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A PORTION OF THE SYSTEM, FERRIC OXIDE-CUPRIC OXIDE-SULPHUR TRIOXIDE-WATER

BY G. TUNELL AND E. POSNJAK

Introduction

The investigation of the system, ferric oxide-cupric oxide-sulphur trioxide-water, was undertaken primarily to gain some knowledge of the processes which take place and the equilibria which may be attained during the natural oxidation of the disseminated iron and copper sulphide ore bodies in altered porphyry. Since these processes presumably take place in the neighborhood of surface temperatures and in not very concentrated solutions, the investigation was restricted to these conditions as it would have required a very large amount of time to work out the quaternary system completely.

Experimental Methods

For the preparation of the initial mixtures, besides normal cupric sulphate and normal ferric sulphate, a basic ferric sulphate and a specially prepared suspension of cupric oxide together with the required amount of water were used. The basic ferric sulphate was obtained some years ago from the firm of J. T. Baker and an analysis (33.61 per cent Fe_2O_3, 42.12 per cent SO_3, and by difference 24.27 per cent H_2O) was found to approach the composition of the basic salt $2Fe_2O_3.5SO_3.17H_2O$. It was extremely fine-grained and for that reason could not be definitely identified microscopically. The suspension of finely divided cupric oxide was prepared by adding a dilute solution of sodium hydroxide to a fairly concentrated warm solution of cupric sulphate, with constant stirring, until it became just alkaline. The greenish-blue precipitate first formed changed at this point to a brownish-black one which was cupric oxide as was evidenced by its X-ray diffraction pattern. The precipitate was washed by shaking it up with hot water and throwing it down by centrifuging. This was continued until the finely divided cupric oxide began to form a suspension which was no longer precipitated by ordinary centrifuging (approximately a relative centrifugal force of 1100 times gravity). The suspension prepared in this way was found by an analysis to be practically free from sodium.

From appropriate amounts of the materials described above mixtures of definite total composition were prepared which, on reaching equilibrium, furnished sufficient amounts of liquid and solid phases for their identification. The total amounts of the mixtures ranged from about 40 to about 100 grams. Each mixture was sealed in a Jena combustion tube, which it about two-thirds filled. These tubes were placed in an air thermostat at 50° in which the variation of temperature was limited to about ± 1°. The time the tubes were kept in the thermostat ranged from about one to about three years and during this time they were shaken up almost every day to promote the establishment of equilibrium.

After the tubes were taken out of the thermostat they were quickly opened and the solid separated from the liquid phase by suction filtration through a dense Jena glass filter. A sample of the solid with adhering mother liquid was examined microscopically for control. The rest of the solid was washed with a mixture of water and alcohol and finally with alcohol or acetone. The air-dry solid was subjected to careful microscopical examination and X-ray analysis to establish the nature of the phase or phases present. Despite the extreme fineness of the precipitates representing the solid phases, it was in all cases possible to establish definitely their crystallinity and crystal individuality even when more than one solid phase was present in the precipitate.

The liquid, or a portion thereof, was weighed and analyzed. The following procedure was used: The copper was removed first by electrolysis of the solution, and weighed. The remaining solution, largely increased in volume due to washing of the copper precipitate, was partially evaporated and at the same time the iron which was reduced during electrolysis was re-oxidized by the addition of a few drops of "perhydrol" to the solution. A double precipitation of the iron with ammonia in the usual way followed and the iron on ignition was determined as oxide. In the combined filtrates the sulphate was finally determined, also gravimetrically, as barium sulphate. This method had been tried out with a mixture of standard solutions of copper and iron sulphates and was found in the absence of nitric acid to give accurate results. Water in all cases was taken by difference.

The Crystalline Phases

Geometrical and optical crystallographic descriptions of all of the compounds found in the portion of the quaternary system investigated have already been published.[1] In this paper the mode of occurrence of all these in the quaternary system will be described and X-ray powder diffraction patterns will be given for two of them, $Fe_2O_3.H_2O$ (goethite) and $3Fe_2O_3.4SO_3.9H_2O$, the patterns of the others having already been published.[2]

$Fe_2O_3.H_2O$ (Goethite).[2a] No single faceted crystals of goethite formed in the quaternary system at 50° (the only temperature at which experiments

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[1] E. Posnjak and H. E. Merwin: The Hydrated Ferric Oxides, Am. J. Sci., 47, 320 (1919); E. Posnjak and H. E. Merwin: The System, Fe_2O_3-SO_3-H_2O, J. Am. Chem. Soc., 44, 1977 (1922); E. Posnjak and G. Tunell: The System, Cupric Oxide-Sulphur Trioxide-Water, Am. J. Sci., 18, 12-23 (1929).

[2] Am. J. Sci., 18, 12 (1929).

[2a] The usage of the term goethite in this paper is the same as that in earlier papers from this Laboratory; the term goethite is thus used as a synonym of α-$Fe_2O_3.H_2O$. It may be added that in this Laboratory the term lepidocrocite is used as a synonym of γ-$Fe_2O_3.H_2O$. These usages are consistent with those of most other authors. Unfortunately, however, by Willmann (Cbl. Min., 1921, 673) and in "Gmelins Handbuch der anorganischen Chemie" (8. Aufl., Teil A, S. 147 (1929)) the term goethite has recently been applied to γ-$Fe_2O_3.H_2O$. For a clear statement of the history and present usages of the terms see "Handbuch der anorganischen Chemie" (Vierter Band, dritte Abteilung, zweiter Teil, B, Lieferung 1, S. B224, B225 (1930)) by R. Abegg, Fr. Auerbach, and I. Koppel. These authors use the terms goethite and lepidocrocite in the same senses in which they are used in the Geophysical Laboratory. Abegg, Auerbach, and Koppel give a good summary in tabular form of the geometrical, optical, and X-ray crystallographic properties, the densities, and some other physical properties of the dimorphic forms of $Fe_2O_3.H_2O$ (S. B226).

were carried out in the quaternary system), or in the ternary system, Fe_2O_3-SO_3-H_2O, at 50° or at any other temperature. Spherulites of goethite, single and in aggregates, were formed in one ternary solution at 50° and in other ternary solutions at higher temperatures. All of the goethite preparations formed in solutions containing all four components at 50° consisted of fibrous or optically amorphous aggregates. In all cases, however, their crystallinity and identity were established by the X-ray powder diffraction method. The apparatus used was one made by the General Electric Company in which the K_α radiation of molybdenum is used and the distance between sample and photographic film is eight inches. As a standard of comparison well-crystallized goethite from Pribram, Bohemia (Harvard Museum No. 80927), was utilized, of which the measured spacings of the diffraction lines and their estimated relative intensities are given in Table I.[3]

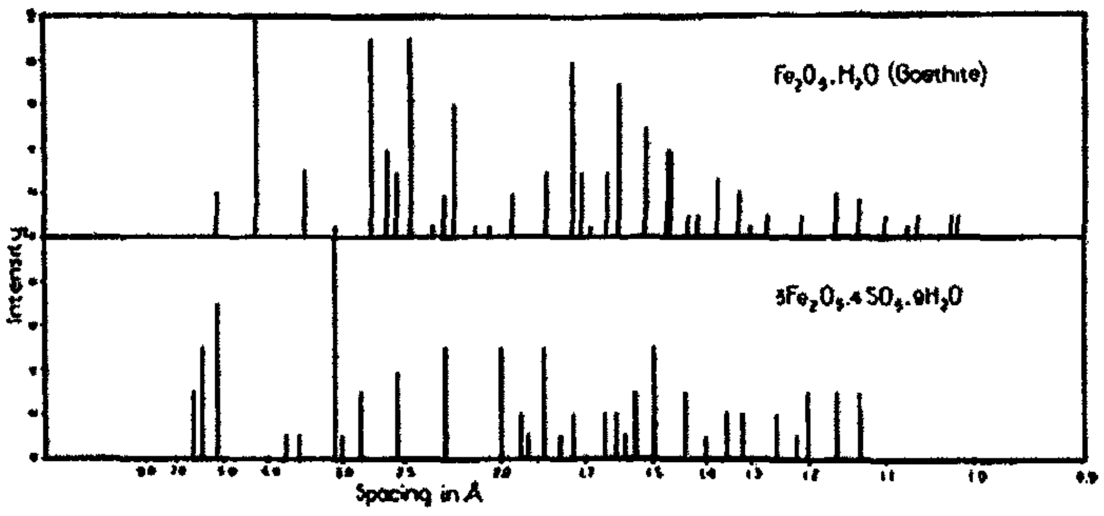

FIG. 1

Diagrams of X-ray powder diffraction patterns of $Fe_2O_3.H_2O$ (goethite) and $3Fe_2O_3.4SO_3.9H_2O$. The relative intensities are visual estimates with ten representing the maximum in each case.

$3Fe_2O_3.4SO_3.9H_2O$. Faceted crystals of $3Fe_2O_3.4SO_3.9H_2O$ and aggregates of fine anhedral grains formed in ternary solutions of Fe_2O_3-SO_3-H_2O at 50°. In solutions containing all four components no faceted crystals formed but only fine-grained (crystalline) aggregates of anhedral, equant grains which were identified microscopically and by means of their X-ray powder diffraction pattern. Crystals of $3Fe_2O_3.4SO_3.9H_2O$[4] precipitated in a ternary solution of Fe_2O_3-SO_3-H_2O were used to obtain the standard X-ray spectrum of this substance. The measured spacings of the lines in the standard spectrum and their estimated relative intensities are given in Table I.

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[3] The diffraction pattern obtained from this specimen was identical with that obtained from one of goethite from El Paso County, Colorado, the analysis of which was No. 5 in Table I and the specific gravity No. 5 in Table VII of "The Hydrated Ferric Oxides" (Am. J. Sci., 47, 316 (1919)). Powder from the specimen from El Paso County, Colorado, was examined under the microscope by Merwin and by Tunell. No impurities were found. The powder consisted of brown, transparent to translucent grains some of which were perceptibly pleochroic between slightly different shades of brown. Grains lying approximately parallel to the perfect cleavage exhibited the characteristic green interference color already mentioned by Merwin and these also showed a biaxial optical figure.

[4] Identified optically. The optical properties of analyzed crystals formed in the system, Fe_2O_3-SO_3-H_2O, had been established previously by Posnjak and Merwin.

TABLE I

Planar Spacings and Estimated Relative Intensities of the X-ray Diffraction Lines of $Fe_2O_3.H_2O$ (Goethite) and $3Fe_2O_3.4SO_3.9H_2O$

$Fe_2O_3.H_2O$ (Goethite)		$3Fe_2O_3.4SO_3.9H_2O$	
Spacing	Intensity	Spacing	Intensity
5.1	2	6.0	3
4.24	10	5.7	5
3.42	3	5.15	7
3.07	0.5	3.69	1
2.72	9	3.54	1
2.61	4	3.10	10
2.52	3	3.00	1
2.475	9	2.84	3
2.325	0.5	2.56	4
2.275	2	2.27	5
2.220	6	1.99	5
2.110	0.5	1.935	2
2.040	0.5	1.890	1
1.940	2	1.840	5
1.820	3	1.780	1
1.732	8	1.745	2
1.704	3	1.631	2
1.675	0.5	1.595	2
1.615	3	1.570	1
1.578	7	1.545	3
1.520	5	1.503	5
1.470 (broad)	4	1.441	3
1.431	1	1.391	1
1.403	1	1.351	2
1.372	3	1.320	2
1.325	2	1.252	2
1.301	0.5	1.230	1
1.271	1	1.200	3
1.208	1	1.160	3
1.157	2	1.134	3
1.131	2	Further weak lines present	
1.100	1		
1.075	0.5		
1.057	1		
1.033	1		
1.018	1		
Further weak lines present			

CuO (Tenorite). No tenorite formed in our solutions containing all four components, and the precipitates which formed in the ternary system, CuO-SO_3-H_2O (which is a part of the quaternary system), have already been described.[5]

$4CuO.SO_3.3H_2O$ (Brochantite). Minute lath-shaped single crystals of brochantite with positive elongation formed in one solution containing all four components.

$3CuO.SO_3.2H_2O$ (Antlerite). Minute lath-shaped single crystals of antlerite, some with negative, a few with positive elongation, were observed which formed in one solution containing all four components. These crystals were elongated parallel to β, like the crystals synthesized in the ternary system, CuO-SO_3-H_2O.

General Experimental Results

The isothermal-isobaric equilibrium relations in a quaternary system may be represented in an equilateral coordinate tetrahedron. The water corner of the tetrahedron, that is to say, the region in which the total composition is 93.5 per cent or more H_2O, 6.5 per cent or less Fe_2O_3, 6.5 per cent or less CuO, and 6.5 per cent or less SO_3, has been investigated at 50°C. and the results are presented in Table II. In order to be sure of the relations of the three-phase space curves inside the limited portion some points were also obtained just outside (that is, in more concentrated solutions), and these are

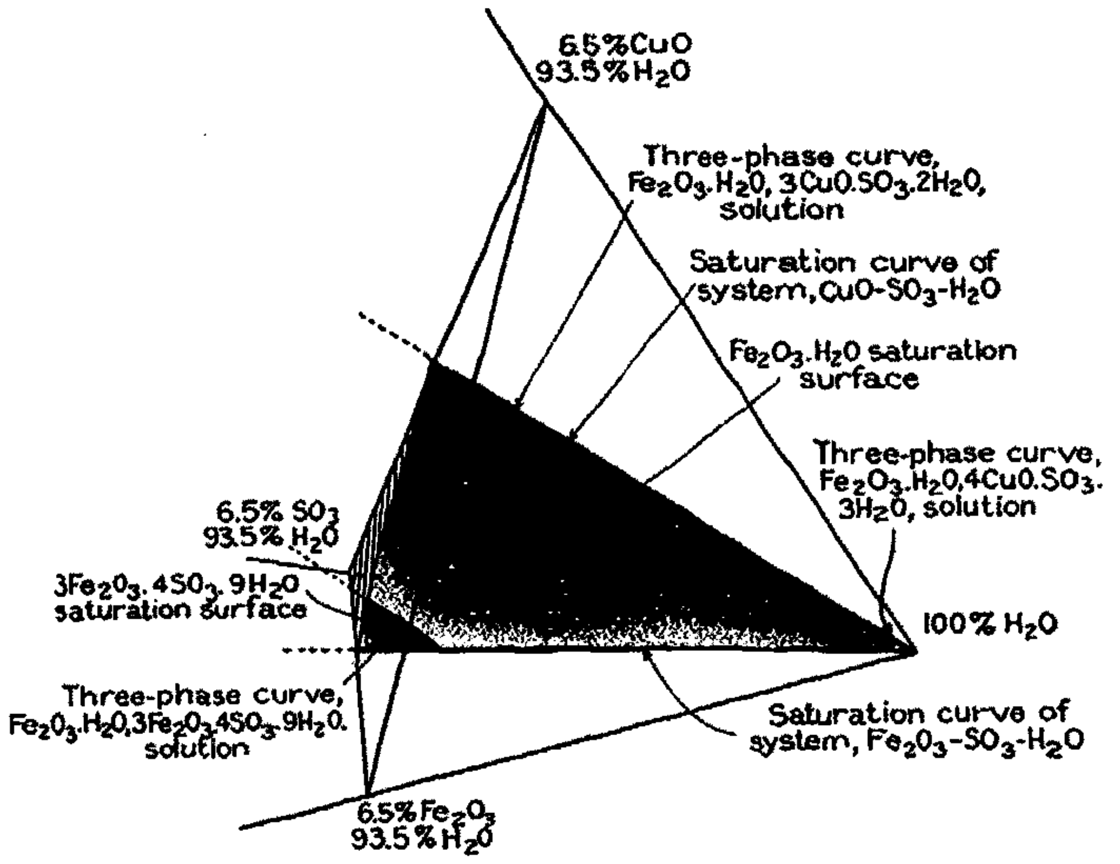

FIG. 2

Perspective view of model of the isothermal-isobaric saturation surface in the portion of the system, Fe_2O_3-CuO-SO_3-H_2O, *in which the total composition* is 93.5 per cent or more H_2O, 6.5 per cent or less Fe_2O_3, 6.5 per cent or less CuO, and 6.5 per cent or less SO_3.

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[5] Am. J. Sci., **18**, 14 (1929).

TABLE II

The Saturation Surface of the System, Ferric Oxide-Cupric Oxide-Sulphur Trioxide-Water, at 50° inside and just outside the Limited Portion of the Tetrahedron

Expt.	Liquid Phase				Solid Phases	Methods of Identification of Solid Phases[3]
	Fe_2O_3 %	CuO %	SO_3 %	H_2O[2] %		
8A	>0 <0.001	0.06	0.06	99.88	$Fe_2O_3.H_2O$[5] & $4CuO.SO_3.3H_2O$[4]	x o x o
9A	>0 <0.001	0.14	0.15	99.71	$Fe_2O_3.H_2O$[5] & $4CuO.SO_3.3H_2O$[7]	x o x
5A[1]	0.05	0.08	0.39	99.48	$Fe_2O_3.H_2O$[5] & $3Fe_2O_3.4SO_3.9H_2O$[7]	x o x
6A[1]	0.17	0.15	0.74	98.94	$Fe_2O_3.H_2O$[5] & $3Fe_2O_3.4SO_3.9H_2O$[7]	x o x
11A	>0 <0.001	0.61	0.64	98.75	$Fe_2O_3.H_2O$[5] & $4CuO.SO_3.3H_2O$	x o x
1A[1]	0.22	0.94	1.64	97.20	$Fe_2O_3.H_2O$[5] & $3Fe_2O_3.4SO_3.9H_2O$[6]	x o x o
7A[1]	0.94	0.24	2.08	96.74	$Fe_2O_3.H_2O$[5] & $3Fe_2O_3.4SO_3.9H_2O$[7]	x o x
2A[1]	0.67	0.93	2.34	96.06	$Fe_2O_3.H_2O$[5] & $3Fe_2O_3.4SO_3.9H_2O$[7]	x o x
3A[1]	1.19	0.90	3.05	94.86	$Fe_2O_3.H_2O$[5] & $3Fe_2O_3.4SO_3.9H_2O$[6]	x o x o
14A[1]	1.37	1.21	3.68	93.74	$Fe_2O_3.H_2O$[5] & $3Fe_2O_3.4SO_3.9H_2O$[7]	x o x
15A[1]	1.72	1.20	4.24	92.84	$Fe_2O_3.H_2O$[5] & $3Fe_2O_3.4SO_3.9H_2O$[7]	x o x
17A[1]	2.44	1.86	5.69	90.01	$Fe_2O_3.H_2O$[5] & $3Fe_2O_3.4SO_3.9H_2O$[7]	x o x
18A	>0 <0.001	5.01	5.22	89.77	$Fe_2O_3.H_2O$[5] & $3CuO.SO_3.2H_2O$[4]	x o x o

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[1] The small amount of $3Fe_2O_3.4SO_3.9H_2O$ left in this experiment is probably due to the extreme slowness of the conversion of $3Fe_2O_3.4SO_3.9H_2O$ into $Fe_2O_3.H_2O$. The point therefore may be assumed to lie on the $Fe_2O_3.H_2O$ saturation surface. See discussion in text.

[2] H_2O by difference.

[3] Denotation of symbols: x, X-ray diffraction pattern; o, optical properties.

[4] Solid phase in faceted crystals.

[5] Solid phase in very fine-grained crystalline (fibrous) aggregates.

[6] Solid phase in very fine-grained crystalline aggregates (anhedral, equant grains).

[7] Solid phase not discernible under the microscope.

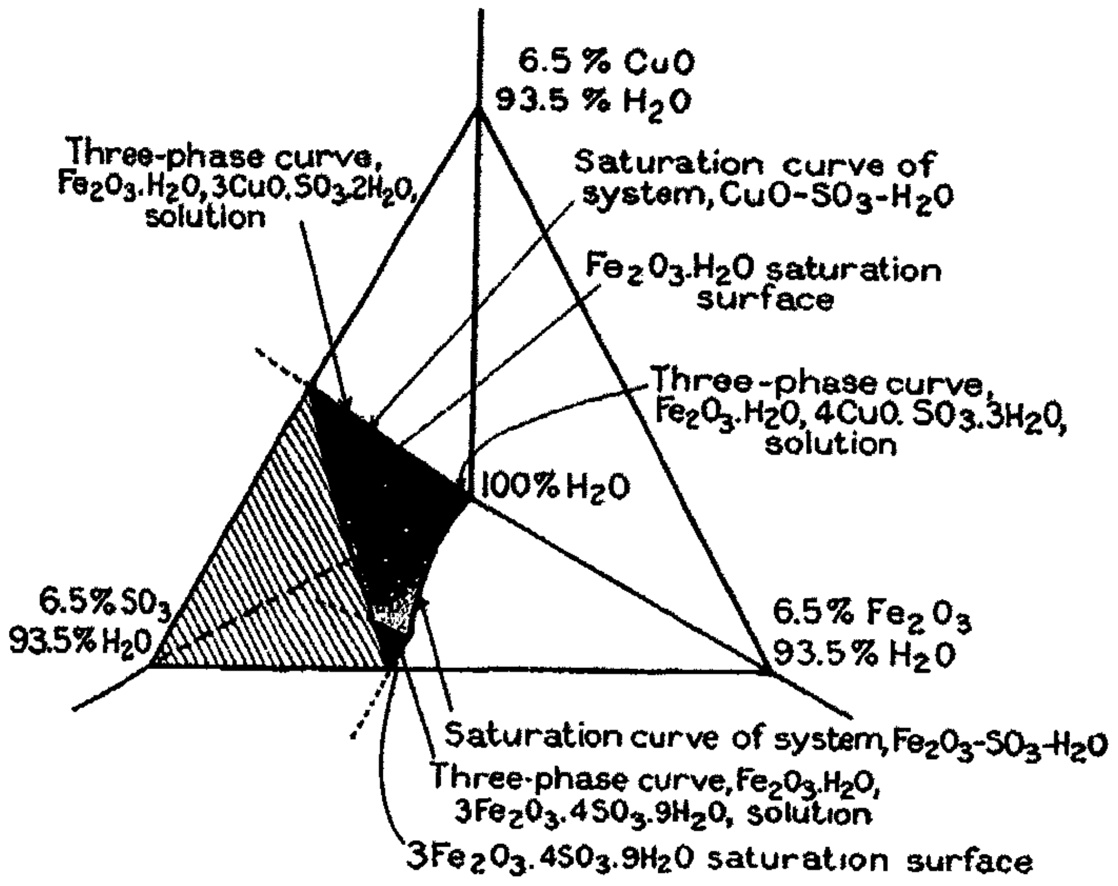

Fig. 3

Perspective view of model of the isothermal-isobaric saturation surface in the portion of the system, Fe_2O_3-CuO-SO_3-H_2O, in which the total composition is 93.5 per cent or more H_2O, 6.5 per cent or less Fe_2O_3, 6.5 per cent or less CuO, and 6.5 per cent or less SO_3.

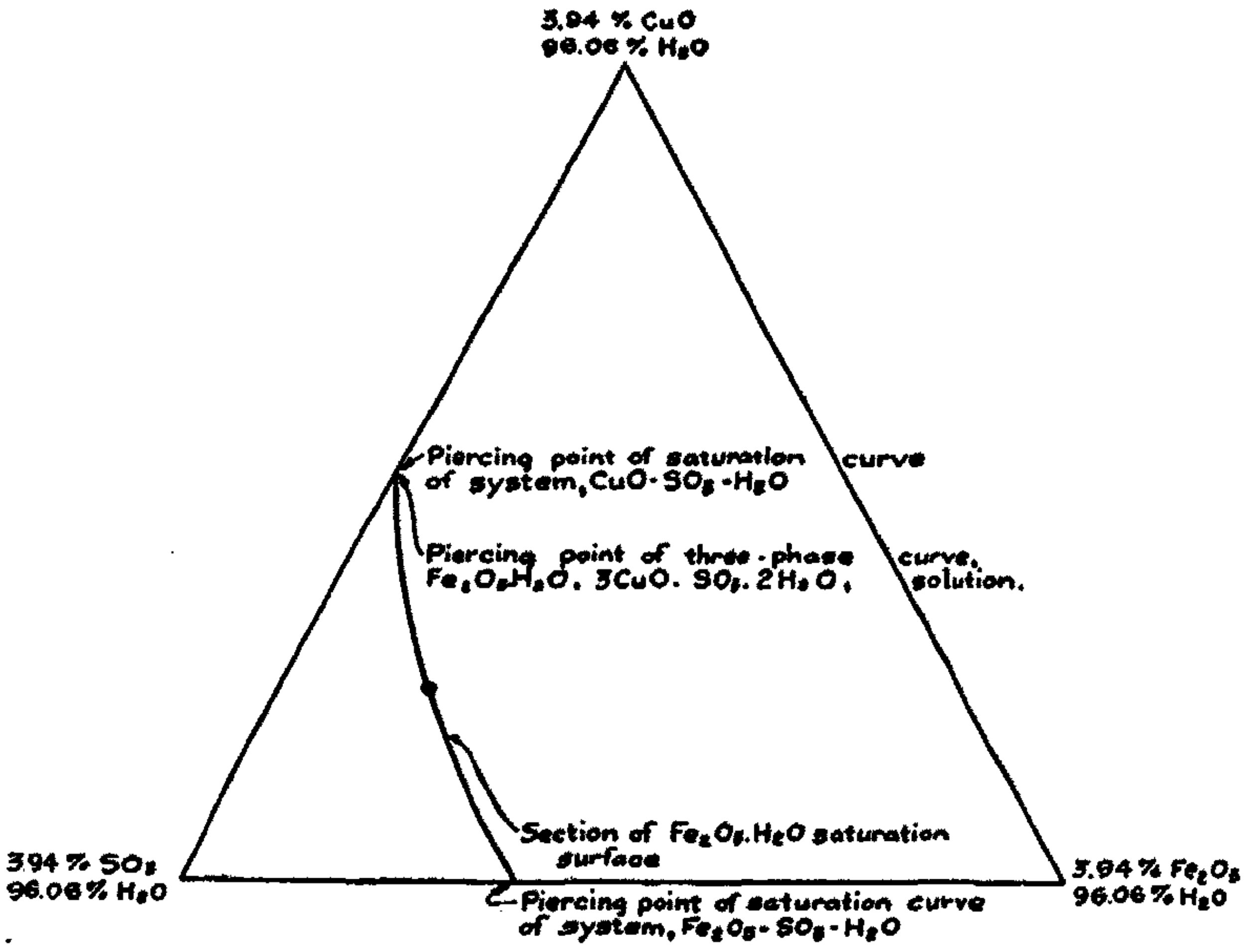

Fig. 4

Section through Fe_2O_3-CuO-SO_3-H_2O coordinate tetrahedron parallel to Fe_2O_3-CuO-SO_3 face (percentage of H_2O at all points in plane of section is 96.06).

also given in Table II. The data refer to mixtures at equilibrium except in cases explicitly noted in which the direction of a reaction was used to obtain information regarding the location of the three-phase curve, $Fe_2O_3.H_2O$, $3Fe_2O_3.4SO_3.9H_2O$, solution. A model of the portion of the tetrahedron and saturation surface has been prepared, and is illustrated in perspective in Figs. 2 and 3. A cross-section of the tetrahedron and saturation surface is given in Fig. 4. The concentrations are expressed numerically and graphically in weight per cent.

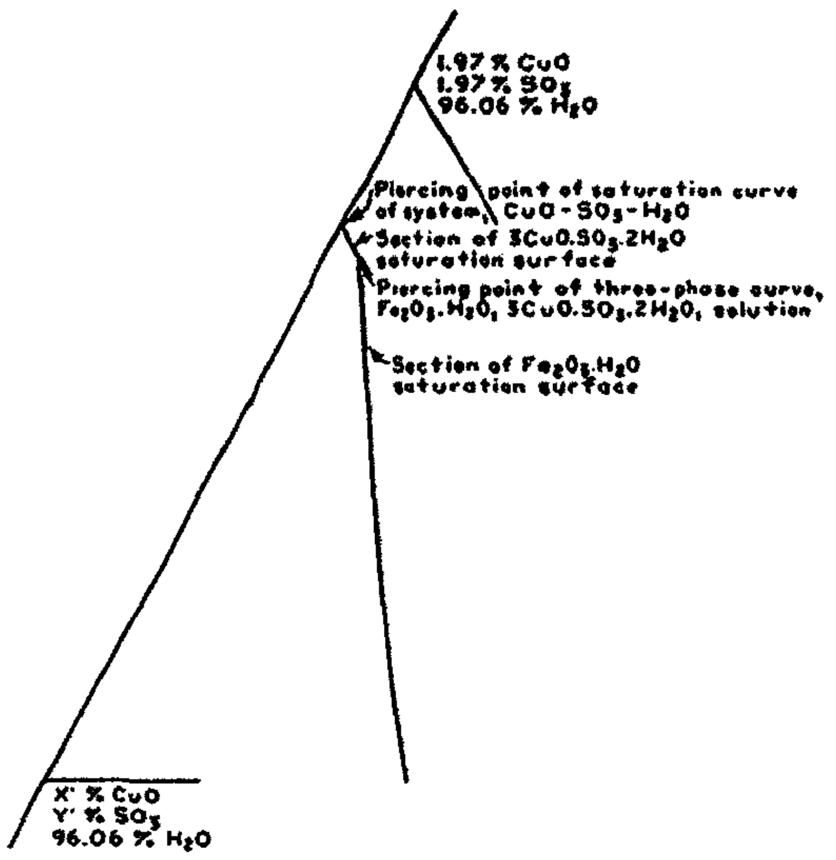

FIG. 5

Sketch showing relations which must exist very near the $CuO-SO_3-H_2O$ face of the coordinate tetrahedron along trace of saturation surface on plane parallel to $Fe_2O_3-CuO-SO_3$ face (percentage of H_2O at all points in this plane is 96.06). Enormously enlarged as compared with Fig. 4.

The saturation surface of the quaternary system necessarily intersects the $Fe_2O_3-SO_3-H_2O$ and $CuO-SO_3-H_2O$ faces of the coordinate tetrahedron in the saturation curves of the respective ternary systems. Numerical values of the data for the saturation curve of the system, $Fe_2O_3-SO_3-H_2O$, have been given by Posnjak and Merwin and for the saturation curve of the system, $CuO-SO_3-H_2O$, by Posnjak and Tunell.[6] Some additional points have been

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[6] In the papers on the systems, $Fe_2O_3-SO_3-H_2O$ and $CuO-SO_3-H_2O$, the results were expressed as isothermal-polybaric equilibria of crystal, liquid, and gas phases. As stated in the paper on the system, $CuO-SO_3-H_2O$, however, the pressure in the gas phase was greater than the vapor pressure of the solution by the pressure of the admixed air. It was also stated in that paper that any one of the diagrams presented would not differ more than the experimental error from the isothermal-isobaric diagram for the equilibria of crystal and liquid phases at the same temperature and the maximum pressure in any of the tubes. In the present paper the equilibria are treated as isothermal-isobaric equilibria of crystal and liquid phases: in the present work the pressures in all of the tubes were practically the vapor pressure of water plus the pressure of the admixed air at 50°C.

determined in these systems. Six points on the saturation curves of the basic cupric sulphates are given in Table III. Also three points on the saturation curves of the normal cupric sulphates are given in Table III.[7] These three points are more accurate than point 81 of Table VI of "The System, Cupric

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[7] Since publication of "The System, Cupric Oxide-Sulphur Trioxide-Water" by Posnjak and Tunell, there has appeared a paper entitled "The System: $CuSO_4$-H_2SO_4-H_2O" by H. D. Crockford and L. E. Warrick: J. Phys. Chem., 34, 1064 (1930). These authors present data for the triple point, $CuO.SO_3.5H_2O$, $CuO.SO_3.3H_2O$, solution, at 40° and at 55°, and for the triple point, $CuO.SO_3.3H_2O$, $CuO.SO_3.H_2O$, solution, also at 40° and at 55°. Interpolation between their values of the SO_3 percentage at 40° and at 55° gives at 50° the SO_3 percentage 35.5 for the triple point, $CuO.SO_3.5H_2O$, $CuO.SO_3.3H_2O$, solution; this value lies within our brackets which are 34.46 and 37.58 per cent SO_3 (Table VI, Am. J. Sci., 18, 33 (1929)). Interpolation between the values of the SO_3 percentage of Crockford and Warrick at 40° and at 55° gives at 50° the SO_3 percentage 44.5 for the triple point, $CuO.SO_3.3H_2O$, $CuO.SO_3.H_2O$, solution, which lies outside our brackets which are 38.50 and 43.04 per cent SO_3 (Table III of present paper). Moreover, interpolation between the less concentrated ends of the brackets of Crockford and Warrick for this triple point at 40° and at 55° gives a less concentrated end at 50° of 44.2 per cent SO_3. This conflicts with the more concentrated end of our brackets at 50°, 43.04 per cent SO_3. Plotting the analyses of the solutions and residues in experiments 8 (55°) and 9 (55°) of Crockford and Warrick and *drawing the tie lines shows that apparently both* $CuO.SO_3.3H_2O$ and $CuO.SO_3.H_2O$ were present in 8 (55°) and also in 9 (55°), provided that their analyses are accurate. It should be noted that they had no evidence except the analyses, as they did not examine the crystalline phases under the microscope. Similarly, plotting the analyses of the solutions and residues in experiments 8 (40°), 10 (40°), 11 (40°), and 13 (40°) and drawing the tie lines shows that apparently again both $CuO.SO_3.3H_2O$ and $CuO.SO_3.H_2O$ were present in each case. The presence of two crystalline phases in more than one experiment at a given temperature is in contradiction to the phase rule and thus it seems that equilibrium in the solid phases was not attained in the experiments of Crockford and Warrick near the triple point, $CuO.SO_3.3H_2O$, $CuO.SO_3.H_2O$, solution, at 55° and at 40°. This is not surprising, as we have found that in a bottle which was kept in the thermostat at 50° much longer than the bottles of Crockford and Warrick, the conversion of the trihydrate into the monohydrate went on over a considerable period of days (even though the bottle was shaken frequently), as was proved by successive microscopic examinations of samples of the crystalline phases.

The general statement can be made that in phase rule studies in which the method of residues is used, the results can be accepted without optical examination only when the tie lines hit points representing known compounds very accurately. In cases in which the tie lines pass by the points representing known compounds or assumed compounds, microscopical studies (or in some cases X-ray studies or both) must be made in addition to chemical analyses to ascertain whether the discrepancies are due to the presence of more than one phase, to adsorption, or to solid solution.

When all of their data are plotted and the tie lines drawn it is evident that Crockford and Warrick are not justified in placing the triple points more closely than within a range of several per cent of SO_3 in many cases.

In passing it may be remarked that the designation of the part of the system, CuO-SO_3-H_2O, studied by Crockford and Warrick, as the system, $CuSO_4$-H_2SO_4-H_2O, is open to criticism since compositions on the line-segment connecting the points representing H_2O and $CuSO_4$ do not form a binary system, at least within the range from room temperature to 200°. Mixtures on part of the line-segment connecting the points representing water and the normal cupric sulphate (5-, 3-, or 1-hydrate depending upon the temperature) on reaching equilibrium consist of solutions in which the ratio of SO_3 to CuO is slightly greater than 1 to 1 (mols per mol) and a small amount of crystalline basic cupric sulphate; mixtures on the rest of *this line-segment on reaching equilibrium consist of the same two phases* plus crystalline normal cupric sulphate. In other words the normal cupric sulphates dissolve incongruently in water, at least from room temperature to 200°. The amount of basic cupric sulphate formed by hydrolysis of normal cupric sulphate in water, although small at 50°, is readily visible to the unaided eye and at higher temperatures it is substantial. Taking $CuSO_4$, H_2SO_4, and H_2O as the components of the ternary system, one must therefore make use of negative masses of one component, H_2SO_4, in order to express the compositions of some of the solid phases present. This is of course permissible, but the use of negative masses of components is probably best avoided if positive masses of the same number of other components will suffice. The compositions of all of the phases can be expressed in terms of CuO, SO_3, and H_2O with use only of positive masses.

TABLE III

Additional Points on the Saturation Curve of the System, Cupric Oxide-Sulphur Trioxide-Water, at 50°[1]

Expt.	Liquid Phase			Solid with Some Mother Liquid		Solid Phase	Methods of Identification of Solid Phase[4]	Methods of Separation of Phases[8]
	CuO %	SO_3 %	H_2O[3] %	CuO %	SO_3 %			
44	0.05	0.05	99.90	25.65	6.52	$4CuO.SO_3.3H_2O$	r o x[5]	f
45	0.13	0.13	99.74	25.92	6.78	$4CuO.SO_3.3H_2O$	r o[5]	f
48[2]	2.20	2.22	95.58			$4CuO.SO_3.3H_2O$ $3CuO.SO_3.2H_2O$	o[5] o[6]	f
35[2]	4.73	4.75	90.52			$4CuO.SO_3.3H_2O$ $3CuO.SO_3.2H_2O$	a o x[5] a o[6]	f
34[2]	5.93	5.96	88.11			$4CuO.SO_3.3H_2O$ $3CuO.SO_3.2H_2O$	a[5] a o[6]	f
36[2]	6.52	6.57	86.91			$4CuO.SO_3.3H_2O$ $3CuO.SO_3.2H_2O$	a x[5] a o x[6]	f
111	3.28	38.50	58.22			$CuO.SO_3.3H_2O$	o[7]	p
112	2.35	43.04	54.61			$CuO.SO_3.H_2O$	o[7]	p
113	1.54	45.40	53.06			$CuO.SO_3.H_2O$	o[7]	f

[1] Cf. Table VI of "The System, Cupric Oxide-Sulphur Trioxide-Water" (Am. J. Sci., **18**, 33 (1929)).

[2] Equilibrium between the solid phases was not attained in this experiment. Very fine-grained crystalline (fibrous) aggregates of $4CuO.SO_3.3H_2O$ were partially converted into euhedral crystals of $3CuO.SO_3.2H_2O$. The solution lies on the $3CuO.SO_3.2H_2O$ side of the triple point.

[3] H_2O by difference.

[4] Denotation of symbols: o, optical properties; x, X-ray diffraction pattern; r, analysis of residue; a, analysis of air-dry solid.

[5] Solid phase in very fine-grained (crystalline) fibrous aggregates.

[6] Solid phase in separate, euhedral crystals.

[7] Coarsely crystalline.

[8] Denotation of symbols: f, filtration; p, removal of solution by means of pipette through glass extension tube containing cotton filter.

Oxide-Sulphur Trioxide-Water," which is therefore discarded as being slightly in error. Three additional points on the saturation curve of the system, Fe_2O_3-SO_3-H_2O, are given in Table IV and are discussed in the following paragraphs.

In the published experiments in each of the systems, Fe_2O_3-SO_3-H_2O and CuO-SO_3-H_2O, at 50° equilibrium in the solid phases was not completely established at points close to the triple point nearest the water corner of the triangle, a combination of unfavorable factors rendering the reactions exceedingly slow near each of these two triple points. The triple point, $4CuO.SO_3.3H_2O$, $3CuO.SO_3.2H_2O$, solution, at 50° in the system, CuO-SO_3-H_2O, was definitely limited, however, by experiments in which very fine-grained crystalline (fibrous) aggregates of $4CuO.SO_3.3H_2O$ were partially converted into separate, single crystals of $3CuO.SO_3.2H_2O$: by these experi-

TABLE IV

Additional Points on the Saturation Curve of the System, Ferric Oxide-Sulphur Trioxide-Water, at 50°[1]

Expt.	Liquid Phase Fe_2O_3 %	SO_3 %	H_2O[2] %	Solid Phases	Methods of Identification of Solid Phases[3]	Method of Separation of Phases[4]
139	0.01	0.10	99.89	$Fe_2O_3.H_2O$[5]	o a	f
97	1.95	2.94	95.11	$Fe_2O_3.H_2O$[6] & $3Fe_2O_3.4SO_3.9H_2O$[7]	o a a	f
62	2.54	3.57	93.89	$Fe_2O_3.H_2O$[6,8] & $3Fe_2O_3.4SO_3.9H_2O$[6]	o a o a	f

[1] Cf. Table IX of "The System, Fe_2O_3-SO_3-H_2O" (J. Am. Chem. Soc., **44**, 1991 (1922)).

[2] H_2O by difference.

[3] Denotation of symbols: o, optical properties; a, analysis of air-dry solid.

[4] Symbol f denotes filtration.

[5] Spherulites, single and in aggregates.

[6] Solid phase in very fine-grained crystalline aggregates.

[7] The $3Fe_2O_3.4SO_3.9H_2O$ left in this experiment is probably due to the extreme slowness of the conversion of $3Fe_2O_3.4SO_3.9H_2O$ into $Fe_2O_3.H_2O$. The point therefore may be assumed to lie on the $Fe_2O_3.H_2O$ saturation curve. See discussion in text.

[8] The small amount of $Fe_2O_3.H_2O$ in this preparation may have formed in the thermostat or possibly at room temperature before the tube was placed in the thermostat. If it formed at 50° the experiment determines the triple point, otherwise a point on the $3Fe_2O_3.4SO_3.9HO$ saturation curve.

ments it was proved to lie either at lower concentrations than CuO 1.65 per cent, SO_3 1.68 per cent, or at exactly these concentrations, the first possibility being the more probable one. Since publication of the paper on the system, CuO-SO_3-H_2O, additional experiments were made over a period of two years in the attempt to partially or completely convert very fine-grained crystalline (fibrous) aggregates of $3CuO.SO_3.2H_2O$ into separate, single crystals of $4CuO.SO_3.3H_2O$ at 50° but these did not result in narrowing down the interval published in that paper, because it was not possible to prove such conversion.[8] In an experiment with the quaternary system, Fe_2O_3-CuO-SO_3-H_2O, at 50° single euhedral crystals of $4CuO.SO_3.3H_2O$ were formed in a solution containing 0.06 per cent CuO,[9] a trace of Fe_2O_3 (less than 0.001 per cent), and 0.06 per cent SO_3, which was kept in the thermostat approximately three years. This experiment proves not only the existence of the $4CuO.SO_3.3H_2O$-solution field at this temperature, but also shows that the triple point, $4CuO.SO_3.3H_2O$, $3CuO.SO_3.2H_2O$, solution, in the ternary system, CuO-SO_3-H_2O, must lie at a sulphur trioxide concentration between (or at) 0.06 per cent and (or) 1.68 per cent.

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[8] At 100° this partial conversion of fine-grained crystalline (fibrous) $3CuO.SO_3.2H_2O$ into separate, single crystals of $4CuO.SO_3.3H_2O$ had already been accomplished, as well as the complete conversion of fine-grained, crystalline (fibrous) $4CuO.SO_3.3H_2O$ into separate, single crystals of $3CuO.SO_3.2H_2O$.

[9] This analysis was published in a footnote at the end of "The System, Cupric Oxide-Sulphur Trioxide-Water" (Am. J. Sci., **18**, 34 (1929)). The percentage of CuO was given there as 0.05. Calculated to the third place the figure is 0.055 so it should have been given as 0.06 according to the accepted convention.

The triple point, $Fe_2O_3.H_2O$, $3Fe_2O_3.4SO_3.9H_2O$, solution, in the system, Fe_2O_3-SO_3-H_2O, at 50° is more difficult to establish accurately because no single, faceted crystals of $Fe_2O_3.H_2O$ have been formed in this system at 50° or at any other temperature. However, excellent round spherulites of $Fe_2O_3.H_2O$ (Preparation 139), single and in aggregates, $n = 2.04 \pm 0.01$, were formed at 50° in solution very near the water corner, containing 0.01 per cent Fe_2O_3, 0.10 per cent SO_3 (that is, in solution far away from the triple point, $Fe_2O_3.H_2O$, $3Fe_2O_3.4SO_3.9H_2O$, solution). These spherulites, although very small (the diameters of the single spherulites are about 0.003 millimeter), show the stationary black cross between crossed nicols and four anisotropic quadrants.[10] The elongation of the fibers is positive (determined with the gypsum plate of first order red). It is true that not only crystalline spherulites but also strained spheres of glass show such a cross. The small spheres of $Fe_2O_3.H_2O$ were formed in solution at 50°, however, and it cannot be assumed that each and every one is a strained sphere of amorphous material. Furthermore, as H. E. Merwin has pointed out,[11] there is no known explanation for their spherical shape except the hypothesis that they are spherulites the fibers of which grew radially. Therefore Merwin and the authors believe that these spheres of $Fe_2O_3.H_2O$ are spherulites, and that they constitute valid evidence of continued crystallization. Such crystallization is strong evidence, in addition to that already published, that $Fe_2O_3.H_2O$ has a stability field at 50° in the system, Fe_2O_3-SO_3-H_2O. Preparations of $Fe_2O_3.H_2O$ formed nearer the triple point are not spherulitic but are anisotropic, fibrous (crystalline). At high concentrations of ferric oxide and sulphur trioxide at 50° single, faceted crystals of $3Fe_2O_3.4SO_3.9H_2O$ were produced. Near the triple point $3Fe_2O_3.4SO_3.9H_2O$ precipitated in aggregates of minute anisotropic, anhedral grains. In all cases of conversion of one solid phase into the other, so far as is known, the conversion was of $3Fe_2O_3.4SO_3.9H_2O$ into $Fe_2O_3.H_2O$. The triple point probably lies at a sulphur trioxide concentration between (or at) 2.94 per cent and (or) 3.57 per cent.[12] This conclusion is based upon the following two experiments at 50°. In the first (97) the solid phase consisted about one-half of $Fe_2O_3.H_2O$ (as examined under the microscope and according to the following analysis of an air-dry sample, Fe_2O_3 65.41 per cent, SO_3 16.82 per cent, H_2O by difference 17.77 per cent) and the composition of the liquid was Fe_2O_3 1.95 per cent, SO_3 2.94 per cent after approximately three months reaction in the thermostat. In the second (62) the solid phase consisted principally of $3Fe_2O_3.4SO_3.9H_2O$ with some $Fe_2O_3.H_2O$ (as examined under the microscope and according to the following analysis of an air-dry sample, Fe_2O_3 56.65 per cent, SO_3 27.08 per cent, H_2O by difference 16.27 per

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[10] Observed by Tunell. Similar but larger spherulites of $Fe_2O_3.H_2O$ which formed at 110° and which made up parts of the solid phases in preparations 115 and 116 mentioned in Table VII of "The System, Fe_2O_3-SO_3-H_2O" (J. Am. Chem. Soc., 44, 1988 (1922)), had been studied in detail by H. E. Merwin and described in that article (Pp. 1972, 1973).

[11] Oral communication to the authors.

[12] The triple point was placed tentatively at 2.30 per cent SO_3 in "The System, Fe_2O_3-SO_3-H_2O" (J. Am. Chem. Soc., 44, 1991 (1922)); but it almost certainly lies at a slightly higher SO_3 concentration.

cent) and the composition of the liquid was Fe_2O_3 2.54 per cent, SO_3 3.57 per cent after approximately three months reaction in the thermostat.

The complete 50° isotherm of the system, Fe_2O_3-SO_3-H_2O, is reproduced in Fig. 6, slightly modified in accordance with the foregoing text. The complete 50° isotherm of the system, CuO-SO_3-H_2O, is reproduced in Fig. 7, also slightly modified in accordance with the foregoing text.

