium, and traces of aluminium were thus precipitated and sodium vanadate remained in solution. The filtrate was made slightly acid with acetic acid, and then ammonia added until just neutral. Practically all the vanadic acid was precipitated out since the solubility of vanadic acid in water is slight. Vanadic acid obtained in this manner consists of both the yellow and red modifications.

The vanadium pentoxide thus obtained was mixed with an equal weight of sugar charcoal, and a dry stream of hydrogen was passed over this mixture in a reduction tube heated to redness and continued until no more moisture was given off. Then a current of dry carbon dioxide was substituted for the hydrogen, and the tube and contents dried thoroughly by heat-

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[1] Phil. Trans., 158, 1 (1868).

[2] Zeit. anorg. Chem., 67, 257 (1910).

ing to redness for an hour. The receiver, a distilling flask, was then sealed on and a stream of dry chlorine was passed over the dry mixture of vanadium trioxide and charcoal. The reaction took place readily and a practically quantitative yield was obtained. The condensed product was wine colored, due to the presence of some vanadium tetrachloride formed at the same time as the vanadium oxychloride.

The crude sample of oxychloride was purified by fractional distillation over metallic sodium in an atmosphere of carbon dioxide. A series of distilling flasks and three-way stopcocks were sealed together in such a way that only the middle portion of the second distillation was collected in the cells. Five cells were filled and sealed off. The purified samples were colored citron-yellow with no vanadium tetrachloride present, and boiled at 124° to 125° under a pressure of 740 mm.

We also tried the method of Ephraim[1] for preparing vanadium oxychloride free from tetrachloride by passing dry hydrogen chloride over a mixture of vanadium pentoxide and phosphorus pentoxide. The latter prevents the decomposition of the vanadium oxychloride by the water formed in the reaction. While practically pure vanadium oxychloride was obtained, the yield was very small, because the reaction mixture caked so badly that only a surface reaction resulted. We had difficulty in breaking up the cake without introducing moisture which is highly objectionable. The samples used in the measurements were all prepared by the method of Roscoe.

There is only one recorded method for the preparation of vanadium oxybromide, $VOBr_3$, that of Roscoe,[2] which involves the same principle as the method for the preparation of vanadium oxychloride.

Considerable difficulty was experienced in preparing this compound in the pure state. Vanadium oxybromide decomposes gradually at ordinary temperature and quite suddenly, according to Roscoe, at 180° into a solid vanadium oxydibromide and free bromine. Most of our failures, however, were

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[1] Zeit. anorg. Chem., 35, 66 (1903).

[2] Ann. Chemie. Pharm. Suppl., 8, 99 (1872).

caused by traces of moisture in the reaction tube. This disturbing factor was remedied by heating the reaction tube to redness for six hours and maintaining a current of dry hydrogen followed by a current of carbon dioxide. After the tube had cooled somewhat a steady stream of carbon dioxide laden with bromine vapor was passed over the mixture in the reaction tube, and vanadium oxybromide was obtained in quantity. The heating of the reaction mixture was conducted in a glazed porcelain tube whose ends fitted into glass adaptors with asbestos packing, which makes a practically air-tight joint. All glass connections were seals. The reaction was carried out at considerably below red heat, contrary to Roscoe's statement that the reaction mixture should be maintained at red heat.

The crude samples of vanadium oxybromide were purified by distillation under diminished pressure. The boiling point at 90 mm pressure was 130°, and 118° at 78 mm. Roscoe gives 130° to 136° at 100 mm pressure. This constant and the specific gravity are the only physical constants of the compound recorded in the literature. The samples used for the measurements were beautiful ruby-red, mobile, transparent liquids having very much the appearance of bromine with the exception of transparency.

The freezing point of vanadium oxybromide lies between —58° and —60°, which was determined by noting the temperature at which the compound previously solidified with liquid air melted as the temperature of a mixture of alcohol and liquid air in a Dewar tube gradually rose. The temperature readings were made with a standardized pentane thermometer. An attempt to solidify the liquid enclosed in a sealed tube by immersing it in a mixture of carbon dioxide snow and ether for fully five minutes failed. As the temperature of the Thilorier mixture is —79° it appears that the liquid can be greatly supercooled.

The samples of vanadium tetrachloride were prepared by the method of Mertes.[1] According to this method dry

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[1] Jour. Am. Chem. Soc., 35, 671 (1913).

chlorine is passed over ferro-vanadium heated in a combustion tube in a furnace. The product contains some ferric chloride from which pure samples of vanadium tetrachloride were obtained by fractioning the liquid twice and distilling the middle portion directly into the measuring cells. The samples obtained were dark red, somewhat viscous and opaque. The boiling point was found to be 150° to 153° under a pressure of 742 mm.

Results.—The values obtained for the dielectric constants at different temperatures are given in the following table:

Compound	No of sample	Temperature	D. C.	Temperature coefficient
Vanadium oxychloride, $VOCl_3$	1	21	3.44	
	2	21	3.47	
	3	21	3.28	
	4	—70	3.38	—0.03%
		26	3.54	
	5	26	3.35	
Vanadium oxybromide, $VOBr_3$	1	20	3.70	
	2	—70	4.38	—0.2%
		30	3.60	
	3	—2	3.93	—0.3%
		26	3.57	
	4	26	3.61	
Vanadium tetrachloride	1	25	3.07	
	2	25	3.03	

The average of the values found for the dielectric constant of vanadium oxychloride at room temperature is 3.42, that of vanadium oxybromide is 3.62, and that of vanadium tetrachloride is 3.05. It is seen that the dielectric constants of these compounds are relatively low, and hence according to the Nernst-Thomson rule the dissociating power of these liquids when used as solvents should be very small. Experiments on the solvent and dissociating power of these compounds have not been made. The electrical conductivity of the liquids is very low.

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A STUDY OF THE TERNARY SYSTEM: CARBON TETRACHLORIDE, ALCOHOL AND WATER

BY HARRY A. CURTIS AND ESBON Y. TITUS

Introduction

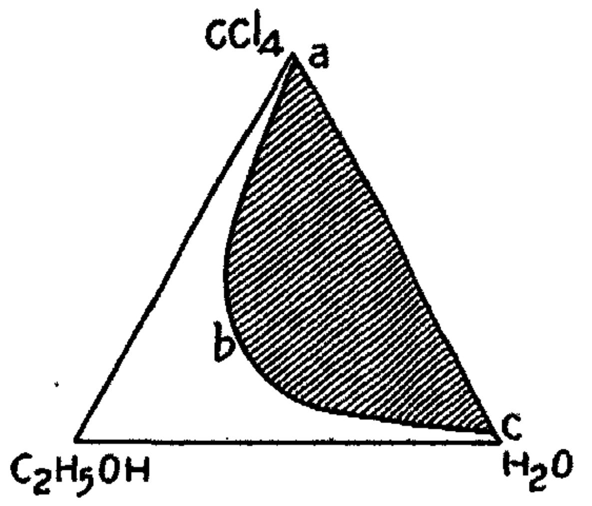

Fig. I

Carbon tetrachloride and alcohol are miscible in all proportions, as are also alcohol and water. Water and carbon tetrachloride, however, dissolve in each other only in very small amounts. A mixture of the three liquids forms either one or two layers, depending upon the relative proportions of the three components present and upon the temperature. If the ternary system be represented in the usual way, Fig. I, there will be a certain region, that shaded in the figure, within which two layers will exist, all mixtures not represented by points within the shaded area forming but one liquid phase. Since the mutual solubility of liquids is, in most cases, increased by increasing the temperature, the critical solubility curve, *a b c*, will approach the CCl_4-H_2O line as the temperature is raised. If temperatures be represented in a direction at right angles to the plane of the triangle the equilibrium between the one and two phase systems will be represented by a surface sloping toward one side of the right prism. The first part of the present paper locates the curve *a b c* for the isotherm 19.75°, and also locates several lines in the critical temperature surface from which the shape of the surface may be inferred. The second part of the paper contains a study of the density and index of refraction of various homogeneous mixtures of the three components. It was at first thought that sufficient data concerning density and refractive index could be gathered to make possible the analysis of any homogeneous mixture of carbon tetrachloride, alcohol and water by simply determining the value of these two properties for the unknown mixture. As the work progressed, however, it became evident that even after the immense amount of necessary data had been obtained, the problem would still remain indeterminate for certain mixtures, as will be shown later. These measurements were therefore discontinued after sufficient data had been taken to show the change in density and index of refraction for any given change in composition of the system.

Chemicals Used

The alcohol was prepared from the laboratory supply of absolute alcohol. This was further dehydrated for two weeks with anhydrous copper sulphate and twice distilled, the middle fraction of the distillate being taken each time. Kahlbaum's carbon tetrachloride was used. It was first distilled, the middle portion allowed to stand over fused potassium hydroxide for a week, and then redistilled. The part used all distilled over within less than one-tenth degree range. The water used was distilled.

Critical Solubility Data

The critical solubility curve *a b c* for the 19.75° isotherm was determined as follows: Six different mixtures of carbon tetrachloride and water were made up, the amounts of each component being accurately weighed. These mixtures were placed in large test tubes and brought to 19.75° in a glass thermostat. Alcohol was then added from a weight burette to each mixture in turn, the mixture being vigorously stirred meanwhile, until the critical point was reached. At the critical point the mixture becomes homogeneous. The various critical concentrations are recorded in Table I, and the results are shown graphically in Fig. II. The points in Fig. II marked thus: ⊖ were obtained by interpolation for 19.75° from Fig. III. It is not to be expected that these points are as accurately located as those determined for the isotherm.

TABLE I

Temperature 19.75°

Percent CCl_4	Percent C_2H_5OH	Percent H_2O
25.46	50.50	24.04
41.94	43.19	14.87
17.00	51.95	31.05
33.07	47.68	19.25
10.53	50.97	38.50
14.02	51.56	34.42

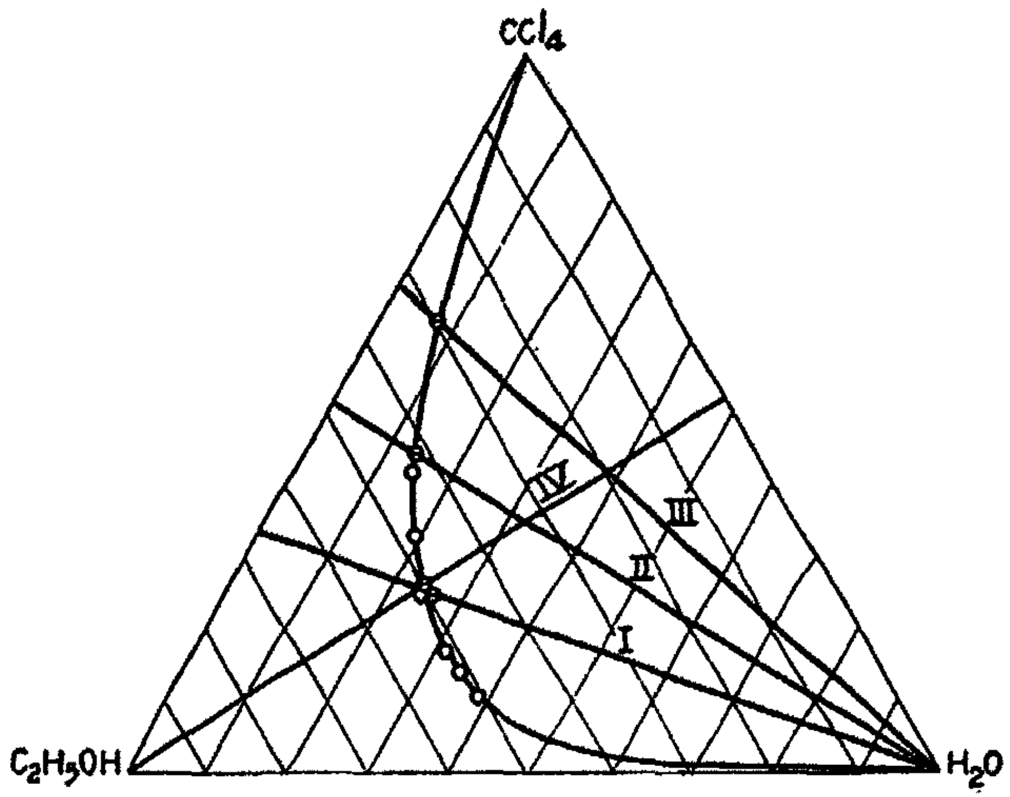

Fig. II

The curve *a b c* intersects the CCl_4-H_2O side of the triangle very near the corners, water and carbon tetrachloride being almost immiscible. Rex[1] gives the solubility of carbon tetrachloride in water as 0.8 g per liter at 20°. This value must be considered as only an approximation, however, since his method did not take into account the solubility of water in carbon tetrachloride.

The effect of temperature on the mutual solubility of

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[1] Zeit. phys. Chem., 55, 355 (1906).

the components, *i. e.*, the shape of the critical solubility surface, was studied as follows: To a known mixture of two of the components, the third component was added in small amounts from a weight burette until, on lowering the temperature, separation into two layers occurred. The critical solubility temperature of this mixture was then determined by raising and lowering the temperature through the critical point several times. A further amount of the third component was then added and the critical solubility temperature again determined. These operations were continued until, at the higher temperatures, the volatility of the carbon tetrachloride prevented further accurate measurements.

It is evident that all the concentrations in this series lie in a straight line drawn from that point on the side of the triangle which represents the original binary mixture to that corner of the triangle which represents the third component, such a line as I in Fig. II.

Consider a plane containing this line and standing at right angles to the plane of the triangle; the various critical solution temperatures plotted against the corresponding amounts of the third component will give a curve lying in this plane and representing the intersection of the plane

TABLE II

I Ratio CCl_4/C_2H_5OH = 0.5048		II Ratio CCl_4/C_2H_5OH = 1.0646	
Percent H_2O	Crit. sol. temp.	Percent H_2O	Crit. sol. temp.
24.25	−1.8°	12.47	2.03°
24.61	+3.6	13.95	23.9
25.13	10.6	14.45	29.8
25.64	17.0	14.85	35.4
26.14	24.5	15.3	39.55
26.59	28.55	15.67	42.75
27.15	31.45	16.02	45.5
27.71	32.75[1]		
28.52	35.5[1]		

[1] Not accurate; CCl_4 distilling off.

Table II—(*Continued*)

III Ratio CCl_4/C_2H_5OH = 2.1012		IV Ratio CCl_4/H_2O = 1.0922	
Percent H_2O	Crit. sol. temp.	Percent C_2H_5OH	Crit. sol. temp.
6.84	12.7°	47.43	44.5°
7.16	21.55	47.56	42.2
7.35	27.2	47.83	39.5
7.54	31.3	48.19	35.1
7.84	36.8	48.6	30.6
8.02	39.75	49.08	25.4
8.28	44.1	49.61	19.9
		50.07	14.6
		50.50	9.15
		51.06	1.6

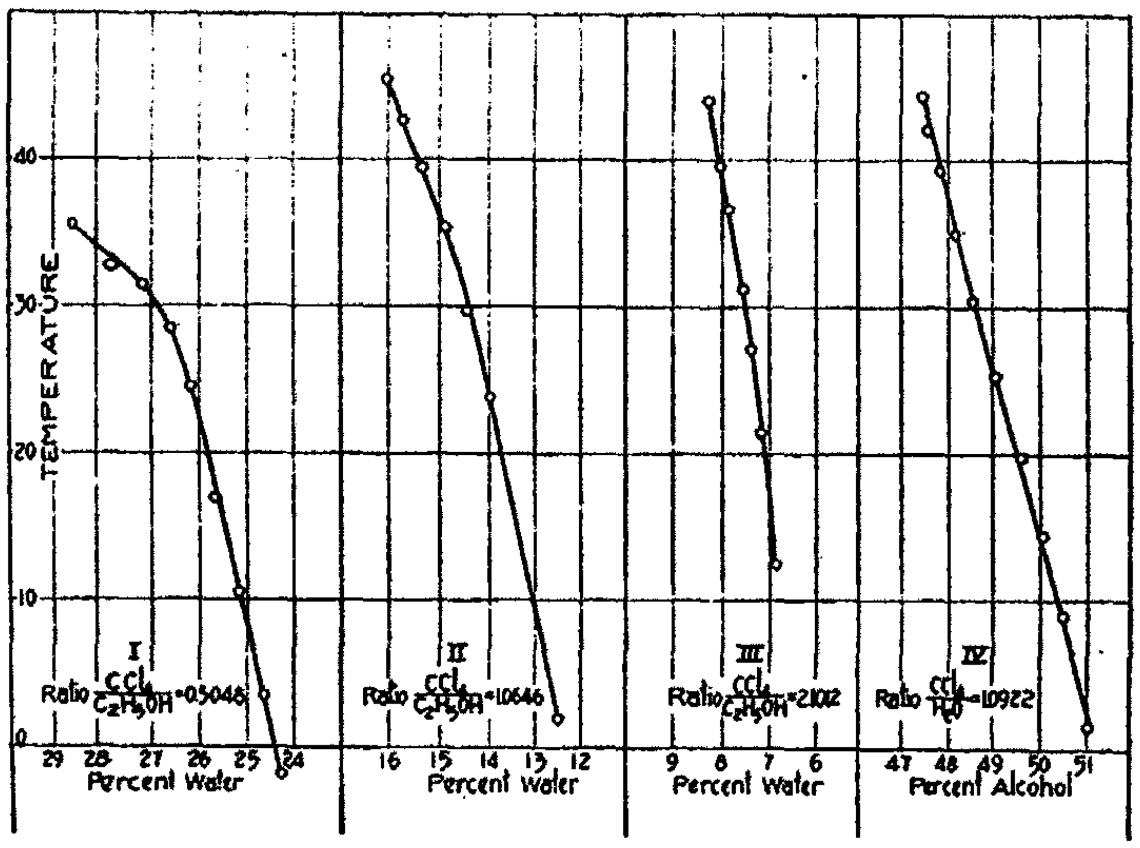

Fig. III

with the critical solubility surface. By determining several of these intersection curves, beginning with different binary mixtures, the general shape of the critical solubility surface may be inferred. In Fig. II, the lines I, II, III and IV represent the various series of ternary mixtures used. Table II gives the various critical solubility temperatures and the corresponding compositions, while Fig. III shows graphically the intersections of the planes containing the lines I, II, III and IV of Fig. II with the critical solubility surface. It will be noted that the percentages of water and of alcohol in Fig. III are plotted on a very much larger scale than is used in the triangle. This was done in order to show more clearly the effect of temperature on solubility. The critical solubility surface rises very abruptly from the triangle, *i. e.*, temperature has very little effect on the mutual solubility of the three components.

Refractive Index and Density

The determination of refractive index and density were naturally limited to such ternary mixtures as form but one liquid phase at the temperature used, *i. e.*, to such mixtures as would be represented by points lying within the unshaded area of Fig. I. Various mixtures of two of the components were made, and to each of these in turn varying amounts of the third component were added, refractive index and density being taken on each ternary mixture thus obtained. The compositions of the ternary systems used are shown on Curves V, VI, VII, etc., of Fig. IV. Tables III, IV, V, etc.,

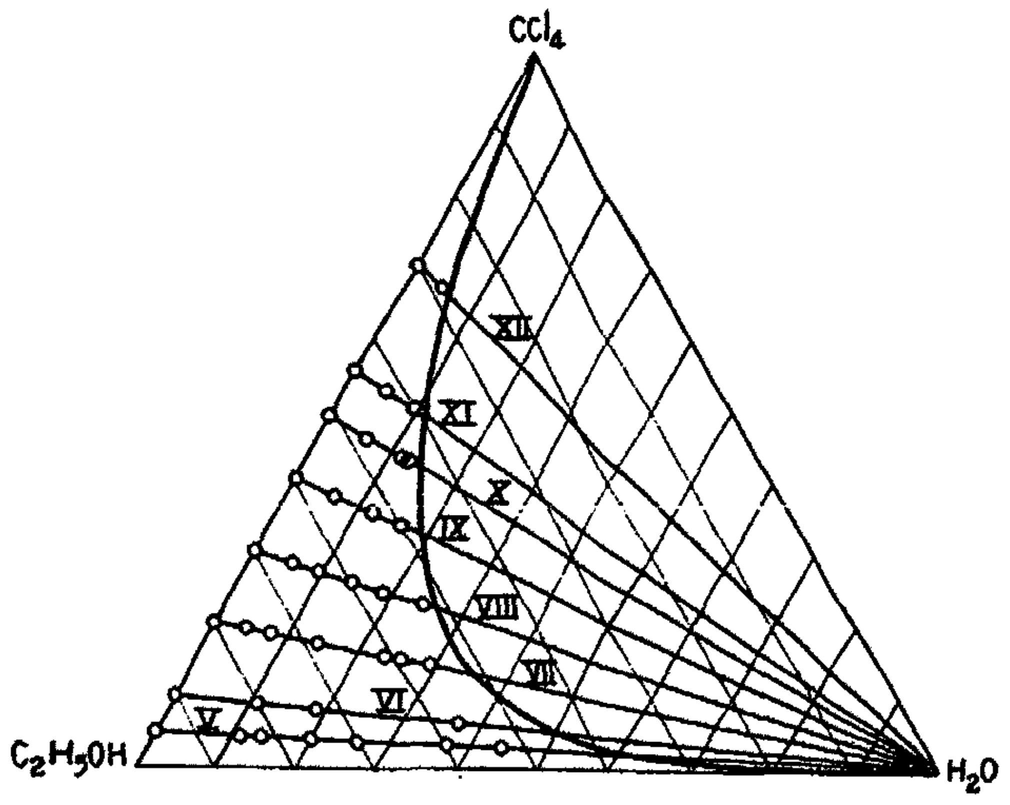

Fig. IV

TABLE III

Series V of Fig. IV. Ratio CCl_4/C_2H_5OH = 0.05086

Percent CCl_4	Percent C_2H_5OH	Percent H_2O	Density	Index
4.84	95.16	0.0	0.8121	1.3637
4.30	84.49	11.21	0.8422	1.3662
4.17	82.00	13.83	0.8485	1.3664
3.86	75.93	20.21	0.8634	1.3665
3.57	70.28	26.15	0.8768	1.3661
3.05	59.97	36.98	0.9004	1.3646
2.71	53.17	44.12	0.9148	1.3630

TABLE IV

Series VI of Fig. IV. Ratio CCl_4/C_2H_5OH = 0.1096

Percent CCl_4	Percent C_2H_5OH	Percent H_2O	Density	Index
9.88	90.12	0.0	0.8339	1.3665
8.78	80.09	11.13	0.8619	1.3687
8.01	73.06	18.93	0.8791	1.3684
6.21	56.60	37.19	0.9156	1.3659

TABLE V

Series VII of Fig. IV. Ratio CCl_4/C_2H_5OH = 0.2555

Percent CCl_4	Percent C_2H_5OH	Percent H_2O	Density	Index
20.35	79.65	0.0	0.8830	1.3727
19.45	76.11	4.44	0.8935	1.3735
18.78	73.47	7.76	0.9005	1.3735
17.38	68.02	14.60	0.9117	1.3732
15.58	60.96	23.46	0.9259	1.3719
15.14	59.26	25.60	0.9315	1.3711
14.36	56.20	29.44	0.9371	1.3705

TABLE VI

Series VIII of Fig. IV. Ratio CCl_4/C_2H_5OH = 0.4319

Percent CCl_4	Percent C_2H_5OH	Percent H_2O	Density	Index
30.16	69.84	0.0	0.9342	1.3788
28.43	65.83	5.74	0.9451	1.3794
27.27	63.15	9.59	0.9510	1.3789
25.79	59.72	14.49	0.9574	1.3782
24.45	56.61	18.94	0.9627	1.3770
22.84	52.89	24.27	0.9686	1.3756

TABLE VII

Series IX of Fig. IV. Ratio CCl_4/C_2H_5OH = 0.6313

Percent CCl_4	Percent C_2H_5OH	Percent H_2O	Density	Index
40.35	59.65	0.0	1.0060	1.3872
37.84	55.95	6.22	1.0114	1.3855
35.45	52.41	12.14	1.0153	1.3845
33.79	49.96	16.25	1.0172	1.3829
33.75	49.90	16.35	1.0167	1.3828

TABLE VIII

Series X of Fig. IV. Ratio CCl_4/C_2H_5OH = 0.9600

Percent CCl_4	Percent C_2H_5OH	Percent H_2O	Density	Index
48.98	51.02	0.0	.0594	1.3936
45.85	47.76	6.39	1.0614	1.3917
43.18	44.98	11.84	1.0619	1.3895
42.74	44.52	12.74	1.0605	1.3888

TABLE IX

Series XI of Fig. IV. Ratio CCl_4/C_2H_5OH = 1.2381

Percent CCl_4	Percent C_2H_5OH	Percent H_2O	Density	Index
55.32	44.68	0.0	1.1093	1.4000
52.37	42.30	5.33	1.1076	1.3978
49.98	40.37	9.64	—	1.3955

TABLE X

Series XII of Fig. IV. Ratio CCl_4/C_2H_5OH = 2.3614

Percent CCl_4	Percent C_2H_5OH	Percent H_2O	Density	Index
70.25	29.75	0.0	1.2346	1.4139
66.92	28.35	4.71	1.2246	1.4118

record the values of density and of refractive index for the various compositions along the Curves, V, VI, VII, etc., of Fig. IV. The densities were taken in a 50 cc pycnometer at 19.4° and refer to water at this temperature. The refractive indices were taken at 19.4° with an Abbe refractometer adjusted for the sodium D line. Water from a large thermostat was circulated constantly through the refractometer. Each mixture was placed for some time in the thermostat before transferring to the refractometer, and it was allowed to stand about two minutes in the refractometer before taking the reading. All thermometers used were compared with a "normal" thermometer standardized by the Reichsanstalt.

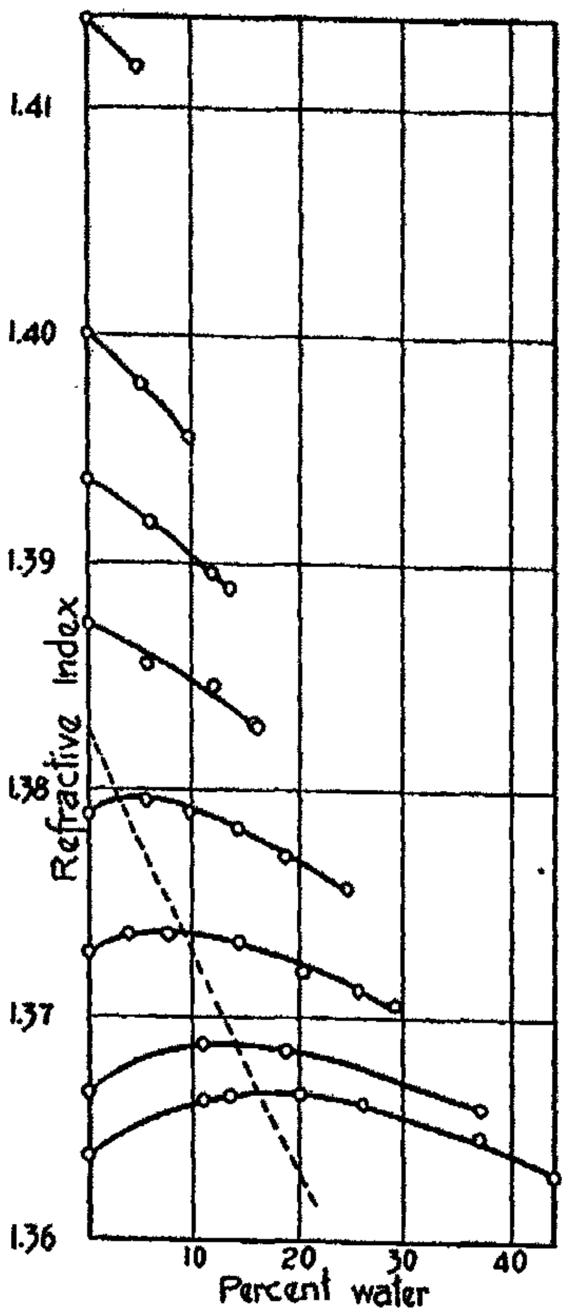

Fig. V

If the refractive indices of Table III be plotted against the corresponding percentages of water, the resulting graph, shown in the lowest curve of Fig. V, represents the behavior of the refractive index as water is added to a mixture containing carbon tetrachloride and alcohol in the ratio 0.05086 : 1. It will be noted that the index passes through a maximum.

If the densities recorded in Table III be plotted against the corresponding amounts of water, the resulting graph, shown in the lowest curve of Fig. VI, represents the behavior of the density as water is added to a mixture containing carbon tetrachloride and alcohol in the ratio 0.05086 : 1. The density curve for this series rises steadily as water is added. It is obvious that the specific refractions of such ternary mixtures as are represented in this series cannot be calculated from the specific refractions of the components.

If the refractive indices of Tables III, IV, V, VI, VII, VIII, IX and X be plotted against the corresponding amounts of water, the curious fact is brought out in Fig. V that the maximum index of refraction is reached with less and less water as mixtures relatively richer in carbon tetrachloride are used, until finally, with mixtures containing initially more than about thirty-five percent of carbon tetrachloride, the addition of water decreases the refractive index continuously.