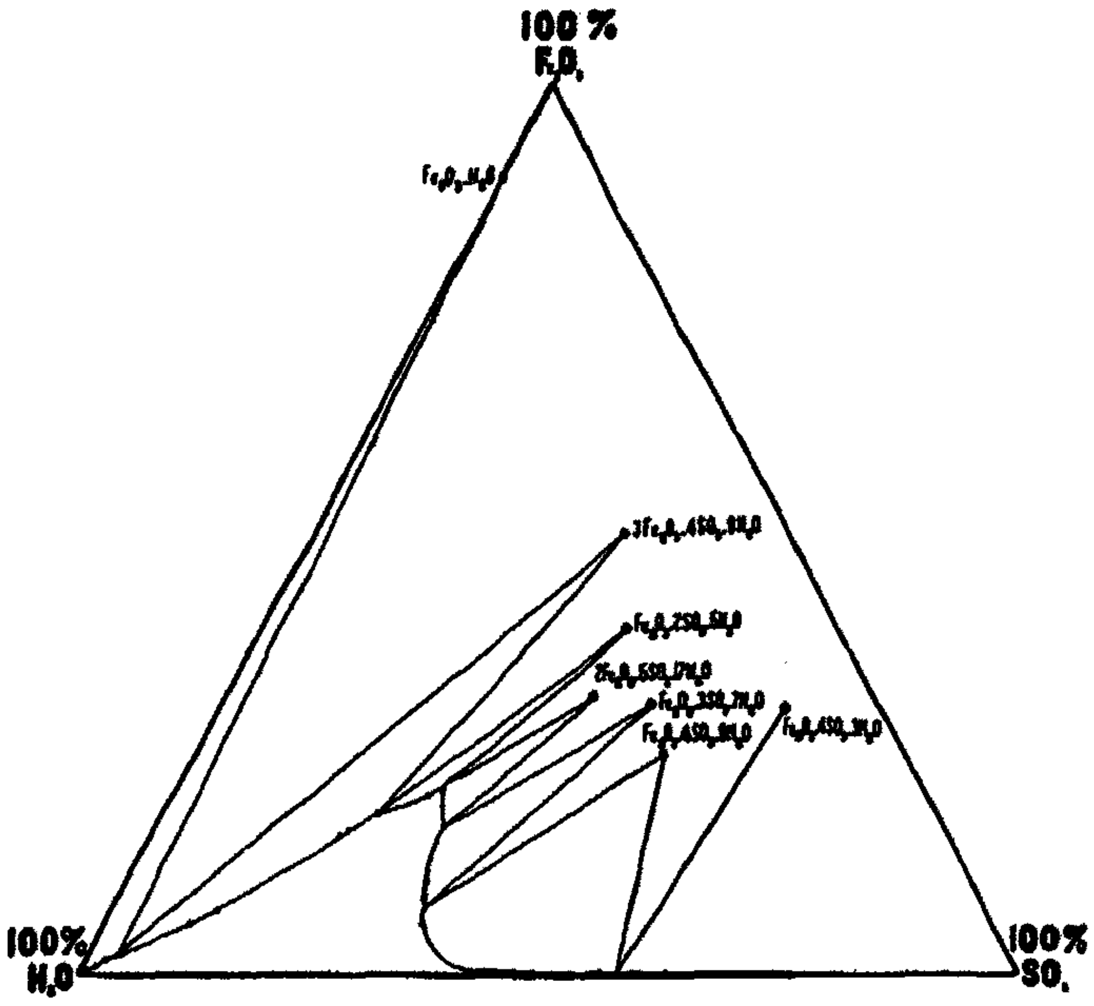

Fig. 6

The 50° isotherm of the system, Fe_2O_3-SO_3-H_2O. (Slightly modified after Posnjak and Merwin as explained in text.)

In the quaternary system at 50°C. the stable crystalline phases existing in contact with the various liquid phases having H_2O percentages above 93.5 are: $Fe_2O_3.H_2O$, $3Fe_2O_3.4SO_3.9H_2O$, CuO, $4CuO.SO_3.3H_2O$, and $3CuO.SO_3.2H_2O$.

The three-phase curves lying in the saturation surface in the portion of the tetrahedron were limited as to location by the following experimental work. The three-phase curve, $Fe_2O_3.H_2O$, $4CuO.SO_3.3H_2O$, solution, was determined experimentally. The three-phase curve, $Fe_2O_3.H_2O$, $3CuO.SO_3.2H_2O$, solution, was sufficiently well oriented by the location of one point, as it is known to intersect the curve, $Fe_2O_3.H_2O$, $4CuO.SO_3.3H_2O$, solution, at an SO_3 concentration between (or at) 0.06 per cent and (or) 1.68 per cent and is almost a continuation of the latter curve. The position of the three-phase curve, $Fe_2O_3.H_2O$, $3Fe_2O_3.4SO_3.9H_2O$, solution, was limited by experiments in which very fine-grained crystalline aggregates (anhedral grains) of $3Fe_2O_3.4SO_3.9H_2O$

were partially converted into crystalline (fibrous) aggregates of $Fe_2O_3.H_2O$. This conversion occurred in the $Fe_2O_3.H_2O$-solution field: it is thermodynamically impossible for it to occur in the $3Fe_2O_3.4SO_3.9H_2O$-solution field. The conversion therefore definitely limited the location of the three-phase curve. The extreme slowness of this conversion near the three-phase curve (complete equilibrium in the solid phases was not attained in these tubes after about three years' reaction in the thermostat) is due in part to the low solubility of both solid phases and probably also in part to a small difference between the chemical potentials. It is probable that the unstable continuation of the $3Fe_2O_3.4SO_3.9H_2O$ saturation surface in the $Fe_2O_3.H_2O$-solution field is very near the $Fe_2O_3.H_2O$ saturation surface in the vicinity of the three-phase curve (which is the intersection of the $3Fe_2O_3.4SO_3.9H_2O$ and $Fe_2O_3.H_2O$ saturation surfaces). Therefore, although in these tubes equilibrium was not completely established in the solid phases after about three years at constant temperature, no appreciable error is introduced by using the analyses of the solutions in them in the establishment of the saturation surface. The three-phase curves, $Fe_2O_3.H_2O$, CuO, solution; CuO, $4CuO.SO_3.3H_2O$, solution; and $4CuO.SO_3.3H_2O$, $3CuO.SO_3.2H_2O$, solution, are extremely short and on the scales of the plotted diagrams do not appear. These are all of the three-phase curves which occur in the portion of the quaternary system under consideration.

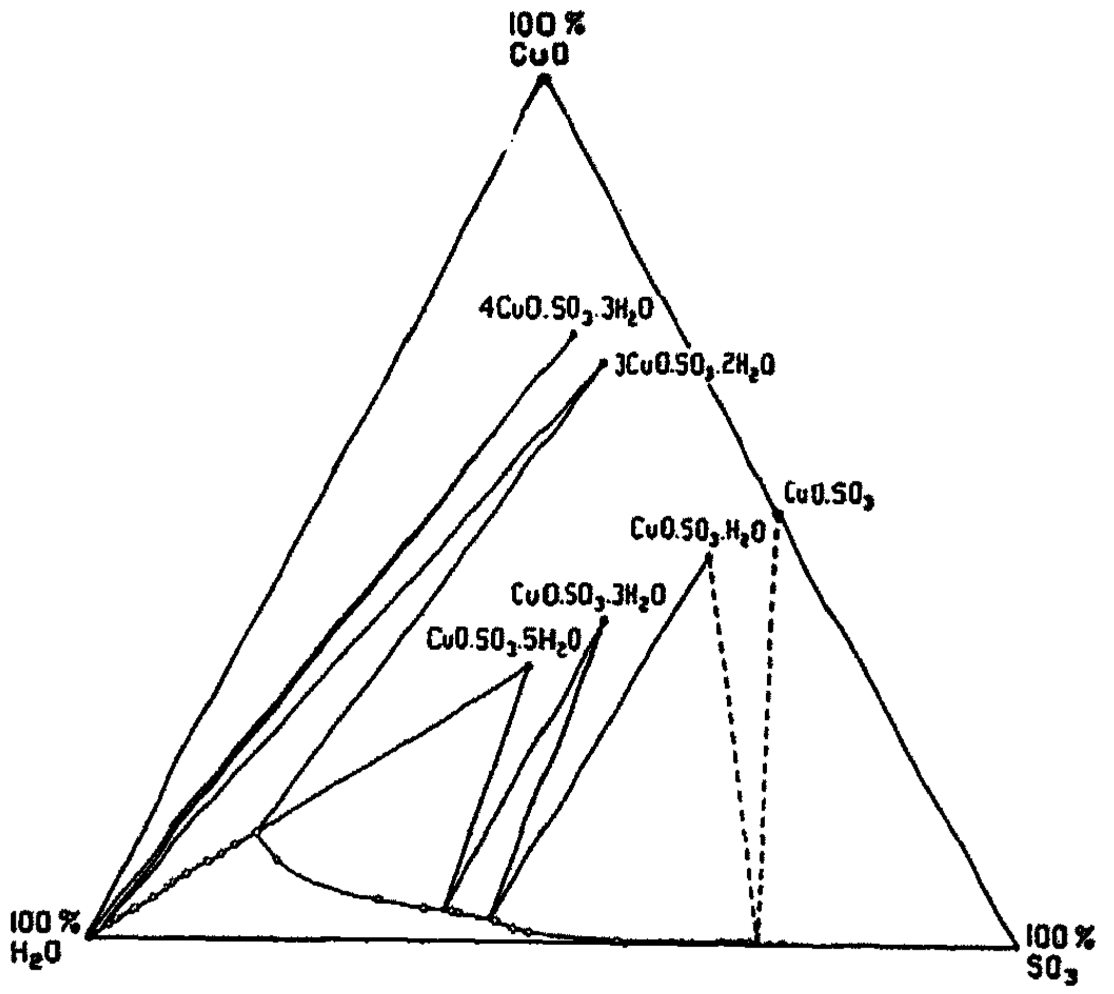

FIG. 7

The 50° isotherm of the system, $CuO\text{-}SO_3\text{-}H_2O$. (Slightly modified after Posnjak and Tunell as explained in text.)

General Properties of the Models for Quaternary Systems in which there is no Solid Solution[13]

The general properties of the isothermal-isobaric tetrahedral models for quaternary systems in which there is no solid solution are as follows. In the tetrahedron the percentages (by weight) of the four components of any arbitrary system are represented by the four normals to the faces of the tetrahedron from a particular point; this point may thus be said to represent the arbitrary system. The arbitrary systems, on reaching equilibrium, consist of one, two, three, or four phases, as shown by the locations of the points representing them in the subregions of the tetrahedron.

Arbitrary systems the total compositions of which are represented by points in the solution field form homogeneous solutions on reaching equilibrium.

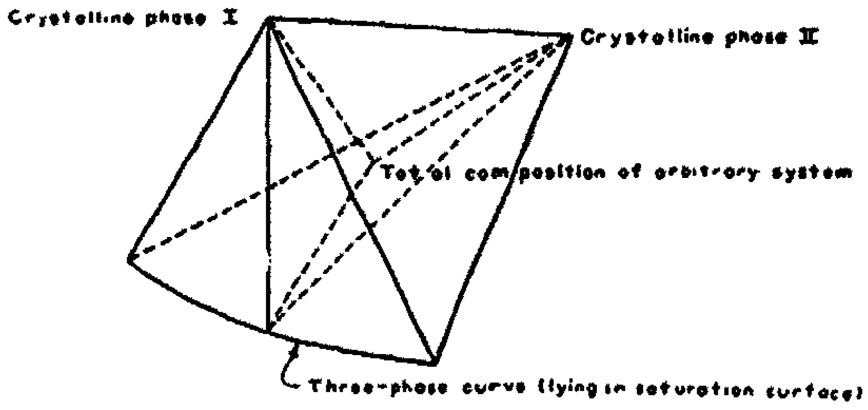

FIG. 8

Schematic illustration, in perspective, of general relations in a quaternary system in which there is no solid solution. The diagram shows the compositions of the crystalline phases and solution phase of an arbitrary system in a three-phase region. The weights of the three phases are to each other as the areas of the three subsidiary triangles opposite the points representing the compositions of the respective phases.

Arbitrary systems the total compositions of which are represented by points in any of the solids bounded by the saturation surface and a cone (noncircular) divide into two phases on reaching equilibrium, crystals the composition of which is represented by the apex and solution the composition of which is represented by the point in which the saturation surface is intersected by a straight line from the apex through the point representing the total composition of the arbitrary system. The weight of crystals is to the weight of solution as the segment of the line between the point representing the composition of the solution and the point representing the total composition of the arbitrary system is to the segment between the apex and the point representing the total composition of the arbitrary system.

Arbitrary systems the total compositions of which are represented by points in any of the solids bounded by two intersecting conical surfaces and two intersecting planes divide into three phases on reaching equilibrium, crystals of two kinds and solution. The compositions of the two kinds of crystals are represented by the endpoints of the segment between the two

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[13] The constructions of this section obviously also apply to parts of quaternary systems in which there is no solid solution although solid solutions may occur in other parts.

conical surfaces, of the intersection line of the two planes; the composition of the solution is represented by the point in which the curve common to the two conical surfaces (this curve lies in the saturation surface) is cut by a plane through the points representing the compositions of the two kinds of crystals and the point representing the total composition of the arbitrary system. The weights of the three phases are to each other as the areas of the three subsidiary triangles opposite the points representing the compositions of the respective phases. The construction of this paragraph is illustrated in Fig. 8.

Lastly, arbitrary systems the total compositions of which are represented by points in any of the nonequilateral tetrahedra (within the equilateral coordinate tetrahedron) divide into four phases on reaching equilibrium, crystals of three kinds and solution, the compositions of which are represented by the vertices of the nonequilateral tetrahedron. The weights of the four phases are to each other as the volumes of the four subsidiary tetrahedra (together composing the nonequilateral tetrahedron) opposite the vertices of the nonequilateral tetrahedron representing the compositions of the respective phases.

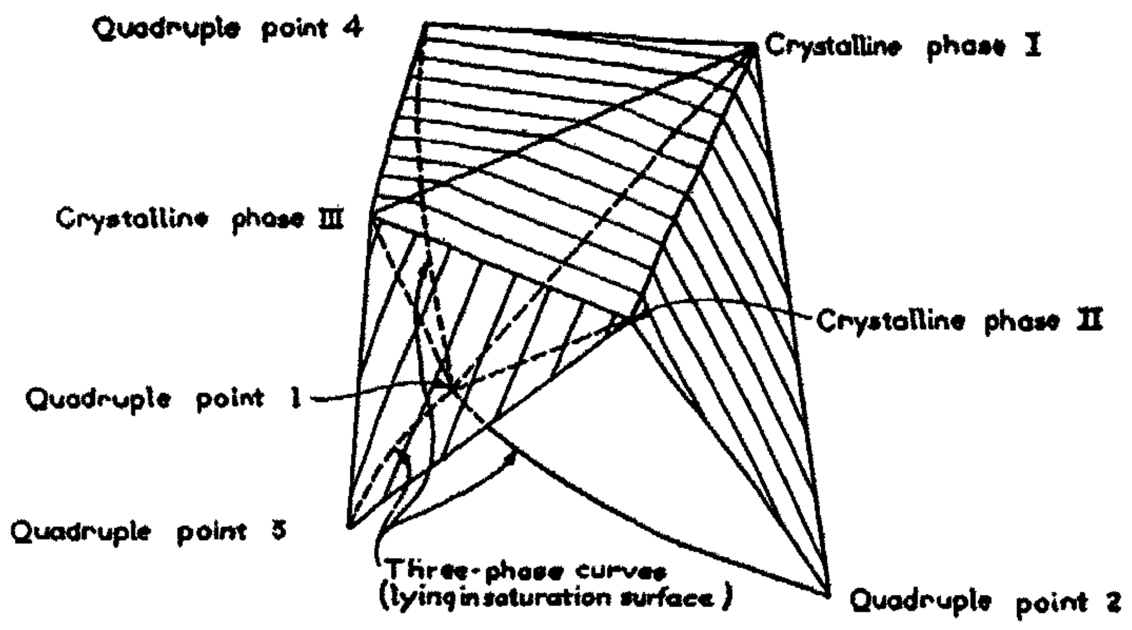

FIG. 9

Schematic illustration, in perspective, of general relations in a quaternary system in which there is no solid solution. The diagram shows the three three-phase curves (lying in the saturation surface) emanating from a quadruple point.

From each of the points representing the composition of a solution which is in equilibrium with three crystalline phases (quadruple points), that is to say, from the solution-vertex of each nonequilateral tetrahedron, there emanate three three-phase curves, points along which represent the compositions of solutions in equilibrium with two crystalline phases. Points in the areas of the saturation surface between the three-phase curves represent the compositions of solutions in equilibrium with one crystalline phase. The relations of this paragraph are illustrated in Fig. 9.

Description of the Three-Phase Curves in the Limited Portion of the System, Ferric Oxide-Cupric Oxide-Sulphur Trioxide-Water

The disposition of the six three-phase curves which occur in the portion of the system investigated is as follows. From the H_2O vertex of the coordinate tetrahedron there extends one three-phase curve, that of $Fe_2O_3.H_2O$, CuO, and solution, but it is extremely short and on the scale of the plotted model does not appear. From the end of this curve there emanate two others, that of CuO, $4CuO.SO_3.3H_2O$, and solution, which extends to the $CuO\text{-}SO_3\text{-}H_2O$ face of the coordinate tetrahedron and is thus too short to be visible if plotted on the same scale, and that of $Fe_2O_3.H_2O$, $4CuO.SO_3.3H_2O$, and solution, which extends almost parallel to the saturation curve of the system, $CuO\text{-}SO_3\text{-}H_2O$, and so near the latter that on the same scale the two curves cannot be shown separately. From the more concentrated end of the three-phase curve, $Fe_2O_3.H_2O$, $4CuO.SO_3.3H_2O$, solution, there emanate two more three-phase curves, that of $Fe_2O_3.H_2O$, $3CuO.SO_3.2H_2O$, and solution, which continues very near the saturation curve of the system, $CuO\text{-}SO_3\text{-}H_2O$, and that of $4CuO.SO_3.3H_2O$, $3CuO.SO_3.2H_2O$, and solution, which extends to the $CuO\text{-}SO_3\text{-}H_2O$ face of the coordinate tetrahedron, ending at the triple point, $4CuO.SO_3.3H_2O$, $3CuO.SO_3.2H_2O$, solution, of the system, $CuO\text{-}SO_3\text{-}H_2O$, and which is thus also too short to be visible if plotted on the same scale. The last three-phase curve is that of $Fe_2O_3.H_2O$, $3Fe_2O_3.4SO_3.9H_2O$, and solution, which extends from the triple point, $Fe_2O_3.H_2O$, $3Fe_2O_3.4SO_3.9H_2O$, solution, of the system, $Fe_2O_3\text{-}SO_3\text{-}H_2O$, to an endpoint not determined; the trend of the curve away from the triple point, $Fe_2O_3.H_2O$, $3Fe_2O_3.4SO_3.9H_2O$, solution, of the system, $Fe_2O_3\text{-}SO_3\text{-}H_2O$, is such, however, that at successively higher CuO percentages the curve intersects planes parallel to the $Fe_2O_3\text{-}CuO\text{-}SO_3$ face of the coordinate tetrahedron in which the percentage of H_2O is successively lower (the planes referred to are those in any one of which the percentage of H_2O is a constant). The three-phase curve, $Fe_2O_3.H_2O$, $3Fe_2O_3.4SO_3.9H_2O$, solution, passes through the plane in which the percentage of H_2O is 93.5 and out of the portion of the tetrahedron under consideration. The three-phase curves, $Fe_2O_3.H_2O$, $3Fe_2O_3.4SO_3.9H_2O$, solution, and $Fe_2O_3.H_2O$, $3CuO.SO_3.2H_2O$, solution, thus do not intersect inside the limited portion of the quaternary system; they may or may not intersect outside.

Summary

The portion of the system, $Fe_2O_3\text{-}CuO\text{-}SO_3\text{-}H_2O$, in which the total composition is 93.5 per cent or more H_2O, 6.5 per cent or less Fe_2O_3, 6.5 per cent or less CuO, and 6.5 per cent or less SO_3, has been investigated at 50°C. with the purpose of applying the results to certain geologic problems.

The modes of occurrence, that is to say the crystallographic habits and states of aggregation, of the five crystalline phases, $Fe_2O_3.H_2O$ (goethite), $3Fe_2O_3.4SO_3.9H_2O$, CuO (tenorite), $4CuO.SO_3.3H_2O$ (brochantite), and $3CuO.SO_3.2H_2O$ (antlerite), encountered in this portion of the system are

described. No double salt has a stability field extending into the limited portion of the system.

Standard X-ray powder diffraction patterns are given for $Fe_2O_3.H_2O$ (goethite) and $3Fe_2O_3.4SO_3.9H_2O$.

The data for the saturation surface inside and just outside the limited portion of the system are presented in tabular form and the saturation surface is also illustrated by means of a model shown in perspective. The disposition of the six three-phase curves which lie completely or partly in the limited portion is described.

It is noteworthy from the geological standpoint that the $Fe_2O_3.H_2O$ saturation surface in the quaternary system extends from the saturation curve of $Fe_2O_3.H_2O$ in the system, Fe_2O_3-SO_3-H_2O, almost to the saturation curves of $4CuO.SO_3.3H_2O$ and $3CuO.SO_3.2H_2O$ in the system, CuO-SO_3-H_2O, the three-phase curves, $Fe_2O_3.H_2O$, $4CuO.SO_3.3H_2O$, solution, and $Fe_2O_3.H_2O$, $3CuO.SO_3.2H_2O$, solution, lying extremely close to the saturation curves of $4CuO.SO_3.3H_2O$ and $3CuO.SO_3.2H_2O$ in the system, CuO-SO_3-H_2O.

It is also of interest for its geological application that the three-phase curve, $Fe_2O_3.H_2O$, $3Fe_2O_3.4SO_3.9H_2O$, solution, extending from the triple point, $Fe_2O_3.H_2O$, $3Fe_2O_3.4SO_3.9H_2O$, solution, of the system, Fe_2O_3-SO_3-H_2O, at successively higher CuO percentages intersects planes parallel to the Fe_2O_3-CuO-SO_3 face of the coordinate tetrahedron in which the percentage of H_2O is successively lower (the planes referred to are those in any one of which the percentage of H_2O is a constant).

Geophysical Laboratory,
Carnegie Institution of Washington,
September, 1930.

THE SOLUBILITY OF POTASSIUM IODIDE IN WATER TO 240°

BY F. C. KRACEK

1. During the progress of another investigation it became desirable to know the course of the solubility curve of KI in water at temperatures above the normal boiling point of saturated solutions. Two series of data in this region are found in the literature, namely, by Tilden and Shenstone,[1] and Étard,[2] reaching to 175° and 213° respectively. There is considerable discrepancy between these two series; as will be seen later, the results of Étard are the more reliable, but the precision of the individual experiments is rather low.

Experimental

2. The solubility measurements were made by the synthetic method in Pyrex tubes. Known amounts of twice-recrystallized KI and distilled water were introduced into the tubes which were then sealed. The tubes were rotated in a stirred air bath which could be kept at any desired constant temperature; the presence or absence of crystals was determined by visual observation.[3] Particular attention was given to the determination of the disappearance of the last traces of crystals in the immediate proximity of the solubility point.

3. The bath was controlled by a five junction Cu-constantan couple actuating a commercial type of controller; the regulating junctions were bare, to minimize lag. The reading thermocouple was also Cu-constantan, enclosed in a small alundum mass, suspended immediately adjacent to the rotating solubility tube. This couple was calibrated with accepted standards, readings being made on a Wolff Feussner type potentiometer mounted in accordance with the usual practice. The control was reliable to better than ± 0.1°, and could be set and maintained at any desired temperature.

4. The solutions acquired a light brown tint due to slight hydrolytic decomposition of KI. This phenomenon is a familiar one, and can be eliminated by small additions of KOH. It was, however, thought better not to attempt to bring about decolorization by such additions, since to do so would alter the K-I ratio in the solutions.

The Results

5. The experimental data obtained in this work are recorded in Table I which gives all the necessary details. A comparison of these results with the older published determinations[4] is given in Fig. 1. The smooth curve is

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[1] Tilden and Shenstone: Proc. Roy. Soc., 35, 345 (1883); Phil. Trans., 175, 23 (1885).

[2] Étard: Ann. Chim. Phys., 2, 503 (1894).

[3] F. C. Kracek: J. Phys. Chem., 35, 417 (1931).

[4] For references see A. Seidell: "Solubilities of Inorganic and Organic Compounds" (1919); also Brönsted's section in Int. Crit. Tables 4, 239; Scott and Frasier: J. Phys. Chem., 31, 459 (1927); Scott and Durham: 34, 1424 (1930).

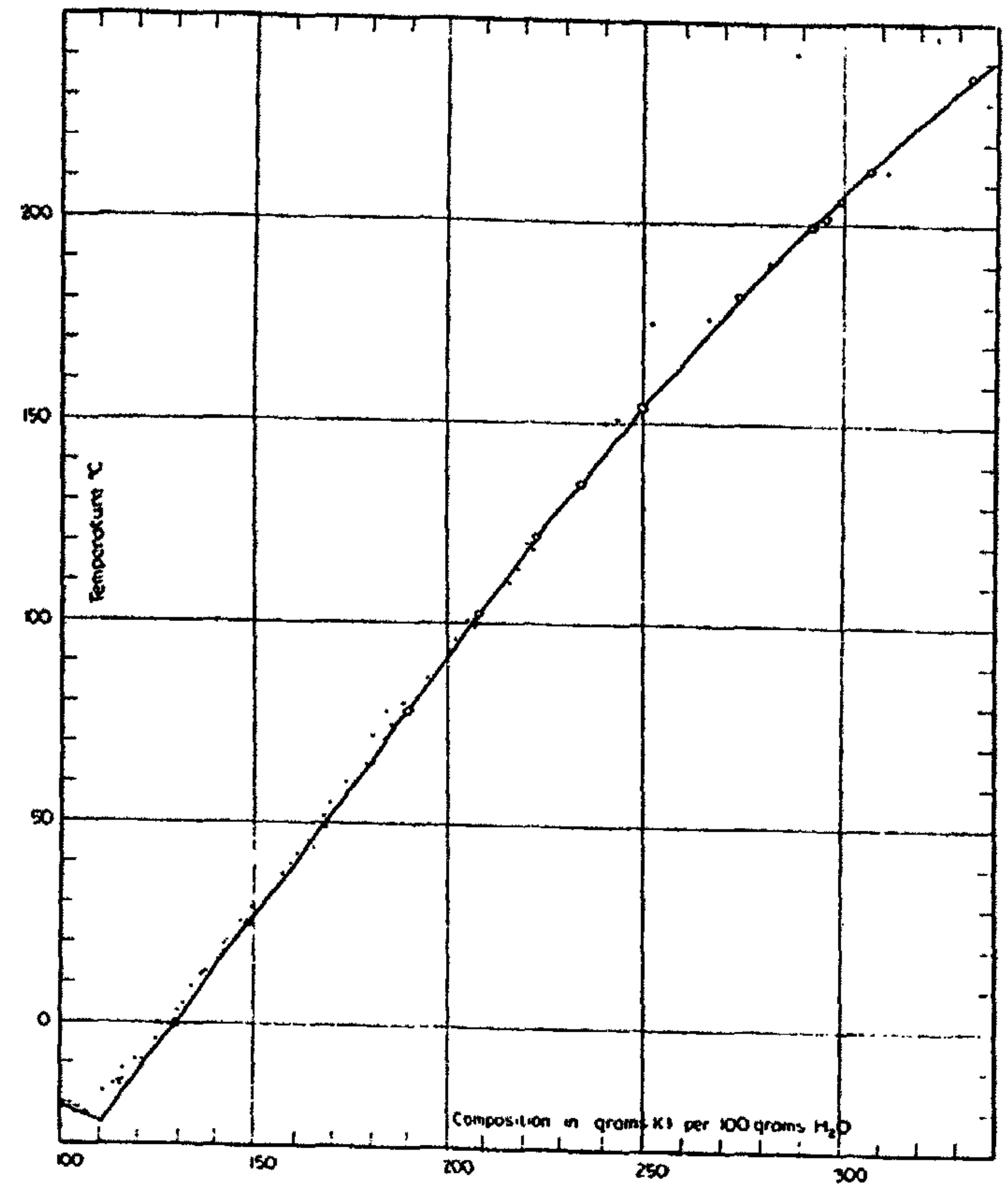

Fig. 1

Solubility of KI in water, in grams of KI per 100 grams of water. The small open circles from 150° upward are by Étard. The triangles at 0° and 25° are by Scott and co-workers, at 100° by Brōnsted. The larger open circles are by Kracek. The small open circles at lower temperatures are taken at random from the literature.

passed thru Scott and Frazier's point at 25°; it also represents quite faithfully the results of Scott and Durham, the most recent published values for the region between 0° and 100°.

In the region of higher temperatures the curve falls generally among the points determined by Étard; the values by Tilden and Shenstone, however, are not even approximately correct.

This investigation is not properly concerned with values at low temperatures, but it may be permissible to point out that there appears to be a consistent deviation in some of the older results in the direction of unsaturation below 25°, and particularly in the determinations below 0°. If we accept Scott and Durham's and Scott and Frazier's determinations at 0° and 25°, both of which are almost directly on the curve as drawn, we must conclude

TABLE I

Determinations of solubility of KI in H_2O

Number	g KI	g H_2O	r_w*	r_m*	Percent KI weight	Percent KI mol	t°C
1	5.6805	2.9930	1.8979	0.20594	65.49	17.08	78.1
2	6.2164	2.9794	2.0865	.22641	67.60	18.46	102.4
3	5.7387	2.5686	2.2342	.24243	69.08	19.51	121.6
4	4.6109	1.9685	2.3423	.25416	70.08	20.265	134.9
5	5.4252	2.1685	2.5018	.27147	71.44	21.35	153.7
6	5.3133	2.1270	2.4980	.27106	71.41	21.33	154.3
7	5.3824	1.9658	2.7380	.29710	73.25	22.91	181.7
8	5.7625	1.9717	2.9226	.31713	74.51	24.08	199.3
9	7.9992	2.7074	2.9546	.32060	74.71	24.28	201.5
10	5.8592	1.9564	2.9949	.32498	74.97	24.53	206.0
11	6.1782	2.0104	3.0731	.33346	75.45	25.01	213.3
12	6.6479	1.9944	3.3333	.36170	76.92	26.56	236.4

* r_w = g KI per g of H_2O.
r_m = mols KI per mol of H_2O.

TABLE II

Solubility of KI in H_2O at even temperatures

t°C	g KI per 100 g H_2O	t°C	g KI per 100 g H_2O
0	129.1 ± 0.5	130	230.3 ± 0.5
10	136.8	140	238.5
20	144.5	150	246.7
30	152.2	160	255.0
40	159.9	170	263.7
50	167.6	180	272.9
60	175.3	190	282.6
70	183.0	200	292.9
80	190.8	210	303.4
90	198.6	220	314.3
100	206.4	230	326.0
110	214.3	240	338.4
120	222.3		

that these deviations are due to failure to obtain complete saturation, a very probable error in view of the high solubility of the salt.

Table II gives the values of the solubility of KI in H_2O at even temperatures, taken from the smooth curve of Fig. 1. The table thus represents the most probable values of the solubilities, arranged to facilitate interpolation at intermediate temperatures.

Geophysical Laboratory,
Carnegie Institution of Washington,
October, 1930.

THE STATISTICAL TREATMENT OF REACTION-VELOCITY DATA. II.

Least-Squares Treatment of the Unimolecular Expression: $Y = L\,(1 - e^{-Kt})$.*

BY LOWELL J. REED AND EMERY J. THERIAULT

Introduction

It has been shown in a previous paper[1] that the usual methods of calculating velocity constants are inadequate and that the least-squares procedures which have been proposed are inapplicable to unimolecular data.

In the present article a statistical treatment will be developed which permits of the ready derivation both of the experimental constants and of their precision values, proper allowance being made for constant errors. The discussion will be limited to the unimolecular expression

$$Y = L\,(1 - e^{-Kt})$$

and the applicability of the proposed method will be exemplified with reference to the data of Pennycuick[2] on the rate of inversion of sugar solutions. It will be shown that these observations conform very closely to the unimolecular type of equation. The data given by Daniels and Johnston[3] for the rate of decomposition of nitrogen pentoxide will also be briefly discussed.

1. Conditions affecting the Applicability of the Least-Squares Criterion

Before applying the least-squares criterion to a series of timed observations it will be necessary to establish the approximate validity of the following assumptions:

a. If all determinations had been made at any single time the absolute errors would have approximated a normal distribution.

b. The variation of this distribution would have been the same irrespective of the particular period of observation selected for the determinations.

c. The time, t, has been determined with a relatively high degree of precision so that the accidental errors in t are negligibly small in relation to the corresponding errors in Y.

d. Proper allowance has been made for constant errors.

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* From the Department of Biostatistics of the School of Hygiene and Public Health, of the Johns Hopkins University, Paper No. 145, and the Stream Pollution Investigation Laboratory, United States Public Health Service.

[1] The Statistical Treatment of Reaction-Velocity Data. I. A Critical Review of Current Methods of Computation. J. Phys. Chem., 35, 673 (1931).

[2] Pennycuick, S. W. (1926): The Unimolecularity of the Inversion Process. J. Am. Chem. Soc., 48, 6-19.

[3] Daniels, F., and Johnston, E. H. (1921): The Thermal Decomposition of Gaseous Nitrogen Pentoxide. A Monomolecular Reaction. J. Am. Chem. Soc., 43, 53-71.

e. As a rule, the equation selected to represent a given process should either be in the linear form or else it should be possible to place it in the linear form without disturbing conditions (a) and (b) regarding the distribution of the errors.

The first assumption is generally valid in measurements based on readings of burettes, polarimeters, manometers, etc., if reference is made to the absolute error. As a rule, therefore, this condition will be fulfilled when the quantity directly observed is Y (or Z) in the equations

$$Y = L\,(1-e^{-Kt}) \tag{1}$$

or,

$$Z = L\,e^{-Kt} \tag{2}$$

It is to be noted, however, that in investigations of supposedly unimolecular reactions, the selection of the quantity to be measured will generally be governed by considerations of analytical convenience. Conceivably (for instance, in potentiometric determinations) the quantity selected for measurement might be $ln\ Z$ (or $ln\ Y$). In this case the equation representing the results would be

$$ln\ Z = ln\ L - Kt \tag{3}$$

In spectrophotometric work the quantity directly observed is a^{-Y} (or a^{-Z}), where "a" is a constant and, if the course of a reaction is followed by measuring a change in electrical resistance, the observed quantity may be $1/Y$ (or $1/Z$). The discussion which follows will be limited to the treatment of equation (1) and of the closely related equation (2). Equation (3) bears a formal resemblance to the Arrhenius expression

$$ln\ K_T = ln\ K_\infty - E/RT$$

and will be considered in a separate paper.

In particular cases the validity of the second assumption regarding the distribution of the errors may be tested out by the examination of pairs of observed values selected from different points along the curve. The assumption will be borne out when the absolute errors, as indicated by the difference between duplicate observations, do not seem to vary systematically with the time. Depending on the variable selected for measurement the percentage error will accordingly increase or decrease progressively with time.

The third assumption regarding the precision of the time measurements will be increasingly valid when slow reactions are considered.

The elimination of constant errors and the linearization of the equations will be considered in the discussion which immediately follows.

2. Allowance for Constant Errors

Let it be assumed that Y and t are the quantities obtained by direct observation and that these observations are supposedly represented by the unimolecular formula,

$$Y' = L'\,(1-e^{-Kt'})$$

where the primes denote that the true values of Y, L and t are being considered. If the constant errors in either Y or t are known to be negligibly small in relation to the accidental (plus or minus) errors it may be permissible to use the above equation without modification. In general, however, it will be necessary to consider the possibility that either Y or t, or both, are affected by constant errors which approach or even exceed the magnitude of the accidental errors. To allow for such a contingency it may be assumed that, after correcting for known errors (lead or lag, etc.) the residual constant error in Y is q and that the corresponding error in t is r where q and r are small constant errors, either positive or negative. The formula which actually corresponds to the observations will then take the form

$$(Y-q) = L' [1-e^{-K(t-r)}]$$

where Y and t refer to the actual observations uncorrected for constant errors. From which

$$Y = L' + q - L' e^{-K(t-r)}$$

Factoring the second member of the above equation and simplifying the resulting expression

$$\begin{aligned} Y &= [L' + q] [1 - \left(\frac{L'}{L' + q}\right) e^{-K(t-r)}] \\ &= [L' + q] [1 - e^{Ks} . e^{-K(t-r)}] \\ &= [L' + q] [1 - e^{-K(t-r-s)}] \\ &= L [1 - e^{-K(t+w)}] \qquad (5) \end{aligned}$$

where,

$$\begin{aligned} \frac{L'}{L' + q} &= e^{Ks} \\ s &= \frac{1}{K} ln \left(\frac{L'}{L' + q}\right) \\ w &= - (r+s) \qquad (6) \end{aligned}$$

and,

$$L = L' + q$$

It follows that constant errors in the determination of Y and t may be accounted for by a shift, w, in the time-axis. It is to be borne in mind, therefore, that w in equation (5) refers not necessarily to a time error but rather to the resultant effect of all constant errors on the time. It is also to be noted that $L = L' + q$ corresponds to the limit which the observations are approaching when, of necessity, no correction can be applied for constant errors.

In experiments where the observed quantity is Z (the amount remaining) instead of Y (the amount decomposed) it will always be possible to express the results in terms of Y, provided that the approximate value of L is known. Thus,

$$Y = L - Z \qquad (7)$$

From the foregoing discussion it is apparent that any constant error introduced by this computation of Y will simply be absorbed in the term q. Equation (5) is therefore applicable to cases where the observed quantity is Z instead of Y.

Similarly it can readily be shown that equation (5) is applicable to results which are reported in terms of fractions (or percentages) of an experimentally determined value of L, without any presentation of the original observations from which the fractional values were derived.

3. Linearization of the Observational Equations

In general, the assumption that the observations Y and t are reasonably free from constant errors will seldom be satisfied in rate-of-reaction experiments. As a rule, therefore, the observations of a supposedly unimolecular process should be referred to the general expression

$$Y = L[1-e^{-K(t+w)}]$$

where, as already explained, w is a small quantity introduced to account for constant errors in the estimation of Y and t. For the purpose of reducing this expression to a linear form let it be assumed that an approximate value of K has first been obtained by any convenient method so that the most probable value of K is given by the relation

$$K = K' + h \qquad (8)$$

where the trial value K′ is a true constant and h is a relatively small number, positive or negative, whose magnitude is to be determined. It will presently be shown that the assumed value of K′ need only be a rough approximation to the actual value of K, so that this assumption does not introduce any special difficulty. Similarly, let the constant w be represented by the relation

$$w = w' + i \qquad (9)$$

where w′ is a first approximation to the value of w and i is a small constant whose magnitude is to be determined. It follows that

$$t + w = t + w' + i = t' + i \qquad (10)$$

where $t' = t + w'$. By substitution in equation (5) we now obtain the equivalent expression

$$\begin{aligned} Y &= L[1-e^{-(K'+h)(t+i)}] \\ &= L[1-e^{-K't'} . e^{-Ki-ht'}] \qquad (11) \end{aligned}$$

By definition, the exponent, $(-Ki-ht') = u$, is a small quantity. Using the relation

$$e^u = 1 + u$$

equation (11) may therefore be written

$$\begin{aligned} Y &= L[1-e^{-K't'} . (1-Ki-ht')] \\ &= L[1-e^{-K't'}] + Lh[t'e^{-K't'}] + LiK[e^{-K't'}] \qquad (12) \end{aligned}$$

$$= af_1 + bf_2 + cf_3 \tag{13}$$

where,

$$\begin{aligned} a &= L \\ b &= Lh \\ c &= LiK = Li\,(K'+h) \\ f_1 &= 1-e^{-K't'} \\ f_2 &= t'e^{-K't'} \\ f_3 &= e^{-K't'} \end{aligned} \tag{14}$$

Equations (12) or (13) may be regarded as the linearized form of equation (5) where Y is a variable affected by accidental errors superimposed on a constant error; a, b, and c are statistical constants of unknown magnitude; and the time functions f_1, f_2 and f_3, are variables relatively free from accidental errors although not necessarily free from small constant errors. When h and i are each equal to zero, equation (12) evidently reduces to equation (1).

When no allowance is made for constant errors, that is, when the observations are referred to equation (1)

$$Y = L\,(1-e^{-Kt})$$

the linearized expression becomes

$$Y = L\,[1-e^{-K't}] + Lh\,[t'e^{-K't}] \tag{15}$$

$$= af_1 + bf_2 \tag{16}$$

where the significance of the symbols is denoted by equations (8) and (14). Equation (15) is obtainable from equation (12) by equating i to zero.

4. Tests for Unimolecularity

Considering the more general case represented by equation (5) or by the corresponding linearized expressions (12) or (13) and assuming that the conditions in regard to the nature and distribution of the errors have been satisfied, the various steps in testing the degree of conformity of a given process to an equation of the unimolecular type will be as follows:

a. Given a series of timed observations Y_1, Y_2, Y_3, etc., and the corresponding times t_1, t_2, t_3, etc., the constants L, K and w in equation (5) will first be determined by least-squares using a procedure which will presently be described.

b. The adjusted values of L, K and w will then be placed in equation (5) and, by assigning appropriate values to t, a series of calculated values, Y_1', Y_2', Y_3', etc., will be obtained which may be compared with the corresponding observations Y_1, Y_2, Y_3, etc.

c. The signs (+ or −) of the differences, $(Y_1 - Y_1')$, $(Y_2 - Y_2')$ etc., may then be examined for the presence of systematic divergencies between the observed and the calculated values. Provided that the observations actually conform to the unimolecular type of expression, a definite trend should not be observed if equation (5) has been used. If equation (1) has been used, the presence of a well-defined trend may indicate either a lack of conformity to the selected type of equation or else a necessity for making proper allowance for the presence of constant errors.

d. In the absence of a trend, the deviation, σ_y, defined by the relation

$$\sigma^2_y = \frac{\Sigma(Y-Y')^2}{n-3} \tag{17}$$

will then be computed. In equation (17) the number of observations, n, has been diminished by 3 to account for the 3 constants (L, K and w) which enter into the computation of Y′ by means of equation (5) (cf. Merriman, "Method of Least Squares," 1904, 8th edition revised, p. 82). When equation (1) is used the deviation σ_y will be given by the expression

$$\sigma^2_y = \frac{\Sigma(Y-Y')^2}{n-2} \tag{18}$$

where the number of observations, n, has been diminished by 2 to account for the 2 constants L and K.

By inspection of equations (17) and (18) it is apparent that, depending on the equation used, at least 3 or 4 observations must be made before any significance can be attached to the values of L and K found by least-squares.

The deviation, σ_y, is a measure of the agreement between the observed and calculated values. However, it should be emphasized that good agreement between observed and calculated values is not, of itself, a sufficient criterion of unimolecularity.

e. A comparison of σ_y with the standard deviation, σ, of the observations themselves, will indicate whether the agreement between the observed and calculated values is within the experimental error.

In favorable cases, the experimental error measured in terms of σ, may be found by the formula

$$\sigma^2 = \frac{\Sigma(Y'-Y'')^2}{2n} \tag{19}$$

where Y′ and Y″ are duplicate observations corresponding to any period of observation. Alternatively, the standard deviation may be found by making a large number of parallel observations at any single point on the curve.

In less favorable cases, it may be either impossible or inconvenient to conduct tests in duplicate or to obtain duplicate readings. Under these conditions it may, nevertheless, be possible to estimate the order of magnitude of σ by a consideration of known errors inherent to the analytical determination of Y.

f. Using σ_y, the deviations of L, K and w will then be computed by formulae which will shortly be derived. From the magnitude of these deviations definite conclusions may be drawn concerning the degree of confidence which can be placed on the agreement between the observed and calculated values of Y.

It will be noted that the above test for unimolecularity depends on the magnitude of the deviations of the constants K, L and w and on the precision measure, σ, of the observations themselves. On this basis K is obtained not as a series of values but as a single, weighted constant; L need not be determined experimentally but appears in the computation as the limiting value which the observations are actually tending to approach; and w is the resultant constant error in L and t. The procedure differs materially, therefore, from the usual criterion based on the possibility of deriving a consistent series of K values using an experimentally determined value of L and disregarding constant errors.

Apart from statistical considerations, it is obvious that the adoption of this method of computation should be advantageous whenever the experimental determination of L is difficult or uncertain (for example, in rate-of-inversion experiments) or in cases where a constant error is necessarily introduced in the measurement of the time (cf. Daniels and Johnston, 1921, p. 56). In such cases the added arithmetical labor may well be compensated for by the avoidance of experimental difficulties.

5. Derivation of the Normal Equations

As already shown (cf. Part I), the derivation of numerical values for the constants L and K from two observational equations of the type

$$Y = L\,(1-e^{-Kt}) = af_1 + bf_2$$

offers no difficulty. Similarly, the derivation of the constants L, K and w (or a, b, and c) from three equations of the type

$$Y = L\,[1-e^{-K(t+w)}] = af_1 + bf_2 + cf_3$$

could readily be accomplished. However, when the number of observational equations exceeds the number of unknown quantities (L, K and w in the above equation) the solution of the equations by the usual algebraic procedures becomes indeterminate. In such cases the most probable values of the unknown constants may nevertheless be obtained by the application of the least-squares criterion, namely, that the values of L, K and w (or the closely related quantities, a, b and c) are to be selected in such a manner that the sum, R, of the squares of the differences between the observed and calculated quantities shall be a minimum.