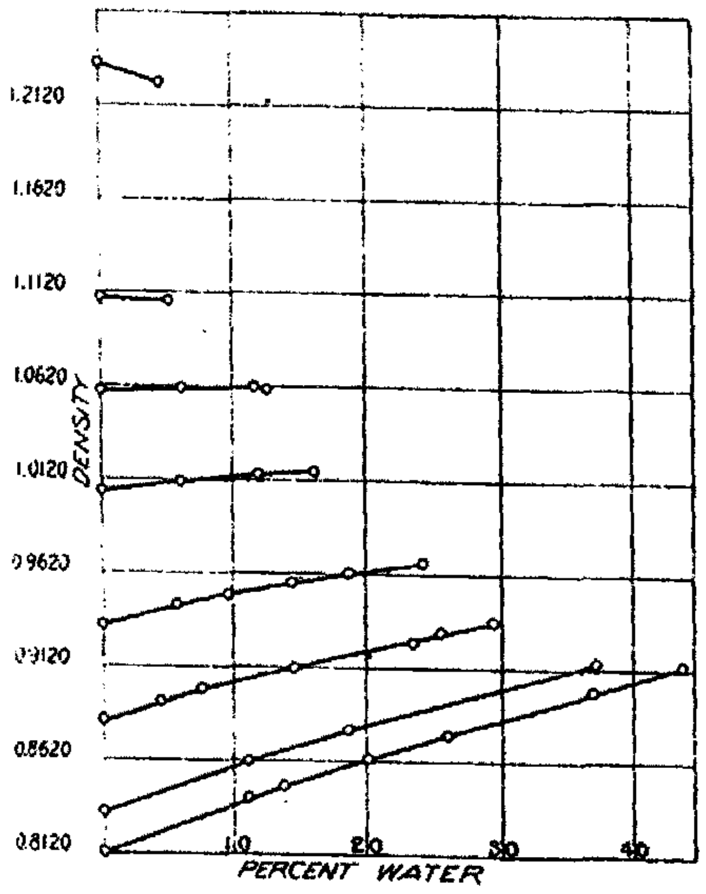

Fig. VI

In Fig. VI, the densities recorded in Tables III, IV, V, VI, VII, VIII, IX and X are plotted against the corresponding amounts of water. As is to be expected, the addition of water to a mixture rich in alcohol increases the density, while the addition of water to a mixture rich in carbon tetrachloride decreases the density. It is to be noted, however, that the slope of the curve does not pass through zero at the point where the density of the initial alcohol-carbon tetrachloride mixture is unity, but at a point considerably higher than this, showing that the volume of the mixture is less than the sum of the volumes of the components.

Since no data regarding the density or refractive index of alcohol-carbon tetrachloride mixtures appear in Landolt and Börnstein's "Tabellen," Table XI has been prepared from measurements taken during the course of the present investigation.

TABLE XI

Percent CCl_4	Percent C_2H_5OH	Density	Index	Percent CCl_4	Percent C_2H_5OH	Density	Index
100.00	0.00	—	1.4604	48.98	51.02	1.0594	1.3936
94.60	5.40	1.5145	1.4499	46.74	53.26	—	1.3918
91.25	8.75	—	1.4440	40.35	59.65	1.0060	1.3872
90.86	9.14	1.4621	1.4432	36.74	63.26	—	1.3838
85.60	14.40	1.3947	1.4348	30.16	69.84	0.9342	1.3788
83.50	16.50	—	1.4319	24.90	75.10	—	1.3755
78.68	21.32	1.3143	1.4251	20.35	79.65	0.8830	1.3727
77.04	22.96	—	1.4234	18.23	81.77	—	1.3717
72.57	27.43	1.2507	1.4174	9.88	90.12	0.8339	1.3665
70.25	29.75	1.2346	1.4139	9.16	90.84	—	1.3661
68.98	31.02	—	1.4135	4.84	95.16	0.8121	1.3637
59.56	40.44	—	1.4031	3.90	96.10	—	1.3633
55.32	44.68	1.1093	1.4000				

It was stated in the introduction to this paper that the determination of the two physical properties, index of refraction and density, of a ternary mixture does not always suffice to determine its composition. The attempt will now be made to establish the truth of this statement.

Consider, in Fig. VII, that the curves C, D, E, F, G and H are a series of such index of refraction curves as shown in Fig. V.. Let the line AB represent the refractive index of the carbon tetrachloride-alcohol-water mixture of unknown composition. The line AB cuts each of the curves C, D, E, etc., in two points. Knowing the ratio of the carbon tetrachloride to alcohol for each of the lines, C, D, E, etc., and the percentage water from the intersection points with AB, there may be plotted on the triangular composition diagram a curve which will obviously represent an infinite number of ternary mixtures having the given index of refraction. Since AB cuts each of the index curves in two points, the curve on the triangular composition diagram will be of some such shape as RST in Fig. VIII.

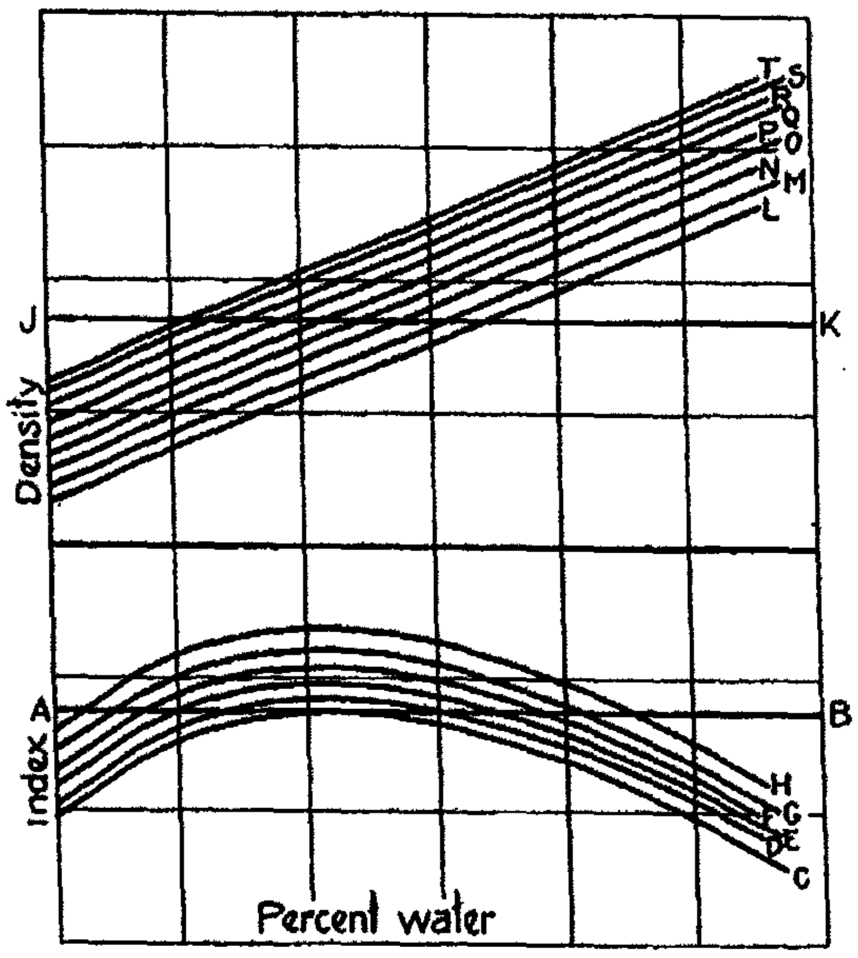

Fig. VII

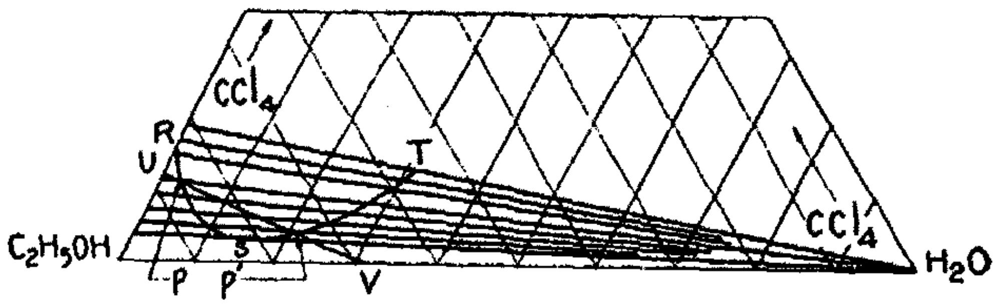

Fig. VIII

Likewise, suppose that Curves L, M, N, O, P, Q, R, S and T are density curves similar to that plotted in Fig. VI, and let the line JK be the density of the unknown mixture. On calculating the compositions as before, these may be plotted on the triangular composition diagram, and the curve thus obtained will represent an infinite number of ternary mixtures having the given density. If the given density be that of a binary mixture of carbon tetrachloride and alcohol of composition U, Fig. VIII, there will obviously be a binary mixture of alcohol and water, say V, having the given density, and the line representing the infinite series of ternary mixtures having the given density will connect these two points on the sides of the triangle. Such a line may cut the index line in two points, such as *p* and *p'*, each of which represents a ternary mixture having both the density and refractive index of the unknown mixture.

Summary

The following data regarding the ternary system carbon tetrachloride, alcohol, and water have been secured in this investigation:

1. The equilibrium line between the one-liquid phase and two-liquid phase systems has been located on the composition diagram for the temperature 19.75° C.

2. The general shape of the critical solubility surface in the composition-temperature prism has been determined over a range of about 50°.

It has been found that this surface rises abruptly from isotherm to isotherm, *i. e.*, temperature has but little effect on the mutual solubility of the three components.

3. The index of refraction has been determined for eight series of homogeneous ternary mixtures. It has been found that as water is added to a mixture of carbon tetrachloride and alcohol rich in alcohol, the index of refraction at first increases and then decreases. As mixtures richer in carbon tetrachloride are used, the maximum refractive index is reached with less and less water, until finally, with mixtures contain-

ing initially more than about 35% of carbon tetrachloride, the addition of water causes the refractive index to decrease continually.

4. The densities have been determined for eight series of homogeneous mixtures. It has been found that the addition of water to a carbon tetrachloride-alcohol mixture rich in alcohol increases the density uniformly, while the addition of water to a mixture rich in carbon tetrachloride lowers the density, as is to be expected. The slope of the density curve does not change sign, however, at the point where the density of the intial carbon tetrachloride-alcohol mixture is unity, but at a point somewhat higher than this, showing that the volume of the ternary mixture is less than the sum of the volumes of the components.

5. It has been found that the determination of two of the physical properties of a ternary mixture does not always fix its composition.

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Boulder, Colorado,
May, 1915

THE ELECTRICAL CONDUCTIVITY OF CERTAIN SALTS IN PYRIDINE

BY EDWARD X. ANDERSON

Introduction

Thus far little work of a systematic nature has been done on the electrical conductivity of salts in pyridine, and this has been limited in every case to one temperature and to the more dilute solutions. Laszczynski and Gorski[1] investigated the conductivity of pyridine solutions containing lithium chloride, and the iodides and thiocyanates of potassium, sodium and ammonium, all measurements being made at 18°. They found that the equivalent curves showed sufficient convergence to render possible the calculation of l_∞ by extrapolation, where l_∞ represents the equivalent electrical conductivity of the solutions at infinite dilution. The maximum values of the equivalent conductivity lie between 40 and 46, and they are, therefore, as large as the values obtained, using ethyl alcohol as a solvent. Lithium chloride showed scarcely any dissociation. Lincoln[2] found that various inorganic salts yielded conducting solutions in pyridine, but values for l_∞ are rarely encountered. Dutoit and Duperthuis[3] determined the conductivities of pyridine solutions containing potassium iodide, potassium thiocyanate and sodium thiocyanate, for dilutions ranging from 1,000 to 20,000 liters per gram-mole of salt. Within these limits Ostwald's dilution law applies in most cases, thus rendering it possible to calculate the degree of dissociation at any given dilution.

Jones and West[4] studied the temperature coefficients of conductivity in aqueous solutions and the effect of temperature on dissociation. In their work the following rela-

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[1] Zeit. Elektrochemie, **4**, 290–293 (1897).

[2] Jour. Phys. Chem., **3**, 457–484 (1899).

[3] Jour. chim. phys., **6**, 699–725 (1909).

[4] Am. Chem. Jour., **34**, 357 (1905); **35**, 445 (1906).

tions were found to exist: a rise in temperature, ranging from 0° to 35° produces a large increase in conductivity due to an increase in ionic mobility. This last effect results from a reduction in viscosity and a simplification of complexes. For any given electrolyte the temperature coefficients of conductivity increase with increasing dilution; with different electrolytes this increase is greatest for those electrolytes with large hydrating power. Voellmer[1] found that the temperature coefficients of electrical conductivity increased with rising dilution for solutions of lithium chloride, and the acetates and iodides of potassium and sodium in methyl alcohol, and also for the solutions of sodium chloride, calcium chloride, silver nitrate and calcium nitrate in ethyl alcohol. The molecular conductivities of various concentrations of the chlorides of nickel, manganese and cobalt in methyl alcohol, ethyl alcohol and acetone, between 0° and 45°, were studied by Rimbach and Weitzel.[2] In contrast with the near constancy of the temperature coefficients on dilution in aqueous solutions, they found that in organic solvents the temperature coefficients increase, as a rule, with increasing dilution. An examination of the work of Jones and Clover,[3] and of Jones and West,[4] however, shows that the temperature coefficients of conductivity in aqueous solutions do increase with increase in dilution and in most cases the increase is quite pronounced.

The results obtained and the conclusions made by the above investigators will be considered more fully in the discussion of the present work.

Pyridine, like water, has the power of combining with salts to form crystalline solids with pyridine of crystallization. This being the case, according to the law of mass action, one should expect these salts to combine with a much larger amount of pyridine when in solution in this solvent.

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[1] Wied. Ann., 52, 328 (1894).

[2] Zeit. phys. Chem., 79, 279 (1912).

[3] Am. Chem. Jour., 43, 187 (1910).

[4] Loc. cit.

Further, as in the case of hydrates, one should expect the complexity of these ionic "pyridinates" to be greatest in the most dilute solutions, and also that the complexity of the solvate at any given dilution should decrease with rise in temperature. This is based on the general law that, the stability of complexes decreases with the rise in temperature. Since pyridine tends to form these "pyridinates," interesting results might well be expected which, in a certain sense, are parallel to those obtained in aqueous solutions.

It was, therefore, thought worth while to make a careful, systematic study of the conductivity of solutions of various salts in pyridine at different temperatures and over as wide a range of concentrations as the experimental conditions would permit.

Experimental

For measuring the conductivity the well known Kohlrausch method, consisting of the Wheatstone bridge, induction coil and telephone receiver, was used. The resistance boxes were certified by the Reichsanstalt and the Bureau of Standards.

The conductivity cells, three in number, were of the type first used by Jones and Lindsay.[1] These were provided with ground glass stoppers and sealed-in electrodes. A 0.02 *N* potassium chloride solution was used, in determining the cell constants. The "chemically pure" potassium chloride was recrystallized from conductivity water and carefully dried by heating for some time at a dull red heat and then cooled in a desiccator. The salt was then dissolved in conductivity water prepared by the method of Jones and Mackay.[2] This water had a specific conductance of $1.5 \cdot 10^{-6}$ r. o. at 25°. The specific conductances of the 0.02 *N* potassium chloride at 0° and 25° were taken as 0.001522 and 0.002768, respectively.[3] The cell constants thus determined were then checked against 0.002 *N* potassium chloride. One set of

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[1] Zeit. phys. Chem., 56, 129 (1906).

[2] Am. Chem. Jour., 19, 90 (1897).

[3] Ostwald-Luther: Messungen, third ed., 474.

constants used for the three cells were 0.0438, 0.2176 and 0.3985, respectively, and the values of l_v for 0.002 N potassium chloride checked to within 0.3 percent.

"Chemically pure" pyridine was allowed to stand over fused caustic potash for several months. It was then decanted and distilled. The fraction passing over between 115° and 116.1° at 74.5 cms was collected, the first and last portions being rejected. The specific conductance at 0° was found to be $0.057 \cdot 10^{-7}$ r. o., at 25°, $0.74 \cdot 10^{-7}$ and at 50°, $1.2 \cdot 10^{-7}$. Lincoln[1] found the specific conductance of this pyridine to be $7.6 \cdot 10^{-7}$ at 25°, a much larger value.

Unless otherwise indicated, it will be understood that Kahlbaum's best grade "C. P." chemicals were used. After complete dehydration, by methods to be mentioned later, the salts were preserved in tightly stoppered weighing bottles over phosphorus pentoxide. Trial solubility tests were made to determine approximately the amount of each salt required for saturation at room temperature. Those salts which do not show hygroscopic properties were weighed out directly and the exact amounts required for a normality conveniently close to that of complete saturation was taken, but for those salts which tend to absorb moisture the method of weighing by difference was used. In diluting the mother solutions every possible care was taken to prevent contact with moisture. Suction was applied directly to the pipette through a calcium chloride drying tube.

All the solutions were prepared at room temperatures, 21°–22°, and transferred to tightly fitting glass-stoppered bottles. The conductivity measurements were made as soon after preparation as possible.

The capacities of the 25° and 50° baths used were 20 and 16 liters, respectively. They were heated by means of immersed electric lights, which were automatically operated by means of a contact toluol regulator and relay system. Stirrers, propelled by a small motor, were used to agitate the

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[1] Jour. Phys. Chem., 3, 457 (1899).

water vigorously and thereby maintain a uniform temperature throughout the baths. By this means both temperatures were automatically kept at 25° ± 0.02 and 50° ± 0.05. A mixture of well washed, finely crushed ice moistened with distilled water was used for the 0° bath. The order of temperatures followed for the conductivity measurements was 25°, 0° and 50°. The temperature 25° was selected as the initial, because the solutions were made up at room temperature. Thermal equilibrium would, therefore, be more quickly attained at this temperature than at either of the others. The temperature 0° was selected as the second in order to permit of the minimum change in the concentration of the solutions by condensation of pyridine on the inside wall of the cells. If the cells had been immersed in the 50° bath before being subjected to a temperature of 0°, there would be more pyridine condensed on the cell walls than if the 25° immediately preceded the 0° bath. Forty minutes were found to be sufficient for establishing thermal equilibrium, because by trial experiments the conductivity was found to remain constant after this amount of time had elapsed.

Silver Nitrate.—The pure crystals were pulverized and kept in the dark over phosphorus pentoxide for several days. This salt dissolves in pyridine with a considerable evolution of heat, probably due to the formation of $AgNO_3 \cdot 2Pyr$, or $AgNO_3 \cdot 3Pyr$, both of which have been found capable of existing in the solid phase.[1] Kahlenberg and Brewer[2] found $AgNO_3 \cdot 3Pyr$ to be stable between —24° and +48.5°, where it changes to $AgNO_3 \cdot 2Pyr$. Below —24° the compound $AgNO_3 \cdot 6Pyr$ is the stable form.

In the following data V denotes the volume of the solution in liters containing one gram-equivalent weight of the salt. l_0, l_{25} and l_{50} represent the equivalent conductivities of the various solutions at 0°, 25° and 50°, respectively. The temperature coefficients are headed by the letters A, B and C where

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[1] Reitzenstein: Liebig's Ann., 282, 267 (1894).

[2] Jour. Phys. Chem., 12, 283 (1908).

$$A = \frac{l_{25} - l_0}{l_0 \cdot 25},\ B = \frac{l_{60} - l_{25}}{l_{25} \cdot 25} \text{ and } C = \frac{l_{60} - l_0}{l_0 \cdot 50}.$$

In the curves which follow, the cube roots of the volumes in cubic centimeters are plotted as abscissae, against the equivalent conductivity l as ordinates. Each space along the abscissa is equal to 2.5 units after the root is extracted. Every space along the ordinate is equal to 10 units after the equivalent conductivity is multiplied by the factor, which will be specified in each case. This factor is used in order to magnify the trend of the curves. It must also be remembered that any errors are likewise highly magnified.

TABLE I

V	l_0	l_{25}	l_{60}
1	1.05	1.55	2.01
2	14.77	19.38	23.28
10	20.68	25.38	27.25
20	22.38	27.05	29.17
100	27.80	34.49	37.92
500	37.31	47.63	55.10

TABLE II

V	A	B	C
1	0.0149	0.0121	0.0183
2	0.0125	0.0081	0.0115
10	0.0091	0.0029	0.0064
20	0.0084	0.0031	0.0061
100	0.0096	0.0040	0.0073
500	0.0111	0.0063	0.0095

From Fig. I it will be seen that, with dilution the equivalent conductivity of silver nitrate increases at first very rapidly and then less rapidly with further dilution for all three temperatures. They do not appear to approach maximum values. The values for l_0 here given agree very closely with those given by Lincoln[1] for the same salt at 25°. The tempera-

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[1] Loc. cit.

ture coefficients (Table II) show distinct minima, decreasing at first very rapidly and then increasing very slowly on further dilution. Although solutions of silver nitrate in pyridine possess a relatively high molecular conductivity, Walden and Centnerszwer[1] found that the molecular weights of silver nitrate in dilute pyridine solutions are normal, while

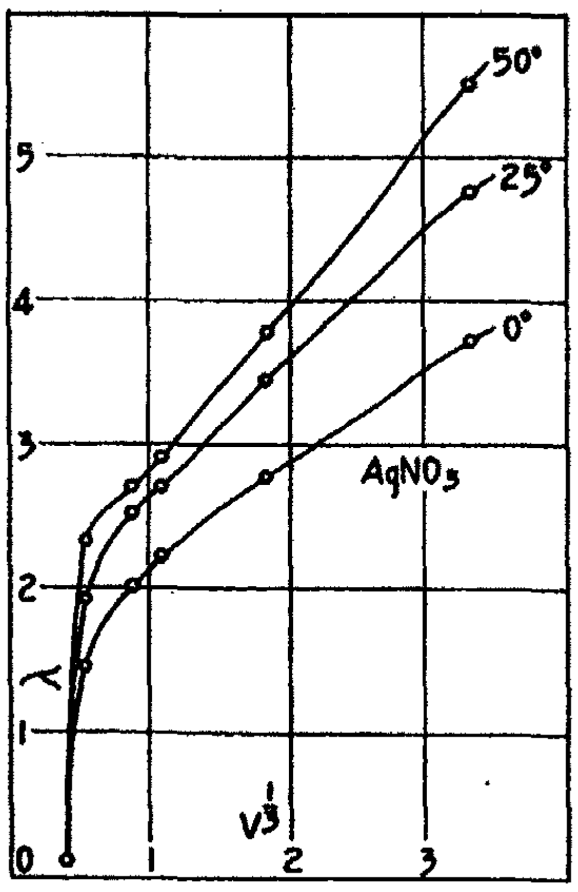

Fig. I

in concentrated solutions (0.1 *N* to 1.0 *N*) the molecular weights are greater than normal, thus indicating association. By the same method Schmuilow[2] found that this salt is apparently non-ionized. Since transference measurements made by Neustadt and Abegg[3] showed that both Ag^+ ions and NO_3 radicle migrated toward the cathode, they assumed that, if ionization does take place, it does so according to the expression

$$(1) \qquad (AgNO_3)_2 \rightleftarrows Ag_2{}^+NO_3 + NO_3{}^-.$$

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[1] Zeit. phys. Chem., 55, 321 (1906).
[2] Zeit. anorg. Chem., 15, 18 (1897).
[3] Zeit. phys. Chem., 69, 486 (1910).

That simple Ag^+ ions are also present to a slight extent is not to be doubted, and, therefore, the more complete equilibrium may be represented by the following equation:

(2) $2Ag^+ + 2NO_3^- \rightleftharpoons 2AgNO_3 \rightleftharpoons (AgNO_3)_2 \rightleftharpoons Ag_2^+NO_3 + NO_3^-$.

Lithium Chloride.—The sample was heated at 120° for several days, with frequent pulverizing in a hot agate mortar until the tendency to cake ceased. The dry, finely powdered salt was preserved in a tightly stoppered weighing bottle.

Lithium chloride dissolves in pyridine with a evolution of heat; it separates from solution as $LiCl \cdot 2Pyr$.[1]

TABLE III

V	l_0	l_{25}	l_{50}
0.59	0.143	0.199	0.239
1.00	0.218	0.264	0.282
2.00	0.254	0.290	0.299
10.00	0.279	0.322	0.346
100.00	0.519	0.573	0.613
1000.00	1.47	1.60	1.68

TABLE IV

V	A	B	C
0.59	0.0160	0.0079	0.0135
1.00	0.0083	0.0028	0.0058
2.00	0.0056	0.0012	0.0035
10.00	0.0061	0.0030	0.0047
100.00	0.0041	0.0028	0.0036
1000.00	0.0037	0.0020	0.0029

An examination of Table III and Fig. II shows that lithium chloride is at best a very poor conductor and is but slightly dissociated at all concentrations and temperatures. The equivalent conductivities do, however, show a rapid increase at first, and then very slight and finally more rapidly, with increasing dilution. The values found by Laszczynski and Gorski[2] for the same solutions are about four times as

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[1] Laszczynski: Ber. deutsch. chem. Ges., 27, 2285 (1894).

[2] Loc. cit.

large, due, perhaps, to the presence of a slight trace of moisture. Increasing dilution has a marked intitial effect on the temperature coefficients (Table IV), the latter passing through a minimum.

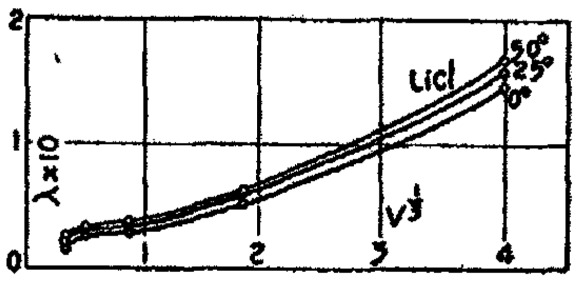

Fig. II

Lithium Bromide.—The anhydrous salt was prepared in a manner similar to that used for lithium chloride.

TABLE V

V	l_0	l_{25}	l_{50}
0.98	—	1.29	1.65
2.00	0.98[1]	1.72	1.98
10.00	2.29	2.44	2.40
100.00	5.43	5.34	4.89
1000.00	13.68	14.15	13.58
10,000.00	24.8	28.7	29.9
∞	(28.5)	(36.3)	(49.0)

TABLE VI

V	A	B	C
0.98	—	0.0109	—
2.00	0.0298[1]	0.0061	0.0202
10.00	0.0026	—0.0006	0.0009
100.00	—0.0007	—0.0034	—0.0020
1000.00	0.0013	—0.0016	—0.0001
10,000.00	0.0063	0.0017	0.0041

A glance at Fig. III reveals the fact that the equivalent conductivity of lithium bromide increases steadily with increasing dilutions, but not at every dilution with a rise in temperature, there being in some cases a decrease in conduc-

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[1] Solidified.

tivity with a rise in temperature. The values for l_∞ at 0°, 25° and 50° were extrapolated and found to be 28.5, 36.3 and 49.0, respectively. The near proximity of the curves signifies that a change in temperature has little effect on the conductivity, there being a slight increase in this effect in the more dilute solutions. The values for the temperature coefficients (Table VI) decrease, at first, with increasing dilution. This decrease is quite rapid in the more concentrated solutions, passing through minima of negative values and then finally increasing at an almost constant rate.

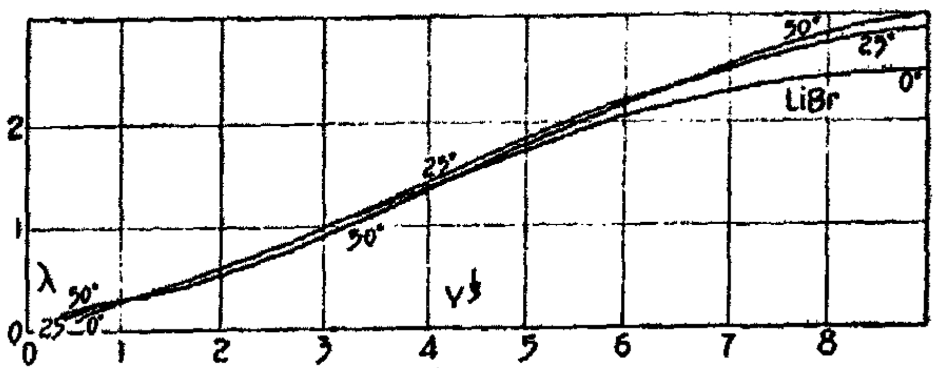

Fig. III

Lithium Iodide.—The salt was carefully dehydrated by constant heating for several days and nights.

TABLE VII

V	l_0	l_{25}	l_{50}
1.0	4.40	7.04	9.82
2.0	7.79	10.98	13.82
10.0	12.76	16.40	18.62
100.0	18.34	23.35	25.98
1000.0	27.10	35.99	42.65
10,000.0	31.2	44.4	50.5
∞	(31.2)	(44.9)	(50.5)

TABLE VIII

V	A	B	C
1.0	0.0224	0.0158	0.0246
2.0	0.0164	0.0103	0.0155
10.0	0.0114	0.0054	0.0092
100.0	0.0109	0.0045	0.0083
1000.0	0.0131	0.0074?	0.0115
10,000.0	0.0169	0.0055	0.0124
∞	(0.0180)	(0.0050)	(0.0124)

From Fig. IV it is observed that lithium iodide is a good conductor. The conductivity increases quite rapidly at the outset, but continuously increases at a decreasing rate and soon attains maximum values. The 0° and 50° curves appear to be asymptotic at a dilution of ten thousand liters; the values for l_v which were actually obtained at this dilution are, therefore, taken as those for l_∞ and are 31.2 and 50.5, respectively. By extrapolation the value for l_∞ at 25° is found to be 44.9. The temperature coefficients fall exceedingly rapidly to minima and then increase very slowly with increasing dilution.

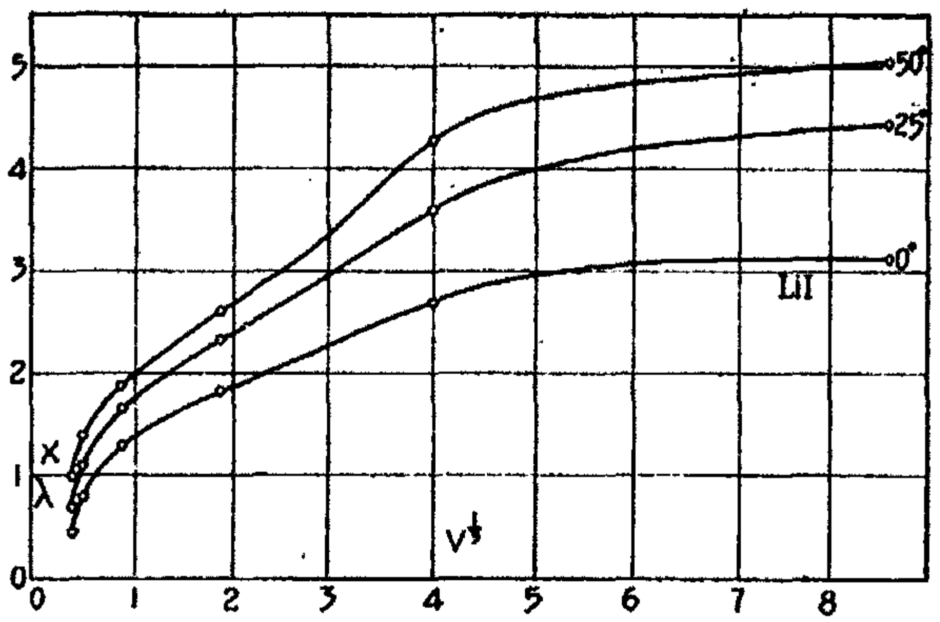

Fig. IV

Sodium Iodide.—The finely powdered salt was thoroughly dried at a temperature slightly exceeding 100°. This substance dissolves in pyridine with considerable evolution of heat.