For equation (5) the difference between an observed and a calculated quantity is evidently

$$r = Y - af_1 - bf_2 - cf_3$$

and the sum, R, of the squares of the residual errors is

$$R = \Sigma\,(Y - af_1 - bf_2 - cf_3)^2$$

By definition, the most probable values of the constants a, b, and c, (corresponding to L, K and w) will be obtained when R is a minimum. From the calculus, the equations defining this condition are,

$$\frac{\delta R}{\delta a} = \Sigma f_1 Y - a\Sigma f_1^2 - b\Sigma f_1 f_2 - c\Sigma f_1 f_3 = 0 \qquad (20)$$

$$\frac{\delta R}{\delta b} = \Sigma f_2 Y - a\Sigma f_1 f_2 - b\Sigma f_2^2 - c\Sigma f_2 f_3 = 0 \qquad (21)$$

$$\frac{\delta R}{\delta c} = \Sigma f_3 Y - a\Sigma f_1 f_3 - b\Sigma f_2 f_3 - c\Sigma f_3^2 = 0 \qquad (22)$$

The solution of equations (20), (21) and (22) by the usual algebraic processes (cf. Woods and Bailey, "A Course in Mathematics," Vol. I, p. 2) gives:

$$a = \frac{[(\Sigma f_2 f_3)^2 - \Sigma f_2^2.\Sigma f_3^2]\Sigma f_1 Y + [\Sigma f_1 f_2.\Sigma f_3^2 - \Sigma f_1 f_3.\Sigma f_2 f_3]\Sigma f_2 Y + [\Sigma f_2^2.\Sigma f_1 f_3 - \Sigma f_1 f_2 \Sigma f_2 f_3]\Sigma f_3 Y}{\Sigma f_1^2[(\Sigma f_2 f_3)^2 - \Sigma f_2^2.\Sigma f_3^2] + \Sigma f_1 f_2[\Sigma f_1 f_2.\Sigma f_3^2 - \Sigma f_1 f_3.\Sigma f_2 f_3] + \Sigma f_1 f_3[\Sigma f_2^2.\Sigma f_1 f_3 - \Sigma f_1 f_2.\Sigma f_2 f_3]} \quad (23)$$

$$b = \frac{[\Sigma f_1 f_2.\Sigma f_3^2 - \Sigma f_1 f_3.\Sigma f_2 f_3]\Sigma f_1 Y + [(\Sigma f_1 f_3)^2 - \Sigma f_1^2.\Sigma f_3^2]\Sigma f_2 Y + [\Sigma f_1^2.\Sigma f_2 f_3 - \Sigma f_1 f_2.\Sigma f_1 f_3]\Sigma f_3 Y}{\Sigma f_1^2[(\Sigma f_2 f_3)^2 - \Sigma f_2^2.\Sigma f_3^2] + \Sigma f_1 f_2[\Sigma f_1 f_2.\Sigma f_3^2 - \Sigma f_1 f_3.\Sigma f_2 f_3] + \Sigma f_1 f_3[\Sigma f_2^2.\Sigma f_1 f_3 - \Sigma f_1 f_2.\Sigma f_2 f_3]} \quad (24)$$

$$c = \frac{[\Sigma f_2^2.\Sigma f_1 f_3 - \Sigma f_1 f_2.\Sigma f_2 f_3]\Sigma f_1 Y + [\Sigma f_1^2.\Sigma f_2 f_3 - \Sigma f_1 f_2.\Sigma f_1 f_3]\Sigma f_2 Y + [(\Sigma f_1 f_2)^2 - \Sigma f_1^2.\Sigma f_2^2]\Sigma f_3 Y}{\Sigma f_1^2[(\Sigma f_2 f_3)^2 - \Sigma f_2^2.\Sigma f_3^2] + \Sigma f_1 f_2[\Sigma f_1 f_2.\Sigma f_3^2 - \Sigma f_1 f_3.\Sigma f_2 f_3] + \Sigma f_1 f_3[\Sigma f_2^2.\Sigma f_1 f_3 - \Sigma f_1 f_2.\Sigma f_2 f_3]} \quad (25)$$

Use will presently be made of some of the coefficients in the above equations in deriving the respective weights of the constants a, b and c. These equations could also be used to determine the most probable values of a, b and c, although the arithmetical work will be shortened if the solution of a, b and c is made to depend directly on equations (20), (21) and (22), after the insertion in these equations of numerical values for the various sums;

$$\begin{array}{lll} \Sigma f_1 Y & \Sigma f_1^2 & \Sigma f_1 f_2 \\ \Sigma f_2 Y & \Sigma f_2^2 & \Sigma f_1 f_3 \\ \Sigma f_3 Y & \Sigma f_3^2 & \Sigma f_2 f_3 \end{array} \qquad (26)$$

6. Derivation of L, K and W

In illustration of the computations use will be made of the data given by Pennycuick (1916; p. 9, his Table II) for the rate of inversion of sugar solutions. Using equation (5) it will be assumed, for simplicity, that w′ is zero, so that $w = w' + i = i$. For convenience of computation the function $e^{-k't'}$ will be placed in the equivalent form $10^{-k't'}$ where

$$k' = 0.4342945\ K'$$

Using rounded numbers, the trial value of 0.001600 will be selected for k′ corresponding to a value of

$$(2.302585)\ (0.001600) = 0.0036841$$

for K′. Within wide limits, the exact numerical value of K′ is without significant influence on the final results.

In Table No. 1, the values of t′ are those given by Pennycuick (1926; p. 9). The values for Y (the sucrose remaining at the time t) were found by deduct-

TABLE I

Computations: Data of Pennycuick (1926, p. 9, His Table II)

($k' = 0.001600$; $w' = 0$)

$t'=t$	Y	$k't'$	$f_3 = 10^{-k't'}$	f_3^2	f_3Y	$f_2 = tf_3$	$f_2Y = t.f_3Y$	$f_2^2 = t^2.f_3^2$	$f_2f_3 = t.f_3^2$
5.97	2.0	0.009552	0.978246	0.956965	1.95649	5.84013	11.68	34.11	5.7131
9.82	3.5	.015712	.964468	.930199	3.37564	9.47108	33.15	89.70	9.1346
21.77	7.4	.034832	.922928	.851796	6.82967	20.09214	148.68	403.69	18.5436
29.80	10.2	.047680	.896025	.802861	9.13946	26.70155	272.36	712.97	23.9253
44.47	14.9	.071152	.848883	.720602	12.64836	37.74983	562.47	1425.05	32.0452
59.60	19.7	.095360	.802860	.644584	15.81634	47.85046	942.65	2289.67	38.4172
79.60	25.4	.127360	.745830	.556262	18.94408	59.36807	1507.95	3524.57	44.2785
93.18	29.0	.149088	.709434	.503297	20.57359	66.10506	1917.05	4369.88	46.8972
119.6	35.5	.191360	.643636	.414267	22.84908	76.97887	2732.75	5925.75	49.5464
142.9	40.9	.228640	.590691	.348916	24.15926	84.40974	3452.36	7125.00	49.8601
179.7	48.4	.287520	.515798	.266048	24.96462	92.68890	4486.14	8591.23	47.8087
239.8	58.9	.383680	.413352	.170860	24.34643	99.12181	5838.27	9825.13	40.9722
299.8	67.2	.479680	.331375	.109809	22.26840	99.34622	6676.07	9869.67	32.9209
359.7	73.9	.575520	.265754	.070625	19.63922	95.59171	7064.23	9137.78	25.4039
522.9	85.9	.836640	.145667	.021219	12.51280	76.16927	6542.94	5801.76	11.0953
589.4	88.9	.943040	.114015	.012999	10.13593	67.20044	5974.12	4515.90	7.6619
639.8	90.0	1.023680	.094694	.008967	8.60768	60.58522	5507.20	3670.57	5.7370
Sums	702.6	—	9.983656	7.390276	258.76705	1025.27050	53670.07	77312.43	489.9611

ing the percentage values for Z given by Pennycuick from 100. As many places of significant figures were retained as appeared necessary to provide about seven significant figures in the sums given at the bottom of Table I.

The computations in Table I will therefore furnish all of the sums listed under (26) with the exception of Σf_1Y, Σf_1^2, Σf_1f_2 and Σf_1f_3. Using the data given in Table No. 1, these sums may conveniently be obtained as follows:

$$\begin{aligned}
\Sigma f_1Y &= \Sigma Y - \Sigma f_3Y &&= 443.833\\
\Sigma f_1^2 &= n + \Sigma f_3^2 - 2\Sigma f_3 &&= 4.42296\\
\Sigma f_1f_2 &= \Sigma f_2 - \Sigma f_2f_3 &&= 535.309\\
\Sigma f_1f_3 &= \Sigma f_3 - \Sigma f_3^2 &&= 2.59338
\end{aligned}$$

Retaining only 6 places of significant figures and substituting in the normal equations (20), (21) and (22), the following numerical expressions are then obtained:

$$\begin{aligned}
&\text{I} && 443.833 - 4.42296\,a - 535.309\,b - 2.59338\,c = 0\\
&\text{II} && 53670.1 - 535.309\,a - 77312.4\,b - 489.961\,c = 0\\
&\text{III} && 258.767 - 2.59338\,a - 489.961\,b - 7.39028\,c = 0
\end{aligned}$$

These equations may now be solved by any of the usual algebraic methods. If a calculating machine is available the following procedure may be found convenient. Equations I, II and III are first divided, in turn, by the coefficients of c to obtain the 3 equations:

$$\begin{aligned}
&\text{IV} && 171.141 - 1.70548\,a - 206.414\,b - c = 0\\
&\text{V} && 109.539 - 1.09255\,a - 157.793\,b - c = 0\\
&\text{VI} && 35.015 - 0.35092\,a - 66.298\,b - c = 0
\end{aligned}$$

Equation VI is then subtracted from equations IV and V, thereby eliminating c, with the result,

$$\begin{aligned}
&\text{VII} && 136.126 - 1.35456\,a - 140.116\,b = 0\\
&\text{VIII} && 74.524 - 0.74163\,a - 91.495\,b = 0
\end{aligned}$$

Equations VII and VIII are next divided by the coefficients of b to obtain

$$\begin{aligned}
&\text{IX} && 0.971524 - 0.0096674\,a - b = 0\\
&\text{X} && 0.814514 - 0.0081057\,a - b = 0
\end{aligned}$$

On substracting X from IX the term b is eliminated, giving

$$\text{XI}\quad 0.157010 - 0.0015617\,a = 0$$

From which

$$a = 100.538$$

By substituting this value of a in IX

$$b = -\ 0.000417$$

and by substitution in IV

$$c = -\ 0.239$$

The arithmetical work may be checked by inserting the numerical values of a, b and c in III and balancing the equation.

Using (14), it follows that

$$\begin{aligned}
L &= a &&= 100.538\\
h &= b/L &&= -0.0000041\\
K' &= 2.302585\ k' &&= 0.0036841\\
K &= K' + h &&= 0.0036800\\
k &= 0.4342945\ K &&= 0.0015982\\
w &= w' + i = i &&= \frac{c}{ak} = -\frac{0.239}{0.369980} = -\ 0.646
\end{aligned}$$

7. Derivation of the Standard Deviation, σ_y

The adjusted values of L, k and w may now be substituted in equation (5) to obtain the series of calculated values given under the heading Y′ in Table II. By inspection, it is apparent that the agreement between the observed and the calculated values is excellent. For this series of observations the standard deviation is

$$\sigma_y = \sqrt{\frac{0.1684}{17-3}} = \sqrt{0.0120} = 0.11$$

corresponding to a probable error of (0.6745) (0.11) = 0.07 per cent. The agreement would not be appreciably altered if the calculation were to be repeated using the trial values k′ = 0.015982 and w′ = − 0.646.

The procedure exemplified in the foregoing pages has also been applied to another series of observations given by Pennycuick (1926, p. 8; his Table I). For these observations the adjusted values of k, L and w are 0.0006004, 100.275 and −0.268 respectively. As shown in Table IIa (17 observations) the agreement between the observed values and the values calculated by equation (5) is good although the general agreement is obviously affected by the presence of one discordant result. When all observations are considered, the value of σ_y is

$$\sigma_y = \sqrt{\frac{2.0809}{17-3}} = 0.39$$

Excluding the discordant observation, the adjusted values of k, L and w become, 100.317, −2.15 and 0.0006010, respectively. A recalculation of the standard deviation on this basis (Table IIa; 16 observations) gives

$$\sigma_y = \sqrt{\frac{0.1642}{16-3}} = 0.11$$

The agreement between the observed and calculated values (Y and Y″) is excellent.

In the absence of data on which a calculation of the deviation, σ, of the observations themselves can be based, it is perhaps safe to assume with Scatchard (1926) that the precision attainable in such measurements is in the neighborhood of 0.2 to 0.5 per cent. If so, it must be concluded that Pennycuick's data conform to the unimolecular type of expression within allowable limits of experimental error. In this sense it appears unnecessary to assume a progressive change of environment in these rate-of-inversion experiments. (Progressive increase in H-ion activity, etc.) However, to confirm this conclusion it will be necessary to obtain a measure of the precision of the constants which were used in deriving the calculated values.

TABLE II

Computation of σ_y for the Data of Pennycuick (1926, p. 9)
$k' = 0.0015982$; $w' = -0.646$; $L = 100.538$)

t	$t' = t + w$	$k't'$	$f_3 = 10^{-K't'}$	$f_1 = 1 - f_3$	Y observed	$Y' = Lf_1$ Calculated	$d = Y - Y'$	d^2
5.97	5.324	0.008509	0.980598	0.019402	2.0	1.95	0.05	0.0025
9.82	9.174	.014662	.966803	.033197	3.5	3.34	.16	.0256
21.77	21.124	.033760	.925210	.074790	7.4	7.52	− .12	.0144
29.80	29.154	.046594	.898268	.101732	10.2	10.23	− .03	.0009
44.47	43.824	.070040	.851060	.148940	14.9	14.97	− .07	.0049
59.60	58.954	.094220	.804970	.195030	19.7	19.61	.09	.0081
79.60	78.954	.126184	.747853	.252147	25.4	25.35	.05	.0025
93.18	92.534	.147888	.711397	.288603	29.0	29.02	− .02	.0004
119.6	118.954	.190112	.645488	.354512	35.5	35.64	− .14	.0196
142.9	142.254	.227350	.592448	.407552	40.9	40.97	− .07	.0049
179.7	179.054	.286164	.517412	.482588	48.4	48.52	− .12	.0144
239.8	239.154	.382216	.414748	.585252	58.9	58.84	.06	.0036
299.8	299.154	.478108	.332577	.667423	67.2	67.10	.10	.0100
359.7	359.054	.573840	.266784	.733216	73.9	73.72	.18	.0324
522.9	522.254	.834666	.146330	.853670	85.9	85.83	.07	.0049
589.4	588.754	.940947	.114565	.885435	88.9	89.02	− .12	.0144
639.8	639.154	1.021496	.095171	.904829	90.9	90.97	− .07	.0049
							$\Sigma d^2 =$	0.1684

TABLE IIa

Computation of σ_y for the Data of Pennycuick (1926, p. 8)

	17 observations				16 observations			
t	Y Observed	Y' calculated[1]	$d = Y - Y'$	d^2	Y Observed	Y'' Calculated[2]	$d = Y - Y''$	d^2
19.80	2.5	2.35	0.15	0.0225	2.5	2.42	0.08	0.0064
39.71	5.0	5.00	.00	.0000	5.0	5.08	−.08	.0064
59.35	7.6	7.56	.04	.0016	7.6	7.63	−.03	.0009
63.01	8.0	8.02	−.02	.0004	8.0	8.10	−.10	.0100
77.50	10.0	9.85	.15	.0225	10.0	9.93	.07	.0049
101.41	13.0	12.79	.21	.0441	13.0	12.88	.12	.0144
181.61	22.0	21.97	.03	.0009	22.0	22.06	−.06	.0036
226.30	26.6	26.67	−.07	.0049	26.6	26.75	−.15	.0225
299.01	34.0	33.71	.29	.0841	34.0	33.80	.20	.0400
371.35	38.7	40.04	−1.34	1.7956	—	—	—	—
490.20	49.3	49.17	.13	.0169	49.3	49.26	.04	.0016
608.70	57.0	56.89	.11	.0121	57.0	56.98	.02	.0004
811.64	67.6	67.50	.10	.0100	67.6	67.59	.01	.0001
1100.60	78.2	78.30	−.10	.0100	78.2	78.38	−.18	.0324
1152.50	80.0	79.82	.18	.0324	80.0	79.90	.10	.0100
1486.40	87.4	87.38	.02	.0004	87.4	87.45	−.05	.0025
2696.40	98.0	97.85	.15	.0225	98.0	97.91	.09	.0081
			Σd^2	= 2.0809			Σd^2 =	0.1642

[1] Basis of L = 100.275; w′ = −2.68; k′ = 0.0006004.
[2] Basis of L = 100.317; w′ = −2.15; k′ = 0.0006010.

8. Derivation of the Weights and Standard Deviations of L, K, and w

Denoting the denominator common to equations (23), (24) and (25) by the symbol D_{abc}, it may readily be shown (cf. Merriman, "Method of Least-Squares," 1904, 8th edition revised, pp. 82-85, 195-198 or Mellor, "Higher Mathematics for Students of Chemistry and Physics," 1913, p. 559) that the weights of a, b and c are given by the expressions:

$$W_a = \frac{D_{abc}}{(\Sigma f_2 f_3)^2 - \Sigma f_2^2 . \Sigma f_3^2} \qquad (27)$$

$$W_b = \frac{D_{abc}}{(\Sigma f_1 f_3)^2 - \Sigma f_1^2 . \Sigma f_3^2} \qquad (28)$$

$$W_c = \frac{D_{abc}}{(\Sigma f_1 f_2)^2 - \Sigma f_1^2 . \Sigma f_2^2} \qquad (29)$$

Given the weights of a, b and c, the deviations of these quantities are found by the formulae

$$\sigma_a = \frac{\sigma_y}{\sqrt{W_a}};\quad \sigma_b = \frac{\sigma_y}{\sqrt{W_b}};\quad \sigma_c = \frac{\sigma_y}{\sqrt{W_c}}$$

(cf. Mellor, p. 511). The calculations in question are exemplified in Table No. 3.

In deriving the deviation σ_K of K it may be considered that $\sigma_K = \sigma_h$ as

$$K = K' + h$$

where K′ is a true constant so that $\delta K = \delta h$.

For the computation of $\sigma_h = \sigma_K$ use is made of the formula

$$h = \frac{b}{a} \pm \frac{\sqrt{\overline{a\,\sigma_b}^2 + \overline{b\,\sigma_a}^2}}{a^2} = \frac{b}{a} \pm \sigma_h$$

(cf. Mellor, p. 529). From which

$$\sigma_K = \sigma_h\,\frac{\sqrt{\overline{a\,\sigma_b}^2 + \overline{b\,\sigma_a}^2}}{a^2} = 0.000013 \qquad (30)$$

Then as k = 0.4343 K, it follows that $\sigma_k = 0.4343\,\sigma_K$.

Finally, on the basis of the formula

$$w = w' + i$$

where w′ is a true constant, we may write $\sigma_w = \sigma_i$. In computing $\sigma_w = \sigma_i$ it is convenient, first of all, to derive the deviation, σ_{aK} of the product, aK (cf. Mellor, p. 528). Thus

$$\sigma_{aK} = \sqrt{\overline{K\sigma_a}^2 + \overline{a\sigma_K}^2} = 0.0014$$

The precision of the quotient

$$i = \frac{c}{aK}$$

is then given by the formula

$$\sigma_w = \sigma_i = \frac{\sqrt{\overline{aK\sigma_c}^2 + \overline{c\sigma_{aK}}^2}}{(aK)^2} = 0.16 \qquad (31)$$

The calculation of the deviations of K, k, aK and w is shown in Table No. 4. As only 2 places of significant figures are required in weights and deviations, it will be noted that the computations of Tables III and IV may conveniently be performed with a slide-rule without introducing any appreciable error.

TABLE III

Computation of the Denominator, D_{abc} and of the Weights and Standard Deviations of a, b, and c, for the Data of Pennycuick (1926, p. 9)

Base data (rounded values; $\sigma_y = 0.11$)

$(1) = \Sigma f_1^2 = 4.42;$

$(2) = \Sigma f_2^2 = 77300.\ ;$

$(3) = \Sigma f_3^2 = 7.39;$

$(4) = \Sigma f_2 f_3 = 490.$

$(5) = \Sigma f_1 f_3 = 2.59$

$(6) = \Sigma f_1 f_2 = 535.$

Derivation of D_{abc}

$(7) = (1) \times (4)^2 = 1,061,000$

$(8) = (2) \times (5)^2 = 519,000$

$(9) = (3) \times (6)^2 = 2,114,000$

$(10) = (7) + (8) + (9) = 3,694,000$

$(11) = (1) \times (2) \times (3) = 2,525,000$

$(12) = (4) \times (5) \times (6) = 679,000$

$(13) = (11) + (12) + (12) = 3,883,000$

$D_{abc} = (10) - (13) = -189,000$

Derivation of W_a and σ_a

$(14) = (4)^2 - (2) \times (3) = 331,000$

$W_a = D_{abc} \div (14) = 0.5710 = (0.76)^2$

$\sigma_a = \sigma_y \div \sqrt{W_a} = 0.14$

Derivation of W_b and σ_b

$(15) = (5) - (1) \times (3) = -26.0$

$W_b = D_{abc} \div (15) = 7,270 = (85.3)^2$

$\sigma_b = \sigma_y \div \sqrt{W_b} = 0.0013$

Derivation of W_c and σ_c

$(16) = (6)^2 - (1) \times (2) = -55,700$

$W_c = D_{abc} \div (16) = 3.39 = (1.84)^2$

$\sigma_c = \sigma_y \div \sqrt{W_c} = 0.060$

TABLE IV

Computation of σ_K, σ_k, σ_{aK} and σ_w

Base data (rounded values)

$a = 100.5$; $\sigma_a = 0.14$; $K = 0.00368$

$b = -0.000417$; $\sigma_b = 0.0013$;

$c = -0.239$; $\sigma_c = 0.060$;

Derivation of $\sigma_K = \sigma_h$ and σ_k

$(1) = \overline{a\,\sigma_b}^2 = 0.0171$

$(2) = \overline{b\,\sigma_a}^2 = 0.0000$

$(3) = (1) + (2) = 0.0171$

$(4) = (3)^{\frac{1}{2}} = 0.131$

$\sigma_K = (4) \div a^2 = 0.000013$

$\sigma_k = 0.4343\,\sigma_K = 0.0000056$

Derivation of σ_{aK}

$(5) = \overline{K\,\sigma_a}^2 = 0.000000265$

$(6) = \overline{a\,\sigma_K}^2 = .000001710$

$(7) = (5) + (6) = .000001975$

$\sigma_{aK} = (7)^{\frac{1}{2}} = .0014$

Derivation of $\sigma_w = \sigma_l$

$(8) = \overline{aK\,\sigma_c}^2 = 0.000492$

$(9) = \overline{c\,\sigma_{aK}}^2 = .000000$

$(10) = (8) + (9) = .000492$

$(11) = (10)^{\frac{1}{2}} = .022$

$\sigma_w = (11) \div \overline{aK}^2 = .16$

With regard to the precision actually attained, the adjusted values of the constants pertaining to the data of Pennycuick (1926, p. 9) therefore become:

$L = 100.54 \pm (\sigma_L = 0.14)$
$w = 0.65 \pm (\sigma_w = 0.16)$
$k = 0.0015982 \pm (\sigma_k = 0.0000056)$

Similarly, for the second set of data given by Pennycuick (1926, p. 8),

$L = 100.28 \pm (\sigma_L = 0.42)$
$w = -2.7 \pm (\sigma_w = 1.4)$
$k = 0.0006004 \pm (\sigma_k = 0.0000061)$

when all observations are considered. When one observation is omitted,

$L = 100.32 \pm (\sigma_L = 0.12)$
$w = -2.15 \pm (\sigma_w = 0.39)$
$k = 0.0006010 \pm (\sigma_k = 0.0000018)$

Deviations in L of the order of 0.1 to 0.4 per cent do not appear improbable in rate of inversion experiments, as the determination of this limiting value is the least precise of all the observations.

A deviation of one per cent or less in the value of k is indicative of a degree of precision seldom achieved in rate-of-reaction experiments (cf. Table VII, data of Daniels and Johnston, 1921).

In interpreting the significance of w in these experiments, it should be borne in mind that this quantity is not simply a time error but that it refers to the resultant effect of all constant errors on the time.

On the whole the conclusion is warranted that the unusually precise data of Pennycuick (1926) do actually conform to an equation of the unimolecular type. It would appear, therefore, that the usual methods of computation may furnish misleading results when the unimolecularity of a given process is being examined. The practical bearing of this conclusion on the various theories which have been proposed to account for apparent departures from the unimolecular formula is obvious.

Logically, the least-squares procedure should be used until the unimolecularity of a given process has either been established or disproved. If the process conforms to the unimolecular formula within known limits of experimental error, it may then appear sufficient, in the absence of large constant errors, to apply the usual methods of computation in deriving numerical values for velocity constants under various experimental conditions. The effect of disregarding constant errors will accordingly be briefly discussed.

9. Effect of disregarding Constant Errors

Let it be assumed that the constant errors in a series of observations on a unimolecular process are known to be negligibly small or else that this source of error is simply disregarded. The equation to be used will then be

$$Y = L\,(1 - e^{-Kt})$$

Now, as already shown (equation 15), the linearized form of this equation is

$$\begin{aligned} Y &= L\,(1 - e^{-K't}) + Lh\,(t'e^{-K't}) \\ &= af_1 + bf_2 \end{aligned}$$

From previous considerations, the normal equations are

$$\delta R/\delta a = \Sigma\, f_1Y - a\,\Sigma\, f_1^2 - b\,\Sigma\, f_1f_2 = 0 \tag{32}$$

and,

$$\delta R/\delta b = \Sigma\, f_2Y - a\,\Sigma\, f_1f_2 - b\,\Sigma\, f_2^2 = 0 \tag{33}$$

The solution of these equations gives

$$a = \frac{\Sigma\, f_2^2.\ \Sigma\, f_1Y - \Sigma\, f_1f_2.\Sigma\, f_2Y}{\Sigma\, f_1^2.\ \Sigma\, f_2^2 - (\Sigma\, f_1f_2)^2} \tag{34}$$

$$b = \frac{\Sigma\, f_1^2.\ \Sigma f_2Y - \Sigma\, f_1f_2.\ \Sigma\, f_1Y}{\Sigma\, f_1^2.\ \Sigma\, f_2^2 - (\Sigma\, f_1f_2)^2} \tag{35}$$

In illustration of this simplified treatment, use will be made of data given by Daniels and Johnston (1921, p. 64; their Experiment 25 at 65°C). Use has already been made of these figures in a preceding section in connection with a discussion of the "chain" formulae for the derivation of velocity constants. For the trial value of k the figure of 0.1880 will be adopted, corresponding to the highest value (K = 0.4340) given by Daniels and Johnston. The derivation of the sums demanded by equations (32) and (33) is shown in Table V. By comparison with Table I, it is apparent that, for an equal number of observations, the arithmetical work is not shortened when no allowance is made for constant errors, although subsequent computations are somewhat simplified.

TABLE V

Computations; Data of Daniels and Johnston (1921; Their Experiment No. 25)

($k' = 0.1880$; no allowance for constant errors).

t	Y	k't	$f_3 = 10^{-k't}$	$f_1 = 1 - f_3$	f_1^2
2	18.6	0.3760	0.420727	0.579273	0.335557
3	22.6	.5640	.272898	.727102	.528677
4	25.1	.7520	.177011	.822989	.677311
5	27.2	.9400	.114815	.885185	.783552
6	29.1	1.1280	.074473	.925527	.856600
7	30.1	1.3160	.048306	.951694	.905721
Sums	152.7				4.087418

t	f_1Y	$f_2 = tf_3$	f_2^2	f_2Y	f_1f_2
2	10.77448	0.841454	0.708045	15.65104	0.487432
3	16.43250	.818694	.670260	18.50248	.595274
4	20.65702	.708044	.501326	17.77190	.582712
5	24.07703	.574075	.329562	15.61484	.508163
6	26.93284	.446838	.199664	13.00299	.413561
7	28.64599	.338142	.114340	10.17807	.321808
Sums	127.51986	3.727247	2.523197	90.72132	2.908950

By the substitution in equations (32) and (33) of the sums given in Table V, the following numerical expressions are obtained:

$$127.5199 - 4.087418a - 2.908950b = 0$$
$$90.7213 - 2.908950a - 2.523197b = 0$$

The solution of these equations gives

$$a = 31.25 = L$$
$$b = 0.07200$$

From which,

$$h = \frac{b}{L} = -0.002304$$
$$K' = 2.302585\,k' = 0.432886$$
$$K = K' + h = 0.430582$$
$$k = 0.4342945\,K = 0.1870$$

The calculated values given in the first part of Table VI were obtained by substituting the values $L = 31.25$ and $k = 0.1870$ in equation (1). By equation (18) the deviation of these values is

$$\sigma_y = \sqrt{\frac{1.09}{6-2}} = 0.52$$

Using rounded numbers, the numerical value of the denominator, D_{ab} common to equations (34) and (35) is

$$\begin{aligned} D_{ab} &= \Sigma f_1^2 . \Sigma f_2^2 - (\Sigma f_1 f_2)^2 \\ &= (4.09)\,(2.52) - (2.91)^2 \\ &= 10.31 - 8.47 \\ &= 1.84 \end{aligned}$$

The weights of $L = a$ and of b accordingly are

$$W_L = \frac{D_{ab}}{\Sigma f_2^2} = \frac{1.84}{2.52} = 0.730$$

and

$$W_b = \frac{D_{ab}}{\Sigma f_1^2} = \frac{1.84}{4.09} = 0.450$$

From which,

$$\sigma_L = \frac{\sigma_Y}{\sqrt{W_L}} = \frac{0.50}{0.854} = 0.585$$

$$\sigma_b = \frac{\sigma_Y}{\sqrt{W_b}} = \frac{0.50}{0.671} = 0.745$$

Then, using equation (30),

$$\sigma_K = \frac{\sqrt{\overline{L \cdot \sigma_b}^2 + \overline{b\, \sigma_L}^2}}{L^2} = 0.024$$

TABLE VI

Computation of σ_Y for the Data of Daniels and Johnston (1921; Their Experiment No. 25)

t	Y Observed[1]	Without Allowance for Constant Errors			Allowing for Constant Errors		
		Y′ Calc.[2]	d = Y − Y′	d^2	Y″ Calc.[3]	d_1 = Y − Y″	d_1^2
2	18.6	18.0	0.6	0.36	18.7	−0.1	0.01
3	22.6	22.7	− .1	.01	22.4	.2	.04
4	25.1	25.7	− .6	.36	25.2	− .1	.01
5	27.2	27.6	− .4	.16	27.3	− .1	.01
6	29.1	28.9	.2	.04	28.9	.2	.04
7	30.1	29.7	.4	.16	30.1	.0	.00
			Σd^2 =	1.09		Σd_1^2 =	0.11

---

[1] Values reported by Daniels and Johnston (1921, p. 64).

[2] Using equation (1); $L = 31.25$; $K = 0.43058$ ($k = 0.1870$).

[3] Using equation (5); $L = 33.805$; $K = 0.28361$ ($k = 0.12317$); $w = 0.8317$.

When no allowance is made for constant errors, the most probable values of L and K for the data in question (Experiment 25 by Daniels and Johnston, 1921) may therefore be written

$$L = 31.25 \pm (\sigma_L = 0.59)$$
$$K = 0.431 \pm (\sigma_K = 0.024)$$

The value of L given by Daniels and Johnston (1921, p. 64) is 32.6. For the value of the velocity constant they deduce K = 0.345 while in their experiments 23 and 24 at the same temperature they report the values 0.290 and 0.293, respectively. Commenting on these results, Daniels and Johnston (1921, p. 65) state: "The velocity constant in Experiment 25 does not check with the others at the same temperature. The errors in it, however, are greatly magnified because the experiment was carried out at a very low pressure in order to contrast it with Experiment 25 in which a high pressure was used. * * * Accordingly, it is excluded in determining the average velocity constant at 65°C."

For purposes of comparison the calculated values which are obtained when proper allowance is made for constant errors are also given in Table No. 6 (Column headed Y″). The deviation of this second set of values from the values observed in Experiment 25 by Daniels and Johnston is

$$\sigma_y = \sqrt{\frac{0.11}{6-3}} = 0.19$$

By inspection, the agreement between the observed and calculated values (Y and Y″) is excellent. It will also be noted that the velocity constant which pertains to this recalculation (K = 0.28361, corresponding to k = 0.12317; see footnote, Table No. 6) is in good agreement with the values (0.290 and 0.293) obtained by Daniels and Johnston in their Experiments 23 and 24. The discrepancy between the observed and calculated values of L (32.6 and 33.805, respectively) is reflected by the relatively high value of w = 0.8317.

On the basis of the agreement between the observed and calculated values, it would appear unnecessary to reject this series of observations although, as will be shown elsewhere*, the weight of this particular series of observations is so small that its omission is without material effect on the general average.

In Table VII the most probable values (in the sense of least-squares) of the velocity constants recalculated from the data of Daniels and Johnston (1921) are compared with the values actually reported by these experimenters. Excluding Experiment 25, the difference between the two sets of constants varies from 0.5 to 12.6 per cent. With less precise data, much greater differences would be observed. If the velocity constants deduced by

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* It is expected that the data of Daniels and Johnston (1921) will be more fully discussed in a separate paper bearing on the statistical treatment of the Arrhenius expression for the dependence of velocity constants on temperature.

least-squares are accepted as most representative of the observations, it must be concluded that the use of the least-squares procedure is the mathematical equivalent of such analytical safeguards as precise temperature control, refined manometric technique, etc. In fact, the difference noted in Table VII are equivalent, on the whole, to temperature variations of 0.1 to 0.2°C., while, as stated by Daniels and Johnston (1921, p. 65), "The thermostat was constant to 0.03°."

Table VII

A Comparison of the Velocity Constants deduced by Least-Squares with the Constants reported by Daniels and Johnston (1921)

Experiment Number	$K \times 10^3$ (Least-Squares)	$K_1 \times 10^3$ Daniels and Johnston	Percentage difference $\frac{100(K - K_1)}{K}$
	At 27°C.		
2	2.120	2.14	— 0.9
3	2.020	2.01	0.5
12	2.017	1.93	4.3
	At 35°C.		
5	7.959	7.89	0.9
6	7.84	8.83	—12.6
11	7.821	7.54	3.6
	At 45°C.		
7	28.43	29.4	— 3.4
8	27.76	29.3	— 5.5
9	29.20	30.9	— 5.8
	At 55°C.		
15	91.7	89.2	2.7
26	92.44	90.9	1.7
	At 65°C.		
23	268.8	290.	— 7.9
24	282.0	293	— 3.9
25	284.0	345[1]	—21.5

[1] This result rejected by Daniels and Johnston (1921).

Summary

1. A statistical treatment applicable to unimolecular data has been developed. The procedure makes it unnecessary to determine experimentally the value of L in the unimolecular formula

$$K = \frac{1}{t-t_0} ln \frac{(L-Y_0)}{(L-Y)}$$

Also, as proper allowance is made for constant errors in Y and t, the quantities Y_0 and t_0 need not be accurately known. Instead of a series of K values, only one properly-weighted velocity constant is obtained.

2. It has been shown that the data of Pennycuick (1926) on the inversion of sucrose do actually conform very closely to an equation of the unimolecular type.

3. In general, the usual methods of computation will furnish misleading indications when the unimolecularity of a given process is being examined.

4. The velocity constants given by Daniels and Johnston (1921) for the rate of decomposition of nitrogen pentoxide have been recalculated. The least-squares values of the velocity constants differ by 0.5 to 12.6 per cent from the values given by Daniels and Johnston.

5. The conclusion is warranted that adherence to the usual methods of computation is inconsistent with refinements of analytical technique. The least-squares procedure should be used whenever a velocity constant is to be determined within an allowable error of, say, 5 per cent.

THE EFFECT OF GELATIN AND SALTS ON CONGO RED*

BY HERBERT L. DAIVS AND JOHN W. ACKERMAN

In the practical application of colloid chemistry no property is more often used than that shown by a number of usually lyophilic colloidal substances by virtue of which they are able to stabilize other colloids, which are for the most part lyophobic. Many examples of this protective action are known and have been studied; but the student of these phenomena can not proceed very far before coming to the point beyond which our knowledge has not gone. This paper will present a contribution to this problem by showing that in certain systems containing gelatin and Congo red in which we should expect a protective action, the phenomena are for the most part to be interpreted on the assumption of an independent existence of these two substances in the mixed sols and only under special conditions does anything like protective action appear and then in a form not usually associated with these phenomena.

A definition of protective action has been given by Thomas:[1] "When a solution of a hydrophilic colloid is added to a less stable dispersion, or suspension, generally there is no change in appearance of the system and the less stable dispersion is found to have become more stable, i.e., it is no longer so sensitive toward coagulation by either the addition of electrolytes or by evaporation to dryness. The less stable dispersion is said to have been 'protected' by the hydrophilic colloid; hence the term 'protective colloid,' which is commonly applied to the hydrophilic colloids, such as gelatin, gum arabic, albumin, etc."

But the addition of gelatin to another colloid is often a much more complex phenomenon than would appear from this simple definition and the literature shows several cases of sensitizations such as are discussed by Bancroft.[2]

"Since a colloid peptized by water may be charged positively or negatively, there is no reason why it should not precipitate another colloid under suitable conditions. We usually consider the colloids peptized by water solely as protecting colloids, but this is clearly an inadequate view, as is shown by the experimental data. Years ago Schulze[3] pointed out that small amounts of gelatin solutions were as effective as lime or alum in causing the rapid sedimentation of clay, and that addition of minute quantities of gelatin to barium sulphate simplified the question of washing and filtration very much. He, of course, gave no adequate explanation of the phenomenon and

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* This work is part of the programme now being carried out at Cornell University under a grant to Professor Bancroft from the Heckscher Foundation for the Advancement of Research established by August Heckscher at Cornell University.

[1] Bogue: "The Theory and Application of Colloidal Behavior," 1, 346 (1924).

[2] "Applied Colloid Chemistry," 309 (1926).

[3] Pogg. Ann., 129, 369 (1866).

the real explanation was given by Billitzer,[1] who called attention to the fact that, while gelatin, agar-agar, etc., ordinarily check the precipitation of colloidal solutions, by electrolytes, small amounts of these same substances may have a precipitating action. This can be detected even when the gelatin produces no precipitation itself. Billitzer cites the experiments of Neisser and Friedemann in which it was found that a mastic emulsion containing a trace of gelatin was precipitated more readily by sodium chloride than when no gelatin is present.[2] Billitzer finds that gelatin precipitated such negative colloids as antimony sulphide and arsenious sulphide in acid or neutral solution, but does not precipitate positively charged sols such as hydrous ferric oxide, Gelatin in ammoniacal solution precipitates hydrous ferric oxide, though no precipitation occurs if ammonia is added to a mixture of gelatin and ferric oxide. Bismarck brown, which is a positive colloid, is precipitated by an alkaline gelatin solution, while eosine is precipitated by an acidified gelatin solution."

A little later, p. 311, Bancroft returns to the more usual protective action and the measure of it. "Coming back to the general problem, if the ratio of gelatin to the other colloid is increased sufficiently, we shall pass through the precipitation range into the range where the colloidal solution is stabilized by gelatin and then behaves more like a water-soluble colloid. Colloidal gold and colloidal silver solutions, when stabilized by gelatin, can be evaporated and redissolved, because the gelatin prevents the irreversible agglomeration. When less gelatin is used it may retard, though not prevent, the change of red colloidal gold to blue. Zsigmondy[3] defines as the gold number the number of milligrams of a protecting colloid which just prevents the color change in a 10 cc red gold solution, containing 0.0053-0.0058 percent gold, when one cubic centimeter of a ten percent sodium chloride solution is added. Of course, a strongly adsorbed non-electrolyte, such as sugar, will act similarly to gelatin; but, in most cases, the adsorption is so much less that these substances are only interesting theoretically as stabilizers."

It is quite generally agreed that the protective action is due to the formation of an envelope or sheath of the protective colloid about the particles of the protected dispersion. As a result of this it is found that the conduct of the coated particles is identical with that of a solution of the protective colloid. This was shown by Loeb[4] who found that collodion suspensions to which gelatin and other protein sols were added lost the properties of the collodion and behaved as sols of the protein alone toward salts, cataphoresis, isoelectric point, etc. In certain cases there was poor protective action and in others there was slight deviation of the properties of the mixed sols from that of the protector, such as in the case of albumin where Loeb believed adsorption on the collodion particles produced an effect analogous to the so-called denaturation of the albumin. But as a general rule a substance which is to act as a

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[1] Z. physik. Chem., **51**, 145 (1905).

[2] Cf. Walpole: J. Physiol., **47**, xiv (1913); Biochem. J., **8**, 170 (1914).

[3] Z. anal. Chem., **40**, 697 (1901).

[4] J. Gen. Physiol., **5**, 479 (1922-3).

protective colloid must be strongly adsorbed by the dispersion to be protected and will impart to the mixture properties of the protecting sol. Contrary to expectation gelatin is but weakly adsorbed by Congo red and the properties of the mixed sols are those of both of its components. Especially prominent among the latter are the properties of dyeing cloth by the mixed sols in the presence of various salts.

The first direct evidence of this state of affairs was the behavior of gelatin swelling in dilute solutions of Congo red. When one gram of powdered gelatin is added to fifty cc of 0.006% solution of Congo red, the swelling gelatin at room temperature is found to contain but little more dye on or within its particles than does the clear supernatant solution which is in turn only slightly lighter than a blank solution to which no gelatin was added. This indicates very clearly that little or no protective action should be expected.

The Effect of Salts on Congo Red Solutions

In spite of the very slight adsorption shown by the Congo red and gelatin there are some phenomena which would ordinarily be interpreted as showing protection. Before proceeding to them it will be well to show some of the properties of the Congo red itself, since these properties indicate Congo red to be somewhat intermediate between the lyophobe and lyophile classifications of colloidal substances. In the first place it can be precipitated by suitable concentrations of sodium and potassium chlorides and iodides. In all these experiments a stock solution containing two grams of Congo red in a liter of solution was employed, usually by adding five cc of the stock solution to sufficient of the other reagents to make 25 cc. The dye solution as diluted finally, then, was 0.04%; samples of 0.01 and 0.02 mol of the halides were dissolved in 20 cc of solution and added to five cc of the stock Congo red. In these low concentrations of salts the precipitation was slow so that the final observations were made after 45 hours. In the case of the solutions which were 0.8 M with respect to the salts the differences were less than in the case of those 0.4 M, for in the more concentrated solution precipitation of the Congo red was nearly complete. Comparison of the precipitates and the supernatant solutions showed, however, that in both dilute and concentrated solutions the effect was in order $KI > KCl > NaI > NaCl$, the potassium iodide having the greatest precipitating effect and the sodium chloride the least effect. This shows that the iodides are more effective than the corresponding chlorides and that the potassium salts are more effective than the sodium salts. The fact that potassium chloride has greater precipitating power for Congo red than sodium iodide has shows that the difference between the metallic ions is greater than that between the chloride and iodide ions. This suggests a Hofmeister series for the coagulation of the negatively charged Congo red micelle[1] and the experiment showed that 0.4 M $BaCl_2$, when added as above, precipitates Congo red almost at once, leaving a clear, colorless, supernatant liquid after ten minutes. In respect to its behavior

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[1] Weiser and Radcliffe: J. Phys. Chem., 32, 1875 (1928).

with salts Congo red acts like a typical lyophobe colloid; but it is readily peptized by water alone and this is a property more often found in lyophile colloids.

The experiments with sodium chloride were continued to greater concentrations and it appears that these systems show a phenomenon akin to the "irregular series." Systems of 25 cc each were made up, each containing five cc of the stock Congo red and sufficient 5N NaCl to make them one, two, three, and four normal with respect to the salt. Although the 4N NaCl system grew quite turbid at once and was soon completely coagulated, the 2N NaCl produced finally much less precipitation of the Congo red than did either the 1N or the 3N systems. Further experiments confirmed this and showed that there is a broad minimum in the coagulating power of sodium chloride when the salt concentration is 1.4–1.6N; systems 1.4–2.0N are not greatly coagulated on standing for several days while systems containing more or less salt are practically completely coagulated and precipitated. This appears to be a case of irregular series as discussed by Kruyt.[1]

"The phenomena observed when a sol is flocculated by means of an electrolyte such as $AlCl_3$ agree well with the changes in boundary potential. When increasing amounts of $AlCl_3$ are added to a negatively charged sol of mastic, we notice that small concentrations cause flocculation, somewhat higher concentrations produce another stable sol of opposite sign, i.e., positively charged, while still higher concentrations bring about another flocculation. . . .

"We have, therefore, first a non-flocculation zone; but as soon as the negative critical potential is reached, flocculation begins. This primary flocculation zone ends when, after reversal of the charge, the positive critical potential is attained. From that concentration on, the $AlCl_3$, instead of causing flocculation exerts a recharging action. Hence the mastic sol is positively charged in this second zone of non-flocculation. But, positive boundary layers are discharged by anions and the positive potential, after going through a maximum value, is reduced by the Cl ions until the critical potential is reached. At that point, a second flocculation zone begins.

"This phenomenon is designated as an *irregular series.* It will always occur when the potential-lowering effect of the cation is far in excess of the potential-raising effect of the anion. This lowering effect may be due either to a high valence of the ion or to a high degree of adsorbability. Polyvalent cations give, therefore, irregular series when they are combined with monovalent anions. But monovalent organic cations act in the same way. For instance, strychnine nitrate, as well as new fuchsin, yields an irregular series with As_2S_3 sol, and $AgNO_3$ with the sol of HgS, because in each case the cation is strongly adsorbed.

"A converse reasoning applies to positively charged sols. Here the anion discharges, while the cation may raise the charge. Whenever there is a great contrast between the two ions, an irregular series will occur; hence we readily

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[1] "Colloids," 89 (1930).

understand why the positively charged sol of iron oxide forms an irregular series with sodium phosphate (monovalent cation *vs.* trivalent anion), and with NaOH (monovalent ions, but anion strongly adsorbable)."

The Congo red sol does not exactly fit this picture, for cataphoresis on the system that was 1.5N NaCl showed that in this zone of non-coagulation the sol is negatively charged as it is in the salt-free condition. In addition to this, small additions of $BaCl_2$ solutions caused immediate turbidity and rapid flocculation and precipitation of the dye in the 1.5N NaCl; systems that were 1.5N NaCl and 0.1N $BaCl_2$ were coagulated somewhat less rapidly but not less completely than systems containing only dye and 0.1N $BaCl_2$. On the other hand, additions of sodium sulphate had no effect on the sodium chloride-Congo red systems except to clear up a slight turbidity produced by the sodium chloride on the dye. If the sol in the non-flocculation zone were positively charged, cataphoresis should have shown it and the sol should have been coagulated on the addition of sodium sulphate instead of barium chloride.

We have here, apparently, an irregular series without the reversal of charge on the colloid. This must be due to a higher adsorbability of the sodium ions on the Congo red, the difference between the adsorbabilities of the sodium and chloride ions being too small to permit a reversal of the charge. The first addition of sodium chloride results in preferential adsorption of positive sodium ions and the reduction of the charge on the Congo red micelles below the critical value. Higher salt concentrations give also some adsorption of chloride ions sufficient to raise the potential above the critical value; and finally sufficient excess of sodium ions are adsorbed to reduce the potential again below the critical value and produce precipitation.

It may be added that sodium sulphate also appears to give with Congo red such an irregular series as is shown by sodium chloride. Molar sodium sulphate produces markedly less coagulation and precipitation than do systems 0.5 or 0.75 M with sodium sulphate.

It has been shown that Congo red may be precipitated by various salts in the proper concentrations. The addition of gelatin to such systems results in a great decrease in the flocculating power of the salts. Systems containing the regular amount of five cc of the stock Congo red solution, sufficient sodium chloride to make them 3.1 and 4.8N respectively, and without or with the addition of five cc of two percent gelatin solution gave the following results in two hours:

	3.1N NaCl	4.8N NaCl
Without gelatin	greatly coagulated	completely coagulated
With gelatin	quite clear	slightly turbid

Solutions of gelatin protected also against precipitation by barium chloride, for whereas 0.1N $BaCl_2$ precipitates the dye rapidly and completely at room temperature, 0.8N $BaCl_2$ produced no observable effect on Congo red in presence of gelatin, even at 95° for an hour. Another experiment with potassium iodide showed that in systems containing up to N KI there was increasing precipitation of the dye while in similar systems containing gelatin there was no coagulation.

These results are typical of the behavior of the dye in the presence of gelatin and one would be inclined to interpret them on the basis of protective action by the gelatin. But if there be little adsorptive attraction between the gelatin and the dye, there can be little protective action and this has been shown to be the case in the absence of salts. In the presence of salts however there does appear to be adsorption of the dye by the gelatin which will explain these phenomena. To demonstrate this, six mixtures were made up, each containing 50 cc of 0.006% Congo red and to this was added the powdered gelatin and the sodium sulphate as shown below.

	A	B	C	D	E	F
Powdered gelatin	0	one gram	0	one gram	0	one gram
Mols of Na_2SO_4	0	0	0.01	0.01	0.02	0.02

Sodium sulphate was chosen because it had been found very effective in salting the dye out of solution, and also because the gelatin would swell less in its solution than in the presence of the halides. The powdered gelatin did swell in all the solutions and took up dye from the solution, comparison of A and B showing that. The addition of salt in C gave a lighter solution than the blank A and for the moment it will be assumed that this change of color is associated with an increase in the size of the colloidal micelles of the Congo red since, of course, there can be no adsorption to decrease the concentration of the dye in the solution and it has already been shown that the addition of more sodium sulphate completes the agglomeration of the dye into particles so large that they are precipitated. The supernatant solution in E is also lighter than that in A but no precipitation of the dye takes place even on long standing. The swelling gelatin in D and F is increasingly darker with the adsorbed dye than is the gelatin in B, and the remaining solution in D and F is increasingly lighter than that in A showing that the gelatin in the presence of increasing amounts of sodium sulphate is adsorbing increasing amounts of the Congo red, or that the salt in concentrations that would otherwise not precipitate the dye can nevertheless cause it to be adsorbed on the gelatin. In the next section it will be shown that the addition of salts causes the dye to be adsorbed more strongly on cloths also. It is not possible to coagulate the dye alone from a system containing 0.04% Congo red and 0.4% gelatin by means of sodium sulphate, for any concentration of this salt that will have any effect is more than the half-saturated solution at which gelatin alone is coagulated and thus carries down the dye with it. The case under discussion is, however, not a case of the carrying down of the dye by the swelling gelatin for there is a definite difference between the systems containing salt and those without the sodium sulphate, the same amount of gelatin being present in each. Further than that, if it were merely a case of filter action, continued shaking should remove all the dye from solution whereas this is not the case. There is a rapid adsorption of the dye on the gelatin which then reaches an adsorption equilibrium leaving a large proportion of the dye still in solution. The final condition is independent of the order of mixing the dye, gelatin, and salt solution.

The assumption introduced above, i.e., that the change of color of the Congo red solution on adding sodium sulphate solution and the increased adsorptive attraction between the altered dye sol and the gelatin are accompanied by a decrease in the dispersion of the dye is not without support in the literature although it is not generally expressed so explicitly. Bancroft[1] discusses the problem in these terms: "With colloids stabilized by an electric charge, we find that the amount of salt necessary to produce precipitation varies with the way in which it is added, more being necessary if the salt solution is added slowly.[2] The precipitation value obtained by adding the electrolyte all at once is such a concentration of the precipitating ion that sufficient adsorption to cause neutralization can result in a definite time. Weiser[3] considers that if the same amount of electrolyte is added very slowly, there results a gradual increase in the size of the particles due to partial neutralization by adsorption. After the addition of enough electrolyte, partial agglomeration takes place. These coagulated particles have adsorbed not only enough to effect their complete neutralization; but the neutralized particles have carried down an additional amount during agglomeration. This adsorption of electrically neutral particles during the fractional precipitation accompanying slow addition of the electrolyte causes such a decrease in the ionic concentration that a greater amount must be added to effect complete neutralization by this fractional process. Rapid addition furnishes at once all the critical concentration of precipitating ion necessary for neutralization by adsorption."

In the experiments reported above, the addition of the precipitating salts has been made all at once, so that question does not enter here. It is suggested however that the addition of the sodium sulphate makes the Congo red particles more instable and therefore more easily adsorbed on the gelatin, which if it were peptized would tend to prevent the precipitation of the dye and thus give the appearance of protection without the existence of any gelatin envelope before the addition of the salt. This problem has been further discussed by Bancroft, p. 299.

"Making a colloidal solution instable will increase the amount of adsorption by a solid adsorbent until the agglomeration of the colloidal particles becomes too great, when the large particles will not be held firmly by the adsorbent. This principle is made use of in dyeing with substantive dyes.[4] Substantive dyes dye cotton direct without a mordant. They are usually sodium salts of color acids and are always in colloidal solution. They are taken up as salts and not as color acids by the fibers. Sodium chloride,

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[1] Bancroft: "Applied Colloid Chemistry," 296 (1926).

[2] Freundlich: Z. physik. Chem., **44**, 143 (1903).

[3] Weiser: J. Phys. Chem., **25**, 404 (1921).

[4] Briggs: J. Phys. Chem., **28**, 368 (1924).

sodium sulphate, and sodium citrate increase the amount of dye forced on the fiber when these salts are used in moderate concentrations. At higher concentrations they strip the dye. Sodium sulphate, therefore, decreases the adsorption of an acid dye by wool and increases the adsorption of a substantive dye by wool or cotton. In both cases the color is in the acid radical; but the acid dye is in true solution and it is the color acid which is adsorbed, while the substantive dye is in colloidal solution and it is the salt which is adsorbed."

Considering the first sentence of the above quotation, it appears obvious that the increase in particle size does not suddenly begin and all take place just at the moment of coagulation or at the concentration at which the particles become too large to be held firmly by the adsorbent. Increase in particle size must begin with the first addition of the precipitating agent and be responsible for the observed increase in adsorbability. In other words the slowly coagulating particle shows an enhanced readiness to adsorb nearly anything such as colloidal substances which would tend to keep it suspended, or, failing that, solid adsorbents such as cloths to be dyed. The drowning man grasps at the straw which would have proved no attraction whatever while he was well able to keep himself afloat. This may be the explanation for the slow precipitations so often observed. Some particles are neutralized by the electrolyte and in turn adsorb other relatively unaffected and stable particles. The particle size thus increases while the charge ratio diminishes until particles grow large enough to be seen and finally settle out.

The theory of dyeing with substantive dyes was formulated and summarized by Briggs in the paper referred to above. In his discussion of the properties of aqueous solutions of these dyes (p. 370), Briggs says: "The dialyzed solutions, like those of the soaps, are excellent conductors; they exert in a collodion osmometer a surprisingly high apparent osmotic pressure; in the absence of a membrane they possess an easily measurable power of diffusion; and they invariably contain amicrons or ultramicrons when viewed in the ultramicroscope. It is possible to bring about an increase in the size of the ultramicrons and a corresponding decrease in the degree of dispersion, without causing any visible or actual flocculation of the suspended dye—a property of the substantive dye solutions which is of the utmost significance in the theory of substantive dyeing. Increase in the size of aggregates is observed as the concentration of the dye is increased, or as the temperature is lowered; at low temperatures concentrated solutions of the substantive dyes set to a jelly. Decreased dispersion is also caused by destabilizing electrolytes, while electrolytes in excess bring about flocculation.[1] The growth of aggregates is opposed by stabilizing protective colloids such as gelatin.[2] Practically all of the very complete evidence now available supports the conclusion that in neutral or alkaline dyebaths the substantive dyes are present as electronegative colloids capable of a very high degree of dispersion in the absence of destabilizing agents.

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[1] Cf. Biltz and von Vegesack: Z. physik. Chem., 73, 481 (1910); Wo. Ostwald: Kolloidchem. Beihefte, 10, 197 (1919); Auerbach: Kolloid-Z., 31, 37 (1922).

[2] Cf. Bayliss: Kolloid-Z., 6, 23 (1910); also Biochem. J., 1, 175 (1906).

"While a flocculating agent will tend to force the suspended colloid into the interface, it should not be present in amounts large enough to produce actual coagulation. If the latter occurs, the agglomerated flocks may be too large to be retained in the interface and will therefore not be adsorbed, at least strongly. Since flocculating agents in amounts insufficient to produce actual coagulation are known[1] to destabilize sols by decreasing their dispersion, such agents will aid in the adsorption of a colloid up to the point of flocculation but beyond this point will act in an opposite direction. The amount of adsorbed colloid in the interface will therefore pass through a *maximum* as the concentration of the flocculating substance is increased beyond its coagulating value. Such adsorption maxima have been observed and they show, in reality, that a dispersed colloid is most strongly adsorbed when its dispersion has some intermediate value, as Wo. Ostwald[2] has suggested.

"Flocculating agents are not the only cause of decreased stability and correspondingly increased adsorption within limits, for the stability of a sol may change with the temperature, with age, and with its previous history. The stability and the dispersion decrease with increase in the concentration of the sol, which may have something to do with the fact, which has puzzled some of us, that more is adsorbed from a concentrated sol than from a dilute one, and the adsorption curve looks like the typical isotherm obtained with a dissolved adsorbed substance,[3] p. 372.

"In terms of the present theory, an acid, base, or salt which acts as an assistant in the substantive dyebath does so because it makes the particles of dye more strongly interfacial between bath and fiber. This in turn it accomplishes by decreasing the dispersion and stability of the dye in the suspension or sol which constitutes the bath. We have seen that electrolytes are known to produce this effect in the case of various organic colloids in suspension and we should expect the same effect with colloidal dyes. Many instances are indeed known, especially among the experiments of Dreaper and his coworkers.[4] Bayliss[5] found that the addition of two percent of sodium chloride to a weak suspension of Congo red trebled the adsorption of this dye by filter paper. Concerning the effect of this salt, he wrote as follows: 'Notwithstanding the fact that no actual precipitation takes place in these experiments, the addition of electrolytes to Congo red, for example, causes an increase in the size of the colloidal particles. . . . so that the solution is on its way to precipitation even when this does not actually occur. The specimen of Congo red used in all my experiments showed the Tyndall phenomenon very faintly in solution in distilled water; but when sodium chloride was added

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[1] Note Linder and Picton's work on the "degradation" of arsenious sulphide sols by sodium chloride. J. Chem. Soc., **67**, 73 (1895).

[2] "Grundriss der Kolloidchemie," 417 (1910). Cf. Traube and Shikata: Kolloid-Z., **32**, 316 (1923).

[3] Cf. Briggs: J. Phys. Chem., **19**, 210 (1915).

[4] Dreaper: "Chemistry and Physics of Dyeing," 251 et seq (1906).

[5] Biochem. J., **1**, 175 (1906).

the beam of light became much more distinct.' . . . The agglomerating and destabilizing action of weak flocculating agents in solutions of the substantive dyes may be regarded as absolutely established at the present time," p. 376.

Kraemer in his chapter[1] on "Colloids" points out some cases of this;

"In many cases a relatively slight aggregation occurs without continuing through the stages of complete coagulation, i.e., an aggregate of primary particles may possess a normal degree of stability. The red-to-blue color change in Faraday gold sols upon the addition of insufficient electrolyte to precipitate them is due to such a partial aggregation. Another is the spontaneous formation of 'tactosols' (aged sols of V_2O_5, Fe_2O_3 or benzopurpurin united into loose swarms) already referred to. Varying degrees of partial aggregation also likely occur in the high-viscosity lyophilic dispersions. Rather direct evidence of such a condition is provided by the rigidity and elasticity, on a microscopic scale, of apparently fluid sols of gelatin or soap."

But the experimental evidence in favor of this view is not universally accepted and that on the gold sols may or may not be true. Therefore it is quite interesting that another method of investigation has brought substantiation to the views here advanced. These experiments have to do with the addition of aluminum sulphate, aluminum nitrate or magnesium sulphate to sols of gold, gum mastic or arsenic trisulphide. Burton and Annetts[2] say:

"The original intention in the present experiments was to use the changes in scattered light to follow changes in samples of colloid to which extremely small amounts of various electrolytes had been added. These results led to the complementary experiment of testing the effects of the coagulation process on the light transmitted by a sample of colloid. The latter in turn led to the discovery of the existence of apparently permanent stages of partial coagulation which do not appear to have been accentuated before." Items in the summary of this paper include: "(1) Experiments have been carried out on the measurement of scattered light and transmitted light from samples of colloidal solutions. These give indication of distinct changes in the colloid on the addition of very small traces of electrolyte even before coagulation sets in. (2) By adding successively very small traces of electrolyte to solutions of gold, mastic and arsenious sulphide, the existence of stages of partial coagulation has been demonstrated." This idea has also appealed to Mullin[3] for he says:

"It is a heretofore unexpected fact, possibly not at all characteristic of dyeing acetate silk only, that certain compounds (dyestuffs) have a much greater affinity for acetate silk when in colloidal solution, possibly in even a rather coarse dispersion, than when they are in true solution. This is particularly the case where the compound is solubilized by means of chemical combination with some solubilizing reagent, such as the solubilization of certain bases by means of hydrochloric acid to form their hydrochlorides, or

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[1] Taylor: "A Treatise on Physical Chemistry," 2, 1695 (1931).

[2] Burton and Annetts: J. Phys. Chem., 35, 48 (1931).

[3] Mullin: "Acetate Silk and its Dyes," 278 (1927).

by sulfonation." A little later we find: "If we neutralize an aqueous base-hydrochloride solution with an alkali such as sodium carbonate, the free base is precipitated as a colloidal or even coarser dispersion in the bath and this free base is rapidly taken up by the acetate silk, as was mentioned in connection with the application of bases for the developed colors on acetate silk, and we get much deeper shades than where we depend only upon the hydrolysis of the dyestuff (base-hydrochloride) to dye the fiber."

Now, obviously, the change in particle size is not the only condition that is changing here since, for instance, in the case of Mullin's dye-hydrochloride adsorption, the addition of sodium carbonate will have a large effect in increasing the hydroxyl ion concentration of the solution and such an increase would, of course, increase greatly the adsorption of the free dye base. Likewise, the addition of salts may have a similar effect on the adsorption of Congo red on the gelatin or cloths. It will be impossible to discover whether increased particle size or the changed ionic environment is responsible for the increased adsorbability until some ready method can be evolved for changing the one of the factors without affecting the other. Boiling effects the coagulation of many sols and we know that, in general, adsorption, such as dyeing, takes place more rapidly in warm solutions. Unless the stages of such coagulation are spontaneously reversed on cooling, cloths should take up increasing amounts of dye from sols that have been boiled for increasing periods and then cooled to room temperature and this should hold nearly to the point of complete precipitation. Increased particle size appears to be the one factor common to increased adsorbability.

Another instance of the protective power of gelatin for Congo red is found in acidifying the solution. Congo red is an indicator changing from red in alkali to blue in acid solution (pH range 3.0-4.0). Addition of hydrochloric acid effects an immediate development of the blue color and a rapid and complete coagulation of the dye. Such a solution gives at once a clear colorless filtrate. If sufficient gelatin be added to the dye to make the final solution 0.4%, the final dye concentration being 0.04%, the addition of sufficient hydrochloric acid to make the final system 0.16N produces as before the deep blue color but no precipitation and the blue sol is stable indefinitely. Boiling for ten minutes, however, coagulates the blue sol completely, and the clear, colorless filtrate appears to have lost permanently the power to protect Congo red from precipitation by acid. If this filtrate be cooled and neutralized, and to it are added new amounts of Congo red and hydrochloric acid immediate coagulation results. This coagulation cannot be due to the sodium chloride produced in neutralization for such a concentration would have no effect on a normally protected sol and did not produce any effect before the addition of the acid. It seems scarcely likely that the dye precipitated in the first instance should have carried down all or practically all the gelatin present.

Dyeing with Congo Red

In recent attempts to dye with certain water-insoluble dyes formed in and protected from precipitation by gelatin, the difficulty was encountered that such sols would not dye satisfactorily, the dye being taken up too little or washing off too easily. This could have but two possible explanations; either the dye sols were dispersions so coarse that sufficient penetration into the fiber was impossible, or the gelatin was being adsorbed with the dye, cutting down the adsorption of the dye itself and also facilitating its removal during the washing process. The latter seemed the more probable explanation and to test this the same procedure was applied to a substantive dye for cotton and one which was therefore known to be fine enough to penetrate properly and to be adsorbed strongly. Gelatin should diminish the adsorption and the fastness to washing of such a dye and methods which might be found to destroy the effects of the gelatin on the ordinary substantive dye should be effective also in making possible satisfactory dyeing with the insoluble dye protected by gelatin.

This procedure had a flaw in its premise and it appears worth while to report the discovery of that flaw while the solution of the main problem is still being sought. The flaw is that at least in the case of Congo red, the substantive dye selected, gelatin does not form a protective film about the dye particles but the two stable sols exist in the mixture as independent colloidal particles, and only under special conditions such as on the addition of salts does any phenomenon such as protection make its appearance. It is found that gelatin swelling in a Congo red solution has but little power to adsorb the dye but that this adsorption is increased somewhat by the addition of suitable salts. If, therefore, the gelatin and the Congo red exist independently in the solution, this is quite a different situation from that which prevails in the case of the para red, an insoluble developed dye which may be protected from precipitation by forming it in the presence of gelatin when the particles of the dye must surely be surrounded by an envelope of gelatin. The problem of breaking such a sheath in such a way as to cause the enclosed dye to be adsorbed on the cloth is quite different from that involved in bringing about the precipitation of dye rather than gelatin from a mixture of the sols.

The Congo red used in the experiments was dissolved two grams in a liter to make the stock solution, and five cc of this added to gelatin, salt, etc., to make 25 cc total volume, the final dye concentration being 0.04%. The gelatin was a powder from Baker and was usually dissolved to make a two percent solution shortly before use; five cc of this solution in the 25 cc gave a final concentration of 0.4% gelatin. The usual procedure was to immerse the cloths for one hour, dry, divide the cloth, and thoroughly soap one half and wash it in warm water.

The first experiments showed that at room temperature pieces of cloth immersed for one hour were dyed much more deeply in the absence of gelatin than in its presence. This is in agreement with the findings of Briggs[1] with

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[1] Briggs: J. Phys. Chem., **28**, 384 (1924).

other substantive dyes. He showed that this action of the gelatin is opposite to the action of salt and made a rough measurement of the effect. In connection with this it is interesting to find that in the absence of gelatin, the addition of sodium chloride resulted in increasing dyeing up to a concentration of 0.25 M. Increased salt concentration caused decreased dyeing until at 4 M approximately half the maximum amount of dye was adsorbed. The dye used in this experiment was Erie Red 4B.

This decrease in dyeing from the 0.4% gelatin-dye sols did not appear when the cloths were dyed at 70°. In the hot solutions the cloths were dyed two to three times more deeply than at room temperature but the difference due to the gelatin was very slight. This effect of the gelatin in the cold solutions is to be ascribed to a blocking effect whereby the gelatin rather than the dye is adsorbed on the cloth. In the hot solutions the penetration of the dye is increased and its stability is decreased with consequent increase in the amount adsorbed by the cloth. Likewise, in the hot solutions the gelatin tends to be peptized, and can thus offer less blocking effect to prevent the dye adsorption. If this is the explanation, the blocking effect might be observable even at higher temperatures if larger quantities of gelatin were present. This was found to be true, for when cotton was dyed at 70° in solutions containing the same amount of dye dissolved in water only or in the presence of 10% gelatin the cloth dyeing in the gelatin system adsorbed much less dye than the one in water only.

The Effect of Salts on Congo Red Dyeing

In the attempt to destroy the effect of gelatin on the dyeing with Congo red, the addition of salts was the first expedient. The effect of salts should be a dual one, on the dye and on the gelatin. As has been shown above, several salts are able to bring about the more or less complete coagulation of Congo red and, as Briggs[1] showed, substances thus effective may be used for the partial destabilization of the sols of such substantive dyes, producing decreasing dispersion and increasing adsorption of the dye by the cloth. The salts employed may be classified roughly into those which exert a liquefying or peptizing action on the gelatin, such as the halides and alkalies, and those which raise the gelation point, such as sodium sulphate.

All of the salts employed of either class have a definite action in forcing the Congo red on cotton. But the portion of dye thus forced on by the salt, either with or without the addition of gelatin, does not penetrate so well nor adhere so firmly as the dye put on from the aqueous sol alone. This is shown by the fact that cloths dyed in the presence of salts are found to be made up of threads which are alternately light (or white) and dark, the light places being those areas of the thread to which the dye did not penetrate merely because of the overlying thread. Threads of cloth dyed in the aqueous sol are much more uniformly dyed even though the intensity of dyeing be less than that found on the surface of the cloths in the sols containing salts. In addition to this, in many cases the extra dye forced on by salt is lost on vigorous soaping

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[1] Briggs: J. Phys. Chem., 28, 368 (1924).

in warm water so that the washed samples may show little effect of the presence of the salt while the unwashed samples show large differences. This is especially true of the liquefying salts at room temperature, and to a lesser extent of sodium sulphate, but it is not true of the cloths dyed in the hot solutions of either type of salts. Apparently in the hot solutions the penetration into the fibers is more complete and the adsorption more irreversible. There may be also some heat coagulation of the adsorbed dye. As was shown by Briggs for other substantive dyes, there is in the case of Congo red also an optimum concentration of salt: increasing concentrations up to this point produce increase dye adsorption by the cloth, while greater concentrations of salt produce decreased dyeing, the dye being flocculated within the solution instead of on the fiber. This agrees with the work of Auerbach[1] who showed that the best dyeing resulted from that concentration of dye which just produced turbidity in the dye solution during the hour of immersion.

Potassium iodide, which has such a well-known peptizing effect on gelatin was one of the first salts used and its effects are typical of the liquefying group of salts. In the absence of gelatin the first addition of potassium iodide (one gram in the 25 cc system) produced a marked increase in the amount of dye put on the cloth in one hour of immersion at room temperature. Two, three, or four grams of the salt gave about the same increased dyeing as shown by one gram; but, while the one gram sample showed only some turbidity, the remaining systems showed increasing coagulation and precipitation of the dye in the solutions during the hour at room temperature. Sols made as those just mentioned but containing five cc of the 2% gelatin in each all show less dyeing than the corresponding sols without gelatin and the difference produced by the first addition of potassium iodide is less than in the absence of the gelatin. The addition of the gelatin is sufficient to prevent the precipitation of any dye in the second set. In both series, soaping thoroughly in warm water removed practically all the excess dye forced on by the salt and while the soaped gelatin-sol dyed cloths are all lighter than the corresponding cloths dyed in the absence of gelatin, the soaped cloths in each series whose dyeing was aided by potassium iodide are of about the same shade as the blank (no salt) in each series.

The explanation of these phenomena is that potassium iodide destabilizes the Congo red making it more readily adsorbed on the surface of the cloth. The dye thus forced on is too coarse to have penetrated far or to be as strongly adsorbed as dye taken up in the absence of salt and is, therefore, less fast to washing. Obviously, the dye adsorbed on the surface will be more effective in making the cloth appear well dyed than that which has penetrated further but the latter which is adsorbed within the fiber will be better protected from removal by washing or rubbing. There is also seen the effect of the gelatin in being adsorbed on the surface and thereby covering it or portions of it so that the dye can not be there adsorbed and must diffuse through to and within the fiber. The potassium iodide therefore, has two effects. It tends to force

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[1] Kolloid-Z., 30, 166 (1922).

the dye out of solution and in the absence of gelatin on to the cloth. It also tends to liquefy the gelatin or to send it into the solution phase as against its being adsorbed on the dye or on the cloth. The fact that the cloths dyed in the gelatin sols are all lighter and that the remaining solutions in that series are clear and without precipitated dye shows that the gelatin is not all peptized from the cloth but still exerts some blocking effect and that the destabilized dye is forced out not only on the cloth but also on the peptized gelatin which is still able to keep it suspended and to prevent its adsorption on the cloth.

Sodium iodide was found to have a similar effect to that shown by potassium iodide in dyeing from the gelatin-dye sols. A comparison was made between sodium iodide and sodium sulphate as these are representatives of the two classes of salts. This comparison shows that sodium iodide is more effective than the equivalent concentrations of sodium sulphate in forcing dye on cotton from gelatin-dye sols because the iodide tends to precipitate the dye but peptize the gelatin while the sulphate tends to precipitate both dye and gelatin on the cloth and thus accentuate the competition between them. Final systems were made up to contain 0.8 and 1.6 N NaI as well as 0.4, 0.8, and 1.6 N Na_2SO_4, each sol being also 0.4% gelatin and 0.04% Congo red. The cloths dyed in the presence of sodium iodide were darker (both original and washed samples) than any of those dyed in the presence of the sodium sulphate. The cloth dyed in the 0.4 N Na_2SO_4 system was the best in that set and was not much inferior to that dyed in the 0.8 N NaI, while the latter was markedly better than the cloth dyed in 0.8N Na_2SO_4. The 1.6 N Na_2SO_4 is distinctly beyond the optimum concentration, producing almost complete flocculation of the dye in solution and dyeing only a little better than the blank containing dye and gelatin only. Both the sodium iodide sols grew turbid during the hour while only the most concentrated sulphate sol did so. It appears, therefore, that the sodium sulphate tends rather to force the adsorption of the destabilized dye on the gelatin rather than on the cloth and that the dye-gelatin adsorption complex is not strongly adsorbed by the cloth for the washing carries off very little dye from the cloths dyed in the presence of the sodium sulphate. In other words the effect of the sodium sulphate is to decrease the dispersion and to increase the adsorptive power of both dye and gelatin for concentrations below that which causes coagulation. On the other hand the effect of the sodium iodide is to decrease the dispersion of the dye and cause it to become more adsorptive but at the same time the peptizing action on the gelatin is one of increasing dispersion and greater stability in the liquid phase and, therefore less adsorptive power. The result is that the Congo red micelles adsorb each other and precipitate instead of adsorbing gelatin and remaining suspended. This is shown by the fact that the sodium iodide samples (in common with those of the other liquefying salts at room temperature) lose considerable dye on washing. It is thus seen that a very important factor in the washing fastness of dyes is the size of the particles of dye on the cloth. The peptized gelatin being little adsorbed permits growth of the dye particles to such size that they are readily washed off, while the greater adsorptive power of the gelatin in the presence of sodium sulphate prevents the development of such large aggregates and the loss on washing is less. The difference here can not be ascribed to a difference in the amount of adsorption of the gelatin on the cloth which might then carry off dye with it on washing for in that case the sulphate samples should have more gelatin on the cloth and wash off worse; actually they wash off less than the iodide samples. Therefore, if this factor enters at all, it is secondary to the factor of particle size and adsorbability.

Conclusions

1. When sols of gelatin and of Congo red are mixed the two sols appear to continue to exist independently.
2. Gelatin adsorbs Congo red so slightly from solution as to render impossible any protection in the ordinary sense.
3. Congo red, in the absence of gelatin, behaves as a sol intermediate between the lyophile and the lyophobe types. It is precipitated by sodium and potassium halides and by various other salts.
4. In the presence of gelatin this precipitation by salts is greatly diminished or entirely prevented. This apparent protection by the gelatin is shown to be due to a decreased stability and decreased dispersion of the dye by virtue of which it is more strongly adsorbed by the gelatin.
5. Salts which liquefy gelatin and salts which precipitate gelatin have different effects on the dyeing of cotton cloth from the mixed sols of gelatin and Congo red.
6. Both types of salts increase the adsorption of dye from the mixed sols, the liquefying salts being more effective because of their action in peptizing the gelatin.

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PHOTO-VOLTAIC EFFECTS IN GRIGNARD SOLUTIONS
II. NATURE OF THE EFFECTS

BY R. T. DUFFORD

Continuing the work described in a previous article,[1] dealing with photo-voltaic effects in cells containing anhydrous ether solutions of Grignard reagents, this paper reports the results of a later series of experiments made under considerably improved experimental conditions; the more important objects were to study the photo-voltaic responses of single electrodes, and to attempt to locate the seat of the effect, but incidental observations in several other directions were also possible, as will be noted later. While much more work is needed on both the questions suggested, sufficiently interesting results were obtained to seem to justify reporting the work, especially since the later extensions planned for the study have been greatly delayed. The results here reported are from observations on about thirty cells which were studied intensively, very long sets of readings being made in many cases. Most of the cells contained solutions of ethylmagnesium bromide or phenylmagnesium bromide, but four solutions not before reported as active are noted below.

While much the same apparatus was used as in the previous work, a number of important improvements were made, which added considerably to the reliability and the accuracy of the observations, and which therefore deserve mention. Experiments at the University of Missouri having shown the feasibility of using more intense illumination, the previous practice of illuminating with a 100-watt lamp was discontinued, and a special tubular-bulb 1000-watt lamp, such as is used for projection purposes, was used instead. The result was an enormous increase in the speed and amount of response of the cells, together with much greater freedom from ambiguity due to slow drift in voltage. For use in the "inner" thermostatic bath (described in the previous article), provision was made for removing the heat by surrounding the lamp with a water-jacket supplied with running water, the water being turned on and off nearly simultaneously with the lamp. Proper regulation of the water supply was obtained by using a gate-valve and stop-cock in series, the gate-valve being left set in the position found by preliminary trials to give the necessary rate of cooling. With this arrangement, the cells could be placed about three inches from the filament of the lamp, but immersed in water; they thus received an illumination comparable with that from noonday sunlight, though the small air bubbles that at times settled on the wall of the water-jacket reduced the illumination somewhat, so that no more precise statement of the value of the illumination would be justified. The temperature changes under this intense illumination were generally less than 1°C., and usually much less, since very long periods of illumination were no longer necessary; hence the temperature control was fully as good as in the previous

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[1] Dufford: J. Phys. Chem., 34, 1544 (1930).

work. A second 1000-watt lamp, used with the small bath, was not water-jacketed since it was outside the bath, usually at a distance, behind a lens. Figs. 1 and 2 give typical response curves obtained under these conditions; the improvement, compared with the curves in the previous article, is very plain. In the outer bath, the temperature could if necessary be held to .01°C. for hours at a time, owing to the use of cooling, good stirring, and a thermostat regulator of unusual sensitivity which was designed by Dr. E. Q. Adams, and will be described by him elsewhere.

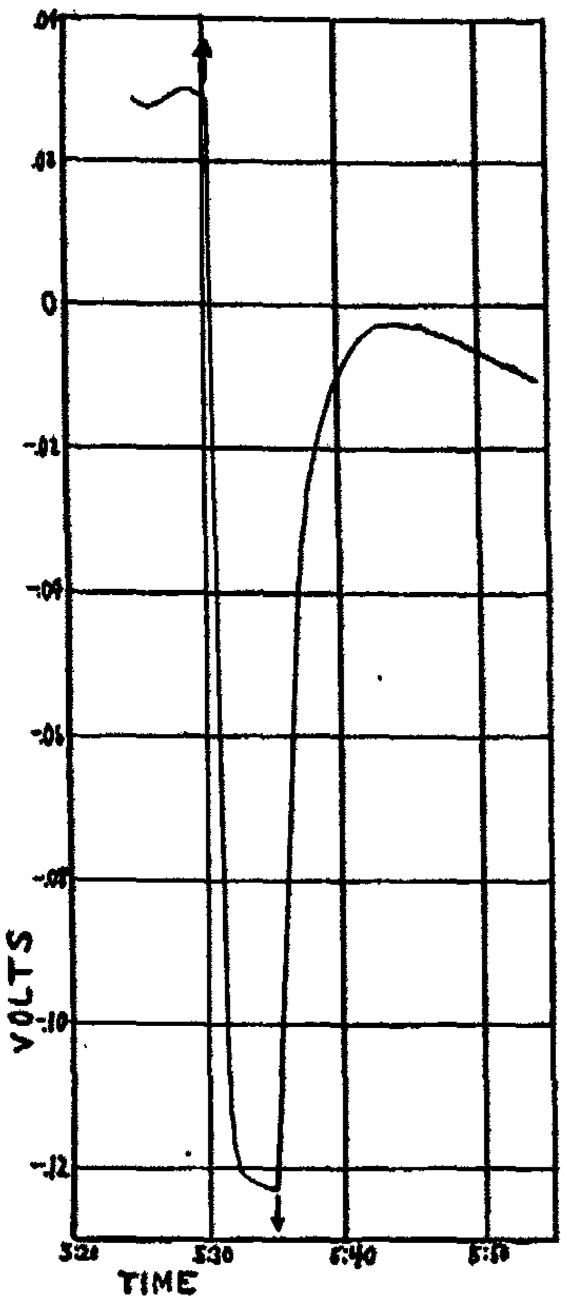

Fig. 1

Response (showing reversal of voltage) and recovery of a Pt/ΦMgBr/Al cell exposed to light from a 1000-watt incandescent bulb; cell was about four inches from filament. Both cell and lamp were immersed in water. Upward-pointing arrow indicates time light was turned on; downward-pointing arrow indicates when light was turned off.

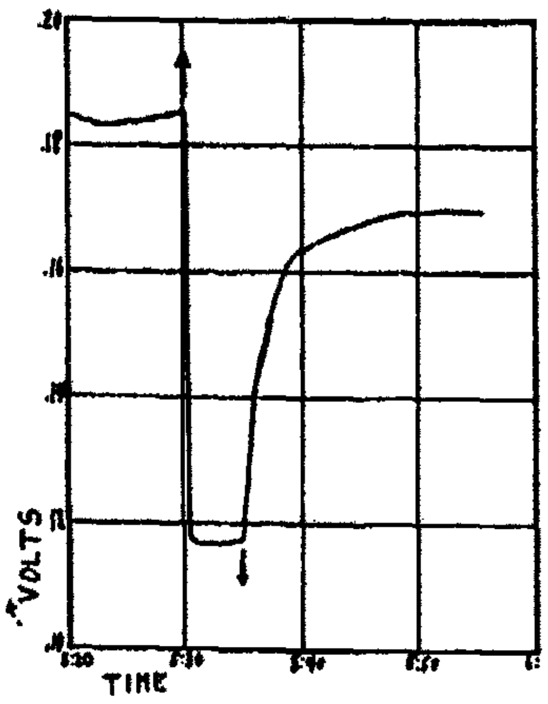

Fig. 2

Voltage response curve of a Pt/ΦMgBr/Al cell which had been depolarized with C_2H_5Br. The response is about half as large as in the similar un-depolarized cell shown in Fig. 1.

Further improvement resulted from the use of a more sensitive galvanometer than was available previously; a 500-ohm Type R instrument, sensitive to about 2 × 10^{-9} amps. per mm., with a universal shunt giving critical damping, was used, with about 0.5 megohm in series for all except the most feeble E. M. F.'s; hence the currents used in balancing were small enough not to produce troublesome polarization effects. In spite of the longer period of this galvanometer, readings could be obtained in 30 to 60 seconds; but because of the rapid changes resulting from the more intense illumination used, it was necessary to confine observations to one cell at a time. The same

Kohlrausch spiral was used as a potentiometer, but on an improved circuit, so that the potentiometer was direct-reading over either of the ranges 0–1 or 1–2 volts, giving twice the sensitivity previously used, and considerable increase in convenience; a switch made the old 0–2 volt range instantly available if needed. In addition, a quadrant electrometer was available for some time, through the courtesy of Dr. Henry Miller.

The ether used in making up the solutions was freshly redistilled over sodium, and was exceedingly dry and free from sodium. This precaution appears not to be entirely necessary, for in no case was any difference in behavior of a cell containing a Grignard solution found which could be attributed to the presence of sodium or its compounds dissolved in the ether. Apparently the same photo-voltaic behavior results if the ether is decanted after standing over sodium, although appreciable amounts of sodium will be dissolved. In order to avoid the presence of oxygen, the ether was distilled under nitrogen, and the compounds were prepared, and so far as possible were handled, under a nitrogen atmosphere. This refinement likewise produces little if any difference in the results. One cannot by this method be absolutely certain that every trace of oxygen has been excluded at every step of the preparation of a cell; and, on the other hand, a compound if properly handled need not be oxidized to any serious extent even if no nitrogen is used, the ether vapor serving the same purpose as the nitrogen, though less effectively, in displacing air.

A thorough set of tests was made on several cells to determine whether the potentiometer method of reading produced any polarization effect that would seriously affect the voltage of a cell. In these tests, the electrometer was left continuously connected to the cell, while the potentiometer was connected for readings and disconnected at intervals. One observer kept close record of the electrometer readings, while another read the potentiometer. On plotting the readings, the curve from the electrometer should show sharp breaks at the points where the potentiometer was connected in, if the voltage were disturbed; but instead, the electrometer curves were very smooth, like the potentiometer curves, on which they could be superposed; the effects due to polarization were less than the errors in reading the electrometer. While these observations are sufficient to give confidence in the potentiometer method of reading, they do not show that polarization effects are nonexistent. On the contrary, tests made on a Pt/ΦMgBr/Al cell showed that, if the cell were deliberately short-circuited for 20 seconds, the recovery curve was very similar to the recovery curve after illumination, with three-quarters of the original voltage recovered in the first ten minutes. The cell used had a "negative" E.M.F. (i.e. Pt negative) of about .083 volts, before being polarized, the value increasing to more than 0.2 on illumination for six minutes; the recovery was somewhat slower than from the polarization, but apparently tended to the same equilibrium value. Forcing a current through the cell in the opposite direction to its normal E.M.F. raised the voltage temporarily, with a quick initial recovery; shaking temporarily raised the voltage, and apparently reduced the equilibrium value slightly. Hence polarization effects exist and must be avoided. Phenyl compounds are much more easily affected by polarization than ethyl compounds, however.

The electrometer was able to settle one question which the potentiometer could not; it showed definitely the existence of a photo-voltaic effect with Pt-Al electrodes immersed in pure ether. The resistance of such a cell is too high to permit balancing a potentiometer. The first response is usually in the "positive" direction (Pt electrode more positive), but after two or three illuminations it becomes and remains negative. The absolutely pure ether showed a slightly larger response than ether containing sodium in solution, but the difference is probably not significant. Addition of a hydrocarbon halide, as phenyl bromide, increases the response, reversing it at once if it is not already negative. If iodine is also added, the response is much larger, and negative; but it sometimes shows the initial momentary throw in the wrong direction when the light is turned on or off. In one cell, some magnesium was also added, so that some phenylmagnesium bromide formed in the solution. This again doubled the response, which was still negative. Even the rapid oscillations of voltage occasionally observed elsewhere have been observed with the electrometer, thus showing them not to be due to polarization from currents during balancing. The effect in pure ether has been studied only with Pt-Al electrode combinations, and much remains to be done in investigating it. But the existence of the effect in pure ether seems to have some theoretical significance, as it appears to rule out certain types of explanations of the effect. This point will be referred to in a later article.

In the preceding paper, it was noted that the initial rate of change of voltage of an illuminated cell was approximately a linear function of the intensity of the illumination. With the increased illumination available, which carried with it the possibility of reaching a definite end-point, much more free from the uncertainties due to voltage drift than readings lasting for longer intervals of time, it was possible to extend the study of intensity effects a step, and test how the end-point depended on the illumination. A long series of readings was made on two $\mathrm{Pt}/\Phi\mathrm{MgBr}/\mathrm{Al}$ cells, one of which was a depolarized cell (the method of depolarizing will be explained below). The end-voltages, or rather the end values of the response, of course increase with the illumination, but apparently not according to any simple law. The curves are approximately logarithmic in form, but with some of the points corresponding to low illuminations somewhat uncertain. The un-depolarized cell was much more sensitive, and gave a more nearly straight line when the logarithm of the illumination was plotted against the response.

Several temperature tests served to confirm the conclusions stated in the previous article, that the temperature effects in those cells are small compared with the photovoltaic effects. Temperature changes can rarely account for as much as ten percent of the observed change in voltage in an illuminated cell. It was found further that the sensitivity of a cell does not vary rapidly with the temperature; cells in ice-water gave practically the same response as cells in water at 25° C.

With the increased illumination, tests could be made to compare the effects of different wave-lengths of light, under much more satisfactory conditions than before. Using monochromatic filters, tests on ten cells confirmed the earlier conclusion that the sensitivity extends from the deep red to the near ultraviolet, at least; but with smaller responses at the red end of the spectrum than at the violet. No cases were found where the responses were different in direction for different wave-lengths. The sensitivity curve for such a cell appears to be flatter than that for a human eye, and broader, and with the maximum at somewhat shorter wave-lengths.

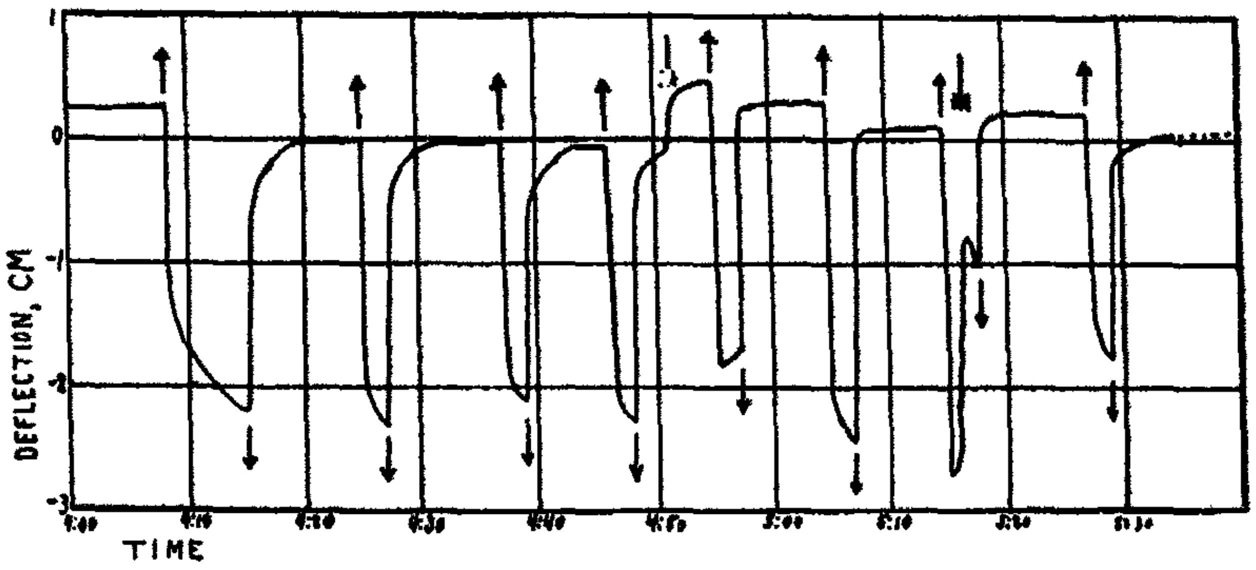

Fig. 3

Current response curve from a Pt/ΦMgBr/Al cell on closed circuit, under same conditions of illumination as in Figs. 1 and 2. Shaking (indicated by astericks) produced a temporary shift in the value of the dark-current. 1 cm. deflection corresponds to 1.78 x 10^{-8} amperes.

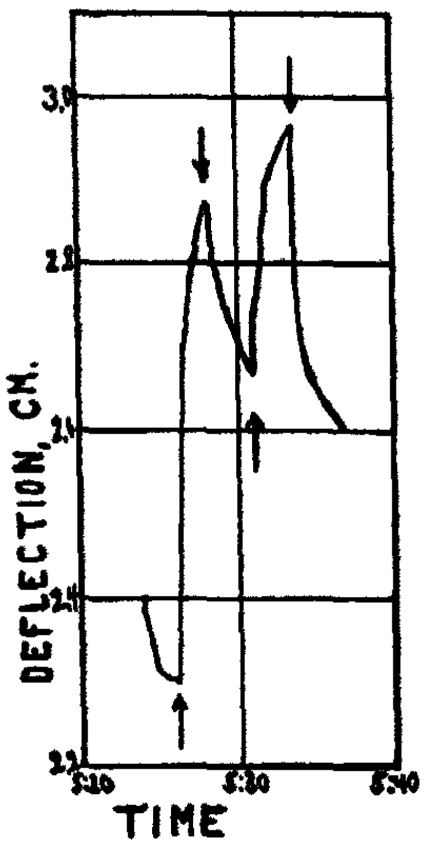

Fig. 4

Current response curve from a Pt/ΦMgBr/Al cell depolarized with C_2H_5Br. 1 cm. deflection corresponds to 1.78 × 10^{-6} ampere. The currents in this test are more than 100 times as large as in the test shown in Fig. 3.

A most interesting method of using cells of this type, is to put them on closed circuit, using the galvanometer as a current-measuring instrument, rather than as a null instrument as with the potentiometer. The voltage is of course not the same as it would be on open circuit. But the current settles down to a very small steady value, usually giving from 1 to 3 mm. deflection on the galvanometer, in a very short time. In most cases, the value of this current is not visibly affected by removing the half-megohm resistance kept in series with the galvanometer; hence the cells have enormous resistances, which appear to be due largely to polarization. Under these conditions, illuminating the cell will increase the current till the deflection is several centimeters, and occasionally so much that it is necessary to use a lower range on the universal shunt. Frequently this response current is in the opposite direction to the small residual current. The response reaches its end-value very quickly, and the recovery is equally rapid. Some typical response curves are shown in Figs. 3 and 4. It will be seen that successive illuminations give much more similar responses than are often obtained on open circuit. While this method of observation probably does not give accurate information concerning the voltage changes on illumination, it does give promise of being an extremely useful method of using such cells. Long life could hardly be expected of a cell on closed circuit; long-time tests were not made, but cells left on closed circuit overnight were still active. The currents observed were too small to read on a coarse instrument like a milliammeter; but no doubt larger currents could be obtained by using larger electrodes.

The writer is indebted to Dr. Wallace H. Carothers for the information that these cells can be depolarized by the addition of such substances as ethyl bromide, methyl iodide, or benzyl chloride. While it has not been possible to make an attack on the question as to why the effect occurs (work in this direction is now being started), it is remarkable how large an effect is produced. The addition of three to five cc. of ethyl bromide to a cell will produce a great increase in the current, sometimes several hundred-fold; and the voltage is also generally increased. The usual rule is that the response to light is decreased somewhat, but not completely destroyed. Good responses are still obtainable on either closed or open circuit. Comparison of Figs. 1 and 2, and of Figs. 3 and 4, will show the nature of the effect.

In order to make a beginning at the problem of locating the seat of the effect, arrangements were made for illuminating only one electrode at a time; the observations would thus show whether one or both electrodes were involved. For this purpose, cells were made in the shape of a H, by connecting a pair of 1-inch test-tubes by a small cross-tube. The H was filled to a height above the cross-tube, the electrodes were pushed well down to near the bottom of the side tubes, and the whole cell was wrapped in black friction-tape except for the region around one electrode. The amount of light that was scattered up to and through the cross-tube and down to the other electrode was very small. The tests so far made have disclosed a photovoltaic response with every electrode used; tests were made with both ethylmagnesium bromide and phenylmagnesium bromide solutions. With phenylmagnesium bromide cells, all the metals studied (Mg, Al, Cu, Zn, Pb, Fe) except platinum gave positive responses, i.e., became more positive with respect to the un-illuminated electrode, when exposed to light. The behavior of platinum, which it was expected would have the most uniform response, proved to be very puzzling, the response being sometimes positive and sometimes negative. The positive responses usually occurred with freshly inserted electrodes, the response usually becoming negative on standing. In the ethylmagnesium bromide cells, the results were similar, but the platinum gave a consistently negative response. It therefore follows, as had been suspected from earlier tests, that the effect in cells with one electrode platinum and the other of a base metal is the sum of the effects from the two electrodes. Also the platinum is shown to be responsible at least in part for the inconsistent behavior often observed in such cells.