TABLE IX

V	l_0	l_{25}	l_{50}
1.33	0.11[1]	0.70	0.84
5.00	10.00	11.14	11.20
10.00	14.56	16.15	15.80
100.00	21.66	23.81	22.87
1000.00	32.99	39.53	41.28
10,000.00	42.20	56.70	63.20

[1] Solid present.

TABLE X

V	A	B	C
1.33	0.2084[1]	0.0076	0.1279[1]
5.00	0.0046	0.0002	0.0024
10.00	0.0044	—0.0009	0.0017
100.00	0.0040	—0.0016	0.0011
1000.00	0.0079	0.0018	0.0050
10,000.00	0.0137	0.0046	0.0099

An examination of Table IX and Fig. V reveals the fact that l_v follows the same general trend as the preceding curves; again, the values of l_v increase on dilution most rapidly in the concentrated solutions. By extrapolation l_∞ was found to be 43.3 at 0°. Laszczynski and Gorski[2] obtained 44.32 for the value of l_∞ at 18°. For 25° and 50°, however, maximum values could not be obtained by extrapolation. At these temperatures the equivalent conductivities continue to increase with dilution more rapidly than at 0°.

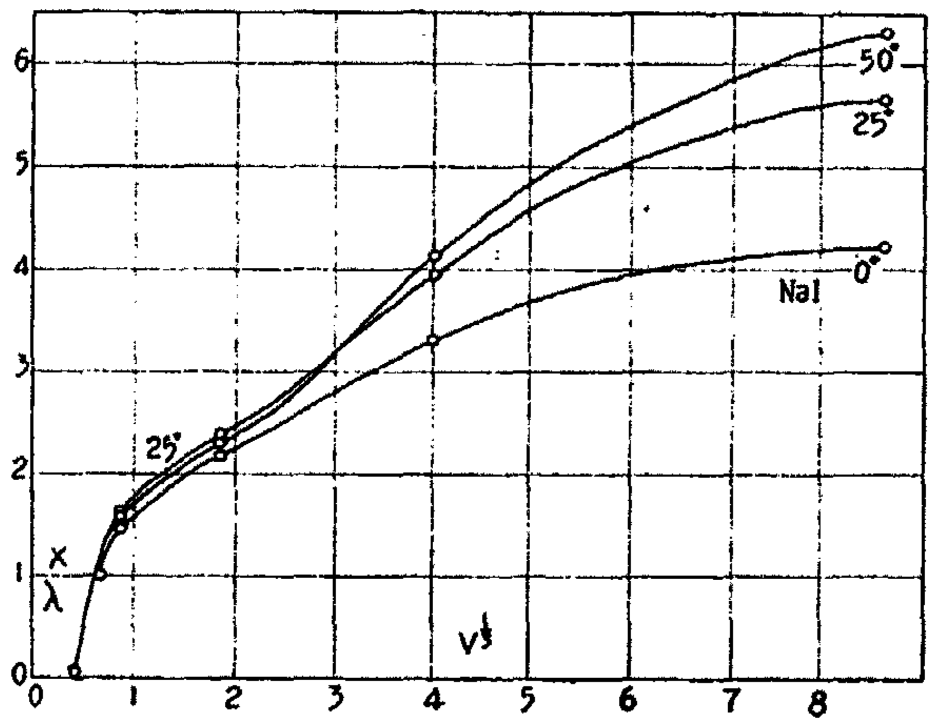

Fig. V

The temperature coefficients show well marked minima.

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[1] Solid phase present.

[2] Loc. cit.

Here, again, negative values appear for temperatures between 25° and 50°.

Potassium Thiocyanate.—The sample used was crystallized from absolute alcohol, washed with absolute alcohol, and dried at 95°. This salt differs from the others studied in that its solubility in pyridine decreases as the temperature rises.

TABLE XI

V	l_0	l_{25}	l_{50}
7.0	5.97	7.12	7.75
14.0	7.20	8.45	9.00
70.0	11.40	13.36	14.54
140.0	14.17	16.77	18.14
1400.0	27.32	33.70	38.31
14,000.0	42.86	58.51	71.30

TABLE XII

V	A	B	C
7.0	0.0077	0.0035	0.0060
14.0	0.0069	0.0026	0.0050
70.0	0.0070	0.0035	0.0055
140.0	0.0073	0.0033	0.0056
1400.0	0.0093	0.0055	0.0081
14,000.0	0.0146	0.0087	0.0133

Referring to Fig. VI, it is obvious that the equivalent conductivity of potassium thiocyanate increases at a more constant rate than most of the conductivities of the preceding salts. By extrapolation 46.5 is obtained for the value of l_∞ at 0°. Laszczynski and Gorski[1] give values in fair agreement with the above, tabulated, comparisons being made at 18°. They did not obtain a value for l_∞ inasmuch as the dilutions at which they worked did not exceed 2870.4 liters. However, the data which they give show that the conductivity is approaching a maximum value. The temperature coefficients exhibit slight minima. In aqueous solutions

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[1] Loc. cit.

the effect of dilution upon the temperature coefficients is greatest in the most dilute solutions, as we should expect.

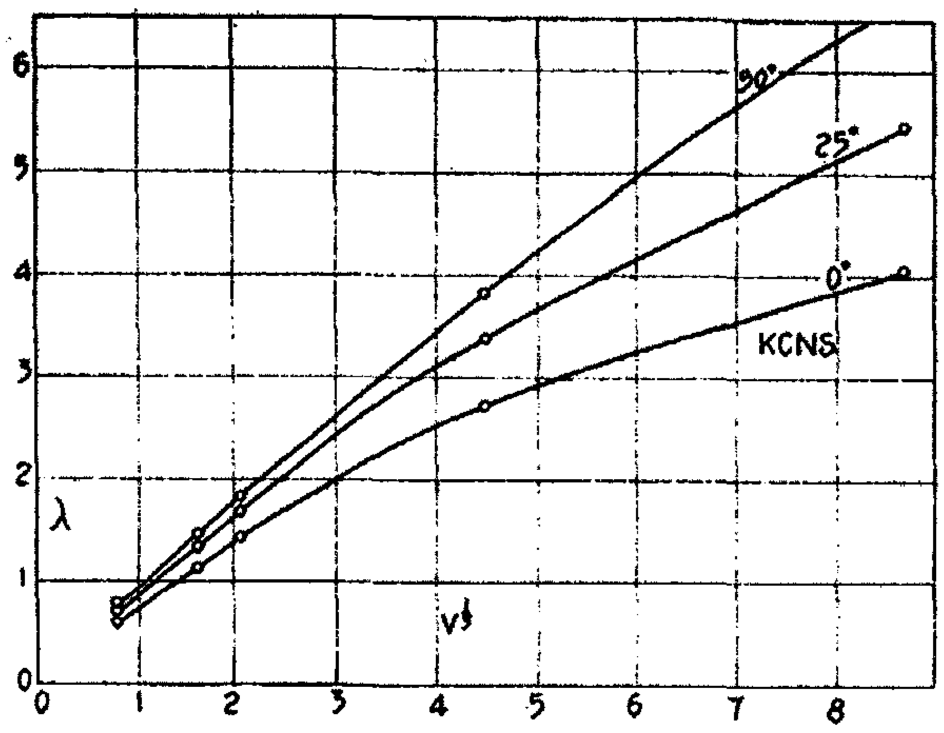

Fig. VI

Ammonium Thiocyanate.—The anhydrous salt was prepared in the same manner as the potassium thiocyanate.

TABLE XIII

V	l_0	l_{25}	l_{50}
0.33	2.10	4.46	7.43
1.00	8.21	11.70	15.12
2.00	10.45	13.76	16.53
10.00	11.96	14.56	16.29
100.00	17.00	20.33	22.18
1000.00	33.57	41.80	47.76

TABLE XIV

V	A	B	C
0.33	0.0451	0.0266	0.0508
1.00	0.0170	0.0117	0.0169
2.00	0.0127	0.0081	0.0116
10.00	0.0087	0.0048	0.0072
100.00	0.0078	0.0036	0.0061
1000.00	0.0098	0.0057	0.0085

From Fig. VII it will be observed that the equivalent conductivity of ammonium thiocyanate behaves somewhat peculiarly, when compared with the previous curves. The conductivity curves rise rapidly at first and then approximate parallelism with the volume axis in the more concentrated solutions, and then increase again with increasing dilution. The values for l_v given in the above table are somewhat larger than those given by Laszczynski and Gorski. They carried the dilution out to 2080 liters and were able to calculate the values for l_∞, which they give as 40.22. In the above curves it may be clearly seen that the 0° curve gives promise of a maximum value for l_v, but the 25° and 50° curves show practically no signs of such a tendency. In connection with the strange conduct of the curves in the vicinity of concentrated solutions, it may be pointed out that the temperature coefficients show equally striking changes, dropping suddenly to minima, and then increasing very slowly in the dilute solutions.

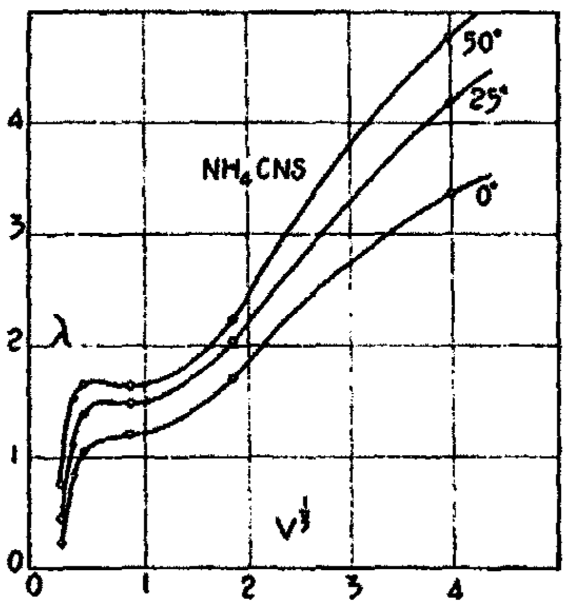

Fig. VII

A relation, exactly analogous to that of the conductivity values shown above, was observed by Franklin[1] for ammonium thiocyanate and tetramethylammonium iodide in liquid sulphur dioxide. The conductivity curves of tetra-

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[1] Jour. Phys. Chem., 15, 675–97 (1911).

methylammonium iodide in liquid sulphur dioxide are almost indentical in form with those here represented for ammonium thiocyanate in pyridine, while those for ammonium thiocyanate in the same solvent are not very unlike those obtained in pyridine. Upon passing from the most concentrated solutions to the most dilute, Franklin found that the molecular conductivity first increases to a maximum, then falls to a minimum value, and finally approaches the usual maximum on further dilution. He explained these results by assuming that the dissociated salt is auto-ionized in the concentrated solutions and that this effect decreases with dilutions. On the other hand, the decrease in viscosity with dilution causes a rise in ionic mobility. These two effects balance each other at the first mentioned maximum. On further dilution the auto-ionization disappears and the conductivity from then on is due to the dissociating power of the solvent. Concentrated solutions of ammonium thiocyanate in pyridine are very viscous; the same is true of a concentrated solution of ammonium thiocyanate in liquid sulphur dioxide.[1] The initial rapid increase in the equivalent conductivities and decrease in temperature coefficients are undoubtedly chiefly due to a rapid decrease in viscosity with slight change in dilution. It is a singular fact that Franklin[2] found the minimum temperature coefficient of conductivity to exist in the solutions of intermediate dilution, where the minimum conductivity was also found. This is in accord with the results here given for ammonium thiocyanate in pyridine. On the other hand, for sulphur dioxide the minimum value of the equivalent conductivity is displaced toward the region of greater dilution, with rising temperature, but this is not so for solutions of the same salt in pyridine. It seems, therefore, that the disturbing influences acting on ammonium thiocyanate when dissolved in liquid sulphur dioxide are, at least in some measure, at work in pyridine.

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[1] Franklin: Loc. cit.

[2] Loc. cit.

Mercuric Chloride.—The sample used was recrystallized from conductivity water and thoroughly dried at 100°–105°.

Lang[1] and Reitzenstein[2] have studied the compound $HgCl_2 \cdot Pyr$, and the formation of $HgCl_2 \cdot 2Pyr$ has been investigated by Pesci.[3] McBride[4] determined the temperature-solubility curve for mercuric chloride in pyridine at temperatures ranging from —33° to +145° and proved the existence of the three compounds, $HgCl_2 \cdot 2Pyr$, $HgCl_2 \cdot Pyr$ and $3HgCl_2 \cdot 2Pyr$.

Table XV

V	l_0	l_{25}	l_{40}
0.5	0.009[1]	0.036	0.045
1.0	0.019	0.025	0.030
2.0	0.016	0.021	0.025
10.0	0.016	0.021	0.027
100.0	0.037	0.061	0.067
1000.0	0.130	0.260	0.400

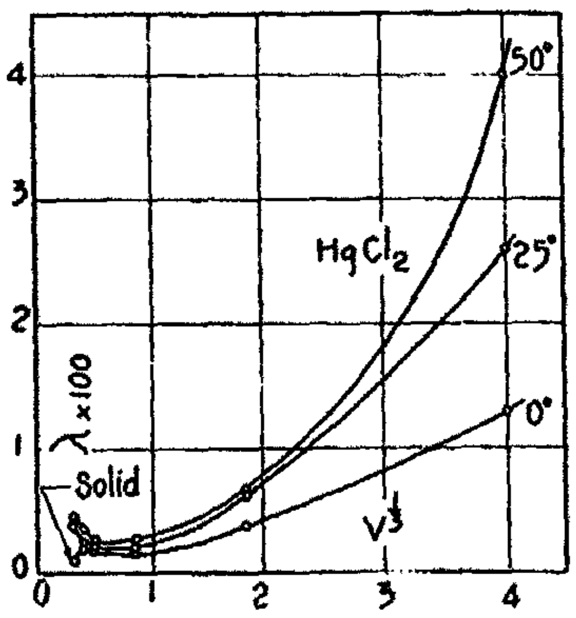

Fig. VIII

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[1] Ber. deutsch. chem. Ges., 21, 1578–88 (1888).
[2] Ann. Phys. Chem., 43, 839–40 (1891).
[3] Gazz. chim. ital., 25, II, 423–33 (1895).
[4] Jour. Phys. Chem., 14, 189–200 (1910).

TABLE XVI

V	A	B	C
0.5	0.1176[1]	0.0104	0.0793[1]
1.0	0.0136	0.0076	0.0119
2.0	0.0126	0.0065	0.0105
10.0	0.0126	0.0119?	0.0141
100.0	0.0260	0.0039	0.0162
1000.0	0.0400	0.0215	0.0415

Mercuric Bromide.—This salt was precipitated from a solution of mercuric chloride with potassium bromide, recrystallized from and thoroughly washed with conductivity water and finally dried at 100°-105°.