Many experiments were made in an effort to learn more concerning the reason for the behavior of the platinum. It was thought that the effects might be associated with films formed on the surface of the platinum electrodes. There is much evidence for the existence of such films, not only from the phenomena of galvano-luminescence,[3] but also from work done by the writer's colleague, Dr. H. E. Hammond,[4] since the present work was finished. The latter work has shown the existence of very large capacitances, larger than a microfarad per square centimeter of electrode surface, between the electrodes and the electrolyte, in cells of the present type; it seems necessary to infer from these results, the existence of films of approximately monomolecular thickness. But these films do not seem to be associated with the photovoltaic effect, nor is it certain, perhaps not even probable, that these thin films are responsible for the galvano-luminescence. But in some preliminary experiments at the University of Missouri, it had been found that a platinum electrode which was coated with either oxidation product or hydrolysis products from a phenylmagnesium bromide solution, and then reinserted in the solution, would take on an unusually high positive potential with respect to the other electrode, and would increase that voltage when illuminated. It might be inferred that the positive response is due to a coating containing oxygen, or oxidation products. Similarly, aluminum electrodes seem to give a somewhat better response if left coated with oxide, just as cut from the sheet, than if carefully cleaned by sandpapering. On this view, the gradual change of the response of the platinum from positive to negative would be due to the loss of a film of oxide, rather than to the formation of a film. On this view, other metals than platinum might possibly give a negative response if they could be put into a condition sufficiently free from oxygen. If this prediction is true, it remains to be verified.

The available evidence is partly for, partly against such a view. Two kinds of experiments seem to support it. If the response is due to changes in a film, changes produced by other than photochemical processes should also cause a similar response. The sensitiveness of certain cells to mechanical disturbance was noted in the preceding article of this series; possibly it may be explained in this way. Tests were made to see if a similar result would be produced by deliberate scraping of the electrode surfaces by a glass scraper introduced through a small hole in the stopper, in the same way that the rectifying film on a Al electrode in a Nodon valve can be punctured. The results were somewhat erratic and unconvincing, but seemed best explained by assuming that the scraping tool brought a fresh supply of oxygen-containing material with it. A second bit of evidence came with the discovery that in Pt-Al cells old enough to have developed the normal negative response, the

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[3] Dufford: J. Opt. Soc. America, 18, 17 (1929). Further work is in preparation for publication.

[4] Hammond: Phys. Rev. (2), 35, 998 (1930).

direction of the response could be reversed by shaking or by bubbling air through the solution a short time. But the response curve after this sort of reversal has a somewhat different shape than usual; the response is weak, and soon dies out under continued illumination. This response may therefore be due to a different process.

If the positive response is due to oxygen, apparently it should be possible to prepare platinum electrodes so free from oxygen that they would give a negative response immediately. Attempts were made to prepare such electrodes by outgassing platinum electrodes by heating in a hydrogen atmosphere at about 800°C. for several hours, allowing them to cool in hydrogen, and to remain in hydrogen until used. No difference in behavior was found between these electrodes and those used after cleaning and heating in a flame. An electrode kept for several days between freshly cut surfaces of sodium metal in ether, and transferred quickly to its cell, showed similar behavior. It is hard to see how these electrodes could have had much occluded oxygen. Hence if the initial positive response is due to an oxygen-carrying film, the film probably gets coated on the electrode when the latter is inserted in the solution.

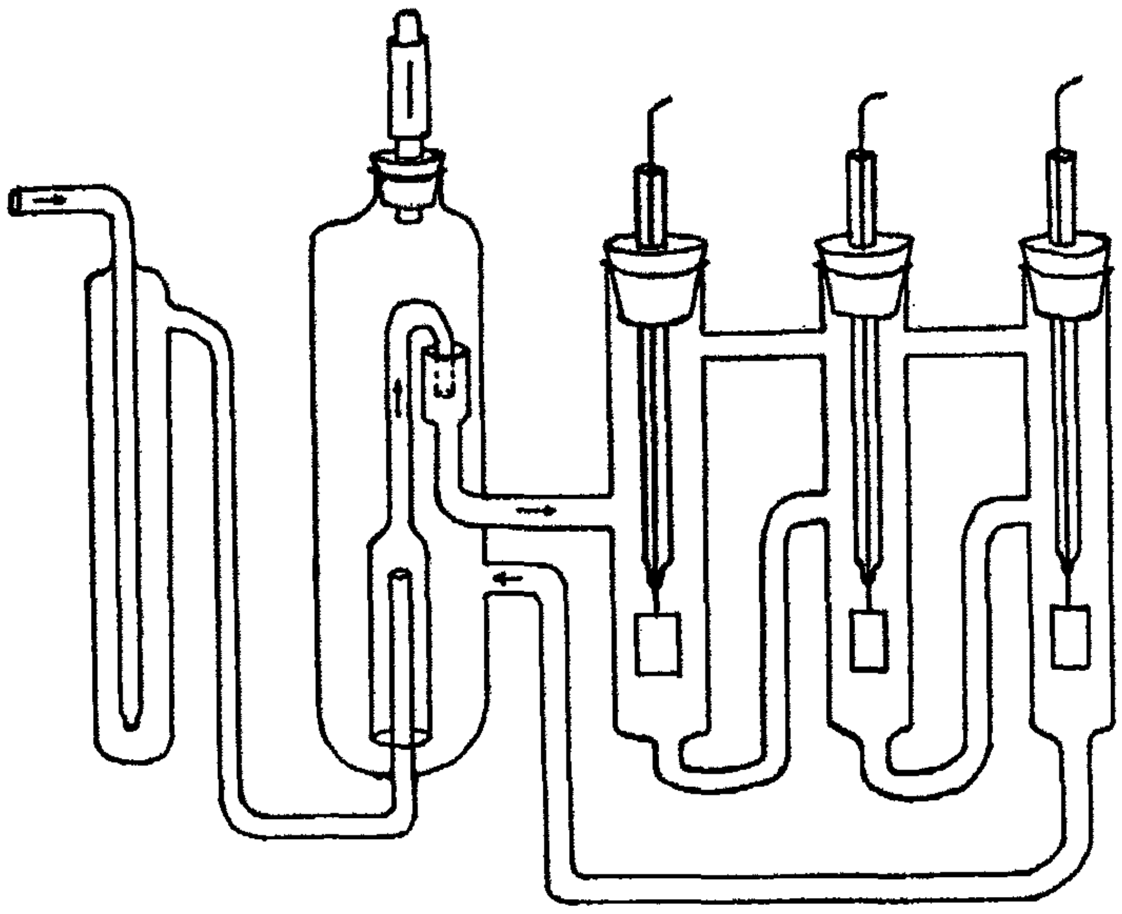

FIG. 5

Circulator used in studying effect of light on electrolytes of photo-voltaic cells.

Experiments of another sort, however, show conclusively that a photo-voltaic effect due to a polarization film cannot possibly be all that exists. To test whether the electrolyte itself is affected by the illumination, a device was constructed which would permit the solution to be circulated, the illuminated electrolyte being carried to an electrode which had been kept in the dark. The experiment was suggested by the work of Lifschitz and Hooghoudt[5] which appeared while the present work was in progress; but the ease with which Grignard compounds unite with oxygen makes the problem of circulating them more difficult than if they could be permitted to come into contact with air. The writer makes grateful acknowledgment to Dr. E. Q. Adams for valuable suggestions regarding the design of the circulator used. As shown in Fig. 5, nitrogen from a tank was purified from traces of oxygen and saturated with ether vapor by bubbling through a separate lot of Grignard solution; it then bubbled through the nitrogen-lift in the reservoir, carrying with it the solution to be circulated, and finally escaped through a Bunsen valve. The solution pumped into the hopper in the reservoir by the nitrogen, passed through the three test-tubes sealed together, and finally returned to the reservoir. Each tube contained a platinum electrode. It was found that the circulation of the solution did not disturb the electrode potentials seriously. Only the middle electrode was illuminated; the electrode upstream from the others served as a reference electrode, and a record was kept of the differences of potential between this electrode and the two downstream from it. With the solution at rest, illuminating the middle electrode did not effect the potential of the electrode downstream from it. With phenylmagnesium bromide solution, circulating the solution seemed to carry a weak effect, reducing the potential of the third electrode, though the response of the middle

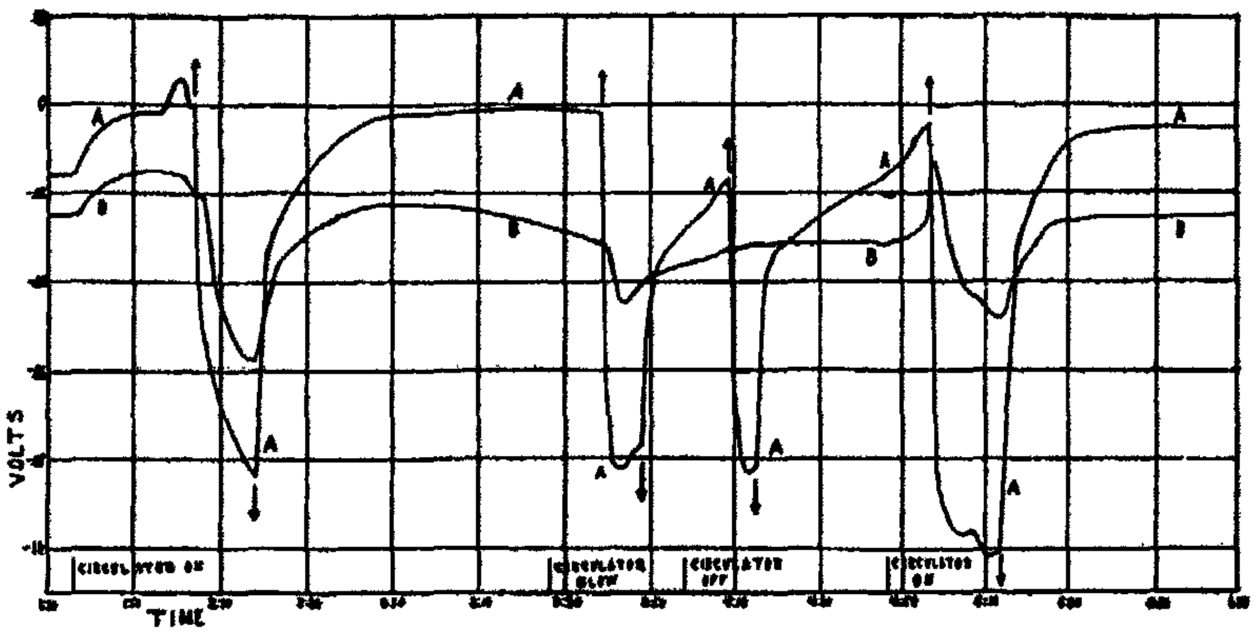

FIG. 6

Curves obtained with circulator shown in Fig. 5. Curve A records the difference of potential between the middle (illuminated) electrode and the upstream electrode; B, the P.D. between the downstream electrode (not illuminated) and the reference electrode. Pt electrodes and C_6H_5MgBr solution were used. The curves show that the solution carried with it an effect which altered the potential of the downstream electrode, but that the alteration became smaller or zero as the circulation was slower or completely stopped.

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[5] Lifschitz and Hooghoudt: Z. physik. Chem., 128, 87 (1927), and later articles. The complete references cited in their articles have made it seem unnecessary to give a complete bibliography here.

electrode was positive. The tests were less satisfactory than might be desired; the response of the third electrode was small. But with ethylmagnesium bromide, the effect was unmistakable; the solution clearly carried with it something that reduced the potential of the electrode downstream. Fig. 6 shows the type of curve obtained. The effect was the same when the middle electrode was pulled up out of the solution, so that only the electrolyte was illuminated.

These experiments seem to indicate that more than one photo-voltaic effect is present; first, an effect carried by the electrolyte, which lowers the potential of a platinum electrode; and second, at least in phenlymagnesium bromide solutions, an effect which raises the potential of a platinum electrode, and is not carried by the solution; this effect may possibly be associated with surface films on the electrodes. The effect noted on introducing oxygen, which gives a somewhat different positive response, may prove to be a third kind of effect. The experiments have not been extended so that the responses of other metals than platinum can be classified. But work in this direction is being started again, and the writer hopes to communicate the results in a later paper.

In the course of the present work, four compounds not previously tested were investigated. An attempt was made to obtain a Grignard compound from ethylene bromide (dibromoethane). The reaction proceeds vigorously, yielding a solution which strongly resembles a Grignard solution, having a brownish color, forming a double layer if sufficiently concentrated, reacting vigorously with water, etc. But the solution is entirely non-luminescent on oxidation (it shows galvano-luminescence, however), and later work at the University of Missouri has shown that a practically quantitative yield of etherated magnesium bromide, usually assumed to be $MgBr_2.2(C_2H_5)_2O$, is obtained. Both layers of this solution give a strong photovoltaic effect. The other compounds studied were the Grignard reagents obtained from ortho-, meta-, and para-bromotoluene. The curves from these compounds (using Pt-Al electrodes) were obtained by electrometer. The para compound gave the largest response, the ortho nearly as large, and the meta compound the least. The order is the same as the order of brightness in the oxy-luminescence of these substances. Study of similar isomeric series of compounds would be desirable; evidently the effect of the position of benzine-ring substituents affects photovoltaic phenomena in a way analogous to the effect on chemiluminescence.

Summary

1. Additional observations, made under considerably improved experimental conditions, are reported, which give further information on the Becquerel effect in cells containing ether solutions of Grignard reagents. Earlier conclusions regarding temperature and wave-length effects are confirmed.

2. Comparisons of electrometer and potentiometer readings show that the potentiometer method of observing, properly handled, is entirely reliable, and not responsible for effects that might have been thought due to polarization while balancing.

3. The voltage response is found to be roughly proportional to the logarithm of the illumination.
4. The existence of an effect in pure ether is shown.
5. The current response of such cells on closed circuit is described.
6. Preliminary study is made of the remarkable increase of current obtainable when certain substances are used as depolarizers. The photovoltaic response is reduced but not destroyed by the depolarizers.
7. The direction of the voltage response of several metals, when single electrodes are illuminated, is noted.
8. Evidence is adduced to show that at least two types of response may occur with platinum electrodes.
9. Four additional compounds are noted to show the effect.

The work described above was done at the Research Laboratory, Incandescent Lamp Department of General Electric Co., Nela Park, Cleveland, Ohio. The writer takes pleasure in expressing his gratitude to Director W. E. Forsythe and to the other members of the staff, who made it possible to carry out the work under unusually pleasant circumstances.

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THE DEGREE OF DISSOCIATION AND THE IONS OF CADMIUM IODIDE IN AQUEOUS SOLUTION

BY JAMES W. McBAIN, PIERRE J. VAN RYSSELBERGHE AND W. A. SQUANCE[*]

During electrolysis of all stronger solutions of cadmium iodide the cadmium moves away from the cathode instead of toward it.[1] Hittorf gave the only possible explanation; namely, that more cadmium is moving in complex anions towards the anode than is traveling in the form of cations toward the cathode. The other properties of these solutions are in accordance with this behavior which seems to be coupled with very incomplete dissociation of the molecules into ions. Thus the lowering of the freezing point is deficient and the concentration of ions as given by measurements of E.M.F. and conductivity is much less than that exhibited by corresponding salts of magnesium or calcium. However, the *difference*, as will appear, is one of degree only, and a careful scrutiny of the data for cadmium salts is therefore of general significance in the search for a valid hypothesis of electrolytic dissociation. We present in this paper a discussion of the data, including a new general method for the calculation of the concentrations of the different ionic species present, based upon migration numbers and E.M.F., and independent of the theory of activity coefficients. The results so obtained are used in the discussion of new diffusion data for cadmium iodide.

In Fig. 1 all the available data for the observed transference of cadmium in solutions of four cadmium salts have been plotted against the logarithm of the concentration.[2] The curves indicate that the migration number is nearly constant from infinite dilution up to a certain low concentration, 0.01 molar in the case of cadmium iodide and 0.056 and 0.11 molar for cadmium bromide and chloride, respectively. For higher concentrations the curves drop rapidly, and the total movement of cadmium is zero in 0.23 molar cadmium iodide, thereafter becoming negative and seeming to tend toward a limit of −0.23. A negative value for the transference number of cadmium in cadmium bromide has been obtained by Gordon (loc. cit.) with a solution containing 29.4 per cent cadmium bromide. In the case of cadmium chloride, a negative value has been obtained by Hittorf (loc. cit.) (1902, 1903) for a concentration of 7.69 gram mols per liter. The similarity between the curves for the three halides is striking; they are almost parallel, a fact which shows that the three

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[*] Died in 1922.

[1] W. Hittorf: Pogg. Ann., **106**, 543 (1859); Z. physik. Chem., **39**, 613 (1902); **43**, 239 (1903); J. W. McBain: Z. Elektrochemie, **11**, 215 (1905); monograph, Proc. Wash. Acad. Sci., (A compilation of the experimental data of the quantitative measurements of electrolytic migration), **9**, 1 (1907); B. Redlich: Z. physik. Chem., **37**, 673 (1901); **38**, 127 (1901); V. Gordon: Z. physik. Chem., **23**, 469 (1897).

[2] See McBain's monograph (loc. cit) and G. Heym: Ann. Physique, **12**, 443 (1919) (the concentrations had to be recalculated); W. W. Lucasse: J. Am. Chem. Soc., **51**, 2597 (1929) (results for $CdBr_2$ were not plotted because they coincide with those of the other authors).

salts dissociate in the same manner and form complexes of the same types at high concentrations.[1] For cadmium iodide the complex anion is almost certainly CdI_3^-.

Similar negative values for the transference number have been obtained for $ZnCl_2$[2], ZnI_2[3] and $CuCl_2$[4]. Movement toward the anode of complex ions containing cobalt has been detected but not measured in mixtures of $CoCl_2$ with concentrated HCl, $MgCl_2$ and $CaCl_2$[4]; complex ions containing iron, copper, move toward the anode in mixtures of $FeCl_3$ and $CuCl_2$ with concentrated HCl[4]. The same result has been obtained in mixtures of $CuCl_2$ with $MgCl_2$, $CaCl_2$, LiCl.[5] Complex anions containing Cu, Fe and UO_2 have been detected in mixtures of $CuSO_4$, ferric and uranyl salts with alkali bicarbonate in excess.[6] Rieger found complex ions in some mixtures; in a solution of potassium ferrous oxalate he found the iron migrating toward the anode.[7]

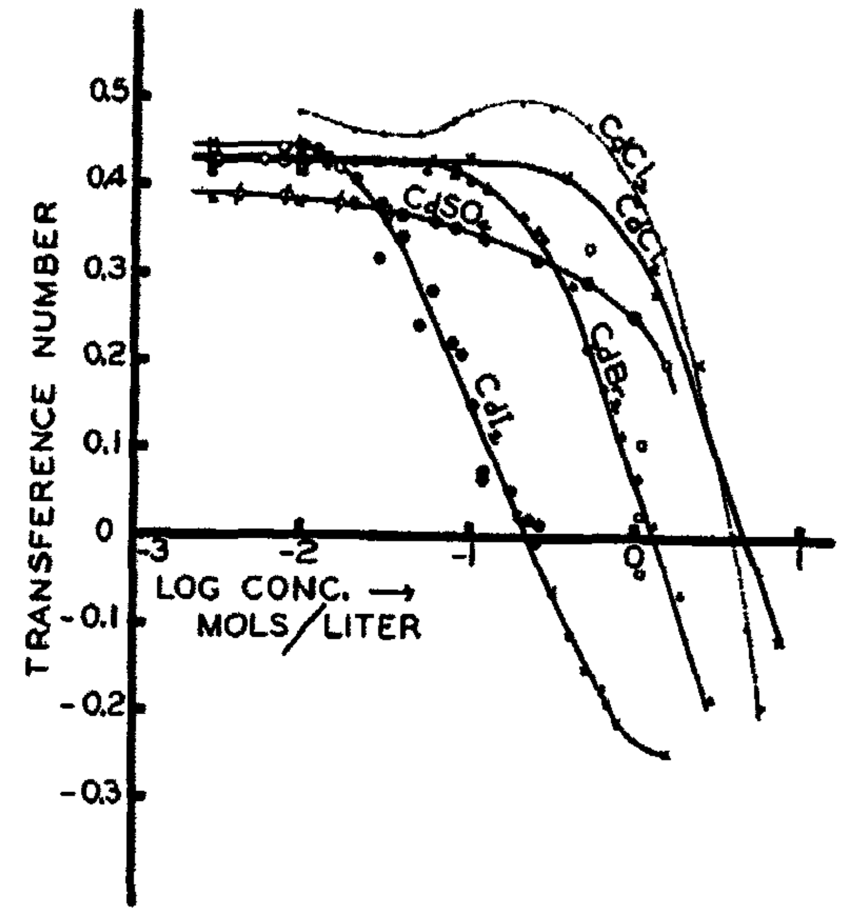

FIG. 1

Transference of cadmium in solutions of four cadmium salts. Hittorf, ×; Goldlust, ϕ; Bukschewski, o; Goldhaber, △; Kummel, *; Gordon, □; Heym, ⊗; Redlich, ●; Lucasse, --●--

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[1] F. Bourion and E. Rouyer (Ann. Chim, (10), 10, 182 (1928); Compt. rend., 184, 598 (1927)) found from ebullioscopic studies of salt pairs that cadmium chloride forms complexes with potassium, sodium and ammonium chlorides just as did cadmium iodide with potassium iodide. See also E. Rouyer: Ann. Chim., (10), 13, 423 (1930); F. Bourion and O. Hun: Compt. rend., 191, 97 (1930).

[2] W. Hittorf: loc. cit.

[3] W. Hittorf: loc. cit. (1859).

[4] V. Kohlschutter: Ber. 37, 1, 1153 (1904).

[5] F. G. Donnan and H. Bassett: J. Chem. Soc., 81, 939 (1902).

[6] R. Luther and B. Krsnjavi: Z. anorg. Chem., 46, 170 (1905).

[7] E. Rieger: Z. Elektrochemie, 7, 863, 871 (1901).

A survey of migration data therefore shows that cadmium iodide is not the only salt of its kind. For almost all the strong electrolytes, the transference number of the slower ion decreases rapidly at high concentrations; negative values are not generally obtained because the solubilities are rarely large enough.

Having admitted complex anions to explain the negative parts of the curves, we have also to admit that such anions are present in more dilute solutions of these salts. For example, in the case of cadmium iodide they are present in sufficient amount appreciably to affect the transport number in all solutions down to 0.01 molar.

The change of transference number with change in concentration in solutions of strong electrolytes has often been interpreted as signifying unequal changes in the mobilities of the ions.[1] This explanation cannot account for negative values, although it is the only one permissible in theories of 100 per cent dissociation. The data just adduced show that cadmium iodide is by no means to be regarded as a unique exception but rather as merely an extreme case.

In previous communications we have shown[2] that negative transport numbers may be obtained for dilute solutions of any salt involving any divalent ion, provided that a sufficient addition of common anion be made to the solution. This is just like the behavior of cadmium iodide to which a solution of potassium iodide has been added.[3] The interpretation of the data for cadmium iodide, therefore, becomes of direct significance for all other solutions.

McBain in 1905 (loc. cit.) explained quantitatively the properties of solutions of cadmium iodide then known by assuming very incomplete dissociation and the presence of the complex anion CdI_3^- and the partially dissociated cation CdI^+. The three dissociations occurring were then

$$CdI_2 = Cd^{++} + 2I^-$$
$$CdI_2 = CdI^+ + I^-$$
$$3CdI_2 = Cd^{++} + 2CdI_3^-.$$

A complex ion of the type CdI_4^{--}, as originally suggested by Hittorf[4], was regarded as improbable, because it is very unlikely that this ion would possess a migration velocity several times greater than the simple Cd^{++} and I^- ions. As a matter of fact it is possible that many types of complexes are present together, but by assuming the existence of one or two definite ones, in some cases reasonable explanations can be obtained for most of the properties of the salt.

Van Name and Brown[5] in 1917 accepted these ions but rejected the calculated concentrations for three reasons. The first was a misunderstand-

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[1] See, for example, G. Jones and M. Dole: J. Am. Chem. Soc., **51**, 1073 (1929).

[2] J. W. McBain and P. J. Van Rysselberge: J. Am. Chem. Soc., **50**, 3009 (1928); **52** 2336 (1930).

[3] W. Hittorf: Ostwald's Klassiker, **23**, 87; J. W. McBain: loc. cit. (1905).

[4] For a revision of Hittorf's calculation of his data see McBain: loc. cit. (1905).

[5] R. G. Van Name and W. G. Brown: Am. J. Sci., **44**, 453 (1917).

ing, whereby, through confusing equivalent and molar conductivity, they thought that the calculated conductivity was only half that observed. The second was because they assumed that simple molecules must freely combine with iodine, whereas they felt that they need not make such an assumption if they assumed double molecules of cadmium iodide. The third reason was that they inferred from E.M.F. data, using an iodine electrode extrapolated to solutions containing no iodine, that the concentration of the I^- ion in such solutions was higher than that calculated by McBain. Actually, for the same reason as indicated above, McBain's value is somewhat higher than theirs. His was for a decimolar solution $0.126 \times 0.2 = 0.0252$ N I^- as compared with their value 0.021 N I^-.

The present paper is divided into two parts. In the first are recorded electromotive force measurements carried out by one of us (W. A. S.) at the University of Bristol in 1922. They are used, together with other electromotive force data obtained by Getman[1] and with migration data, in the calculation of the concentrations of the various ionic species present in aqueous solutions of cadmium iodide. In the second part, diffusion data obtained by Dr. Tsun Hsien Liu at Stanford in 1930 are presented and discussed in the light of the information obtained in Part I as to the composition of aqueous solutions of cadmium iodide.

PART I

Experimental

Measurements were made of the E.M.F. of the following cells together with two in which KI was added to the CdI_2:

Cd	CdI_2	KCl	KCl, Hg_2Cl_2	Hg
	0.001–	satd.	0.1 N solid	
	0.4 M			

Hg	Hg_2I_2,	KI	KCl	KCl,	Hg_2Cl_2	Hg
	solid	0.1	satd.	0.1 N	solid	
		and				
		0.05 M				

Hg	Hg_2I_2,	CdI_2	KCl	KCl,	Hg_2Cl_2	Hg
	solid	0.1 M	satd.	0.1 N	solid	

Merck's pure cadmium was fused to a stout copper wire without solder and the copper, including about 1 cm. of the cadmium beyond the joint, was sealed into a glass tube with shellac, sealing wax or piccin. Other materials were Kahlbaum's purest chemicals. The Weston cadmium cell was standardized by the National Physical Laboratory. Decinormal calomel electrodes were made and used in duplicate. It was assumed that the satu-

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[1] F. H. Getman: J. Phys. Chem., 32, 941 (1928).

rated KCl had eliminated diffusion potential. All vessels and instruments used were calibrated. A large Kohler precision potentiometer was employed together with a delicate Leeds and Northrup ballistic galvanometer.

After each series of measurements on a solution of one concentration, the cell was taken apart and the cadmium electrode washed and then rubbed with a fresh piece of emery cloth to ensure removal of any oxide or other contamination. It was found impractible to use a dilute solution of ammonia to remove the oxide film, as suggested by Richards, except when piccin was used instead of shellac for insulating material, because on standing the ammonia attacked the shellac. The cadmium electrodes were tested immediately before use, and a potential difference of ±0.0002 volt was considered sufficiently small to proceed with the actual measurement of the electromotive force of the combination cell employing one of these electrodes.

The electromotive forces given in Table I are the means of a series of observations and in several cases represent the average of two or more entirely independent series made upon solutions of the same concentration. The negative sign indicates that the named electrode was negative as compared with the mercury of the calomel electrode. The concentrations are expressed as mols per liter, and the values for the electromotive force are considered accurate at room temperature to within ±0.002 volt.

TABLE I

E.M.F. of Cells at 20° consisting of Solutions of Cadmium Iodide and Potassium Iodide, alone and together, measured against N/10 Calomel Electrodes through Saturated Solutions of KCl

Electrode	Concentration of salt Mols per liter	E. M. F. Volts
Cd/CdI_2	0.001	−0.8133
”	0.01	−0.8061
”	0.05	−0.8028
”	0.1	−0.7958
”	0.2	−0.7896
”	0.3	−0.7808
”	0.4	−0.7718
Hg/Hg_2I_2, KI	0.05	−0.2927
”	0.1	−0.3094
Hg/Hg_2I_2, CdI_2	0.1	−0.2799
Hg/Hg_2I_2, K_2CdI_4	0.025	−0.2916
Cd/K_2CdI_4	0.025	−0.8238

A. Mobilities of the Simple and Complex Ions.

We shall suppose that the mobilities of the simple ions Cd^{++} and I^- vary with concentration but remain proportional to their values at infinite dilution. For CdI_2 the transference numbers of Cd^{++} and I^- at infinite dilution are, respectively, 0.45 and 0.55. Our assumption on the mobilities means that, at any concentration, the ratio of the mobilities of the Cd^{++} and I^- ions is equal to 0.45/0.55.

The mobility of the ion CdI_3^- was calculated by McBain (loc. cit. 1905) who used two different methods. The first one is based upon migration data for pure CdI_2 in concentrated solutions; the second is based upon a recalculation of Hittorf's experimental data for migration in the mixture $2KI + CdI_2$. If we assume that in very concentrated solutions we have only Cd^{++} and CdI_3^- ions, a hypothesis corroborated by E.M.F. data, the transference number of CdI_3^-, or better the ratio of its mobility to the sum of the mobilities of Cd^{++} and CdI_3^-, is given by $1.23/3 = 0.41$. This value 0.41 means that the complex ions CdI_3^- carry 41 per cent of the total current carried by the ions resulting from the dissociation

$$3CdI_2 = Cd^{++} + 2CdI_3^-$$

or that the mobilities of Cd^{++} and CdI_3^- are in the ratio of 0.59 to 0.41.

McBain had to assume that the CdI^+ ion had the same mobility as the Cd^{++} ion, because no data were available for the calculation of its exact value. In part B, we shall show that this mobility can be deduced from E.M.F. data. The calculation gives the ratio between the mobilities of CdI^+ and I^- equal to 0.16/0.55.

B. Evaluation of the Data for E.M.F.

In the first type of cell used in Table I the E.M.F. depends solely upon the concentration of Cd^{++} ions, and for any two concentrations the difference in E.M.F. observed is

$$E_1 - E_2 = 0.029 \log \frac{(Cd^{++})_2}{(Cd^{++})_1}$$

where changes in activity coefficient are neglected.

Getman[1] has recently measured cells of the type Cd | CdI_2, AgI | Ag, and for any two concentrations the difference in E.M.F. observed is

$$e_1 - e_2 = 0.029 \log \frac{(Cd^{++})_2(I^-)_2^2}{(Cd^{++})_1(I^-)_1^2}$$

Hence

$$e_1 - e_2 - E_1 + E_2 = 0.058 \log \frac{(I^-)_2}{(I^-)_1}$$

Thus the two series of data, considered together, furnish the ratios of Cd^{++} ions as well as I^- ions in the two solutions.

To obtain absolute amounts, we have assumed that the concentrations of Cd^{++} ion and I^- ion in 0.005 molar CdI_2 are given by conductivity. It was shown in McBain's paper (loc. cit. 1905) that for low concentrations the data for freezing point and conductivity are in close agreement, and similar freezing point data were since obtained by Van Name and Brown (loc. cit.). Hence we take the concentrations in 0.005 molar CdI_2 as 0.00315 molar Cd^{++} and 0.0063 I^-, the degree of dissociation being 63 per cent.

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[1] F. H. Getman: J. Phys. Chem., 32, 941 (1928).

In Table II the calculation of the concentrations of the cadmium and iodine ions relative to their concentrations in a 0.005 molar CdI_2 solution are given, using smoothed values for both Squance's and Getman's curves for E.M.F. and converting Getman's concentrations into mols per liter by means of the densities given in International Critical Tables.

TABLE II

Concentrations in Mols per Liter of Iodine and Cadmium Ions deduced from E.M.F. Data of Squance and Getman and the Degrees of Dissociation of the Two Ions.

Total cadmium	$-e_2$ volts	$-E_2$ volts	(I^-)	(Cd^{++})	$\frac{\frac{1}{2}(I^-)}{(CdI_2)}$	$\frac{(Cd^{++})}{(CdI_2)}$
0.005	0.6078	0.8082	0.0063	0.00315	0.630	0.630
0.01	0.5933	0.8061	0.0103	0.0037	0.515	0.370
0.02	0.5701	0.8050	0.0148	0.0040	0.370	0.200
0.05	0.5605	0.8028	0.0228	0.0048	0.228	0.096
0.1	0.5512	0.7958	0.0252*	0.0084	0.126*	0.084
0.2	0.5380	0.7896	0.0285	0.0138	0.071	0.069
0.5	0.5285	0.765	0.0181	0.0973	0.018	0.194

* The same fraction was obtained from the freezing point data by McBain in 1905, but ignoring any CdI^+ present (loc. cit., compare page 1001 above).

C. Migration Data applied to the Calculation of the Concentrations of Complex Ions.

1. Calculation of the mobility of the CdI^+ ion.

Let us suppose (see Fig. 1) that for a concentration of 0.01 mol/l. the concentration of the CdI_3^- complex is 0. Then the apparent transference number of the Cd^{++} ion is given by the general expression[1]

$$N_{Cd} = \frac{2(Cd^{++}) \cdot \frac{m_{Cd}}{m_I} + 2(CdI^+) \cdot \frac{m_{CdI}}{m_I} - 2(CdI_3^-) \cdot \frac{m_{CdI_3}}{M_I}}{2(Cd^{++}) \cdot \frac{m_{Cd}}{m_I} + (CdI^+) \cdot \frac{m_{CdI}}{m_I} + (I^-) + (CdI_3^-) \cdot \frac{m_{CdI_3}}{m_I}}$$

where the m's represent the respective mobilities referred to any common unit. For the concentration 0.01 mol/l. we have

$$N_{Cd} = \frac{2(Cd^{++})\frac{0.45}{0.55} + 2(CdI^+)\,\frac{m_{CdI}}{0.55}}{2(Cd^{++})\frac{0.45}{0.55} + (CdI^+)\,\frac{m_{CdI}}{0.55} + (I^-)} = 0.45$$

E.M.F. data gave:

$$(Cd^{++}) = 0.0037$$
$$(I^-) = 0.0103$$

As $(CdI_3^-) = 0$,

$$(CdI^+) = (I^-) - 2(Cd^{++}) = 0.0029$$

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[1] Miss M. E. Laing: J. Phys. Chem., 28, 673 (1924).

Hence the equation when solved for m_{CdI} gives:

$$m_{CdI^+} = 0.16,$$

expressed in the same units as give $m_{I^-} = 0.55$. That is, the equivalent conductivity of CdI^+ is 0.16/0.55. or 29 % of that of the I^- ion.

2. Calculation of (CdI_3^-) as a function of (Cd^{++}), (I^-) and N_{Cd}.

In the same way,

$$N_{Cd} = \frac{2(Cd^{++}) \cdot \frac{0.45}{0.55} - 2(CdI_3^-) \cdot \frac{0.41}{0.59} \cdot \frac{0.45}{0.55} + 2(CdI^+) \cdot \frac{0.16}{0.55}}{2(Cd^{++}) \cdot \frac{0.45}{0.55} + (CdI_3^-) \cdot \frac{0.41}{0.59} \cdot \frac{0.45}{0.55} + (CdI^+) \cdot \frac{0.16}{0.55} + (I^-)}$$

Replacing (CdI^+) by (I^-) + (CdI_3^+) − 2(Cd^{++}) and solving for (CdI_3^-) we obtain:

$$(CdI_3^-) = \frac{(0.26 - 0.58\,N_{Cd})\,(Cd^{++}) + (0.32 - 0.71\,N_{Cd})\,(I^-)}{0.4727\,N_{Cd} + 0.3054}$$

It is easily seen that, when $N_{Cd} = 0.45$ (corresponding to the migration number for extreme dilution), (CdI_3^-) = 0. Again, the equation is reduced to an identity when N_{Cd} is put equal to −0.23, (I^-) equal to 0 and (CdI_3^-) equal to 2 (Cd^{++}). Knowing the values of N_{Cd}, (Cd^{++}) and I(−), it is then possible to calculate (CdI_3^-) for different concentrations. (CdI^+) is deduced from

$$(CdI^+) = (I^-) + (CdI_3^-) - 2(Cd^{++}).$$

Table III gives the values of (Cd^{++}), (I^-), (CdI_3^-) and (CdI^+) corresponding to total concentrations of CdI_2 ranging from 0.005 mol/l. to 0.5. The values obtained for this latter concentration must only be considered as approximations, one of the values for the E.M.F. having been determined by extrapolation.

TABLE III

Concentrations in Mols per Liter of each of the Ions present in Aqueous Solutions of Cadmium Iodide

Total cadmium	(I^-)	(Cd^{++})	(CdI_3^-)	(CdI^+)	Total CdI_2 dissociated
0.005	0.0063	0.00315	0.0000	0.0000	0.00315
0.01	0.0103	0.0037	0.0000	0.0029	0.0066
0.02	0.0148	0.0040	0.0011	0.0079	0.0130
0.05	0.0228	0.0048	0.0064	0.0196	0.0308
0.1	0.0252	0.0084	0.0153	0.0237	0.00474
0.2	0.0285	0.0138	0.0350	0.0359	0.0847
0.5	0.0181	0.0973	0.1769	0.0004	0.2746

In Table IV we give for comparison the conductivity ratios and the activity coefficients as calculated by Getman (loc. cit.) and the ratios $1/2C[(Cd^{++}) + (I^-)/2)]$, where C is the total concentration of CdI_2, and also the ratios $1/C\,[(I^-) + (CdI_3^-)]$.

TABLE IV

Comparison of the Ionic Concentrations deduced from Migration Data and and E.M.F. with Arrhenius' Degrees of Dissociation and with Activity Coefficients

Total cadmium	Activity coefficients	$1/2C[(Cd^{++})+(I^-/2)]$	$1/2C[(I^-)+(CdI_3)]$	Conductivity ratios (25°C)
0.005	0.56	0.63	0.63	0.63
0.01	0.40	0.44	0.51	0.53
0.02	0.26	0.28	0.40	0.43
0.05	0.14	0.16	0.29	0.30
0.1	0.09	0.10	0.20	0.23
0.2	0.06	0.07	0.16	0.19
0.5	0.03	(0.11)	(0.19)	0.16

It is interesting to notice that the conductivity ratios and the values of $1/C\left[(I^-) + (CdI_3^-)\right]$ are in close agreement, and also that the activities calculated by Getman are of the same order of magnitude as the values of $1/2C\left[(Cd^{++}) + (I^-)/2\right]$. This seems to prove that, for CdI_2, the conductivity ratios fairly closely represent the percentage of ions present in the solution in Arrhenius' sense. The activity coefficients deduced from E.M.F. measurements correspond to the total percentage of the simple ions measured by the electrodes used, in this case Cd^{++} and I^-, and ignoring the complexes CdI^+ and CdI_3^-.

PART II

Table V contains diffusion coefficients measured for various concentrations of cadmium iodide, at 25°C., by the method of McBain and Liu.[1]

TABLE V

Concentration m/l.	Diffusion coefficients	Concentration, m/l.	Diffusion coefficients
0.005	0.956	0.05	0.788
0.005	0.964	0.05	0.790
0.005	0.965	0.15	0.732
0.005	0.951	0.5	0.690
0.01	0.859		

The diffusion coefficient corresponding to infinite dilution, i.e., to complete dissociation into Cd^{++} and I^- ions, is given by Haskell's equation for infinite dilution, which is an extension of the Nernst formula to the case of unsymmetrical salts:

$$D_\infty = RT\,\frac{m_{Cd^{++}} \cdot m_{I^-}}{m_{Cd^{++}} + m_{I^-}}\left(\frac{1}{2} + \frac{1}{1}\right)$$

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[1] J. W. McBain and T. H. Liu: J. Am. Chem. Soc., 53, 59 (1931).

At 25°C. the limiting mobility of I^- is 75.4. From the ratios of mobilities used in Part I we deduce

$$m_{Cd^{++}} = 61.6,\ m_{CdI_3^-} = 42.8,\ m_{CdI^+} = 22.0$$

At a finite concentration at which the only ions present are the simple Cd^{++} and I^- ions, the degree of dissociation being α, the part of the diffusion coefficient due to those ions is given by:

$$D = D_\infty \times \alpha$$

We have, at 25°C.:

$$D_\infty = 0.023 \times \frac{61.6 \times 75.4}{137.0}\left(\frac{1}{2}+\frac{1}{1}\right) = 1.170$$

McBain and Liu proposed the following general equation for the diffusion coefficient of any electrolyte at any concentration:—

$$D = \frac{iRT}{\Sigma \frac{C}{m}}$$

in which C is the fraction of the total concentration which is in the form of ions or molecules of mobility m. The summation is extended to all the ions, simple and complex, and to the neutral molecules. i is van't Hoff's coefficient. At any concentration of cadmium iodide where, beside neutral molecules, simple Cd^{++} and I^- ions only are present, this equation gives for 25°C.

$$D = \frac{0.023\ i}{\frac{2\alpha}{m_{I^-}} + \frac{2\alpha}{m_{Cd^{++}}} + \frac{1-\alpha}{m_{CdI_2}}}$$

i is deduced from freezing point measurements.[1] At the lowest concentration studied by us (0.005 molar)

$$i = 1 + 2 \times 0.63 = 2.26$$

In the first part of this paper we assumed as a first approximation, since the conductivity ratio is 0.63 at that concentration, that the degree of dissociation is equal to 0.63. Now we shall consider the degree of dissociation at 0.005 molar and the mobility of the CdI_2 molecule as two unknowns. We are going to determine their values by requiring that Haskell's formula and the McBain-Liu formula give at the concentration 0.005 molar the experimental value 0.959, recorded in Table V.

At 25°C. and 0.005 molar, $D_{Cd^{++}+I^-} = 1.17 \times \alpha$. The difference between 0.959 and $1.17 \times \alpha$ is then due to the diffusion of the neutral molecules. The mobility of the CdI_2 molecule must then be given by:

$$m_{CdI_2} = \frac{0.959 - 1.17\alpha}{(1-\alpha)\,RT} = \frac{0.959 - 1.17\alpha}{0.023\,(1-\alpha)}$$

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[1] Compare J. W. McBain: Z. Elektrochemie, 11, 215 (1905).

We then have the two simultaneous equations:

$$\begin{cases} 0\,959 = \dfrac{2.26 \times 0.023}{\dfrac{2\alpha}{75.4} + \dfrac{2\alpha}{61.6} + \dfrac{1-\alpha}{m_{CdI_2}}} \\[2ex] m_{CdI_2} = \dfrac{0.959 - 1.17\alpha}{0.023\ (1-\alpha)} \end{cases}$$

or

$$\begin{cases} \alpha m_{CdI_2} - 0.921\ m_{CdI_2} - 17\alpha + 17 = 0 \\ \alpha m_{CdI_2} - m_{CdI_2} - 50.9\alpha + 41.6 = 0 \end{cases}$$

These two equations represent hyperbolae. Drawing the two curves, one finds for their intersection point:

$$m_{CdI_2} = 22.3$$
$$\alpha = 0.675$$

The actual degree of dissociation at the concentration 0.005 molar is thus, as expected, a little higher than the conductivity ratio 0.63. All our calculations in Part I could be modified accordingly. We will not do so, because the new value obtained for the degree of dissociation at the concentration 0.005 molar is probably not yet the final one. We only attempt to calculate as well as possible the orders of magnitude of the concentrations of the various ionic species. Taking the concentrations given in Table IV (except for the 0.005 molar solution for which the new value of the degree of dissociation is used) the diffusion coefficients listed in Table IV are obtained from the McBain-Liu formula.

TABLE VI

Concentration, mols per liter	van't Hoff's i	D calculated	D measured or interpolated
0.005	2.26	0.959	0.959
0.01	2.08	0.883	0.859
0.02	1.88	0.844	0.831
0.05	1.52	0.740	0.789
0.1	1.25	0.654	0.750
0.2	0.96*	(0.524)	0.720

* By extrapolation.

The results show that at low concentrations the agreement is to be regarded as fairly satisfactory. It should be pointed out that the calculated values are exceedingly sensitive to a slight change in the mobility of one of the constituents. If, for instance, we deduce the mobility of the CdI_2 molecule from Haskell's formula and from the value 0.63 for the degree of dissociation of 0.005 molar CdI_2, we find 26.1 This value when used in the McBain-Liu formula for the concentration 0.005 molar gives 1.02 for the diffusion coefficient instead of 0.959.

It is probable that if all the concentrations given in Table IV were corrected by taking 0.675 instead of 0.63 for the degree of dissociation of 0.005 molar CdI_2, a better agreement between calculated and measured values of the diffusion coefficient than that shown in Table VI would be obtained; this because of the fact that the term corresponding to the molecules CdI_2 in the McBain-Liu formula would be decreased.

However, the chief reason for the very significant difference between observed and calculated values for higher concentrations is that the observed values were obtained by diffusion into pure water instead of into slightly less concentrated cadmium iodide. The experimental data are therefore integral values, whereas those calculated refer only to the concentration indicated. McBain and Liu have shown for other cases that integral values diverge in this manner.

On the whole the preceding calculations show that the concentrations of the various ionic species calculated in Part I give reasonably good values of the diffusion coefficients.

Summary

(1) Measurements have been made of the E.M.F. of cells containing cadmium iodide in concentrations from 0.001 to 0.4 molar. These measurements have been combined with those for other cells measured by Getman to deduce the concentrations of the simple ions.

(2) Using the general formulation of migration of Laing and McBain, the concentrations and mobilities of the complex cations and anions have been evaluated.

(3) It is found that the sum of the concentrations of the simple ions follows closely or is equal to the activity coefficients and that, further, for the weak electrolyte, cadmium iodide, the total dissociation is substantially in agreement with (and slightly more than) the conductivity ratio of Arrhenius.

(4) Diffusion coefficients have been measured for solutions of cadmium iodide for concentrations from 0.005 to 0.5 molar. From these measurements and from the combination of the Haskell and McBain-Liu diffusion formulae the mobility of the cadmium iodide molecule and a more accurate value of the degree of dissociation of 0.005 molar cadmium iodide have been deduced. The concentrations of the various molecular species present in solutions of cadmium iodide have been used to calculate the diffusion coefficients. Fairly good agreement with the experimental values has been obtained.

(5) The behavior of cadmium iodide with respect to the dissociation and formation of complexes differs only in degree from that of all other salts containing divalent ions.

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COPPER QUADRANTOXIDE

BY M. J. MURRAY

Mellor[1] is not very certain that there is such a substance as copper quadrantoxide, Cu_4O. "H. Rose[2] prepared what he regarded as copper quadrantoxide, Cu_4O, or copper tetritaoxide, by adding freshly prepared and moist cuprous chloride to a dilute solution of stannous chloride in potassium hydroxide; if the solution be not dilute enough or if too much stannous chloride be employed, metallic copper is precipitated. The same product was obtained by using a solution of cuprous sulphate instead of cuprous chloride. . . . Gladstone and Tribe[3] also say that if a copper-silver couple be placed in a solution of cupric nitrate, a film of this oxide may be deposited on the silver plate. Recoura[4] obtained Rose's oxide by the decomposition of cuprous oxide. Rose thus describes the properties of copper quadrantoxide. The olive-green powder is stable if kept under water out of contact with air, and it gradually becomes denser and less readily oxidized; but it cannot be dried without change. When the oxide is heated in a limited supply of air, it acquires a yellow film of cuprous oxide. Dilute sulphuric acid converts it into copper and cupric sulphate in the proportions $Cu:CuSO_4 = 3:1$ (nearly); the equation is presumably $Cu_4O + H_2SO_4 = 3Cu + CuSO_4 + H_2O$. Since cuprous oxide is soluble in dilute sulphuric acid, Moser[5] says that the quadrantoxide is either decomposed by the dilute acid or else it is a mixture of cuprous oxide and copper. Hydrochloric acid first darkens the quadrantoxide—possibly forming copper subchloride—and then furnishes a mixture of copper and cuprous chloride; and hydrocyanic acid forms a black substance—possibly copper subcyanide—soluble in dilute nitric acid. Hydrogen sulphide transforms copper quadrantoxide into a black homogeneous substance—possibly copper subsulphide—which gradually gives off hydrogen and forms a higher sulphide. The quadrantoxide is insoluble in aqua ammonia or in an ammoniacal solution of ammonium carbonate. Gladstone and Tribe add that silver nitrate is reduced to filiform silver by copper suboxide. Analyses of the product correspond with 95 percent Cu_4O and 5 percent stannous oxide. The chemical individuality of the quadrantoxide has not therefore been established, and, when further investigated, it may prove to be a hydrogel of variable composition. Wöhler and Balz[6] observed no signs of the quadrantoxide in their study of the dissociation $2CuO \rightarrow Cu_2O \rightarrow 2Cu$."

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[1] "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", **3**, 116 (1923).

[2] Pogg. Ann., **120**, 1 (1863).

[3] Chem. News, **25**, 193 (1872).

[4] Compt. rend., **148**, 1105 (1909).

[5] Z. anorg. Chem., **64**, 200 (1909).

[6] Z. Elektrochemie, **27**, 406 (1921).

Moser[1] is quite definite as to the non-existence of copper quadrantoxide. "When cupric or cuprous compounds are reduced by stannous salts in alkaline solution or by sodium hydrosulphite in presence of hydroxyl ions, one gets no quadrantoxide, but mixtures of cuprous oxide and copper, or only metallic copper. It is easy to understand the error made by Rose in thinking that he had a lower oxide of copper, because many of the properties of the mixtures could be considered as those of a lower oxide. Especially significant is the fact that the green precipitate turns yellow when the surface is exposed to the air. If hydroxyl ions are present, this process takes place more rapidly, and the finely divided copper is oxidized to the yellow cuprous oxide. This can easily be observed if one adds ammonia to the green, washed, precipitate. In the absence of aif there is no change in a short time. If oxygen gets in, there is, almost suddenly, a formation of amorphous, yellow, cuprous oxide at the surface of the suspension. It was this process that Rose considered as the oxidation of the lower oxide when he added ammonia to the wash-water in order, as he says, to make the precipitate agglomerate more readily. Since the concentration of ions in the liquid was very low because of the repeated washings, addition of ammonia, an electrolyte, causes the hydrosols of copper and cuprous oxide to form gels. The precipitate becomes, as Rose says, 'denser' as it settles to the bottom. On the other hand, if ammonia is added with the most scrupulous exclusion of air, only a small portion of the cuprous oxide dissolves to form the complex molecules $(Cu.nNH_3).OH$. This increases the relative amount of copper in the precipitate, which thereby becomes more dense and consequently settles more rapidly. The further observation by Rose that addition of hydrochloric acid dissolves the quadrantoxide to a dark-colored subchloride, which soon decomposes with precipitation of copper and formation of cuprous chloride is true to the extent that the copper comes out at first in a colloidal form on addition of hydrochloric acid to the amorphous cuprous oxide gel, so that it looks as though one had a dark-colored solution.

"The two, practically identical, results which Rose obtained by decomposing the substance with dilute sulphuric acid in the absence of air, can be accounted for because Rose worked to a definite, green color of the precipitate, which therefore corresponded in the two cases to the same amounts of the two components.

"By mixing finely divided copper with yellow cuprous oxide it was possible to obtain mixtures which had identically the same properties as the hypothetical quadrantoxide. If the solution is alkaline, the finely divided copper on the surface oxidizes on the surface to cuprous oxide and one believes that the green precipitate becomes yellow in contact with the air. Also, on addition of ammonia, the same phenomena occur as have been described. On addition of sodium thiosulphate, it is possible to dissolve the cuprous oxide with formation of complex ions, leaving the finely divided copper behind. This phenomenon, which was observed in both cases, is characteristic of a mixture."

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[1] Z. anorg. Chem., **64**, 212 (1909).

The preceding paragraph is a very disappointing one. Moser does not say how he made his finely divided copper or in what proportion he mixed it with his also undescribed cuprous oxide. If the copper was not of the same grain size as in Rose's alleged compound, the two colors cannot have been identical. If it was of the same particle size, Moser has not offered any proof that his mixture remained a mixture. It may have reacted to form the quadrantoxide. It is probable that Moser had a mixture; but there is a difference between probability and proof, and Moser has overlooked that difference. While sodium thiosulphate would dissolve cuprous oxide out of a mixture of cuprous oxide and copper, it might also dissolve it out of a compound. We have a double salt, $CuCl_2.2KCl.2H_2O$, even though absolute alcohol will dissolve the cupric chloride and leave the potassium chloride behind. Moser would have concluded from this experiment that he had a mixture of cupric chloride and potassium chloride, and he would have been wrong even if he had mixed his two salts in presence of a trace of water. Moser's conclusion that there is no definite copper quadrantoxide is not justified by his experiments.

Some years ago, Mr. J. Y. Riffe, now of Charleston, West Virginia, did some work on this problem while a graduate student at the University of Colorado, under the direction of Professor F. E. E. Germann. The results were never published and Mr. Riffe very courteously placed them at the disposal of Professor Bancroft. It was to supplement this material that I did the few experiments which will be described later.

Mr. Riffe points out that "Sabatier and Espil[1] proved, to their own satisfaction, that the suboxide of nickel, Ni_4O, is a definite compound by means of the data obtained by the reduction of nickel oxide by hydrogen, plotting percentage reduction against time, and observing that a more or less definite break occurred in the curve at about 70-75 percent reduction. This evidence was sufficient for Rideal and Taylor[2] to take up the study of nickel as a catalyst from the standpoint of the formation of Ni_4O as an intermediate compound."

Chiefly on the basis of the work by Wöhler and Balz,[3] the existence of nickel quadrantoxide as a definite chemical compound is discredited by Roscoe and Schorlemmer[4] and by Wagner.[5]

Mr. Riffe goes on to say that "as copper is next to nickel in importance as a catalyst in organic synthesis, Sabatier and Espil attempted to prove the existence of Cu_4O in the same way, by the reduction curve. In this they were not very successful as the curve failed to show signs of a break, although a critical examination of the points of reference of their published curve seems

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[1] Compt. rend., 159, 668 (1914).

[2] "Catalysis in Theory and Practice,"

[3] Z. Elektrochemie, 27, 406 (1921).

[4] "Treatise on Chemistry," 2, 1370 (1923).

[5] Thorpe: "Dictionary of Applied Chemistry," 4, 530 (1922).

to indicate that they might just as well have drawn straight lines with breaks at fifty and seventy-five percent reductions corresponding to the compounds, Cu_2O and Cu_4O.

"The most extensive and thorough work on the reduction of copper oxide by hydrogen was done by Wright, Luff and Rennie.[1] Their investigation covered a wide range of conditions, temperatures, rate of gas flow, etc. They came to the conclusion that the reduction curve was without breaks. However, in no case did they make the reduction slower than about six hours for about ninety percent reduction. Pease and Taylor[2] repeated part of the work of Wright, Luff and Rennie, with the object of studying the action at the Cu-CuO interface, and the inhibiting action of water vapor and oxygen upon the rate of reduction. They verified the previously made observation that, after a period of incubation during which there was apparently no reduction, the reaction started from minute particles of a red color within the mass of oxide and spread in all directions. This was thought to be conclusive evidence that the reaction went much more rapidly at a copper-copper oxide interface and they verified this conclusion by mixing with the copper oxide some completely reduced copper, a proceeding which shortened the period of incubation.

"From the data given in the experimental part of this article and from the fact that cuprous oxide can also be red, it may well be that the reduction spread from the CuO-Cu_2O interface. In fact, our results seem to permit no other interpretation. However, no method other than interpretation of the curve suggested itself for proving this point. If some Cu_2O were to be mixed with the CuO, one would not expect a long period of incubation before reduction began.

"With all the above in mind, we wished to prove the existence of the lower oxide of copper, Cu_4O, both by reduction and by oxidation methods. One of us [Riffe] had observed several years ago that a freshly prepared solution of copper in ammoniacal copper sulphate would precipitate metallic copper if acidified, and that the amount of precipitate depended upon the time which had elapsed between dissolving the copper and acidification. This promised to be a convenient method for studying the rate of oxidation of copper in solution. The only method which readily suggested itself for studying the rate of reduction was by the often-tried one of reduction of the oxide in a stream of hydrogen; but this had been done so often and so well that it seemed rather presumptuous to expect any new light from it. However, we could not help but feel that the rate of reduction should show up differently for the different oxides of copper and that, if we could get the proper conditions for bringing out the presence of the well-known oxide, Cu_2O, we might be able to do likewise for the less stable oxide, Cu_4O. So at first our attention was directed to reduction under some possible conditions for bringing out the presence of cuprous oxide. The catalytic action of inter-

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[1] J. Chem. Soc., 35, 475 (1879).

[2] J. Am. Chem. Soc., 43, 2179 (1921).

faces and of water vapor was minimized as far as possible by suitably designed apparatus, and, when the reaction velocity was slowed down to about one-fourth of that used by previous workers, we were able to get results that indicated not only the presence of Cu_2O very clearly, but also that of the lower oxide, Cu_4O.

"In both the oxidation and the reduction investigations, it was found that one-fourth of the oxygen carried by cupric oxide was bound to the copper more firmly than the rest. To be more exact, it was found that this much of the oxygen was dislodged at a slower rate than the rest, and taken up at a much faster rate, other conditions being fairly constant. We are of the opinion that this is rather definite proof of the existence of the suboxide of copper, copper quadrantoxide, under certain definite, but rather limited, conditions."

Mr. Riffe describes the following experiments on oxidation. "A solution of ammoniacal cupric sulphate, of known copper value, was heated to some definite temperature between 40° and 80°, and a stirring device, fashioned out of copper gauze and copper wire, was rotated rapidly in it for a definite length of time. A certain amount of copper was dissolved from the stirrer, the amount depending on the temperature of the solution and the concentration of the copper sulphate. The amount of copper dissolved was determined by weighing the stirrer before and after. The ammoniacal solution containing the dissolved copper was allowed to stand for definite lengths of time, which varied from only a few seconds to several hours, during which it absorbed oxygen rapidly from the air. Sulphuric acid (1:1) was then added until the solution became neutral or slightly acid. At the neutral point a heavy precipitate of metallic copper was thrown down.

"When the copper sulphate solution was filtered off and tested for copper, it was found that there was an appreciable increase in strength, and the sum of the copper precipitated and that found in the increase of copper sulphate in solution was, of course, equal to the total copper dissolved. The ratio of the amount precipitated and that dissolved was found to be a variable one. This variable was a function of the time allowed for the dissolved copper to oxidize by absorption of atmospheric oxygen. The percentage of the total dissolved copper which could be precipitated varied from seventy-five per-cent, if precipitated immediately after solution, to zero if allowed to stand for several hours."

Mr. Riffe's explanation of the phenomenon is not right. He postulates that no copper would dissolve from the stirrer in the absence of oxygen, which is not true. He also postulates that the copper dissolves as Cu_4O, which may be true but which is not necessarily so.

What actually happens when air is excluded is that metallic copper reduces the ammoniacal cupric oxide to cuprous oxide which of course in moderate concentrations remains in solution. One equivalent of copper dissolves and the solution becomes colorless. On acidification the following reaction takes place:

$$Cu_2O + H_2SO_4 = Cu + CuSO_4 + H_2O$$

The one equivalent of copper which dissolved is reprecipitated and the original concentration of copper compound is again produced.

Of course if air is allowed to come in contact during the stirring, the solution will not become colorless, i.e., oxidation will proceed continuously, with the result that not all of the copper which dissolves can be reprecipitated as metallic copper. The solution when acidified will show more and more cupric compound. If the correct amount of air is stirred in only 75% of the copper which dissolved will be reprecipitated and it might appear that the copper had dissolved as quadrantoxide; but if no air is stirred in or allowed to enter after the reduction, all the copper is reprecipitated.

Experiments designed to illustrate this were conducted as follows: 25 cc. of an approximately M/10 $CuSO_4$ solution were put in a 50 cc. wide-mouth, glass-stoppered bottle. A roll of freshly-cleaned, weighed copper gauze was put in the copper sulphate solution and the bottle filled with concentrated ammonium hydroxide. This operation was carried on in an atmosphere of hydrogen and the solutions were freed of air before using. The bubble entrapped when the stopper was inserted being hydrogen could not cause oxidation. The bottle and contents were shaken at room temperature, 20°C, and in a few minutes the solution had become entirely colorless. Shaking was continued for two hours. At the end of this time the bottle was opened, again in an atmosphere of hydrogen and the contents poured into a beaker containing dilute sulphuric acid in slight excess of the amount required to neutralize the ammonium hydroxide.

The loss in weight of the copper gauze was 160 milligrams while 25 cc. of the $CuSO_4$ solution used contained by electrolytic determination of the copper, 156 milligrams. Considering the great affinity which the solution has for oxygen the slight difference is readily accounted for.

Another experiment in which air was purposely allowed to enter showed that the amount of copper dissolved was increased just as it should be.

One other experiment was tried in this line—that of using dilute ammonium sulphate solution instead of the copper sulphate solution. In this case only a very slight trace of copper dissolved from the roll of gauze.

Mr. Riffe also made a study of the rate of reduction of cupric oxide in an atmosphere of hydrogen. "The apparatus was designed to eliminate as far as possible the effect of the heat of reaction and of the water vapor formed. This was done by spreading the material over the bottom of a 500 cc. flask. We also wanted to study the effect of the rate of flow of the gas stream, the difference in rate of reduction at different temperatures, and, particularly, to have an apparatus that would operate over hours and even days under absolutely uniform conditions. The set-up which answered our purpose very well was constructed as shown in Fig. 1. The hydrogen from the tank flowed throughout a "Purox" pressure reducer, set so that the gauge B gave two pounds pressure to the line through a glass stop-cock which could be adjusted for any rate of flow, then through a differential flow-meter of the type shown. This flow-meter gave reasonably accurate readings for rates of flow from ten to a hundred cc of hydrogen per minute and was made by inserting a piece of capillary tubing of about .25 mm bore between two lengths of ordinary size tubing and by-passing with a small-size tubing which ran into an oil reservoir at an angle of about 10°. The reservoir was filled with a light non-volatile oil (3 in 1), up to the zero mark on the sloping tube. It was calibrated by finding the depression of the oil column for four known rates of flow into a gasometer and then constructing the straight line curve. After passing the flow-meter, the hydrogen was passed into a combustion tube and across a platinum wire heated electrically to a white heat. This served to transform the small amount of oxygen present into water, which was then removed by passing the gas through a U-tube filled with phosphorus pentoxide. The dried and purified gas was then run into the reaction flask placed in a Freas constant-temperature oven. The copper oxide was scattered over the bottom of the flask in a thin layer. The hydrogen, plus the water vapor formed in the reduction, was then passed through one or two tared U-tubes connected into the chain in parallel and containing P_2O_5, through another flow-meter to get an estimate of the amount of hydrogen used up and to have a quick method of detecting leaks in the apparatus, and then to the atmosphere. After given intervals of time the tared U-tubes H and J were wiped to constant weight and accurately weighed. Care was taken at this point to weigh the tubes after intervals of not more than ten minutes from the time they were removed from the apparatus and placed in the balance case in order to minimize as far as possible the diffusion of hydrogen. The difference in weight of the U-tube filled with hydrogen and filled with air was greater than the usual amount of water vapor caught.

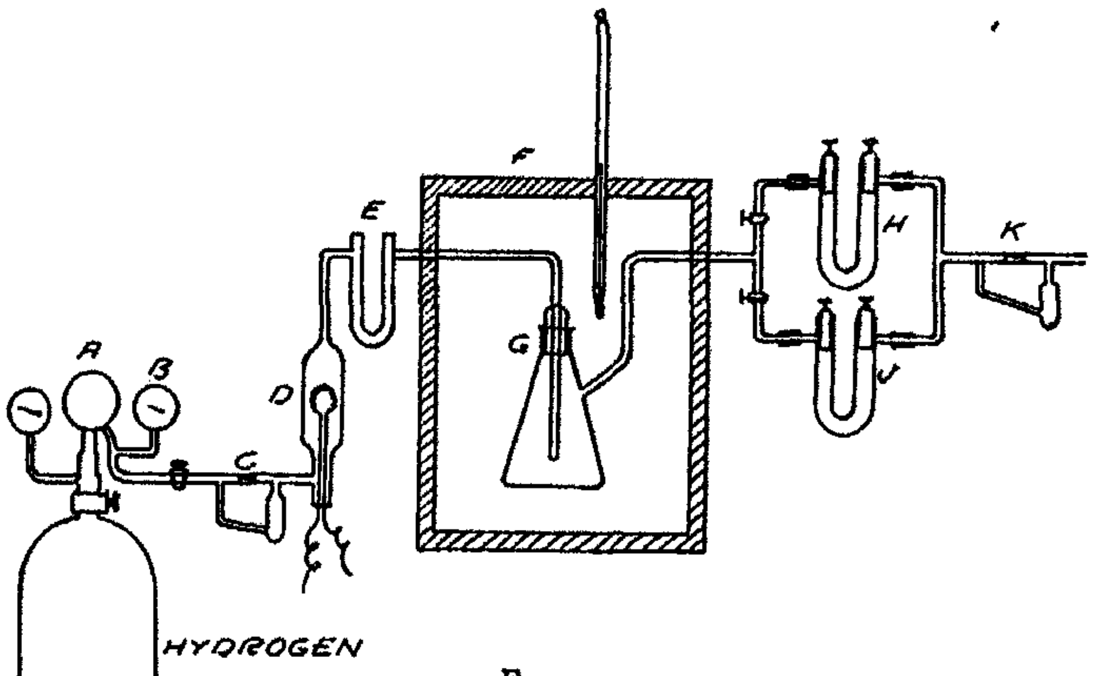

Fig. 1

Apparatus for Reduction of Copper Oxide

A—Tank pressure reducer
B—Line pressure gauge
C—Differential flowmeter
D—Oxygen remover
E—Phosphorus pentoxide
F—Freas electric oven
G—Reduction flask
H—Phosphorus pentoxide tube
J—Same
K—Differential flowmeter

"The advantages of having the copper oxide scattered over the bottom of a large flask are very apparent: the heat of reaction does not affect the temperature of the rest of the copper oxide to an appreciable extent, the water vapor formed rises immediately out of the reaction zone, and, as the oven was equipped with a glass door, the progress of the reaction could be observed.

"Fig. 2 was plotted from results obtained by exceedingly slow oxidation. As a further precaution towards minimizing the influence of interface catalysis the sample of CuO was ground in a pebble mill with SiO_2 for a couple of hours. The reducing value of this mixture was determined by reduction of a weighed sample at a temperature of 250° in hydrogen, and as a check, by an electrolytic determination of the copper. The copper oxide used was a sample of Kahlbaum finely-ground reagent which analyzed 19.4 per cent available oxygen. About four parts SiO_2 to one part CuO was used. The reduction was carried on at 130°C. The hydrogen flow was 45 cc/min.

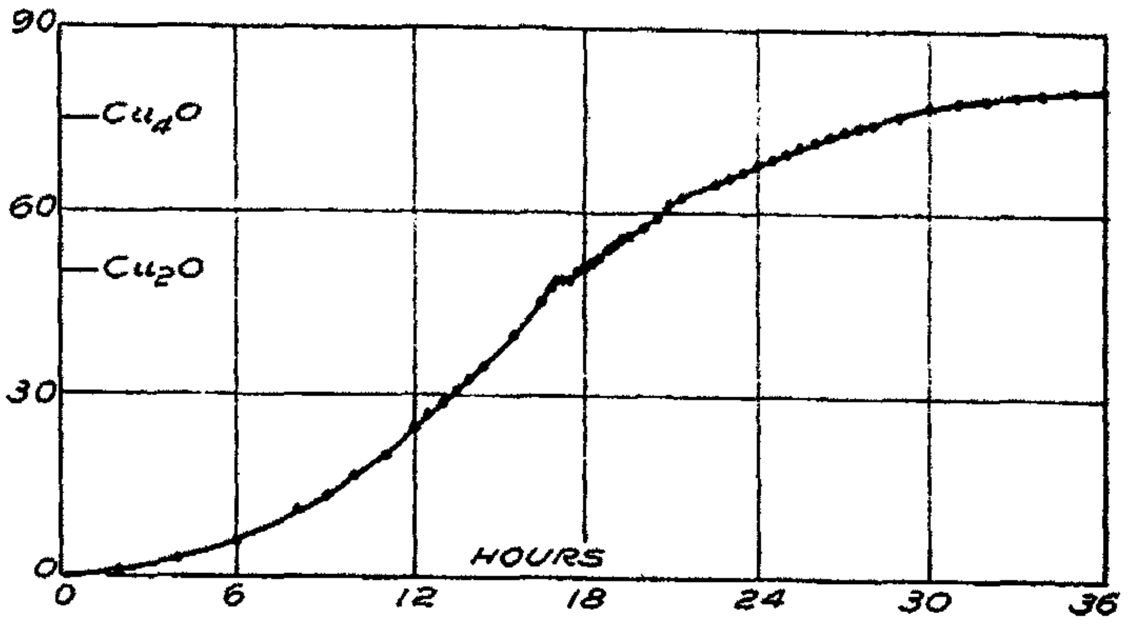

Fig. 2
Copper Oxide Reduction

"This curve can be divided into three parts: the first part starts from CuO which is reduced very slowly at the start but with perfectly regular increasing acceleration until a maximum rate is reached just before the point of half reduction. This corresponds to the conversion of all the CuO to Cu_2O if the mass is homogeneous throughout, and as the time necessary for reaching this stage is a matter of some 16 hours it is safe to assume homogeneity. When all the copper is in the form of Cu_2O there is a very decided decrease in the rate of reduction, amounting in this case to actual cessation for a period of half an hour. Then there is a short period of fluctuating rates of reduction (clearly shown in Fig. 3 which is a section of the same curve on a large scale) followed by an increasing rate of reduction until a maximum is reached which is about half the value reached in the previous maximum, then there is a gradual but uniformly decreasing rate of reduction until in the vicinity of 75 per cent reduction the rate reaches a value of about 5 per cent of the maxima. This point corresponds to the formation of Cu_4O. From this point the rate of reduction becomes constant within the limits of experimental error and the curve continues in a straight line. This last statement about the straight line may be subject to correction if we ever have the time, patience, and luck to keep the apparatus going long enough to determine a

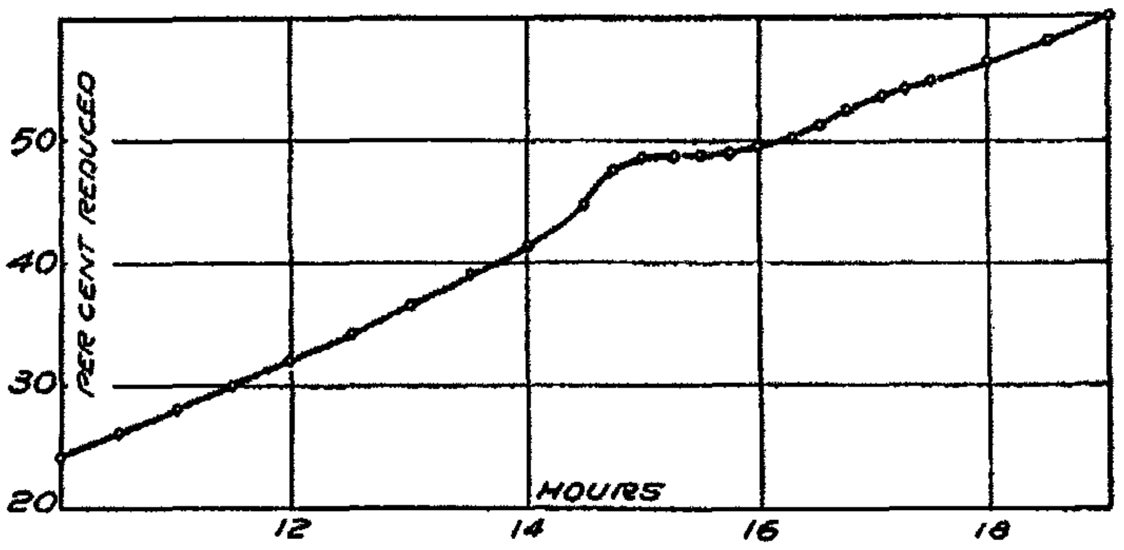

Fig. 3

Copper Oxide Reduction
Temperature 130°.
Hydrogen Flow 45 cc/min.
Diluted with SiO_2.

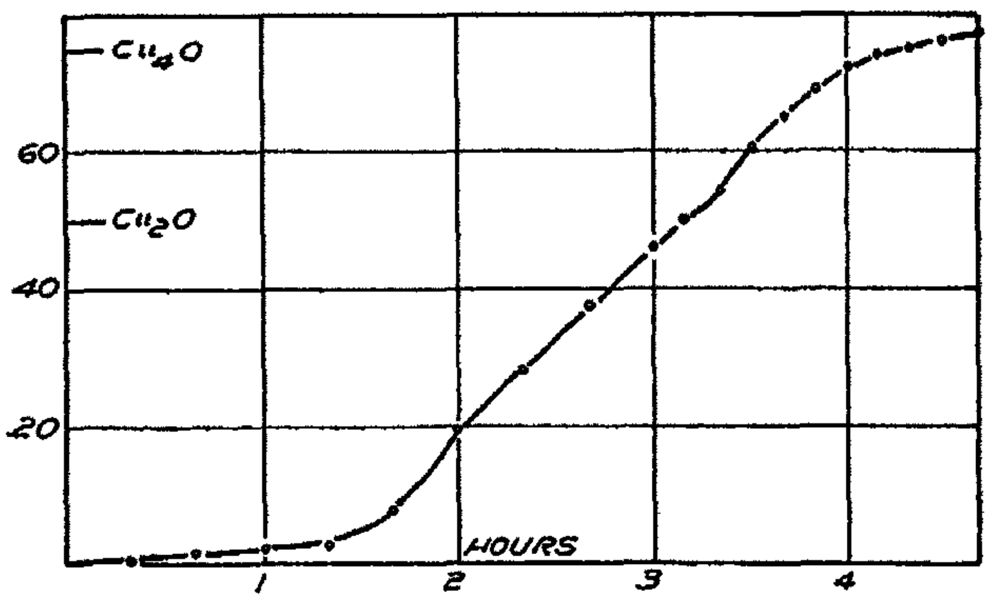

Fig. 4

Copper Oxide Reduction

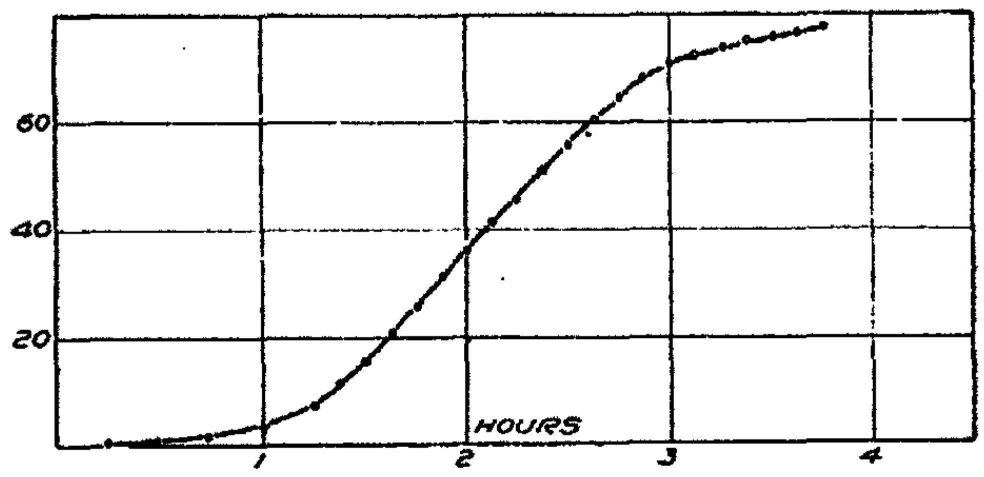

Fig. 5

Copper Oxide Reduction

TABLE I

Hours	Water gms $\times 10^{-4}$	Total Water gms $\times 10^{-4}$	Reduction per hour	Percent Reduction
2:00	11	11	0.25	0.5
4:00	46	57	1.2	2.7
6:00	57	114	1.5	5.3
8:00	102	216	2.7	10.6
9:00	63	279	3.1	13.1
10:00	75	354	3.5	16.5
11:00	73	427	3.4	19.9
12:00	73	530	3.4	24.7
12:30	40	570	3.7	26.6
13:00	40	610	3.7	28.5
13:30	42	652	3.9	30.5
14:00	44	696	4.1	32.5
14:30	46	742	4.3	34.7
15:30	106	848	5.0	39.7
16:30	122	970	5.7	45.3
16:45	56	1026	10.5	47.9
17:00	20	1046	3.7	48.8
17:15	0	1046	0.0	48.8
17:30	0	1046	0.0	48.8
17:45	14	1070	2.6	50.0
18:00	10	1080	1.9	50.5
18:15	20	1100	3.7	51.4
18:30	18	1118	3.4	52.2
18:45	28	1146	5.3	53.6
19:00	24	1170	4.5	54.7
19:15	10	1180	1.9	55.1
19:30	14	1196	2.6	55.8
20:00	32	1228	3.0	57.4
20:30	38	1266	3.6	59.1
21:00	40	1304	3.7	61.0
21:30	28	1332	2.6	62.3
22:30	48	1380	2.2	64.5
23:00	22	1402	2.1	65.5
23:30	26	1428	2.4	66.7
24:00	20	1448	1.8	67.6
24:30	24	1472	2.2	68.8
25:00	20	1492	1.9	69.8
25:30	20	1512	1.9	70.7
26:00	16	1528	1.5	71.3
26:30	20	1548	1.9	72.3
27:00	16	1564	1.5	73.1
27:30	18	1582	1.7	74.0
28:00	16	1598	1.5	74.7
29:00	32	1630	1.5	76.0
30:00	32	1662	1.5	77.6
31:00	13	1675	0.61	78.3
32:00	11	1686	0.51	78.8
33:00	12	1698	0.56	79.3
34:00	10	1708	0.48	79.8
35:00	9	1717	0.43	80.3
36:00	10	1727	0.48	80.7

sufficient number of points in such a slowly moving reaction. However, several runs each lasting several days with points at six and twelve hour intervals give an exactly straight line. If this reaction is to be explained by interface catalysis at all, under these conditions, it is necessary to make the compound Cu_2O the accelerating medium. As the amount of this substance increases, the rate of reduction increases until a maximum rate is reached just before all the cupric oxide is converted into the cuprous form. Then there is a state of equilibrium with no reaction taking place until a small nucleus of the still lower oxide is formed. A maximum reduction is soon reached under these conditions which when there is almost exactly half Cu_2O and half Cu_4O, then the rate of reduction gradually decreases as the amount of Cu_2O becomes smaller until a constant value is obtained when there is nothing but Cu_4O present. From the fact that the rest of the curve is a straight line, we assume that there is no accelerating effect due to the presence of metallic Cu in with the Cu_4O as the reduction proceeds.

TABLE II

Two-gram sample of the oxide dried at 135°C. Temperature of reduction 127°

Time in Hours	Water in gms. $\times 10^{-4}$	Total Water gms $\times 10^{-4}$	Reduction per hour	Percent Reduction
:20	22	22	1.5	.5
:40	30	52	2.1	1.2
1:00	36	88	2.5	2.0
1:20	36	124	2.5	2.8
1:40	224	348	15.4	8.0
2:00	516	864	35.5	19.5
2:20	366	1230	25.2	28.1
2:40	424	1654	29.2	37.9
3:00	358	2012	24.6	46.1
3:10	192	2204	26.4	50.5
3:20	176	2380	24.2	54.5
3:30	272	2652	37.4	60.8
3:40	200	2852	27.5	65.3
3:50	178	3030	24.4	69.3
4.00	116	3146	15.9	72.2
4:10	94	3240	12.9	74.2
4:20	48	3288	6.6	75.2
4:30	46	3334	6.3	76.3
4:40	44	3378	6.0	77.2
6:10	118	3496	1.8	79.3

"Fig. 4 is plotted from the results obtained with the same sample of copper oxide, reduced at the same temperature and with the same rate of gas flow: the only difference being that it was not diluted with SiO_2. This curve has the same characteristics as Fig. 2, but it will be noticed that the time of reduction is very materially reduced and the break at the point corresponding to half reduction is less noticeable.

"Attempts were made to slow down the rate of reduction by reducing the temperature in order to get a curve which would have the same time factor as curve 1 but without success. This was principally due to the fact that the change in rate of reduction per degree difference in temperature increased very rapidly in the region of 120°-130° and the constant-temperature oven available would not permit of sufficiently accurate adjustment.

"Fig. 5 is plotted from the results of work duplicating as nearly as possible the conditions under which previous investigators worked and confirms their conclusions that there is no break in the reduction curve as carried out by them.

"The accompanying Tables I, II and III contain the data from which curves 1, 3 and 4 are plotted.

TABLE III

One-gram sample of the oxide dried at 135°. Temperature of reduction 132°

:15	6	6	1.1	.2
:30	10	16	1.8	.7
:45	16	32	2.9	1.4
1:00	42	74	7.7	3.4
1:15	88	162	16.1	7.4
1:22	88	250	32.2	11.5
1:30	94	344	34.4	15.8
1:37	112	456	41.0	20.9
1:45	104	560	38.1	25.6
1:52	116	676	42.5	31.1
2:00	112	788	41.0	36.1
2:07	108	894	39.5	41.0
2:15	104	998	38.1	45.6
2:22	120	1118	43.9	51.0
2:30	100	1218	36.6	55.7
2:37	102	1320	37.3	60.4
2:45	92	1412	33.7	64.7
2:52	70	1482	25.6	68.0
3:00	56	1538	20.5	70.4
3:07	40	1578	14.6	72.2
3:15	32	1610	11.7	73.7
3:22	28	1638	10.2	75.0
3:30	22	1660	8.1	75.8
3:37	12	1672	6.7	76.5
3:45	12	1684	6.7	77.1

"Since the above was written, our attention has been called to an article by W. G. Palmer[1] in which he studied the oxidation of copper and the reduction of copper oxide by precipitating a very thin film of the metal on a china rod and observing the course of the oxidation or reduction by means of measuring the changes in reductance of the film. He confirms our observation that in the oxidation process the rate of oxidation is very high at first but he does not draw the same conclusion from this fact. He states that the rate of oxidation is abnormally high due to two causes: first, the increase of resistance of the film owing to the increase of temperature, and secondly, the stimulating effect of the reducing agent remaining in the film and rod on the oxidation.

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[1] Proc. Roy. Soc., 103A, 444 (1923).

"The curves for the reduction which he reproduces are, in the main, similar to those already published and show no break for the oxides. This is not surprising when we consider that he was able to get only a very few hasty readings in the ten minutes or so necessary to reduce the film completely.

"In general it might be said that Mr. Palmer's view as to the mechanism of the reduction of copper oxide by hydrogen does not coincide with those of Pease and Taylor nor with the evidence presented in this article. The method which he used, however, seems to promise excellent results if the reaction on such a thin film could be slowed down sufficiently to permit of a sufficient number of accurate readings."

While these curves may make it probable that copper quadrantoxide exists, the breaks in the curves as plotted are not marked enough to be very convincing. It seemed desirable to find some other method which would be less arbitrary. Such a method had been suggested implicitly by Rose when he said that the precipitate which he called copper quadrantoxide did not dissolve in ammoniacal solutions, which do dissolve cuprous oxide. Since there are a number of cases in which a precipitate, once formed, does not dissolve readily, it seemed best to work under conditions which preclude the formation of the wrong precipitate. If we take an ammoniacal solution of cuprous oxide and reduce it still further we cannot, by definition, get a mixture of copper and cuprous oxide precipitating. We shall get a one-phase precipitate either of copper quadrantoxide or of metallic copper.

N/10 $CuSO_4$ solution was made strongly ammoniacal and dilute sodium hydroxide was added. Then sodium hydrosulphite was added as the reducing agent. The deep blue color first disappeared and on further addition of reducing agent metallic copper (not an olive green precipitate) was obtained. If Cu_4O had formed and could possibly have remained in the solution, metallic copper could not have made its appearance on the addition of a little more than one equivalent of the reducing agent. Besides the compound is supposed to be insoluble in NH_4OH.

If in the above experiment the ammonium hydroxide is omitted, an olive green precipitate is obtained.

In an additional experiment the first step in the reduction of the copper was carried out in ammoniacal solution by means of a roll of copper gauze. To the colorless solution was added dilute sodium hydroxide and a small amount of sodium hydrosulphite. Metallic copper alone was precipitated.

While we do not know why the precipitate of the so-called copper quadrantoxide is olive-green, there is a very similar case cited by Roscoe and Schorlemmer.[1] "When powdered sulphur and fine copper-filings are well mixed together, a green-colored powder results, in which, however, a microscope will show the particles of sulphur lying by the side of the particles of copper." Professor Clyde Mason suggests that the copper particles act like a black, thus giving an olive green.

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[1] "A Treatise on Chemistry," 1, 47 (1920).

The significance of the results is unmistakable. When the solution is able to dissolve or peptize cuprous oxide, metallic copper appears as solid phase. When the solution cannot dissolve or peptize cuprous oxide, an olive-green precipitate is obtained. Since this must contain metallic copper, the other constituent cannot be copper quadrantoxide but must be a mixture.

The general results of this paper are:

1. The evidence proves that copper quadrantoxide does not occur as a stable solid phase at room temperature.

2. Rose's experiments to show that copper quadrantoxide can be made to precipitate from an alkaline solution and cannot be dissolved or peptized by ammoniacal solutions are vitiated by adsorption and therefore prove nothing.

3. Metallic copper precipitates when a cuprous salt is reduced in an alkaline solution under conditions such that cuprous oxide cannot precipitate. An olive-green precipitate is obtained when cuprous oxide can precipitate.

4. The olive-green precipitate cannot be copper quadrantoxide and must be a mixture of metallic copper and hydrous or anhydrous cuprous oxide.

Cornell University.

SOLUTIONS FOR COLORIMETRIC STANDARDS. IV.

Some Factors affecting the Color of Indicator Solutions*

BY M. G. MELLON AND G. W. FERNER

In some earlier work it was observed that certain indicators intended for use in the colorimetric determination of hydrogen ion concentration seemed to give erroneous results for the pH range through which they were supposed to undergo their transformation of color. The variation in hue for the same indicator supplied by different manufacturers was particularly disturbing.

This experience raised the question as to whose indicators one might use with most assurance, and whose method of use should be followed. If either or both of these points are of significance, any information regarding them should be of interest to individuals in various kinds of experimental work involving the use of such compounds. It is of special importance to those attempting to prepare permanent standards designed to match the color of indicator solutions.

The present work was undertaken with the object of securing information regarding the effect on certain indicator solutions of the following factors: (1) the source (or degree of purity) of the indicator itself; (2) the method of preparation of the stock solution of any given indicator; and (3) aging, particularly the effect of light.

Previous Work

Of the earlier relevant work mention may be made of some of the significant contributions. Several authors have noted variations in the hue of indicators from different sources. Hunter,[1] on testing samples of congo red from four manufacturers, found a divergence of 40 to 75 percent from the hue values for a purified product. Methyl orange showed a similar variation. After testing six different samples Collins[2] stated that methyl orange for indicator work should be so specified when ordering. Schlegel and Steuber[3] found that brom thymol blue from different sources, or successive lots from the same source, may give widely divergent results.

Similar observations have been made upon the method of preparing the stock solutions of indicators, and the effect of different substances, such as ethanol, upon the change of hue of indicators. Thiel and Springemann,[4] Thiel, Wülfken and Dassler,[5] and Michaelis and Mizutani[6] investigated the effect

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* Presented before the Division of Physical and Inorganic Chemistry at the meeting of the American Chemical Society at Cincinnati, Ohio, September 8-12, 1930.

[1] Biochem. J., **19**, 42 (1925).

[2] J. Ind. Eng. Chem., **12**, 800 (1920).

[3] Ind. Eng. Chem., **19**, 631 (1927).

[4] Z. anorg. allgem. Chem., **176**, 64 (1928).

[5] Z. anorg. allgem. Chem. **136**, 406 (1904).

[6] Biochem. Z., **147**, 7 (1924).

of ethanol. Kolthoff[7] states that little is known about the influence of different solvents on the sensitivity of indicators. Although he has called attention to a significant "alcohol error" for several indicators in solutions containing from 10 to 70 percent alcohol, the concentration is very much less than the smaller of these values when one is using one ml. of a 95 percent alcoholic solution in 50 ml. of a buffer solution. Clark[8] states that brom cresol purple dissolved directly in alcohol has a different hue than when prepared according to his method.

In connection with the stability of indicator solutions Thiel and Springemann[9] showed that various indicators fade when exposed to light in the presence of organic solvents. Some faded samples regained their color on standing. Brightman and others[10] made a spectrophotometric study of the end point and fading of phenolsulfonphthalein indicators. Marsh[11] found that indicator solutions react with the bottles in which they may be stored, while Schlegel and Steuber[3] recommended keeping the solutions in Pyrex flasks, or coating ordinary glass with paraffin or wax.

Experimental Data

Preparation of Materials. In purifying the materials used and in preparing the solutions the usual precautions for careful work were observed, such as using "conductivity water," recrystallizing salts three times, preserving solutions in Pyrex containers, and adhering to Clark's directions[12] in preparing buffer solutions. The latter were made from the stock solutions just before use.

In addition to regular commercial material, intended for use as indicators, samples of methyl orange[1] and methyl red[13] were purified according to methods given in the respective references. Otherwise the other indicators were used as purchased, since most individuals probably use them in this form, both because various authors so recommend and because of a natural hesitancy to purify materials retailing at their present price. In this case also it was of particular interest to ascertain whether different samples were equally good. Most of the indicators were purchased from such reputable firms as the National Aniline Company, Coleman and Bell, Hynson, Wescott and Dunning, the LaMotte Chemical Company, and the J. T. Baker Chemical Company, each of whom stated that they prepared their own products. In this data reference to the source of each indicator used was purposely omitted since it is not the object of the paper to advertise any concern's product. In case of any marked variations among the results for several different products one should use this particular indicator with suspicion. Most of the indicators

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[7] "Indicators," 92, 183, 184 (1926).

[8] "Determination of Hydrogen Ions", 95 (1927).

[9] Z. anorg. allgem. Chem., 176, 112 (1928).

[10] J. Am. Chem. Soc., 40, 1940 (1918).

[11] Science, 59, 216 (1924).

[12] "Determination of Hydrogen Ions", 192 (1927).

[13] Desvergnes; Ann. chim. anal. chim. appl., 2, 209, (1920).

were purchased shortly before use, but a few had been in stock at least five years before the solutions were prepared. In some cases the solid indicators from the several manufacturers appeared much alike; in others there was a marked difference in the colors, little of which was observable, however, when the solutions were prepared.

Stock solutions of the indicators were prepared by several different methods. One tenth percent aqueous solutions of methyl orange were used throughout, as recommended by Kolthoff.[14] Two hundredths percent solutions of methyl red in 60 percent ethanol were prepared according to Coleman and Bell's directions.[15] Tropaolin OO was prepared in 0.1 percent aqueous solutions,[16] and in 0.1 percent solutions in 50 percent ethanol.[15] The recommendation of Coleman and Bell[15] was followed in preparing a 0.02 percent solution of cresolphthalein in 95 percent ethanol. Three types of solutions were used for the indicators of Clark and Lubs: (1) aqueous solutions prepared according to Clark's directions[16] by adding definite amounts of sodium hydroxide to 0.1 g. of the indicator and diluting to 250 ml.; (2) alcoholic solutions made by dissolving 0.1 g. of the indicator in 52 ml. of neutral 95 percent ethanol, adding the amount of sodium hydroxide specified by Clark, and diluting with water according to Taub's procedure[17]; and (3) according to Kolthoff[14] by dissolving 0.1 g. of the solid in 50 ml. of 95 percent ethanol and diluting with water to 250 ml. With the exceptions noted, Clark's directions were followed in preparing solutions for the comparison of the different products and for the determination of the effect of ultraviolet radiation; likewise, a single product was used in testing different methods of preparation and in preparing the solution for exposure to ultraviolet radiation.

With the exception of tropaolin OO, a sample of each indicator was exposed for two hours to a quartz mercury lamp (Cooper-Hewitt type, designed for operation at four amperes and 220 volts) by placing a thin layer of the solid on a glass about 30 cm. from the lamp. Solutions were then prepared similar to those for the unexposed samples.

Determination of Color. Observations of the various lots of the different indicators, in solutions of different kinds, prepared before and after exposure to ultraviolet radiation, were made by means of a Keuffel and Esser color analyzer (Model C). The procedure followed differed from that reported in an earlier paper[18] only in the use of two 400 w. Mazda lamps for illumination of the samples in the five cm. tubes.

Solutions for the determination of the spectral transmission curves were prepared by diluting one ml. of the stock solutions to 50 ml. with appropriate buffer solutions. Most of the buffers selected were 0.2 pH unit beyond the limits of the useful range of the indicators in order to insure a practically com-

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[14] "Indicators", 63, 64, 72 (1926).
[15] "Catalog and Price List", 68 (1928).
[16] "Determination of Hydrogen Ions", 94 (1927).
[17] J. Am. Pharm. Assocn., 16, 118 (1927).
[18] Mellon and Martin: J. Phys. Chem., 31, 161 (1927).

plete conversion to either the basic or acidic color. One sample of each solution so prepared, except tropaolin OO, was exposed in a quartz container to the same conditions of ultraviolet radiation as were the solids.