Groos[2] and Reitzenstein[3] made the compound $HgBr_2 \cdot 2Pyr$.

TABLE XVII

V	l_0	l_{25}	l_{50}
0.5	0.012[1]	0.034	0.043
1.0	0.020	0.026	0.032
2.0	0.018	0.023	0.026
10.0	0.017	0.023	0.028
100.0	0.031	0.047	0.053
1000.0	0.13	0.28	0.29

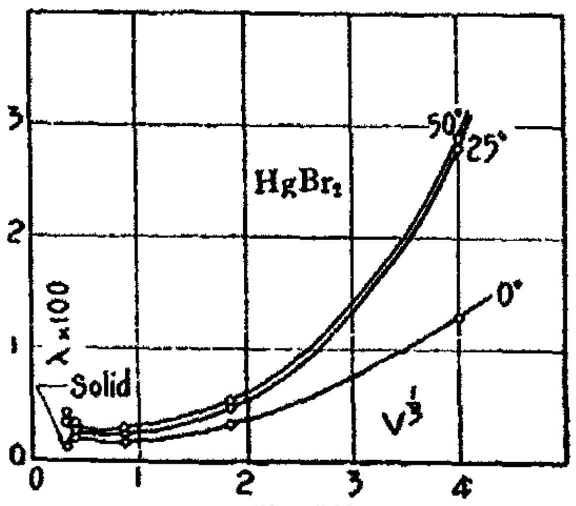

Fig. IX

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[1] Solid phase present.
[2] Arch. Pharm., (3) 28, 73-8.
[3] Loc. cit.

TABLE XVIII

V	A	B	C
0.5	0.0742[1]	0.0108	0.0525[1]
1.0	0.0121	0.0090	0.0119
2.0	0.0104	0.0063	0.0092
10.0	0.0128	0.0092	0.0124
100.0	0.0207	0.0051	0.0142
1000.0	0.0462	0.0014	0.0246

Mercuric Iodide.—A method similar to that used for the preparation of mercuric bromide was followed in preparing this salt, using potassium iodide as the precipitant. Complete desiccation was assumed after the salt had been kept for some time at the transition point of the iodide.

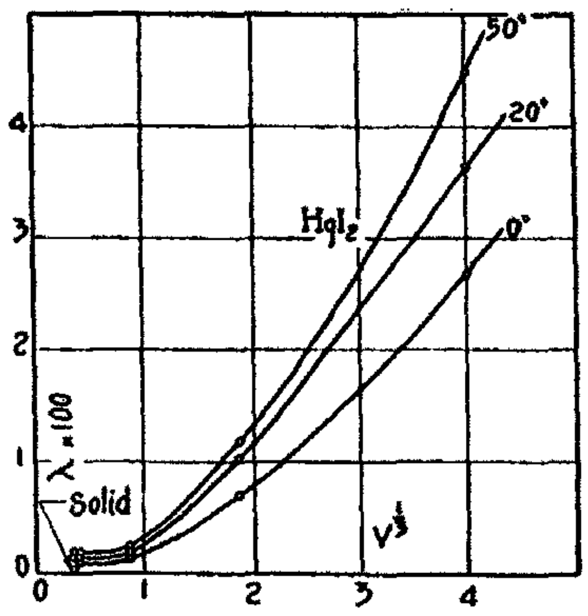

Fig. X

The compound $HgI_2 \cdot 2Pyr$ has been prepared by Groos.[2]

TABLE XIX

V	l_0	l_{25}	l_{50}
0.67	Solidified	0.013	0.018
1.00	0.009	0.013	0.018
2.00	0.008	0.012	0.015
10.00	0.013	0.019	0.024
100.00	0.069	0.102	0.117
1000.00	0.266	0.364	0.448

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[1] Solid present.

[2] Loc. cit.

TABLE XX

V	A	B	C
0.67	—	0.0162	—
1.00	0.0186	0.0130	0.0188
2.00	0.0170	0.0118	0.0169
10.00	0.0198	0.0099	0.0173
100.00	0.0190	0.0059	0.0139
1000.00	0.0148	0.0093	0.0137

As a general rule the mercuric halides when dissolved in organic solvents exhibit a strong tendency either to polymerize, or to unite with the solvent to form complex solvent-solute molecules. Walden and Centnerszwer[1] determined the molecular weights of the three halides in pyridine by the boiling-point method and found them to be approximately normal in the dilute solutions. In the concentrated solutions, however, the molecular weights are less than normal, which, since the low conducting power is evidence of slight ionization, must indicate in the solution the presence of solvent-solute complex molecules and complex ions.

As was to be expected, the equivalent conductivities of the three salts are extremely low. The effect of temperature is relatively slight; the conductivity values for corresponding dilutions are of the same order of magnitude and show a minimum conductivity in the regions of greatest concentration.

The values of l_v for mercuric iodide are much smaller than those obtained by Lincoln[1] at 25°.

Owing to the low conductivity of these solutions and the fact that very slight errors are enormously magnified in the calculation, no emphasis is made of the exactness of the temperature coefficients; they show, nevertheless, distinct minima.

Cupric Chloride.—This salt was heated for several hours in an atmosphere of dry hydrogen chloride at 160°–165°, then heated at the same temperature in a current of dry

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[1] Loc. cit.

hydrogen and cooled in a current of the latter; lastly, it was heated in an air bath at about 160° for several hours and preserved as above described.

Lang[1] isolated the compound $CuCl_2 \cdot 2Pyr$.

TABLE XXI

V	l_0	l_{25}	l_{40}
25.0	0.053	0.062	0.074
50.0	0.066	0.076	0.086
100.0	0.088	0.098	0.111
200.0	0.130	0.146	0.171
500.0	0.203	0.216	0.216
1000.0	0.302	0.365	0.410

TABLE XXII

V	A	B	C
25.0	0.0073	0.0076	0.0082
50.0	0.0059	0.0052	0.0059
100.0	0.0045	0.0055	0.0053
200.0	0.0050	0.0068	0.0063
500.0	0.0027	0.0000	0.0014
1000.0	0.0084	0.0049	0.0072

The curves (Fig. XI) for cupric chloride show an apparent transition for the values of l_v. The equivalent conductivity increases steadily with increasing dilution. The large factor 100, by which l is multiplied, is responsible for the marked break in the curves. The temperature coefficients show minimum values.

Ley[1] obtained a blue solution when he dissolved cupric chloride in pyridine; this solution gave $l_{30} = 0.05$, in close agreement with the results given in this work for the same dilution. Ley assumes that the blue color of the pyridine solution is due to an undecomposed cupric chloride-pyridine compound and not to copper ions. Kohlschuetter[2] states

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[1] Loc. cit.

[2] Ber. deutsch. chem. Ges., 37, 1153 (1904).

that cupric chloride dissolved in pyridine gives a blue solution, that is, the color of the solution corresponds to the color of the hydrated salt, and, since its molecular weight as found by the boiling-point method is normal, its color may be attributed to that of the undissociated cupric chloride. In these pyridine solutions there may be complexes of solvent and solute of the order of $CuCl_2 \cdot 2Pyr$, corresponding to $CuCl_2 \cdot 2H_2O$, or of a higher order. Naumann[1] states that cupric chloride dissolves in pyridine with evolution of heat, giving a blue solution and therefore assumes that the complex $CuCl_2 \cdot 2Pyr$ is present in the solution. All these investigators affirm that cupric chloride dissolved in pyridine gives rise to a blue solution. All of the cupric chloride solutions used in this work had a beautiful, deep green color without the least indication of a bluish tint and, furthermore, the solutions remained green for several months,—until finally rejected. On the other hand, in making one of the trial solubility tests, an attempt was made to weigh directly a sample of the dry cupric chloride. The salt absorbed

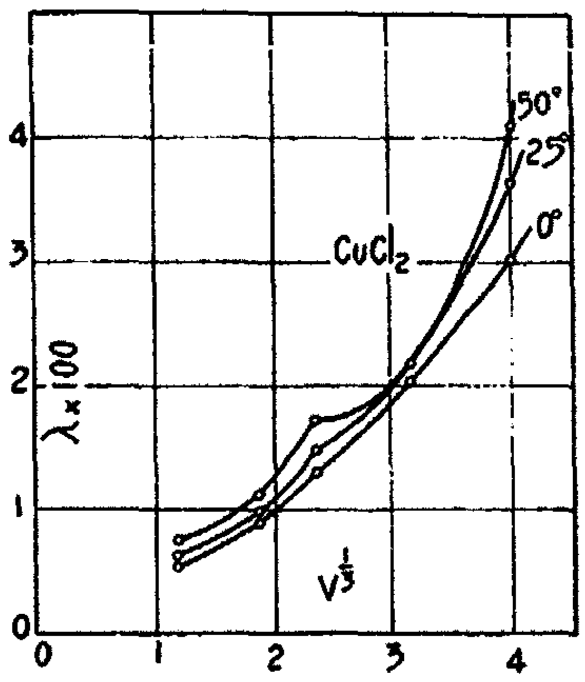

Fig. XI

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[1] Ber. deutsch. chem. Ges., 37, IV, 4609 (1904).

moisture so rapidly that accurate weighing was impossible. Although it was noticed that the edges of the salt mass had taken on a greenish blue color, the salt was quickly transferred and dissolved in pyridine, and, as might be expected, the solution was distinctly blue. When, however, the cupric chloride was quickly weighed by difference, a deep green solution was obtained. It is evident, therefore, that the blue color observed by Kohlschuetter, Lang, Ley and Naumann is due to the presence of a slight trace of moisture. It is safe to assert that the green color of a solution of cupric chloride in pyridine is due to the presence of $CuCl_2$ 2Pyr, and the blue color often obtained when supposedly dry cupric chloride is dissolved in the same solvent is due to the presence of $CuCl_2 \cdot 2H_2O$. The values given by Lincoln[1] at 25° for l_v (recalculated from those given for μ) are much higher than the above or those given by Ley.[1]

Copper Nitrate.—The anhydrous salt was prepared by the method of displacement used by Kahlenberg.[2] A 0.1 *N* solution of silver nitrate in pyridine was treated with an excess of finely divided, reduced metallic copper and allowed to stand until the solution gave no test for silver.

Copper nitrate crystallizes from pyridine solutions as the complex $Cu(NO_3)_2 \cdot 4Pyr$.[3]

TABLE XXIII

V	l_0	l_{25}	l_{60}
10.0	9.68	12.94	14.96
20.0	5.00	7.21	8.88
40.0	8.57	11.60	14.16
100.0	12.08	16.43	20.43
1000.0	16.41	22.88	29.71
10,000.0	19.42	27.24	35.71

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[1] Loc. cit.

[2] Jour. Phys. Chem., 3, 379 (1899).

[3] Grossmann: Ber. deutsch. chem. Ges., 37, 1253–7 (1904).

TABLE XXIV

V	A	B	C
10.0	0.0135	0.0062	0.0109
20.0	0.0176	0.0093	0.0155
40.0	0.0142	0.0088	0.0131
100.0	0.0144	0.0097	0.0138
1000.0	0.0158	0.0119	0.0162
10,000.0	0.0161	0.0124	0.0168

A study of Fig. XII discloses the fact that copper nitrate is peculiar in its behavior, in that, like the mercuric halides, it gives minimum conductivity values. After passing through the minima the values for l_v first increase at a moderate rate and then exceedingly slowly with increasing dilution.

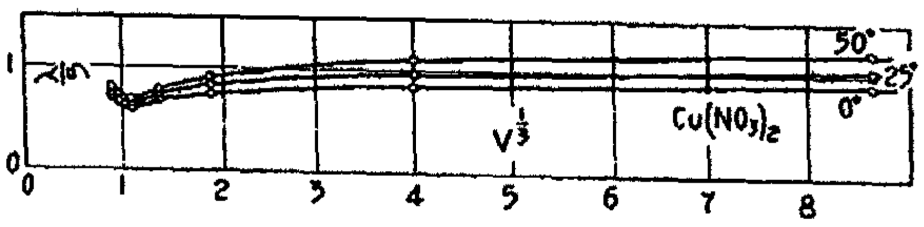

Fig. XII

Here again, the temperature coefficients show minimum values.

Cadmium Nitrate.—The pure anhydrous salt was prepared by the displacement of silver in a 0.1 *N* solution of silver nitrate by means of chemically pure cadmium.

TABLE XXV

V	l_0	l_{25}	l_{50}
10.0	0.141	0.160	0.122
20.0	0.322	0.348	0.288
40.0	0.402	0.433	0.340
100.0	0.694	0.733	0.630
1000.0	2.37	2.31	2.44
10,000.0	7.40	8.60	9.80

TABLE XXVI

V	A	B	C
10.0	0.0052	—0.0095	—0.0028
20.0	0.0033	—0.0070	—0.0021
40.0	0.0031	—0.0086	—0.0031
100.0	0.0023	—0.0056	—0.0018
1000.0	—0.0010	0.0023	0.0006
10,000.0	0.0065	0.0056	0.0065

The equivalent conductivities of cadmium nitrate (Fig. XIII) increase quite steadily with increase in dilution. The curves obtained by plotting the temperature coefficients are somewhat irregular, but in general show minima of negative value. The curves run quite closely together, diverging only to an appreciable extent in the more dilute solutions.

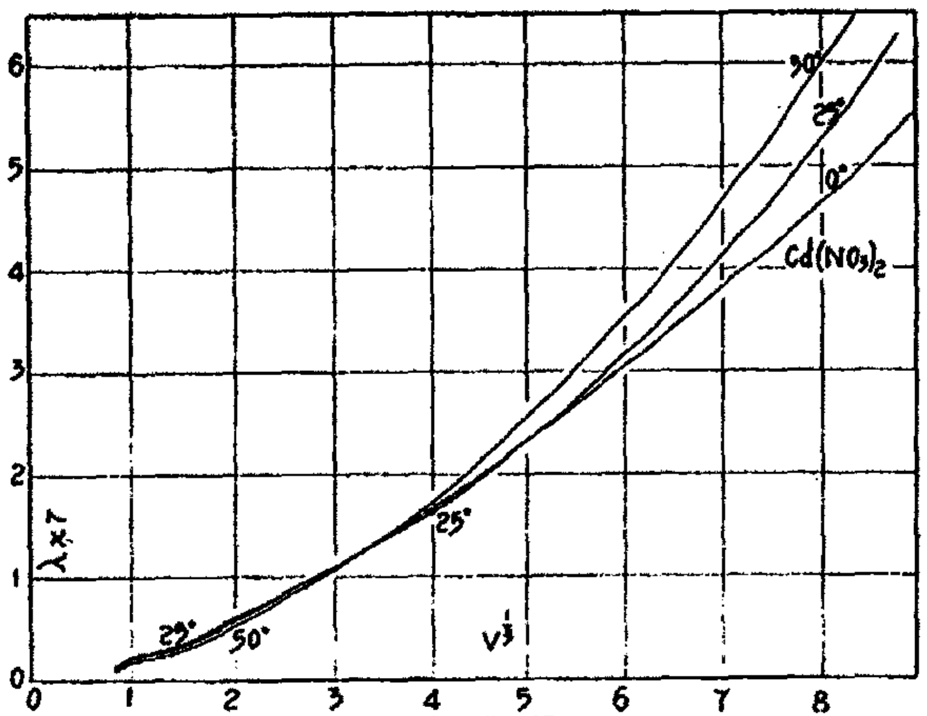

Fig. XIII

Cobalt Chloride.—The sample used was partially dehydrated *in vacuo* over phosphorus pentoxide, then heated in an atmosphere of dry hydrogen chloride at 140° for twenty-four hours, and finally in a current of dry hydrogen for fifteen hours. The product was of a pale blue color. Reitzenstein[1] prepared the compound $CoCl_2 \cdot 4Pyr$. Cobalt chloride

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[1] Loc. cit.

dissolved in pyridine gives a red solution at 0°, a violet at 25°, and a deep purple solution at 50°.