The data obtained are plotted on a semilogarithmic basis using the percent transmittancy as ordinates and the wave length in millimicrons as abscissas. All of the curves for a given indicator, except thymol blue, are on the same graph. The point used in locating the position of the curves at each interval of ten millimicrons represents the average of five readings on the color analyzer. Of the fourteen indicators studied the curves for cresolphthalein

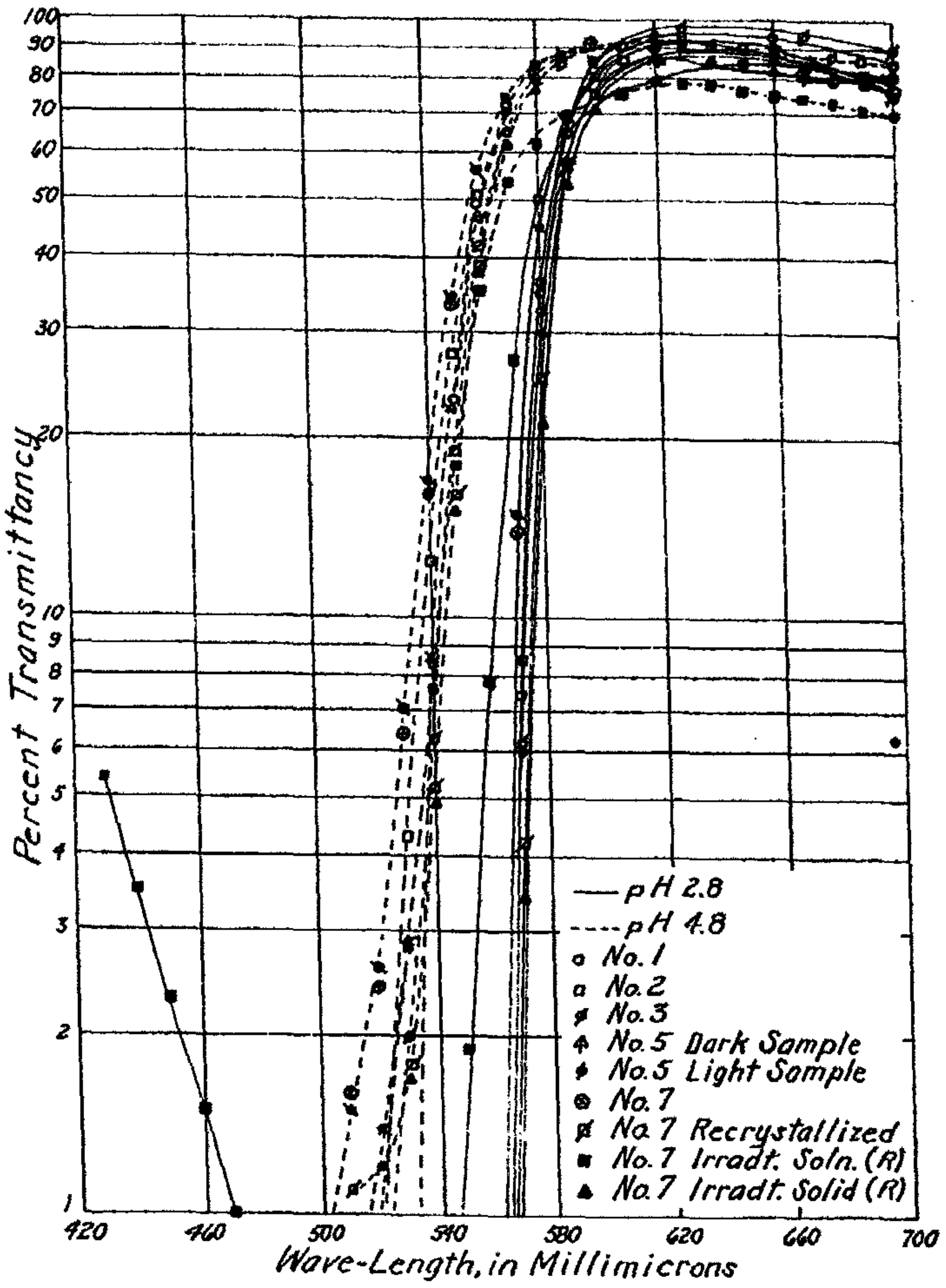

Fig. 1

METHYL ORANGE. Curves showing the effect of different samples and different conditions on the spectral transmittancy values for a 5 cm. tube containing a solution made by diluting one ml. of a 0.1 percent solution to 50 ml. with a buffer solution.

alone have been omitted since they checked each other so closely. On all the graphs a given number of curve, as No. 1, refers to the product of the same manufacturer.

It may be mentioned that similar spectral transmission curves have already been published[19,4,5,9] for individual samples of practically all of the indicators studied, but in these cases the object was not to determine spectrophotometrically differences of color.

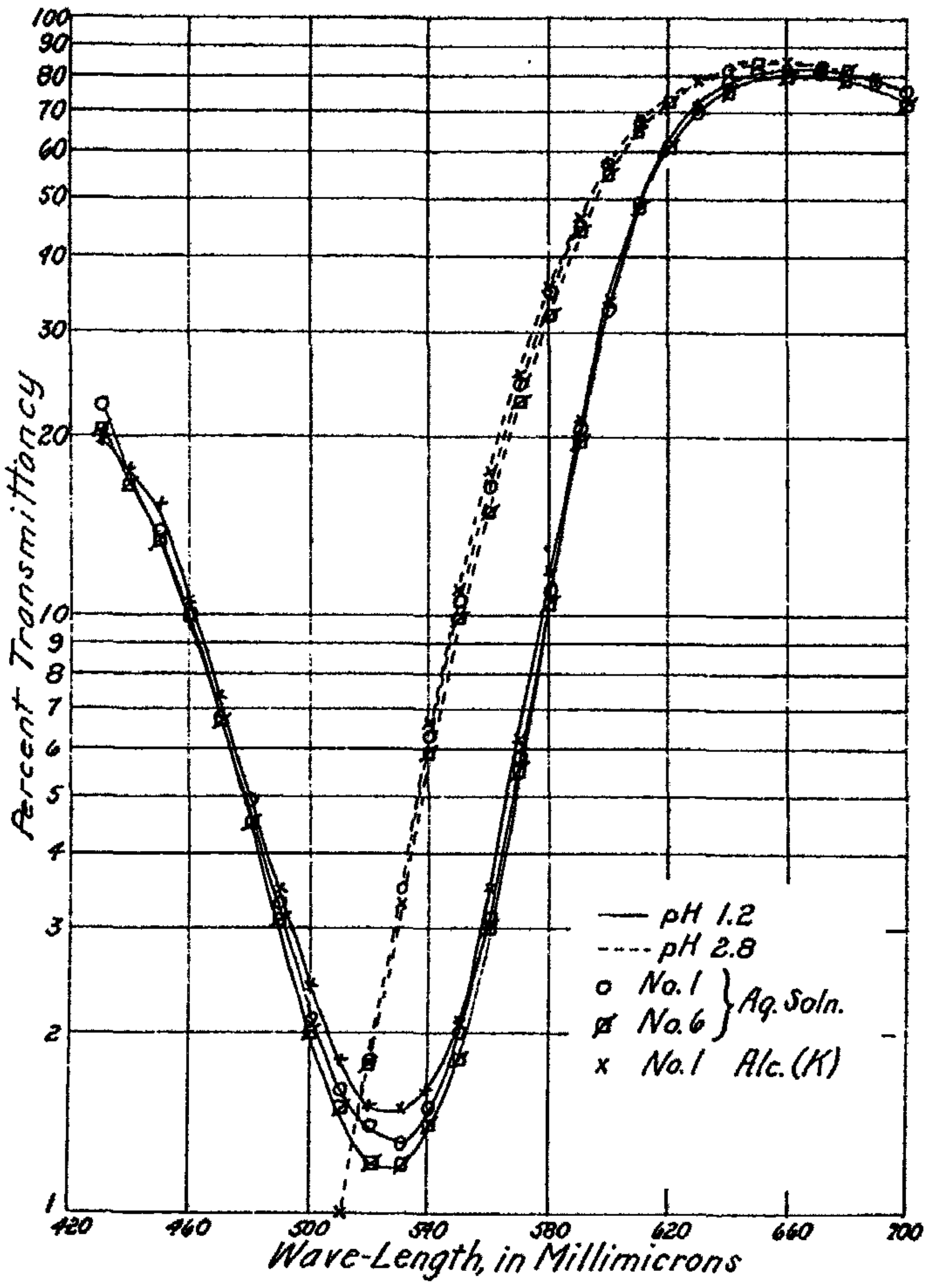

FIG. 2

TROPAOLIN OO. Curves showing the effect of different samples and different conditions on the spectral transmittancy values for a 5 cm. tube containing a solution made by diluting one ml. of a 0.1 percent solution to 50 ml. with a buffer solution.

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[19] Brode: J. Am. Chem. Soc., 46, 581 (1924); Mellon and Martin: Ref. 18; Baker and Davidson: Phot. J., 62, 375 (1922); Gibbs and Shapiro: J. Am. Chem. Soc., 50, 2798 (1928).

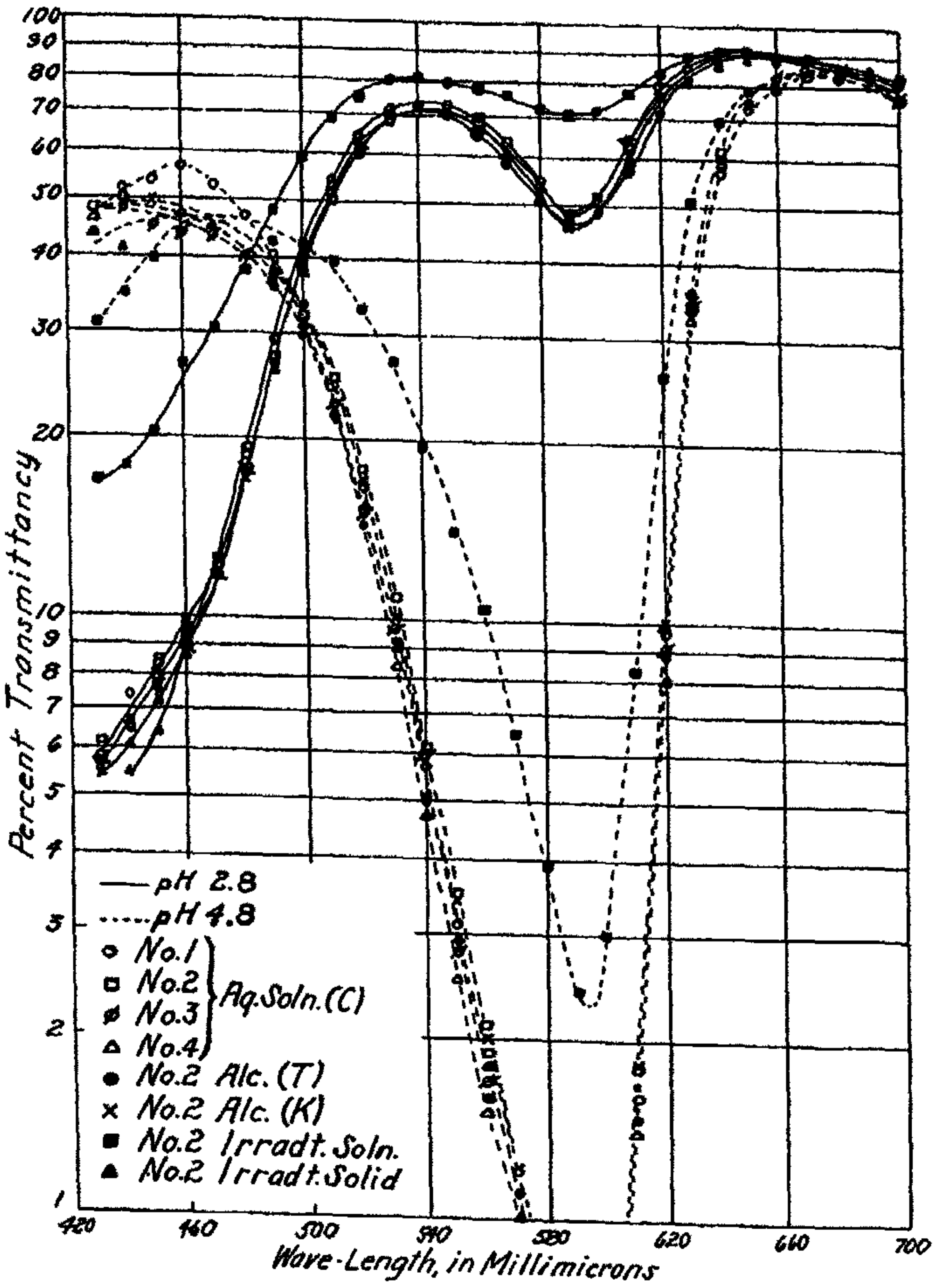

Fig. 3

BROM PHENOL BLUE. Curves showing the effect of different samples and different conditions on the spectral transmittancy values for a 5 cm. tube containing a solution made by diluting one ml. of a 0.04 per cent solution to 50 ml. with a buffer solution.

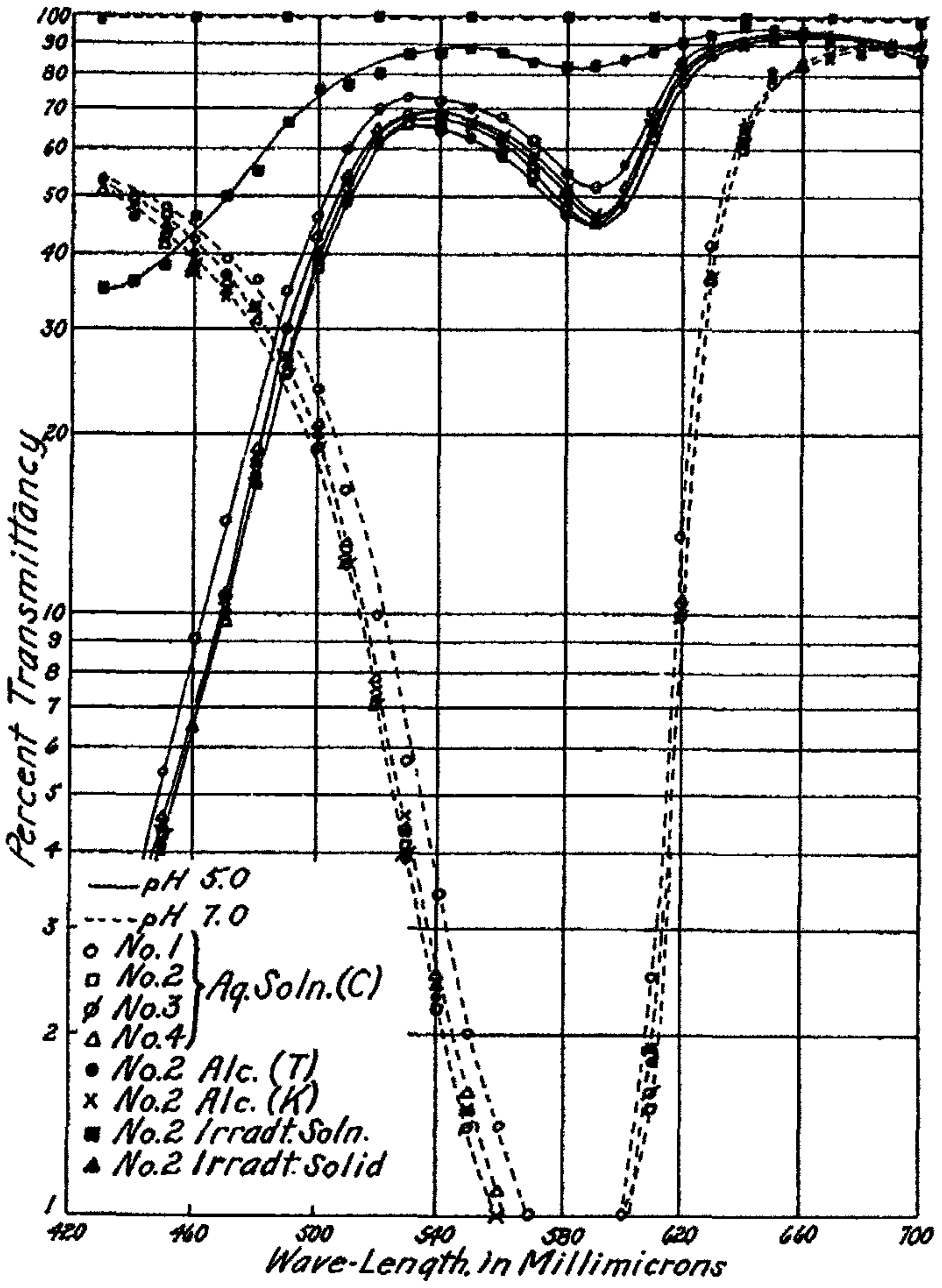

Fig. 4

BROM CRESOL PURPLE. Curves showing the effect of different samples and different conditions on the spectral transmittancy values for a 5 cm. tube containing a solution made by diluting one ml. of a 0.04 percent solution to 50 ml. with a buffer solution.

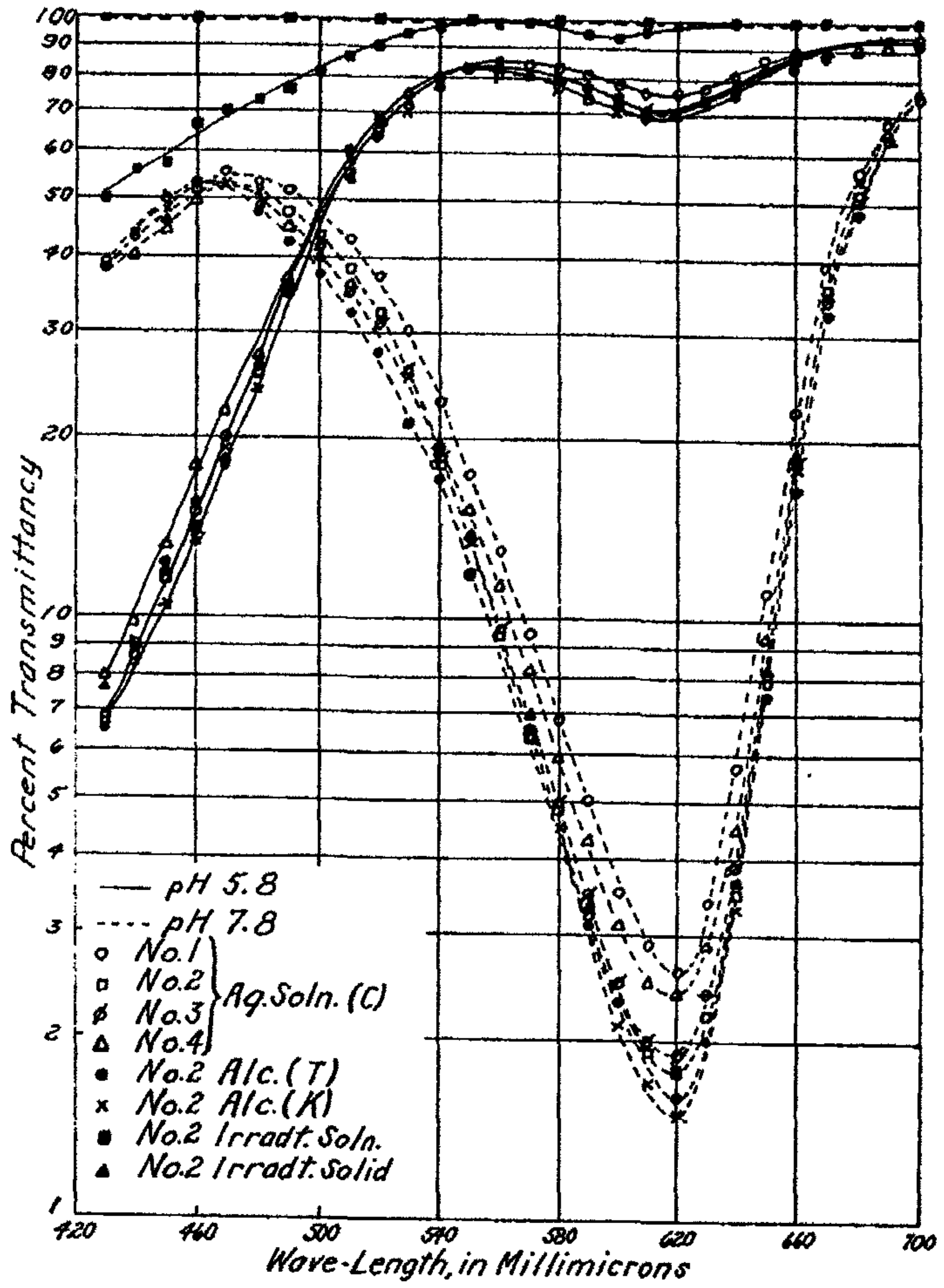

Fig. 5

BROM THYMOL BLUE. Curves showing the effect of different samples and different conditions on the spectral transmittancy values for a 5 cm. tube containing a solution made by diluting one ml. of a 0.04 percent solution to 50 ml. with a buffer solution.

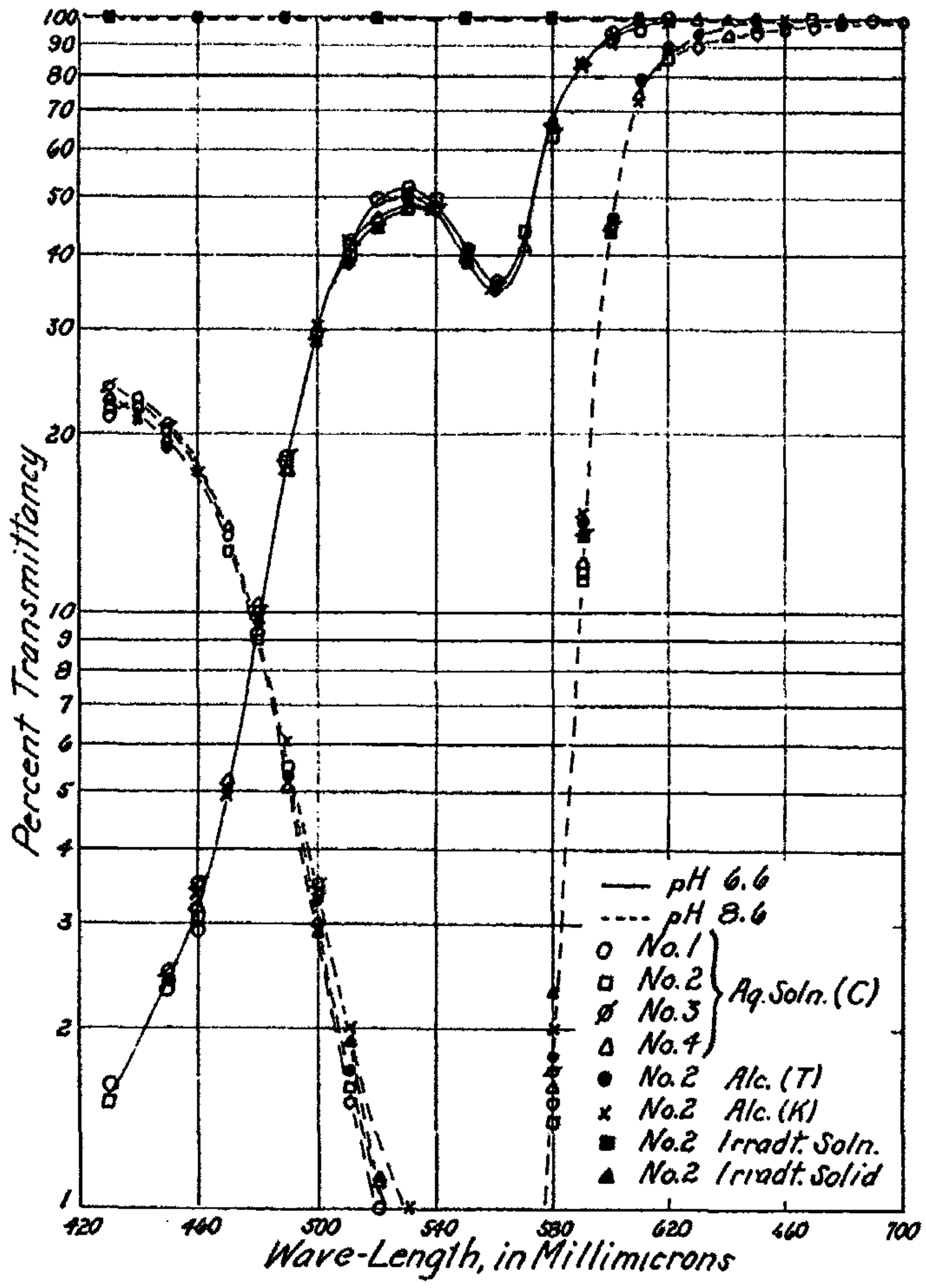

Fig. 6

PHENOL RED. Curves showing the effect of different samples and different conditions on the spectral transmittancy values for a 5 cm. tube containing a solution made by diluting one ml. of a 0.04 percent solution to 50 ml. with a buffer solution.

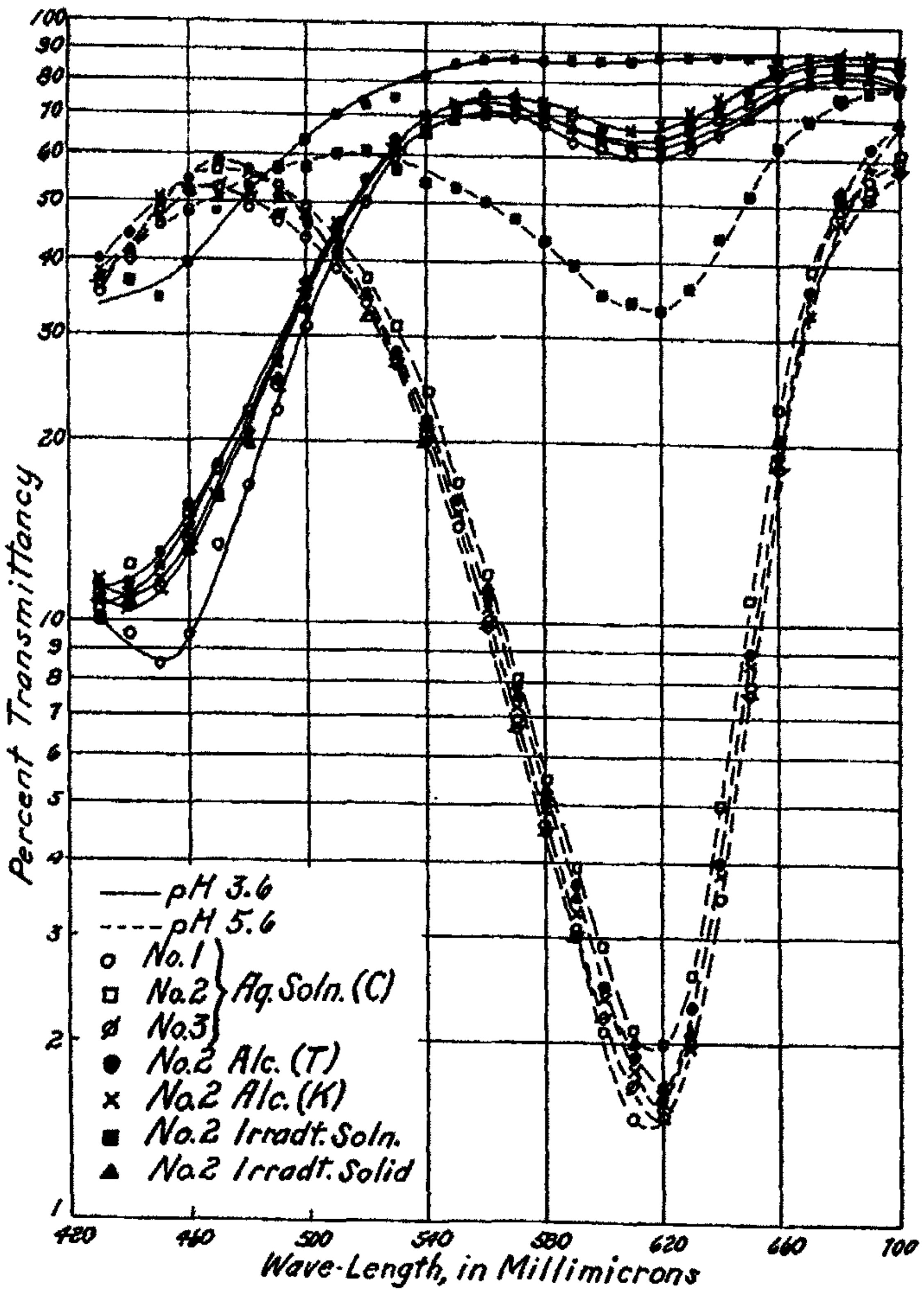

Fig. 7

BROM CRESOL GREEN. Curves showing the effect of different samples and different conditions on the spectral transmittancy values for a 5 cm. tube containing a solution made by diluting one ml. of a 0.04 percent solution to 50 ml. with a buffer solution.

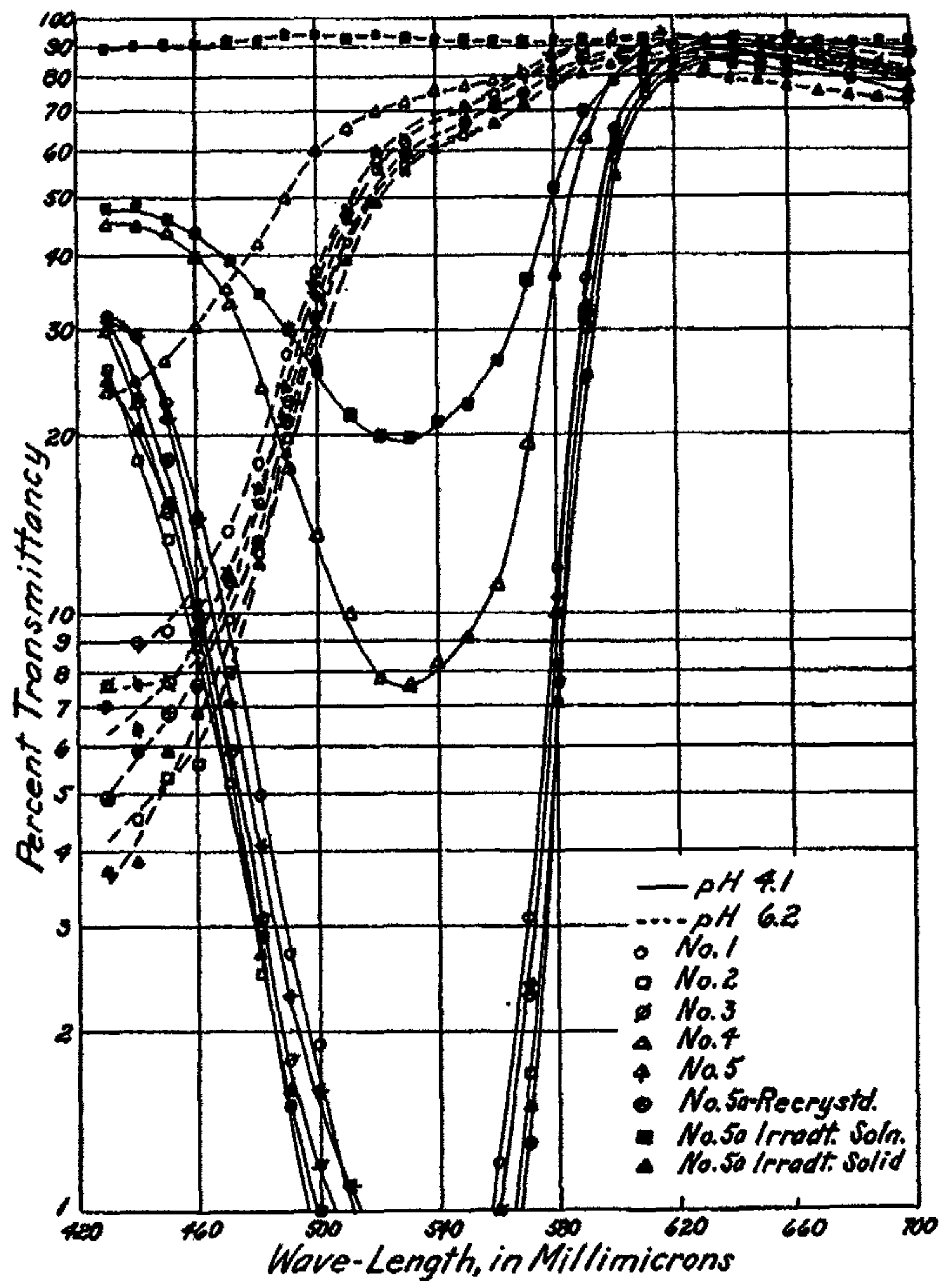

FIG. 8

METHYL RED. Curves showing the effect of different samples and different conditions on the spectral transmittancy values for a 5 cm. tube containing a solution made by diluting one ml. of a 0.02 percent solution to 50 ml. with a buffer solution.

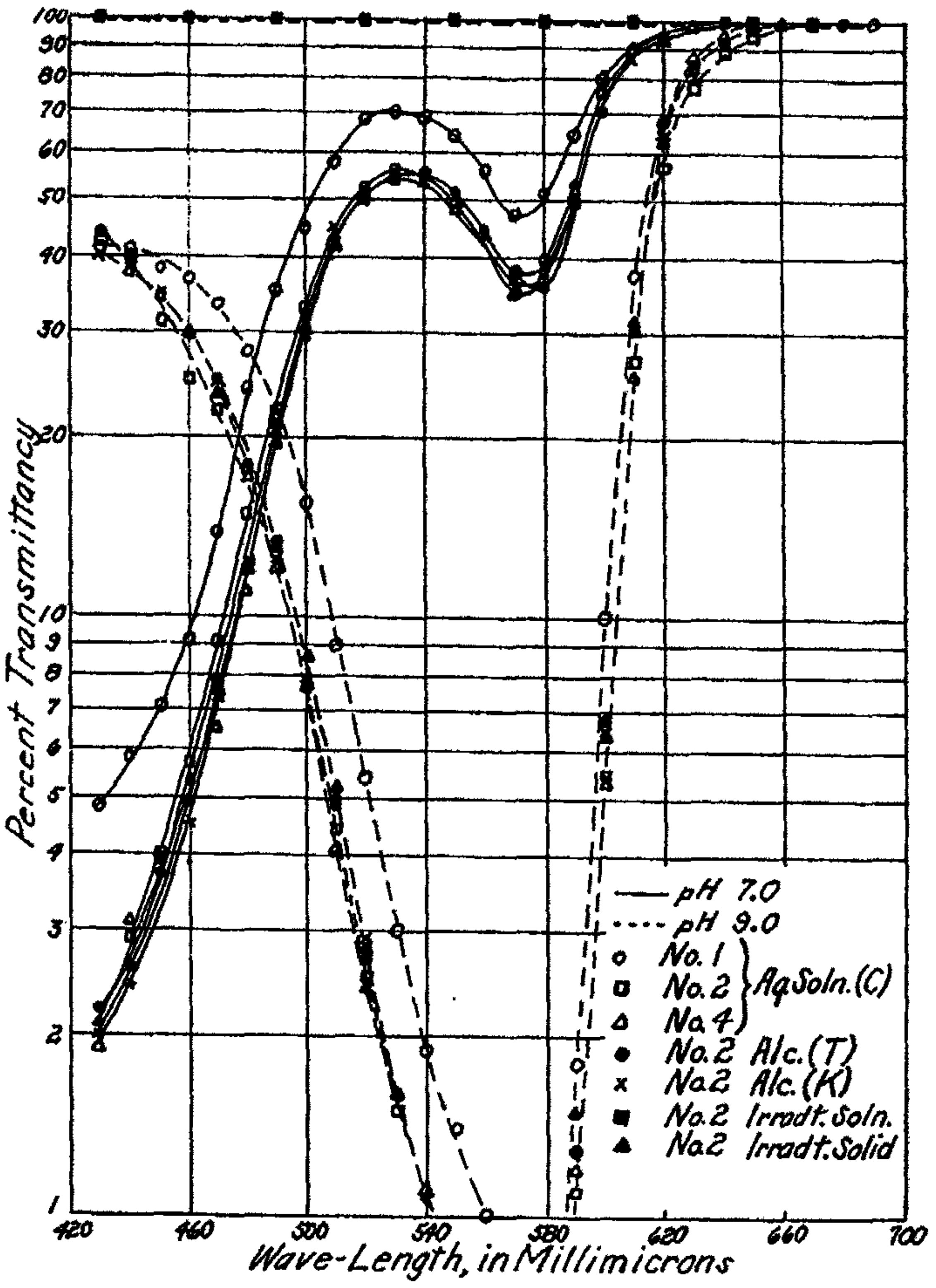

Fig. 9

CRESOL RED. Curves showing the effect of different samples and different conditions on the spectral transmittancy values for a 5 cm. tube containing a solution made by diluting one ml. of a 0.04 percent solution to 50 ml. with a buffer solution.

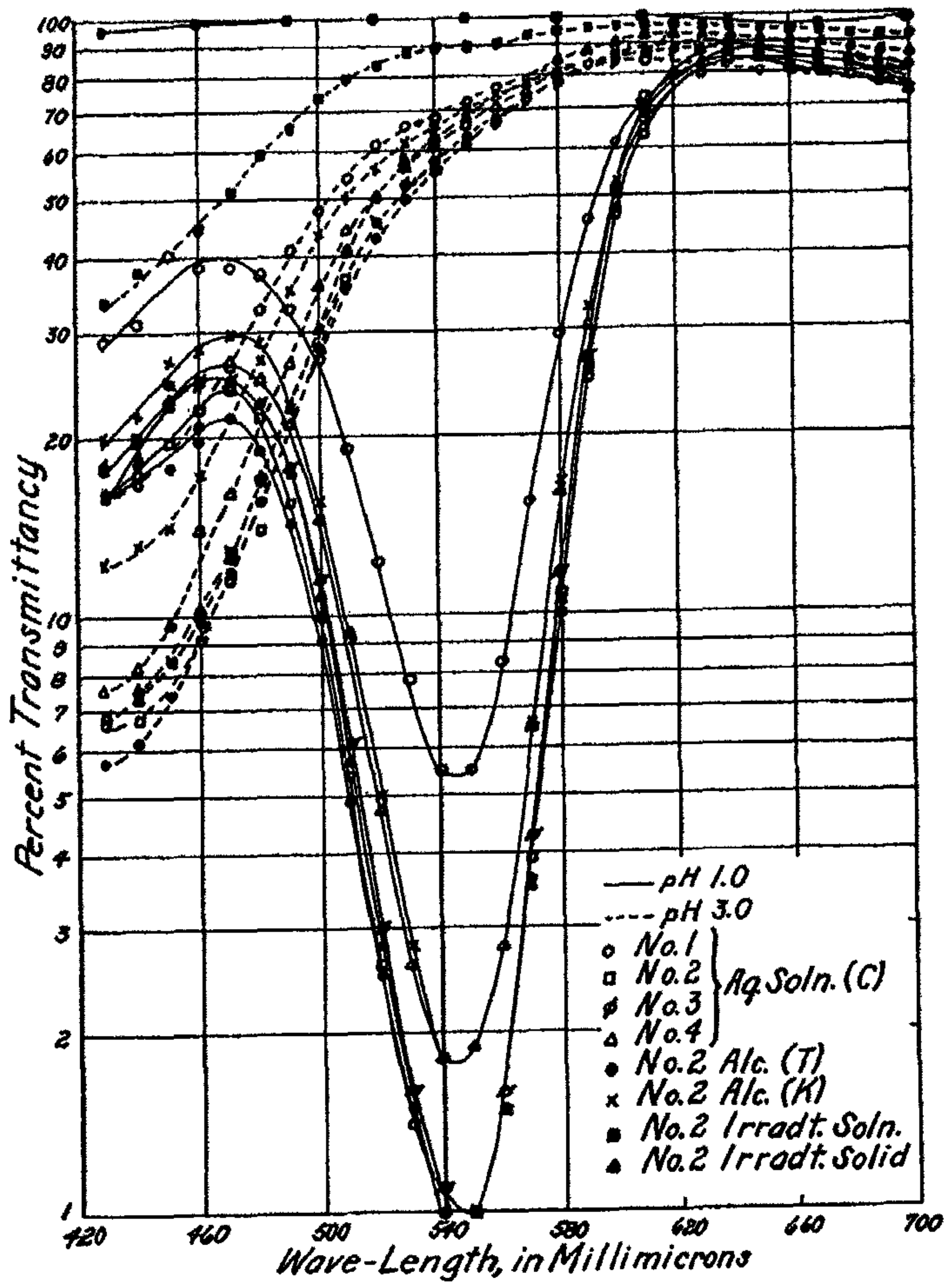

FIG. 10

THYMOL BLUE. Curves showing the effect of different samples and different conditions on the spectral transmittancy values for a 5 cm. tube containing a solution made by diluting one ml. of a 0.04 percent solution to 50 ml. with a buffer solution.

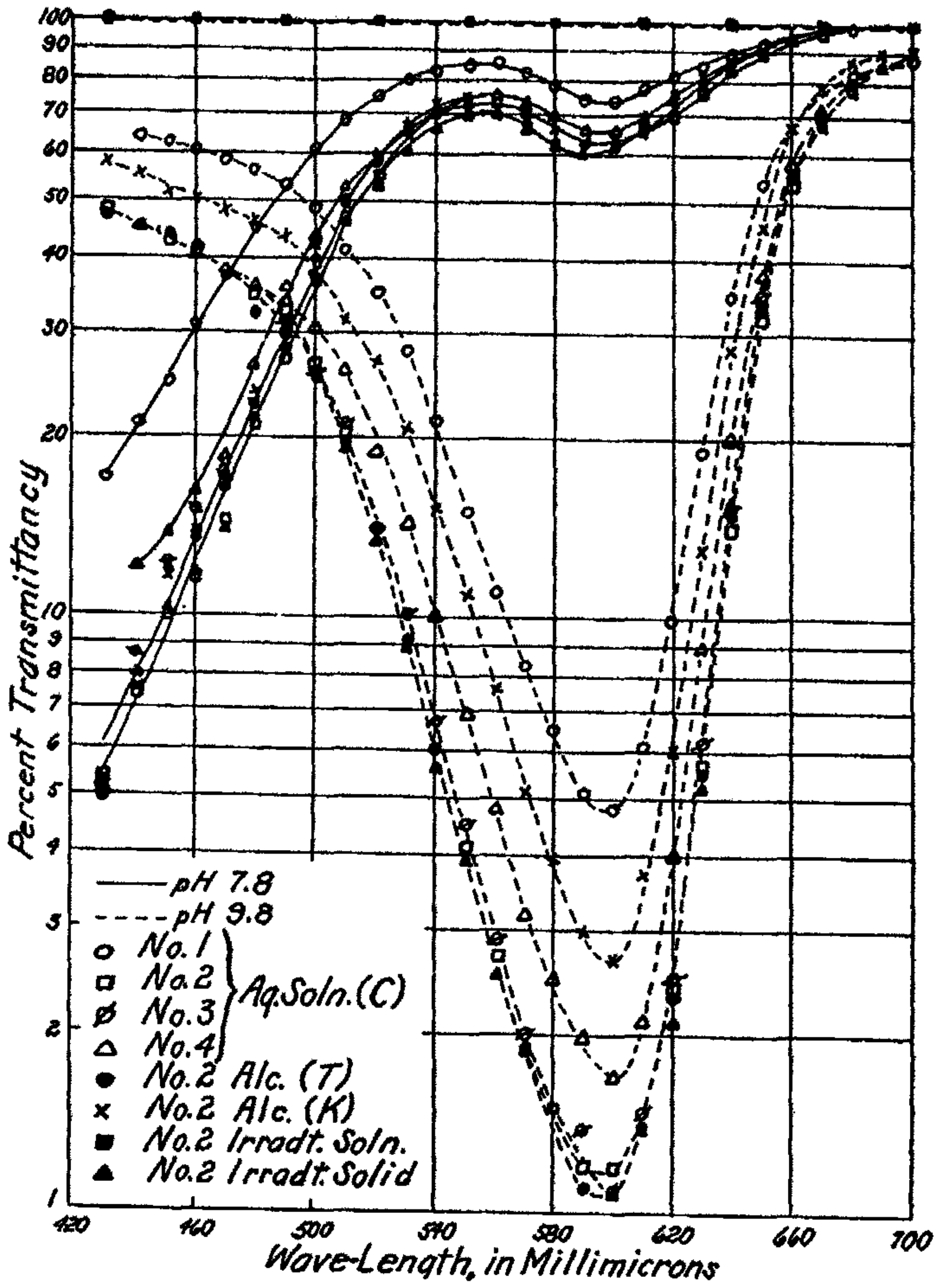

FIG. 11

THYMOL BLUE. Curves showing the effect of different samples and different conditions on the spectral transmittancy values for a 5 cm. tube containing a solution made by diluting one ml. of a 0.04 per-cent solution to 50 ml. with a buffer solution.

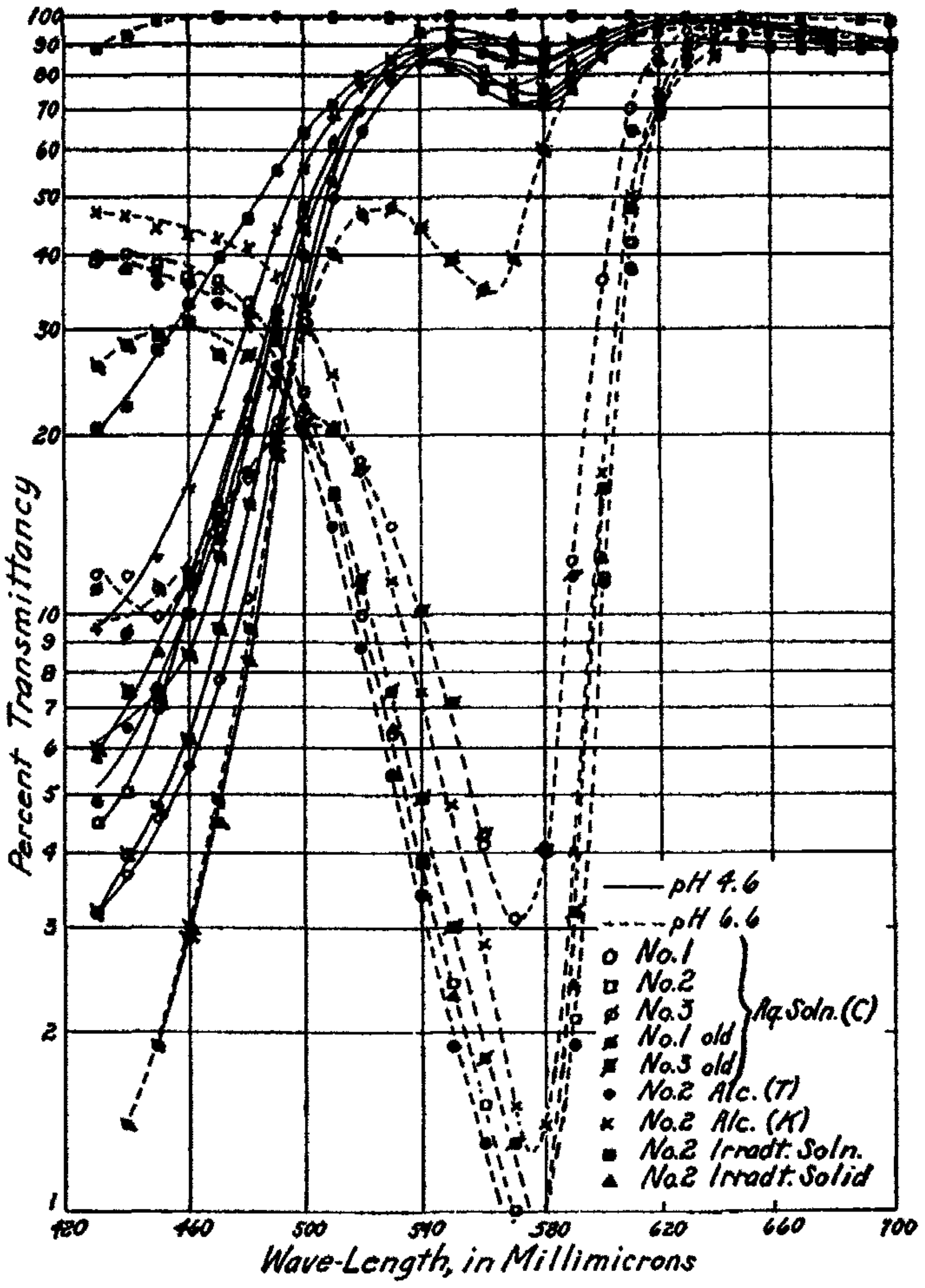

FIG. 12

CHLOR PHENOL RED. Curves showing the effect of different samples and different conditions on the spectral transmittancy values for a 5 cm. tube containing a solution made by diluting one ml. of a 0.04 percent solution to 50 ml. with a buffer solution.