TABLE XXVII

V	l_0	l_{25}	l_{50}
10.0	0.009[1]	0.012	0.012
20.0	0.015	0.015	0.022
40.0	0.021	0.020	0.024
100.0	0.042	0.045	0.041
1000.0	0.220	0.230	0.310
10,000.0	0.600	1.000	1.100

TABLE XXVIII

V	A	B	C
10.0	0.0149[1]	0.0319	0.0293[1]
20.0	0.0019	0.0174	0.0101
40.0	—0.0021	0.0082	0.0028
100.0	0.0028	—0.0036	—0.0005
1000.0	0.0018	0.0139	0.0082
10,000.0	0.0267	0.0040	0.0167

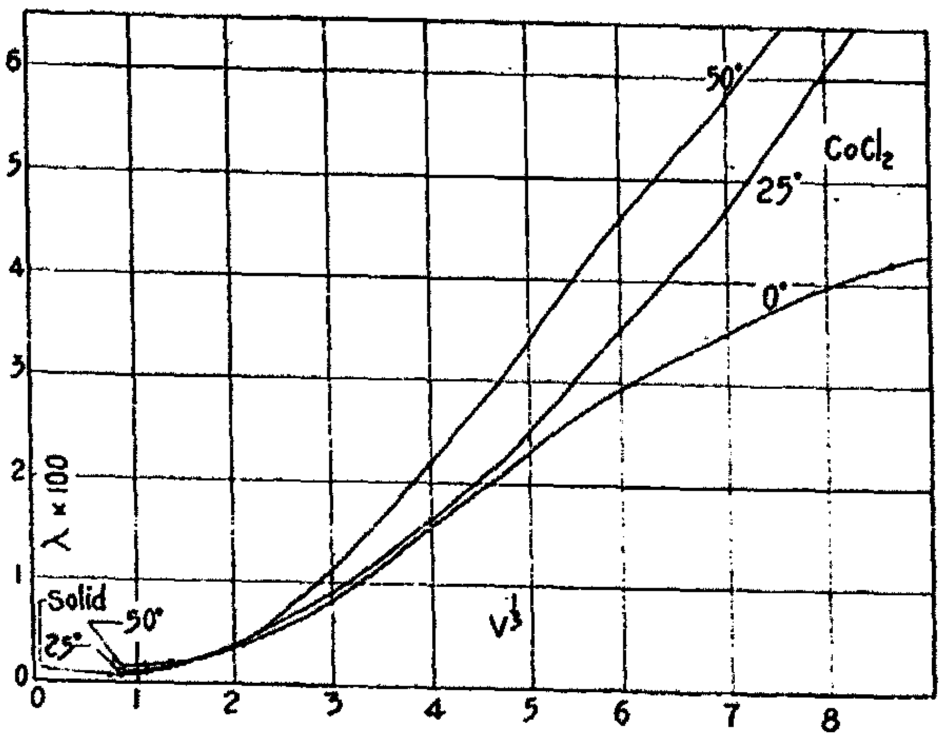

Fig. XIV

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[1] Solid present.

Cobalt chloride in pyridine solutions is at best an exceedingly poor conductor. By some, its solutions are considered as non-conductors. Consequently, slight errors in the work are highly magnified. The results obtained show a continuous increase in equivalent conductivity with dilution for all temperatures. Again, Lincoln's[1] values for l_v at corresponding dilutions are very much higher than the values here quoted. The temperature coefficients are likewise subject to considerable error, yet even these show definite minima at which negative coefficients are observed.

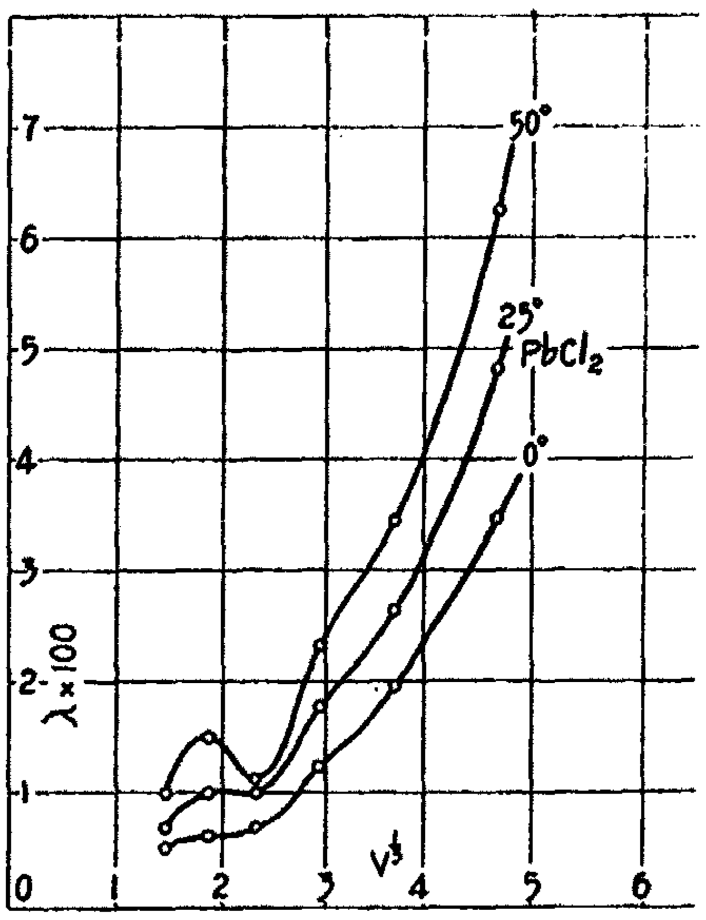

Fig. XV

Werner[1] and his co-workers found by the ebullioscopic method that cobalt chloride has the normal molecular weight in pyridine.

Lead Chloride.—The salt was precipitated from chemically pure lead nitrate by pure hydrochloric acid. It was then thoroughly washed with water and heated to dryness at 120°.

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[1] Loc. cit.

Pyridine forms three crystalline compounds with lead chloride, e. g., $3PbCl_2\ 4Pyr$,[1] $4PbCl_2 \cdot 3Pyr$,[2] and $PbCl_2\ 2Pyr$.[3] It crystallizes from aqueous solutions in the form of the anhydrous salt and should have small hydrating power and low temperature coefficients of conductivity. Jones and Winston[4] find, however, that the temperature coefficients in aqueous solutions are relatively high. Apparently the temperature coefficients are not entirely dependent upon the amount of solvent separating with the solute when solvates crystallize from solution.

TABLE XXIX

V	l_0	l_{25}	l_{50}
50.0	0.05	0.07	0.10
100.0	0.06	0.10	0.15?
200.0	0.07	0.10	0.11
400.0	0.12	0.18	0.23
800.0	0.20	0.26	0.35
1600.0	0.35	0.48	0.63

TABLE XXX

V	A	B	C
50.0	0.030	0.019	0.020
100.0	0.025	0.021	0.030?
200.0	0.019	0.005?	0.013
400.0	0.018	0.013	0.018
800.0	0.014	0.012	0.015
1600.0	0.016	0.012	0.016

Discussion

The power of a solution to conduct electricity depends upon the dielectric constant of the solvent, the degree of dissociation of the electrolyte, the number of ions present and their velocities. The degree of dissociation is determined

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[1] Zeit. anorg. Chem., 4, 100–110 (1893).
[2] Ibid., 14, 379–403 (1897).
[3] Jour. Phys. Chem., 15, 373 (1912).
[4] Am. Chem. Jour., 46, 368 (1912).

by the dielectric constant of the solvent and the electro-affinity of the ions. For a given potential gradient the ionic velocities are in turn dependent upon the viscosity of the solution, the mass or the volume of the ions. The mass and volume of either or both ions may be further augmented by combination with the molecules of the solute to form complex ions, or with the molecules of the solvent to form more or less highly solvated ions.

For solutions in a large number of solvents the molecular conductivity behaves normally, *i. e.*, it increases with increasing dilution. There are, however, numerous instances like those shown by the mercuric halides in pyridine in which the equivalent conductivity decreases, passes through a minimum and then rises with increase in the concentration of the solute. Such phenomena are considered by many as being incapable of explanation on the basis of the Arrhenius theory. That increase in molecular conductivity with increase in concentration in some organic solvents is peculiar only to the concentrated solutions has been shown by Pearce[1] and others. He, like Sachanov,[2] found that the molecular conductivity of various salts in aniline decreased with increase in dilution to a minimum and then increased normally upon further dilution.

Franklin[3] explains the increase in molecular conductivity with increasing concentration as due to an increase in auto-ionization, which more than compensates for the decrease in molecular conductivity due to an increase in viscosity.

In their study of the conductivity of various inorganic salts and non-salt organic solutes in the liquid halogen acids Archibald, McIntosh and Steele[4] found that the molecular conductivity increases with increasing concentration. They assumed that, while the original solute may of itself be incapable of ionizing in the solvent, it may combine with the

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[1] Unpublished results.

[2] Jour. Russ. phys. chem. Soc., 42, 683–690 (1910).

[3] Loc. cit.

[4] Zeit. phys. Chem., 55, 129 (1907).

solvent to form a complex solvent-solute molecule which behaves as an electrolyte. Accordingly, the number of complexes must increase with the concentration and, likewise, the molecular conductivity must increase, due to an increase in the total number of ions. These investigators used the expression

$$M_v = \alpha K' = \chi V^n,$$

where α, χ and V represent the degree of dissociation, the specific conductance and the volume, respectively. K′ is a constant and n is the number of simple molecules of solute combined with m molecules of solvent. By means of this relation they calculated the molecular conductivity and found it to increase normally with dilution. It is obvious that when α is equal to unity,

$$M_\infty = K'.$$

Evidently these investigators did not consider the fact that the amount of solvation per molecule of solute will vary with the dilution and must necessarily decrease as the concentration of the solute is increased. Where solvation is possible it is difficult to conceive how the complex, say, (n) solute-(m) solvent can remain unchanged throughout a wide range in concentration.

Sachanov has studied the molecular conductivity of various solutions in acetic and propionic acids[1] and in aniline, methylaniline and dimethylaniline.[2] In practically every case the molecular conductivity was found to increase with increasing concentration. All of these solvents have low dielectric constants and slight dissociating power. In a later article,[3] he states that a decrease in molecular conductivity with increasing dilution is just as characteristic for solvents with low dielectric constants as is an increase in molecular conductivity for solutions in solvents with high dielectric constants. He[4] asserts that electrolytic dissociation does

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[1] Jour. Russ. phys. chem. Soc., **43**, 526 (1911).

[2] Ibid., **44**, 324 (1912); **42**, 683 (1910).

[3] Zeit. phys. Chem., **80**, 13 (1912).

[4] Ibid., **80**, 20 (1912).

not depend solely on the magnitude of the dielectric constant, but also on the solvates and complex ions. The formation of such ions favors electrolytic dissociation because the electro-affinity of these complex ions is greater than that of the simple ions. In solvents with low dielectric constants only the complexes which yield complex ions of high electroaffinity can undergo electrolytic dissociation. The decrease in electrolytic conductivity in such solvents is explained as being due to the composition of these polymerized solute molecules on dilution.

An examination of the curves plotted from the data will show that the electrolytes used in this work are of two types. First, those which give minimum conductivity values at all temperatures, *viz.*, the mercuric halides and copper nitrate. Second, those like the nitrates of silver and cadmium, the chlorides of lithium, cobalt, copper and lead, the iodides of lithium and sodium, lithium bromide, and the thiocyanates of potassium and ammonium, which upon dilution give increasing values of l_v.

The phenomenon of the molecular conductivity increasing with increasing concentration is considered by some as being at variance with the Arrhenius theory. However, an attempt will be made in the present discussion to show that this anomalous behavior is due entirely to the presence and the properties of the polymerized solute molecules which are present in solutions showing such phenomena.

The most dilute solutions studied by Walden and Centnerszwer[1] correspond to those concentrations which give the minimum conductivity values in this work, and hence we have no experimental evidence as to the state of aggregation in the very dilute solutions. Assuming only the ionization of simple molecules, their results would seem to show that these molecules are ionized in the concentrated, but undissociated in the dilute solutions, which is contrary to common experience. That some ions are present at all dilutions is evident from the conducting power of these solutions.

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[1] Zeit. phys. Chem., 55, 231 (1906).

The abnormal boiling-point results noted must, therefore, be due to such an equilibrium between the various forms of the electrolyte present in the solution, *viz.*, simple and complex molecules, simple and complex ions and the pyridinated forms of each, as would give the molecular weights obtained.

Let us consider, as an example of the first type, the solutions of mercuric chloride, and what is said concerning them will apply, for the most part, to the other salts which give minimum conductivity. This salt is very soluble and has a strong tendency to combine with pyridine to form stable salts with pyridine of crystallization. Naturally, then, we would expect it to combine with still more pyridine when in solution in this solvent. Walden and Centnerszwer[1] have found that the mercuric halides exhibit a strong tendency to polymerize in pyridine solutions, just as they do in most solvents.

We should expect to find in these solutions the simple and polymerized molecules of mercuric chloride, the simple and complex ions and the solvated ions and molecules. The number and kind of each will depend upon the dilution. The equilibria between the different forms of the solute may be represented thus:

$$(1) \qquad HgCl_2 + m_1Pyr \rightleftarrows HgCl_2 \cdot m_1Pyr$$

$$(2) \qquad 2HgCl_2 \cdot m_1Pyr \rightleftarrows (HgCl_2)_2 \cdot m_2Pyr$$

As the concentration of the solute is increased the equilibrium will naturally be disturbed and the resulting effect will be a corresponding increase in the concentration of the polymer. Hence the reaction will proceed from left to right, as in (2). It is evident from the increase in conductivity in the most concentrated solutions that the dissociation of the polymerized molecules must be greater than that of the simple molecules. The conditions of equilibria may be represented by the following relations:

$$(3) \quad (HgCl_2)_2 \cdot m_2Pyr \rightleftarrows \overset{++}{Hg} \cdot m_3Pyr + \overset{--}{HgCl_4} \cdot m_4Pyr$$

In the most dilute solutions where the simple molecules predominate, we shall have the equilibrium represented by

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[1] Loc. cit.

$$(4)\quad HgCl_2 \cdot m_1Pyr \rightleftharpoons Hg\overset{+}{Cl} \cdot m_5Pyr + \overset{-}{Cl} \cdot m_6Pyr,$$

and possibly to a slight extent,

$$(5)\quad Hg\overset{+}{Cl} \cdot m_5Pyr \rightleftharpoons \overset{++}{Hg} \cdot m_3Pyr + \overset{-}{Cl}\ m_6Pyr.$$

In the intermediate concentrations all of these equilibria will be found to a greater or lesser extent. The degree of pyridination of the various solute particles (m_1, m_2, etc.) will depend upon the dilution.

Inasmuch as the molecular weight of mercuric chloride in pyridine approximates the normal value, and, therefore, the effect due to polymerization must approximately annul that due to dissociation and solvation, the extent of the polymerization must be slight, because the conductivity is low. Hence we may attribute to the polymerized molecules a strong ionizing power and, consequently, a high degree of dissociation in these solutions.

All the solutions used in the present work were made up under the assumption that no polymerization of the solute takes place. It is, therefore, evident that the actual normalities of the concentrated solutions with respect to the ionizing polymers are less than assumed in preparing the solutions. For example, if exactly one gram-molecular weight of mercuric chloride is dissolved in pyridine and then diluted to one liter and, if it is assumed that all the simple molecules combine in pairs to form single molecules of the polymerized form, the normality with respect to the polymer will be 0.5 *N* instead of 1.0 *N*, as would be the case, if no polymerization takes place. If, on the other hand, only a fraction of the simple molecules combine to form the polymerized form, the normality of the ionizing polymers will be still less, and will always be one-half the fractional molar concentration of the simple molecules which have become polymerized. If we are then dealing with ionizing polymers, the degree of dissociation for a given solution in the concentrated regions will be relatively much higher than it would be if we were actually dealing with the normality at which the solutions are originally made up.

In order to explain minimum conductivity the following equilibrium equation will be used as a guide:

$$2Hg^{++} + 4Cl^- \rightleftarrows 2HgCl^+ + 2Cl^- \rightleftarrows 2HgCl_2 \rightleftarrows (HgCl_2)_2 \rightleftarrows Hg^{++} + HgCl_4^{--}$$

In the concentrated solutions the ions present will result from the dissociation of the polymers. There will be only a very slight tendency towards simple ionization and this will be impeded by the repression of ionization due to the mercury ions. As the most concentrated solutions are dilute the equilibrium will be disturbed and polymers will change over into simple molecules in obeyance to the law of mass action. Hence the concentration of the ions formed from the polymers will decrease, although the dissociation of the remaining polymers will become more and more complete with continued dilution. The result will be a decrease in the equivalent conductivity. As dilution is continued the influence of the simple ionization will soon become effective on account of the polymers being converted almost completely into simple molecules. These in turn furnish a preponderance of simple ions which will cause the repression of the complex ionization. The equivalent conductivity should, therefore, begin to rise again and continue to do so with an increase in dilution. This, then, would mean that the minimum values would be encountered for the equivalent conductivity. Of course viscosity changes as well as solvation effects are taking place with dilution. The latter would naturally change the sizes of the ions and, therefore, alter the freedom with which they would move. The decrease in viscosity would also result in greater freedom to the mobility of the ions. However, all these last mentioned factors would be subordinated to the changes in the concentrations of the various kinds of ions, as just outlined.

Solutions of silver nitrate, lithium bromide, lithium iodide, and the thiocyanates of ammonium and potassium all possess high conductivity values. The most concentrated solution of each is noticeably viscous. On the other hand, cadmium nitrate and the chlorides of lithium, cobalt, copper and lead are only slightly soluble in pyridine. Their most concentrated solutions have apparently low viscosities. The equivalent conductivities shown by these electrolytes are very low. Hence, within the limits of these facts, the viscosity is not the predominating effect in their conductivity.

Another point in connection with the salts just mentioned is the fact that, generally speaking, the binary salts are the better and the ternary salts the poorer conductors.

The existence of minima of temperature coefficients of equivalent conductivity seems to be a general phenomenon in pyridine solutions. The solvation per molecular weight of the solute is greatest in the more dilute solutions. Owing to the greater concentrations of the solute, however, the concentrated solutions will contain a much greater percent of combined pyridine, the degree of solvation decreasing with increasing concentration. The instability of these solvates increases not only with increase in complexity but also with increase in temperature.

The minima of the temperature coefficients may be explained on the basis of viscosity and ionic solvation. We would expect the greatest temperature changes in the most concentrated solutions. Here the viscosity is greatest and the percent of pyridine locked up as that of solvation is at a maximum. The effect of the decrease in the complexity of the solvates due to a rise in temperature would be to increase the amount of the pure solvent. This in itself means a decrease in the viscosity of the solution. Then, too, the rise in temperature results in a decrease in the viscosity of the pure solvent. For these reasons the solvated ions, which in themselves may or may not have suffered an appreciable change, due to the rise in temperature, are able to migrate more rapidly. In the less concentrated solutions the viscosity changes due to a rise in temperature will be less pronounced. Hence the values of the temperature coefficients will decrease. While the decrease in the viscosity change with dilution is going on the ionic solvation is increasing. The instability of the solvated ions with rise in temperature is also increasing with dilution. As the temperature is raised the decrease in the complexity of the solvated ions will cause an increase in their mobility. Thus we can readily understand how the solvated-ion effect can annul that of the viscosity. It is this condition which gives rise to the minimum temperature coefficient values. As the increase in dilution continues the ion solvation effect becomes the sole factor and hence we obtain a steady increase in the values of the temperature coefficients.

Another point to be noted is that the temperature coefficients are greater between 0° and 25° than those obtained for the interval 25°-50°. Since the decrease in the complexity of the solvated ions caused by a rise in temperature must be greatest in the region of greatest complexity, a greater change should be expected at temperatures favorable to a higher degree of complexity, *i. e.*, between 0° and 25°.

No explanation can be offered for the negative temperature coefficients in the cases of lithium bromide, sodium iodide, cobalt chloride and cadmium nitrate.

Comparing the magnitudes as well as the relative changes of temperature coefficients with dilution for the different electrolytes there seems to be no direct relation between these and the amount of pyridine with which they are combined when they crystallize from solution.

In general, the binary salts show the highest equivalent conductivity. The ternary give the lowest. There are, however, two notable exceptions to this generalization: lithium chloride, a binary salt, gives very low, while copper nitrate, a ternary salt, gives comparatively high values of the equivalent conductivity.

So far as the effect of solvation on conductivity is concerned, there is no reason for assuming the combination of solute and solvent as essential to the increase of electroaffinity, as Sachanov[1] has done. After the ions are once

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[1] Loc. cit.

formed then combination of the same with the solvent may modify their electro-affinity to some extent.

Inasmuch as the dielectric constant of pyridine (20) varies little within the temperature range studied its effect must be practically constant throughout. Since pyridine is considered as a non-associated solvent[1] this factor would not enter into the problem.

Summary

A study of the equivalent electrical conductivity of solutions of fifteen salts in pyridine has been made at three temperatures, *viz.*, 0°, 25° and 50°.

Two classes of electrolytes are to be observed. (1) Those for which the equivalent conductivity increases throughout with increasing dilution; (2) those which give minimum values of equivalent conductivity.

The values of the temperature coefficients between 0° and 25° are higher than those between 25° and 50°. An explanation is offered.

An explanation for the minimum values of equivalent conductivity has been advanced.

It has been shown that the anomalous behavior in equivalent conductivity is due entirely to the presence and properties of the ionizable polymerized solute, which predominates in the concentrated solutions.

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[1] J. L. R. Morgan: Jour. Am. Chem. Soc., 30, 1068 (1908).

NEW BOOKS

The Chemistry of Colloids. *By W. W. Taylor. 14 × 19 cm; pp. viii + 328. New York: Longmans, Green & Co., 1915. Price: $2.00 net.*—Any book on colloid chemistry written in English is helpful nowadays. The author divides the subject into four parts: general properties of colloids; methods of preparation; adsorption; applications of colloid chemistry. Under general properties of colloids the headings are: introduction; general differences between suspensoids and emulsoids; diffusion and dialysis; osmotic pressure and molar weight; optical properties; Brownian movement; the size of particles and ultrafiltration; electrical properties; precipitation; protection and mutual precipitation; the properties of gels. Under methods of preparation the chapters are: introduction; crystallization methods; solution methods; electrical dispersion methods. Adsorption is treated under the three subdivisions: surface phenomena; surface concentration; adsorption. Under applications of colloid chemistry the author discusses: semi-colloids; dyeing; tanning, the soil, and purification of sewage; applications of colloid chemistry to biology.

The book is frankly a compilation, the author contributing practically nothing, not even a point of view. It seems to the reviewer that the general arrangement is faulty. Since colloidal solutions owe their stability in general to adsorbed substances, the phenomena of adsorption should be taken up first and not last. Unless one does this, the treatment is necessarily empirical.

The author spells cathode in the German fashion. There is practically nothing on emulsions except a couple of references to Hatschek's oil emulsions and there is not even a reference to the possibility of two types of emulsions. It is not the author's fault that his chapter on dyeing only comes down to 1913; but it is a singular piece of hard luck for him that he should have chosen that particular topic for one of the applications. As a matter of fact he has not read Pelet-Jolivet's book with any thoroughness, though he refers to it. The reviewer does not like the statement, p. 274, that "as a broad generalization mordants may be said to be 'colloidogenic' substances, *i. e.*, they are themselves truly soluble, but by various changes give rise to colloids, either sols, or more usually gels." The author is considering aluminum acetate and stannic chloride as mordants, whereas the reviewer believes that the mordants are aluminum oxide and stannic oxide.

On p. 264 the author says that "casein is insoluble in water, but is essentially acid, as is shown by the reddening produced by pressing moist casein on to blue litmus paper." This involves the same fallacy as the one about acid soils. It is not a mistake which a writer on colloid chemistry should make.

While the book is distinctly a disappointment when one considers what it might have been or should have been, it is perhaps fairer to judge it as the only English text-book available. Since it has no competitors, it is necessarily the best of its kind.

Wilder D. Bancroft

Surface Tension and Surface Energy and Their Influence on Chemical Phenomena. *By R. S. Willows and E. Hatschek. 13 × 19 cm; pp. viii + 80. Philadelphia: P. Blakiston's Son and Co., 1915. Price: $1.00 net.*—"The present small book is based on a course of lectures delivered at the Sir John Cass Technical Institute by one of the authors, in response to the wishes of a number of the students who had attended the course on colloids."

The general treatment is: existence and theory of surface tension; relations between surface tension and other physical constants; relations between surface tension and chemical constants; factors affecting distribution of a solute in solution; effect of electric charge on surface tension. There is an interesting passage, p. 31, in regard to Traube's theory that surface tension phenomena are the cause of osmotic pressure. "It may be remarked here that Traube's theory is rather a theory of osmosis than of osmotic pressure and that, as regards the latter, it has proved incapable of giving any numerical results. It is also open to a number of grave objections, which we will state very briefly. A solution of salicin in water has lower surface tension than water, yet water passes into it through a membrane, as it also does into a mixture of ethyl alcohol and water. According to Traube's theory this should be impossible. A further deduction from Traube's theories has also proved untenable. According to them, no diffusion through a membrane from a solution into the solvent should be possible if the former has a higher surface tension than the latter; in other words, the membrane behaves as an impermeable membrane to this system. Traube assumes that it becomes permeable, *i. e.*, that diffusion takes place, if a substance is added which reduces the surface tension below that of the solvent. This assumption has also been proved incorrect by experiment.

"In view of the great importance of osmotic phenomena in organisms and of the difficulty of explaining many of them by the classical theories, Traube's views have received some attention from biologists and have given rise to various investigations, one of which deserves mention. This was carried out by Czapek, with the object of determining the 'surface tension' of the contents of plant cells. He made solutions of various organic substances, in which the cells were immersed, and noted the concentrations at which the contents just began to diffuse outwards. In accordance with Traube's theories he assumed that at this point the surface tension of the solution and that of the plasma were equal. Exosmosis occurred with all solutions when their surface tension was reduced to 0.65 and 0.68 that of water, whence Czapek concludes that this is the surface tension of the cell contents. While we cannot consider this conclusion warranted, the fact that solutions of equal surface tension produce exosmosis is certainly remarkable. It seems probable that an explanation may be found in adsorption as has been the case with many 'poisoning' phenomena which could not be explained by osmotic pressure alone."

It is unfortunate, almost inexcusable, that no references are given.

Wilder D. Bancroft

Elektrochemie wässeriger Losungen. *By Fritz Foerster. Second edition. 16 × 24 cm; pp. xviii + 804. Leipzig: J. A. Barth, 1915. Price: 30 marks paper, 31.50 bound.*—The first edition was reviewed ten years ago (9, 782). The new edition is quite a different book and far superior to the first, though the general treatment is the same as before and there is no change either in the number or in the headings of the chapters. The whole book is so good that it is almost unfair to cite special sections. The paragraphs on electrical endosmose are very good, p. 108, and the pages on electrolytic addition agents, p. 333, are the best that the reviewer has seen. There is a very clear account of the working of the different accumulators, p. 200, though the reviewer thinks that a reference to the elimination of sulphating by use of a sodium sulphate solution would have been wise. The process is a very useful one and is interesting theoretically. The author has given a very clear account of the phenomena of passivity, pp. 186, 367. While one may not agree with the view, p. 269, that overvoltage is due to the formation of hydrogen alloys, the author has presented his case well. He has done as well as could be expected with the very unsatisfactory subject of ozone and hydrogen peroxide, p. 297. The author now classifies methods of electrolytic analysis, p. 400, explicitly as constant voltage and constant current methods, and consequently has corrected the erroneous statement in the first edition that rapid methods cannot be used for electrolytic separations. The theory of slow electrolytic reductions, p. 509, is put in a very good form and of course the author's special chapter on the electrolysis of halogen compounds is very well done. Besides these major points there are a number of minor points throughout the book which were of great interest to the reviewer. There are so many sloppy books published nowadays that it is a real pleasure to find a first-class book, written with care by a man who knows his subject.

Wilder D. Bancroft

The Electrical Nature of Matter. *By Harry C. Jones. Third edition. 22 × 16 cm; pp. viii + 212. New York: D. Van Nostrand Company, 1915. Price:* $2.00.—The third edition does not differ materially from the second (15, 508). An occasional line has been changed, a paragraph has been put in here and there where there was a blank half page, and there has been added a page, p. 204, in regard to the work on the atomic weight of radioactive lead. The most interesting of the added paragraphs is the one on p. 48.

"The recent work of Laue, Bragg and others has changed our conception as to the nature of the X-ray. If the rays were a regular series of vibrations in ether, with wave-lengths say of molecular dimensions, when allowed to fall on a grating with a distance between the lines also of molecular dimensions, we would have produced an X-ray spectrum. A crystal is just such a space-grating. When X-rays are reflected from a crystal, we have produced spectra of various orders. From the positions of the spectra of the various orders, and the intermolecular distances in the crystals, we can calculate the approximate wave-lengths of the X-rays. These wave-lengths vary, but are of the magnitude of an Ångström unit. This means that X-rays are not a series of irregular pulses in the ether as Stokes supposed, but like light a series of regular vibrations. The X-rays differ from light in that the lengths of the ether waves are much less. This explanation of the nature of the X-ray is in harmony with its properties."

Wilder D. Bancroft

NAME INDEX

To Papers

NAME INDEX

To New Books

SUBJECT INDEX

Exclusive of New Books