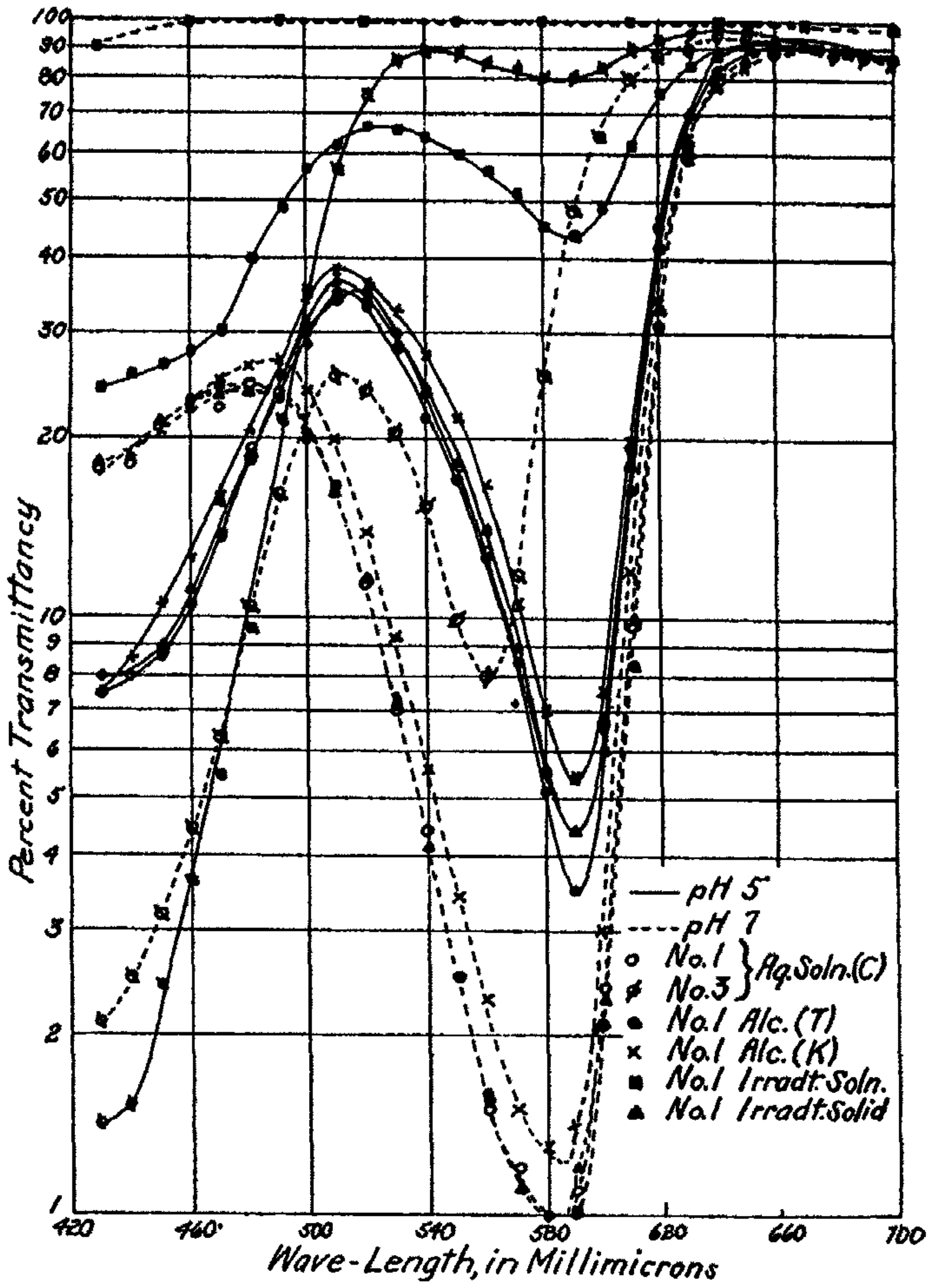

FIG. 13

BROM PHENOL RED. Curves showing the effect of different samples and different conditions on the spectral transmittancy values for a 5 cm. tube containing a solution made by diluting one ml. of a 0.04 percent solution to 50 ml. with a buffer solution.

Discussion

For the purpose of the present investigation it seemed that curves coordinating transmittancy and wave length would be of most value as a basis for formulating conclusions. If two solutions, for example, yield curves practically superimposable upon each other, within the limits obtainable with the spectrophotometer used, one may conclude that the samples exhibit the same color. But if there is a marked divergence between the curves for two different solutions, this fact in itself is definite evidence of divergence in the colorimetric characteristics of the two systems. Obviously, the spectrophotometric curves show merely whether there is a difference between samples; where a difference is found little direct evidence is provided to indicate the cause.

Having in mind that our present interest is in the divergence of the curves for any given indicator, we may consider the data from the view point of several different factors thought to be of possible significance in connection with the use of indicator solutions. These factors are discussed separately below.

Effect of Ultraviolet Radiation. The chief visible effect of ultraviolet radiation on the solid indicators was to cause considerable darkening during exposure of brom phenol blue, brom cresol green, brom cresol purple, and brom thymol blue. Solutions of the exposed solids gave curves which were practically identical with those for the solutions of the unexposed solids. Any differences of appearance of the irradiated solids did not extend to the hue of the solutions. In view of the effect on the solutions, however, perhaps a longer exposure would have produced more significant results.

Fading, varying from an almost negligible amount to a complete disappearance of hue, occurred in all of the solutions which were exposed to ultraviolet radiation. Absence of color would indicate the destruction in the solution of whatever had been functioning in the system as a selective absorber of visual radiation. Such effects raise the question of the possible action of sunlight on any solutions found to be sensitive to ultraviolet radiation.

Effect of the Method of preparing the Solutions. From a study of the curves it is evident that differences in the method of preparing the indicator solutions had no appreciable effect in the case of tropaolin OO, brom phenol blue, brom cresol green, brom cresol purple, brom thymol blue, phenol red and cresol red. Only one kind of solution was used for methyl orange, methyl red and cresolphthalein.

For the remaining indicators the curves obtained for the different solutions varied more or less. In most cases the solutions prepared according to Taub's method compare quite favorably with those prepared following Clark's directions. Those prepared according to Kolthoff's suggestion varied to a greater or less extent from those prepared by the other two methods. From the curve it would seem that the small amount of alcohol used in preparing the solutions made no appreciable difference in the color. It is a question whether the variations in the solutions prepared by Kolthoff's method were due to the absence of sodium hydroxide in the stock solutions or to the presence of alcohol. Since the solutions prepared by Taub's method contained alcohol and agreed fairly well with those prepared by Clark's method, it is reasonable to assume that the differences are connected with the neutralization of the indicator in preparing the solutions, rather than with the presence of the alcohol.

Effect of the Source of the Indicators. The appearance of the solid indicators from the different sources varied considerably. While these differences were quite marked, they did not extend to the solutions; in fact, some of the solids appearing most nearly alike showed the greatest variation in their spectral transmission curves.

The curves for the different samples of methyl orange, tropaolin OO, brom phenol blue, brom cresol green, brom cresol purple, phenol red, and cresolphthalein, compare quite favorably with each other. The small variations in these indicators would probably be of no significance in the colorimetric determination of pH values. The remaining indicators, presenting variations more or less marked, are considered individually.

For methyl red the agreement was fairly good with the exception of one old sample (more than five years) and of the region of shorter wave lengths at pH 6.2.

For thymol blue, at both sets of pH values, two samples stand out as being different in color. One of these (No. 4) was an old sample.

The curves for chlor phenol red show the widest variation, especially at the higher pH value and for one old sample (No. 1). Qualitative tests on this sample showed its pH range to be approximately 6.4 to 7.6 instead of the normal range of 4.8 to 6.4. Thus, the hue of the solution was still yellow at a pH value where it should have been fully red*.

The two available samples of brom phenol red, one of which was old (No. 1), gave curves quite different from each other. In connection with this indicator, as also with chlor red phenol, it may be mentioned that the manufacturer of the old sample stated it is their belief that results, such as those encountered with chlor phenol red, may be due to a decomposition of the indicator or to an incomplete halogenation at the time of preparing the solid material. In the present instance the old sample of chlor phenol red was not showing its normal transformation range at the time of purchase.

For brom thymol blue the chief variation occurred, curiously, at the minimum point for the higher pH value.

For cresol red one sample stands out as having a high transmittancy. In all such cases it may be kept in mind that a high transmittancy means that the solution is absorbing less visible radiation and hence may be referred to as being paler or having a higher relative brilliance. Presumably such a solution contains a smaller concentration of the selective absorber due to the lower degree of purity of the solid indicator.

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* Harden has just published [J. Am. Chem. Soc., 52, 4611 (1930)] a note regarding variations in different samples of chlor phenol red.

Summary and Conclusions

As a result of the foregoing spectrophotometric study of certain indicators, it may be concluded, on the basis of the curves obtained, that the source of the compounds, the method of preparing their solutions, and the action of ultraviolet radiation upon the latter are all of more or less significance in affecting the color of the solutions. These effects vary with the different compounds, but in general the actions may be summarized as follows:

1. The decolorizing effect of ultraviolet radiation on buffer solutions of indicators shows their photochemical sensitivity. In view of this action, and of the change in hue of some of the solids on irradiation, such systems probably should be protected from strong sources of photochemically active radiant energy.

2. Differences in the method of preparing the indicator solutions may have an observable effect upon the hue obtained. It would seem advisable, therefore, to specify a uniform method of preparing such solutions whenever any variation would be liable to produce significant variations in the results obtained with the use of the indicator.

3. Indicators from different sources may show considérable variation in the color of their solutions. Whatever may be its cause, the fact of this variation's occurrence makes necessary a careful inspection of any sample intended for use wherever the several attributes of color, hue, relative brilliance, and colorimetric purity, must have definite values, as in the possible preparation of permanent colorimetric standards to match indicator solutions. For any work of this kind indicators should meet definite specifications.

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THE DECOMPOSITION OF DIETHYL ETHER IN CONTACT WITH PLATINUM AND TUNGSTEN

BY H. AUSTIN TAYLOR AND M. SCHWARTZ[1]

The recent theories that have been suggested to account for the existence of homogeneous unimolecular gas reactions have as their basic principle the fact that the loss of activated molecules due to reaction must be compensated for in one way or another. The number of active molecules must of necessity be a constant fraction of the reactant concentration for the reaction to be of first order. If the temperature of the reactant as a whole be raised, a point may be reached where the Maxwellian distribution will provide active molecules at a rate sufficient to allow reaction to proceed with a measurable velocity. Alternatively, it should be possible to supply this necessary concentration of active molecules in an atmosphere, otherwise relatively cold, by furnishing a source from which molecules could absorb energy, for example by collision with a heated filament.

Such a condition would appear the more probable if the view first suggested by Lindemann[2] to account for unimolecular reactions be adopted. On this view the molecule may become activated by collision with other molecules but possesses a mean life before reaction. Such a condition would be favored by complexity of the molecule since energy may then be stored in a large number of degrees of freedom. Complex molecules therefore would appear to be able to maintain rheit necessary energy above the average for some time after the instant of having received it, whatever the actual mechanism of the reception may have been.

Under the conditions postulated then, the reaction would appear to be homogeneous, that is, independent of the material forming the filament and would be of the same order and possess the same energy of activation as the reaction studied under the more normal conditions of higher temperature throughout the gas as a whole. Such would appear to be the explanation of the decomposition of acetone in contact with platinum recently studied by one of us.[3]

It should be emphasised at this stage that the above conditions must not be confused with those obtaining in typical heterogeneous reactions where a definite adsorption for a period of time must be postulated. Even the rather exceptional heterogeneous decomposition of nitrous oxide in contact with gold which Hinshelwood[4] has shown may be accounted for on the assumption that nearly every molecule striking the wire decomposes, is entirely different. In

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[1] Abstract from a thesis presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy at New York University.

[2] Trans. Faraday Soc., **17**, 598 (1922).

[3] Taylor: J. Phys. Chem., **33**, 1793 (1929).

[4] Proc. Roy. Soc., **108A**, 211 (1925).

this reaction, the homogeneous decomposition is bimolecular with an energy of activation of 58,500 calories per two moles, whilst on platinum and gold the reactions are of first order with energies of 32,500 and 29,000 calories respectively. In the acetone decomposition the energy of activation was the same in the truly homogeneous reaction as in the presence of the heated filament, the apparently heterogeneous condition.

The possibility of distinguishing between the two methods of obtaining the necessary concentration of active molecules, and at the same time actually confirming the correctness of the mechanism here suggested, presents itself in the existence of reactions whose velocities studied under the more usual conditions fall off as the pressure is decreased. The rate of production of active molecules by collision then becomes less than their rate of decomposition and the reaction is no longer unimolecular. Activation by a heated filament would not suffer from this peculiarity until probably much later in the course of the reaction or at much lower pressures. Unfortunately the decomposition of acetone has not been studied at low pressure so that a test of the above could not be applied in that case. For that reason the decomposition of diethyl ether was studied in the above manner since it has been found[1] that below a pressure of about 150 mms. the velocity constant falls considerably, it being anticipated that no falling off would be observed under the changed conditions until much lower pressures were reached.

The apparatus and method of procedure was similar to that described in the previous work on acetone. The manometer and capillary connecting tubes were maintained at a temperature above the boiling point of the ether, whilst the reaction vessel was immersed in a thermostat at 35°C.

Measurements were made at four different temperatures using various initial pressures of ether. The total pressure increase obtained during the reaction at the various temperatures are shown in Table I.

TABLE I

Temp. ° C.	Total increase / Initial pressure	Temp. ° C..	Total increase / Initial pressure
846	2.17	942	2.42
892	2.34	968	2.45

The ratios are slightly larger than those observed by Hinshelwood but actually are closer to the 2.5 ratio to be expected on the basis of the assumed mode of decomposition.

$$C_2H_5OC_2H_5 = 2CH_4 + 1/2\ C_2H_4 + CO$$

In all probability then the decomposition is the same as that in the homogeneous reaction. Table II gives the times in minutes observed for 25, 50 and 75 percent decomposition.

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[1] Hinshelwood: Proc. Roy. Soc., **114A**, 84 (1927).

TABLE II

Initial pressure (mms)	t_{25}	t_{50}	t_{75} mins.
A. Temperature 846° C.			
160	3.6	9.8	20.3
171	3.5	9.4	21.5
184	3.5	9.7	23.0
196	3.4	9.5	22.0
205	3.5	9.6	22.5
217	3.4	9.2	21.5
Mean	3.5	9.5	21.8
B. Temperature 892° C.			
149	1.2	3.2	8.2
160	1.2	3.4	8.3
173	1.2	3.4	8.5
186	1.2	3.3	8.2
196	1.2	3.2	8.0
206	1.2	3.2	8.0
Mean	1.2	3.3	8.2
C. Temperature 942° C.			
142	.43	1.1	2.8
153	.42	1.2	2.8
165	.45	1.2	2.9
177	.43	1.2	3.0
192	.46	1.2	2.9
199	.42	1.1	2.8
Mean	.44	1.2	2.9
D. Temperature 968° C.			
134	.27	.70	1.8
146	.26	.69	1.7
157	.25	.69	1.7
173	.25	.68	1.6
186	.26	.66	1.6
196	.27	.64	1.5
Mean	.26	.68	1.7

The obvious constancy of these times over the pressure range studied is ample evidence of the unimolecular nature of the reaction. The constancy of the three-quarter life is especially remarkable, and would suggest that a constant value would be obtained for calculations of the velocity constant. Table III shows the results obtained in a typical determination.

TABLE III

Temperature 846° C. Initial Pressure 205 mms.

Time (mins)	Pressure Increase (mms)	k	Time (mins)	Pressure Increase (mms)	k
1	39	.0919	25	347	.0609
2	71	.0872	30	368	.0588
3	99	.0842	35	382	.0563
4	123	.0811	40	395	.0551
5	145	.0791	50	412	.0526
7	183	.0759	60	425	.0525
10	229	.0726	70	435	.0549
15	284	.0681	80	442	0675
20	321	.0642			

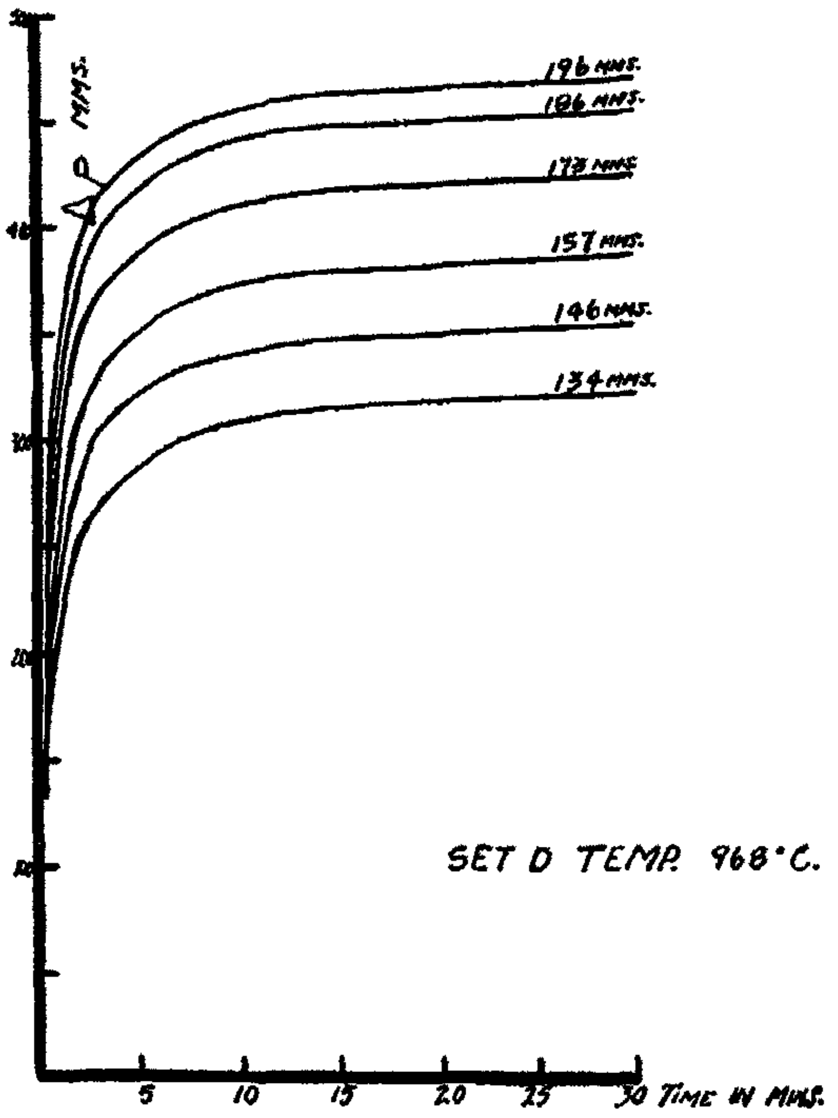

FIG. 1

The value of k the unimolecular velocity constant, it will be observed, falls steadily as the reaction proceeds, even in the first few minutes of reaction. One might be tempted to account for this on the basis that the reaction was deviating from its unimolecular nature as the reactant concentration decreased. In view however of the constancy of the three-quarter life such an explanation is hardly tenable. What appears more probable is that the reaction is not a simple one but is probably composed of two simultaneous unimolecular reactions each with its own velocity constant. Such might account also for the deviation observed between the total pressure increase and that theoretically to be expected.

The results obtained for the rate of pressure increase with time are shown in a typical case in Fig. 1.

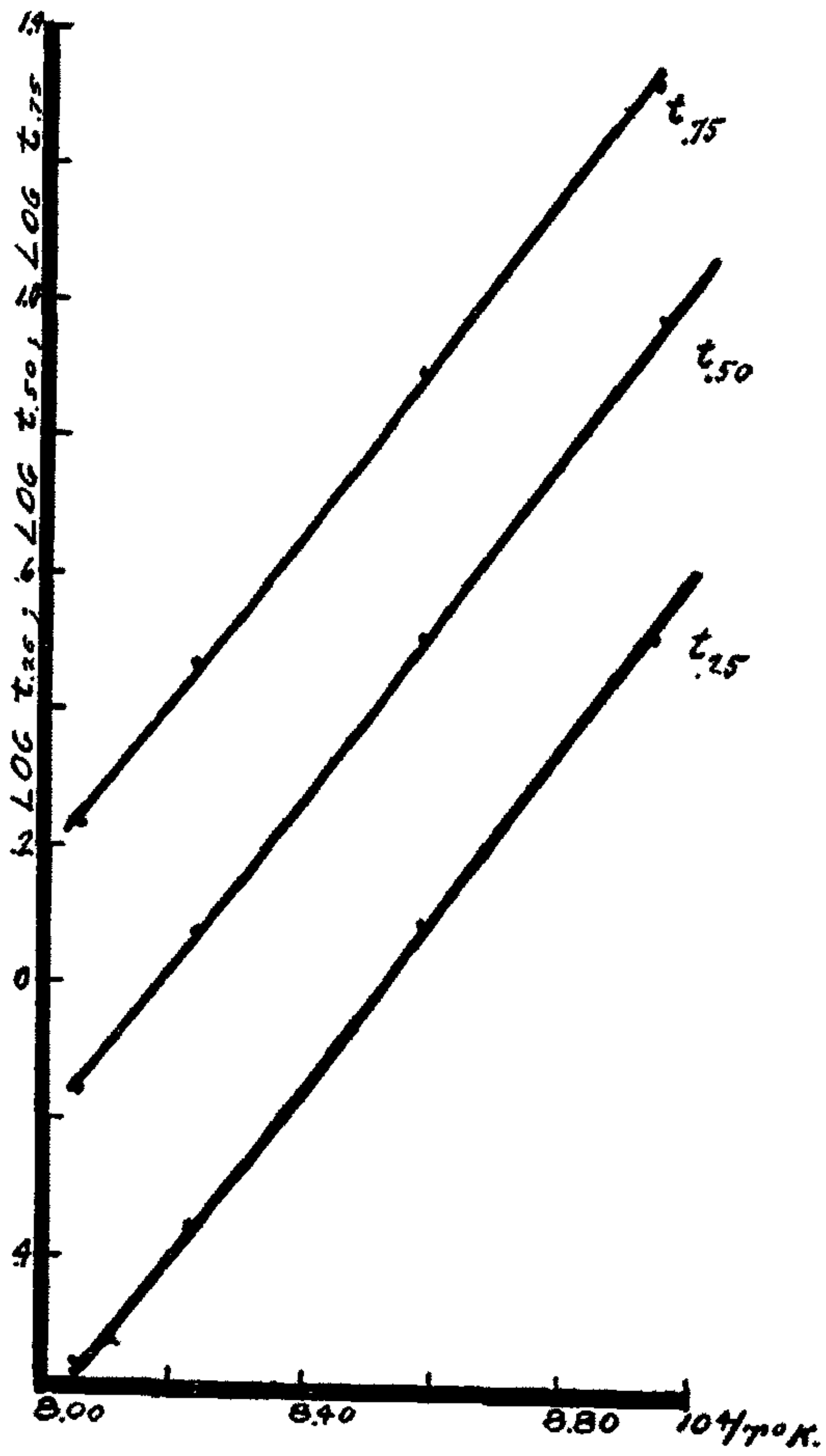

FIG. 2

The calculation of the heat of activation from the times of quarter, half and three-quarter decomposition give the results shown in Table IV.

TABLE IV

Sets	Energy of Activation from t_{25}	t_{50}	t_{75}
A-B	58,200	58,200	54,000
B-C	57,250	57,250	58,500
C-D	55,100	59,900	55,100

Fig. 2 shows the straight lines obtained by plotting the logarithm of the time against the reciprocal of the absolute temperature. The average energy of activation is 57,000 calories which is at least of the same order of magnitude as that obtained by Hinshelwood namely 53,000. The difference however would appear to be outside the limits of experimental error. In order to determine therefore whether this deviation was due in any way to the presence of platinum in the system the experiments were repeated using a tungsten filament. It was found that the results were not as reproducible with tungsten as with platinum since experience showed that if the tungsten filament was allowed to glow during evacuation of the reaction vessel marked evaporation of tungsten occurred and the characteristics of the wire changed considerably. It was necessary then to evacuate with the filament cold and probably therefore the surface conditions were not as reproducible as in the case of platinum since it must be remembered that carbon monoxide is one of the products of decomposition.

Measurements were again made at four different temperatures. The tungsten was of approximately the same diameter as the platinum previously used, the temperatures with tungsten being higher than with platinum for a given speed of reaction.

Table V gives the times for 25, 50 and 75 percent decomposition.

TABLE V

E. Temperature 915° C.	t_{25}	t_{50}	t_{75} (mins)
157	3.0	9.3	21.5
170	3.2	9.3	22.0
182	3.2	9.7	22.7
Mean	3.1	9.4	22.1
F. Temperature 934° C.			
172	2.0	6.4	15.5
184	1.9	6.3	15.9
208	2.1	7.1*	17.5*
221	2.2	7.2*	17.0*
185	1.7*	6.3	15.5
Mean	2.1	6.3	15.7
G. Temperature 953° C.			
160	1.2	4.2	10.8
176	1.3	4.3	11.1
182	1.3	4.3	11.0
195	1.3	4.5	11.5
Mean	1.3	4.3	11.1
H. Temperature 973° C.			
159	.95	2.4	6.2
170	.89	2.8	7.5
184	.88	2.9	8.0
193	.92	2.9	8.0
Mean	.91	2.8	7.8

* Not included.

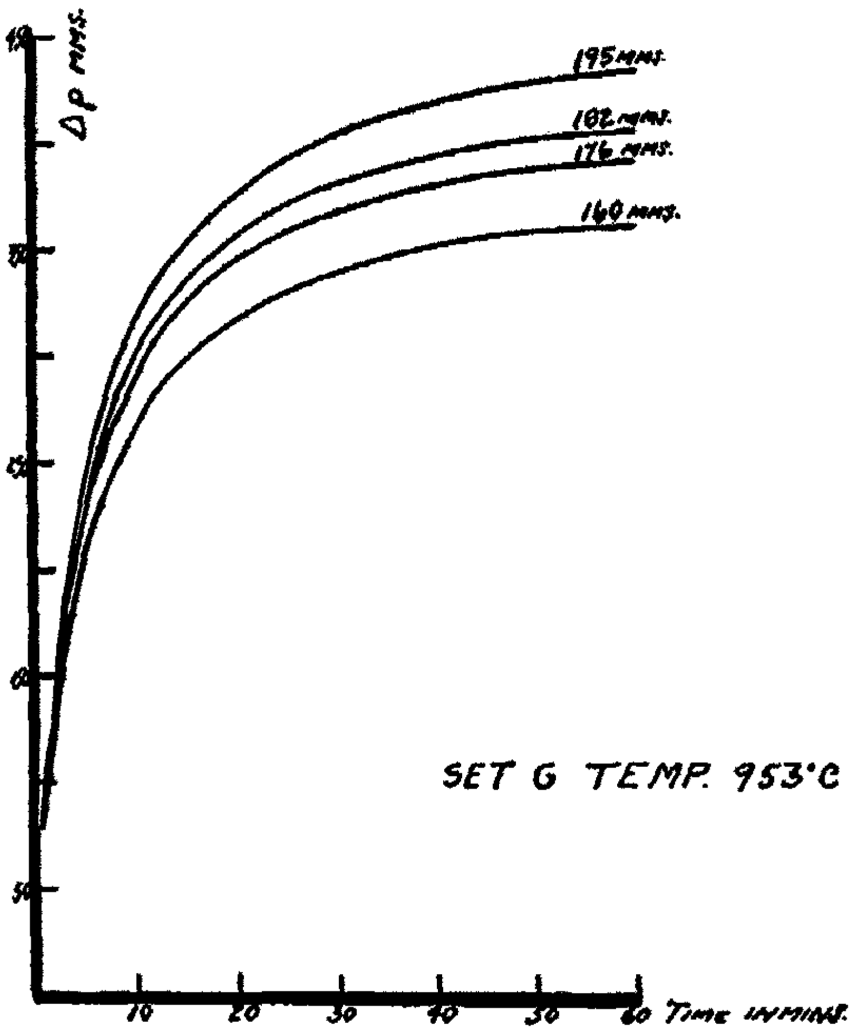

Fig. 3

The reaction again therefore is unimolecular. The velocity constants as in the case of platinum likewise exhibit a similar steady falling trend, shown in Table VI.

Table VI

Temperature 915° C. Initial Pressure 157 mms

Time (mins)	Pressure Increase (mms)	k
1	43	.134
2	67	.109
3	86	.097
4	102	.089
5	118	.085
7	147	.080
10	179	.074
15	220	.069
20	250	.066
25	270	.062
30	285	.060
40	305	.056
50	319	.054
60	328	.053
70	335	.056

No comparison can be made naturally between the actual values of the constants in the two cases of platinum and tungsten since each will depend on the specific dimensions of the apparatus. That the reaction however is probably the same in both cases may be seen from the similarity of the ratios of total pressure increase to initial pressure for tungsten as in Table VII, and those for platinum previously given.

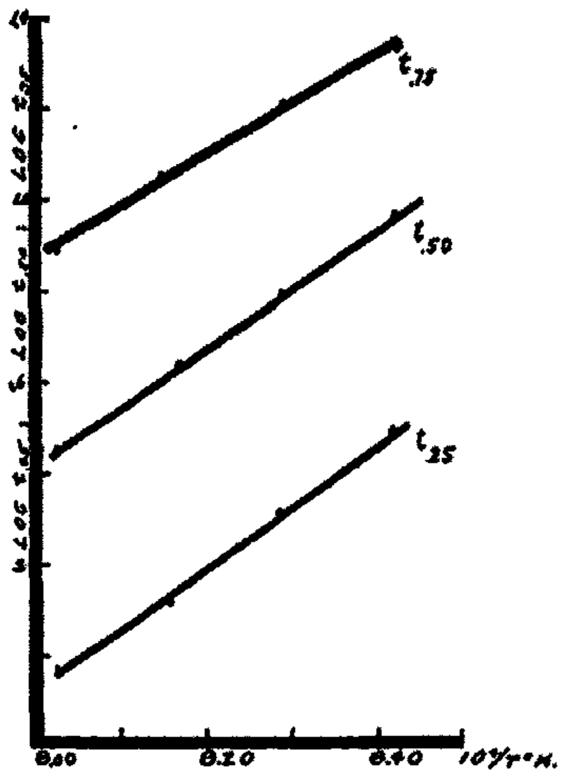

Fig. 4

TABLE VII

Temp. °C.	$\frac{\text{Total increase}}{\text{Initial pressure}}$	Temp. °C.	$\frac{\text{Total increase}}{\text{Initial pressure}}$
915	2.15	953	2.25
934	2.23	973	2.31

Fig. 3 gives a typical example of the pressure increase-time curves obtained using tungsten.

The calculation of the heat of activation from the times of 25, 50 and 75 percent decomposition as made previously for platinum gives an average value of 58,000 calories for tungsten as against 57,000 for platinum. The plot of the logarithm of the times against temperature is shown in Fig. 4.

There can be no doubt therefore that the reaction in presence of the heated filaments is truly homogeneous. The temperatures used were chosen so that the observed rate of reaction would be of the same order as those found by Hinshelwood, and it will be noted that there is no deviation from unimolecularity in the neighborhood of 150 mms. and in fact down to 100 mms.

This does not preclude the possibility that the constant might fall at still lower pressures or as Hinshelwood has shown, at comparable pressures when the total reaction rate is slower, that is, at lower temperatures.

The fact that the energies of activation for platinum and tungsten are in such good agreement is significant. Whether the discrepancy between the average value 57,000 calories here obtained and the 53,000 previously quoted is significant, cannot definitely be said. Judging from the change in the calculated energy of activation caused by an error of only five seconds in the time of 25 percent decomposition, the discrepancy would appear to be within the limits of error at least for tungsten where the reproducibility was not so good as for platinum.

TABLE VIII

Temperature °C.	Time for 50 percent pressure increase mins.	Heat of Activation
	Bulb No. 2.	
825	6.5	
800	11.0	49,300
775	17.8	43,100
750	28.6	40,500
725	76	79,400
700	164	59,400
	Bulb No. 1 secs.	
800	58	
750	192	52,300
700	585	44,000

There exists however the possibility that under the conditions used a molecule having become activated by collision with or proximity to the hot filament might, in passing into the colder atmosphere in the reaction bulb, radiate some of its energy. Such a molecule would require to absorb an energy greater than the critical energy in order that it should still have the necessary activation at the end of its active life before decomposition.

During the preparation of the manuscript for the above paper the authors[1] called our attention to a similar research. Their conclusions are in agreement with ours although their particular apparatus has allowed them to realise the deviation from unimolecularity at higher pressure. The energy of activation, 52,000 calories, obtained graphically by them would seem to be in closer agreement with Hinshelwood's value than ours. If however the values for

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[1] Steacie and Campbell: Proc. Roy. Soc., 128A, 451 (1930).

the various temperature intervals are calculated separately the agreement is seen to be fortuitous. Table VIII gives these values in detail.

It is obvious therefore that no particular stress can be laid on the absolute value of the energy term.

Summary

The decomposition of diethyl ether in presence of heated filaments of both platinum and tungsten has been shown to be identical with the ordinary homogeneous reaction. The presence of the filament serves merely to furnish the necessary stationary concentration of active molecules.

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THE ENERGY DIAGRAM OF SODIUM CHLORIDE

BY PIERRE J. VAN RYSSELBERGE

Introduction

In recent times, under the influence of various theories and experimental facts, such as the Lewis theory of valence, the results of the X-ray analysis of crystals, the properties of electrolytes, etc., it has been customary to consider salts of the type of sodium chloride as polar compounds. In such compounds the bond existing between the two constituents consists mainly of the electrical attraction of two oppositely charged ions. A crystal of sodium chloride is considered as a purely ionic lattice, in which the various ions are held together at definite distances from one another in a certain geometrical pattern because of the interplay of two kinds of forces: the Coulomb electrical forces and the Born repulsive forces of which the wave mechanics of Schrödinger has recently given an interpretation.[1] In solution, such a crystal dissociates into free ions which in dilute solutions obey, with a fairly good approximation, the laws of the Debye-Hückel theory of electrolytes. Departure from these laws has been explained by Bjerrum[2] as due to partial physical association. Using Bjerrum's terminology,[3] we say that a crystal of sodium chloride is completely ionized but also completely "associated" and that aqueous solutions of sodium chloride are completely ionized but partially "associated," or clustered.

Nernst and his co-workers,[4] on the basis of measurements of heats of dilution of strong electrolytes, were able to determine directly the degrees of association and the heat involved in the dissociation into single ions of those associated groups (Na-Cl, for instance) which if we choose to we may call neutral molecules. In order to explain these results it was found necessary to modify the Debye-Hückel theory in a fundamental way. The fact that the degrees of association found by Nernst and the resulting dissociation constants explain rather well the properties of mixtures of potassium and sodium chlorides[5] makes it plausible to suppose that in such solutions we are dealing with actual neutral molecules in which a pair of electrons is shared between the two atoms.

The existence of individual molecules of the alkali halides in the vapor state is obvious as shown for instance by the discussion of the photochemical decomposition of these molecules by Kistiakowsky.[6]

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[1] L. Pauling: J. Am. Chem. Soc., 49, 765 (1927); A. Sommerfeld: "Atombau und Spektrallinien. Wellenmechanischer Ergänzungsband," p. 116 (1929).

[2] N. Bjerrum: Det. Kgl. danske Vidensk. selskab. Math-fys. Medd., VII, No. 9 (1926).

[3] N. Bjerrum: Ber., 62B, 1091 (1929).

[4] W. Nernst: Z. physik. Chem., 135, 237 (1928).

[5] J. W. McBain and P. J. Van Rysselberge: J. Am. Chem. Soc., 52, 2336 (1930).

[6] G. B. Kistiakowsky: "Photochemical Processes," p. 31 (1928).

London[1] gives a method of deciding whether a compound is polar or homopolar. The expression

$$\Phi = E_\infty - \frac{z_+ z_- e^2}{r} \qquad (1)$$

represents the potential energy of the system of two ions (Na^+ and Cl^- for instance) for large values of r. E_∞ is the sum of the ionization energy of the cation and of the electroaffinity of the anion. z_+ and z_- are the valences of the two ions, e the elementary charge, r the distance between the centers of the ions.

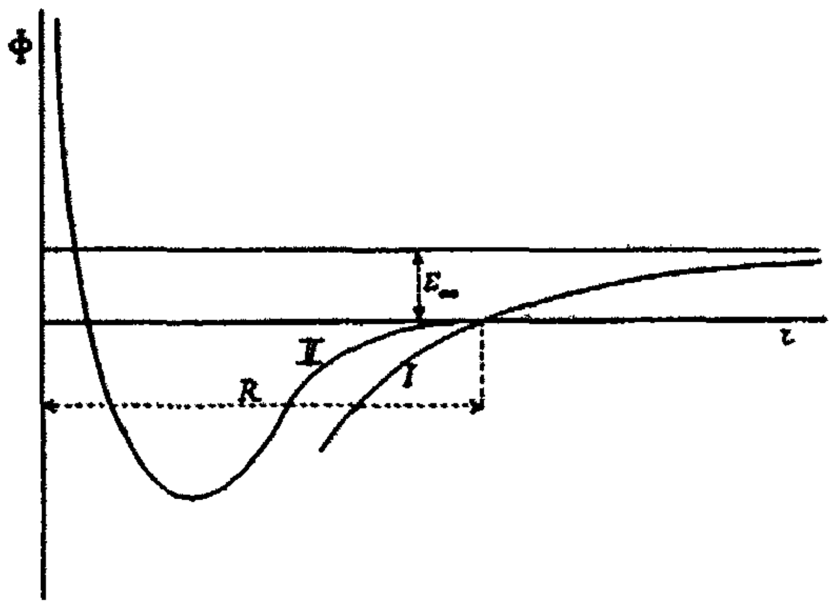

Fig. 1

For $\Phi = 0$ we have:

$$R = \frac{z_+ z_- e^2}{E_\infty} \qquad (2)$$

If we express E_∞ in volt electrons we obtain:

$$R = \frac{z_+ z_- \times 14.3}{E_\infty} \text{Å} \qquad (3)$$

The potential energy for the system of neutral atoms passes through a minimum, then coincides very rapidly with the horizontal axis. This is a generalization of the consequences of the theory of Heitler and London[2] explaining the formation of a molecule of hydrogen from two neutral atoms, on the basis of the perturbation theory of wave mechanics.

At the distance R given by equation (3) the curves corresponding to the ions (polar curve), I, and the one corresponding to the neutral atoms, II, intersect each other as shown on Fig. 1.

According to London, we have the following criterion: if the distance R is much larger than the known distance between two oppositely charged ions in the crystal, the compound is polar; if R is of the order of magnitude of the distance between the atoms in the molecule, the compound is homopolar.

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[1] F. London: Z. Physik, 46, 455 (1927).

[2] W. Heitler and F. London: Z. Physik, 44, 455 (1927).

London found, for instance, that hydrogen halides are probably homopolar, a conclusion already drawn by Franck,[1] and that alkali halides are decidedly polar. Another test to determine whether a compound is polar or non-polar is given by Pauling[2]: "if the internuclear equilibrium distance calculated for a polar structure with the aid of the known properties of ions agrees with the value found from experiment, the molecule is polar; the equilibrium distance for a shared electron bond would, on the other hand, be smaller than that calculated."

Williams[3] suggests that a compound like sodium chloride exists under two forms: a purely polar one and a homopolar one having a structure analogous to that of a hydrogen molecule, in which a pair of electrons with opposite spins is shared between the two atoms. According to the state (vapor, crystal or solution) of sodium chloride, variable amounts of both types of molecules are present. Such a picture would replace the idea of continuous transition from the homopolar to the polar bond, often proposed by chemists.

In the presence of these new ideas and of the rather uncertain views about the nature of chemical bonds, it seemed useful and important to us to determine a complete interaction energy diagram for sodium chloride, using trustworthy data on ionization potential, electroaffinity, heat of dissociation in the vapor state and in solution, crystal structure, etc. Such a diagram, besides being a novelty, brings into light a few interesting facts, as we proceed to show.

II. Gaseous Ions, Dissolved Ions. Ionization Potential, Electroaffinity

The difference between gaseous ions and dissolved ions has been clearly explained by Fredenhagen.[4] If we call dissolution energy the one corresponding to the transformation of a dissolved ion into a gaseous atom, ionization energy the one corresponding to the transformation of a gaseous atom into a gaseous ion, and solvation energy the one corresponding to the transformation of a dissolved ion into a gaseous ion, the following relation must hold[5]:

dissolution energy	+	ionization energy	=	solvation energy
dissolved ion		gaseous atom		dissolved ion
→gaseous atom		→gaseous ion		→gaseous ion

The dissolution energies should not be confused with the normal electrode potentials. The dissolution energy corresponds to the transformation of one gas atom into a dissolved ion, when the concentrations of the atoms in the gas phase and of the ions in the solution are equal.

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[1] J. Franck, H. Kuhn, and G. Rollefson: Z. Physik, **43**, 155; J. Franck and H. Kuhn: 169 (1927).

[2] L. Pauling: Proc. Nat. Acad. Sci., **14**, 359 (1928).

[3] A. T. Williams: Physik. Z., **31**, 367 (1930).

[4] K. Fredenhagen: Z. physik. Chem., **128**, 1, 239 (1927); **134**, 33 (1928); **140**, 65; **140**. 435; **141**, 195 (1929).

[5] See specially: K. Fredenhagen: Z. physik. Chem., **140**, 69 and seq. (1929).

In the case of Na and Cl, we have the energy relationships given by Fig. 2. 5.13 V. is the ionization potential of sodium, 3.7 V. is the electroaffinity of chlorine. If we consider as a reference energy that corresponding to a system composed of neutral sodium and chlorine atoms in the gaseous state, the system gaseous Na^+ + gaeous Cl^- will have an energy content of:

$$5.13 - 3.70 = +1.43 \text{ V. e.}$$

The system dissolved Na^+ + dissolved Cl^- will have an energy content of:

$$-(3.49 + 2.46) = -5.94 \text{ V.e,}$$

according to the dissolution energies given by Fredenhagen.[1]

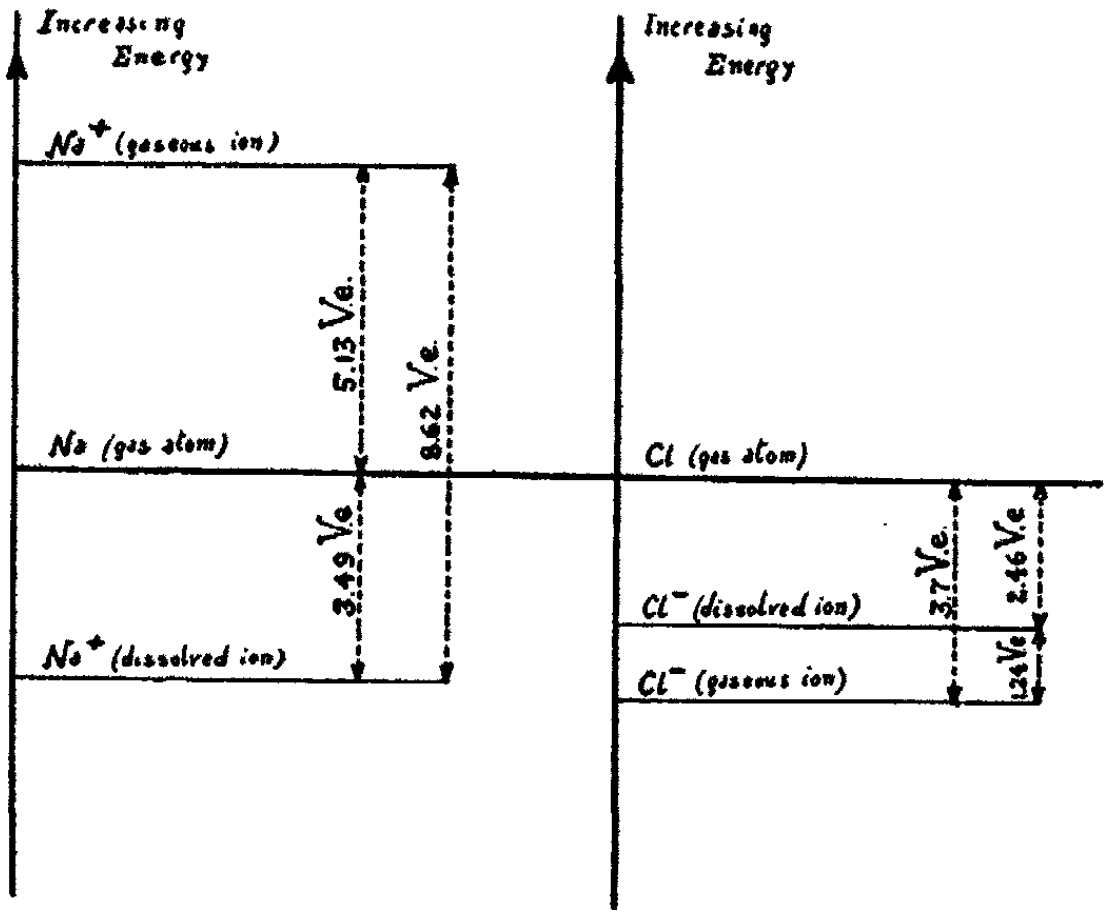

FIG. 2

On Fig. 3 where the interaction potential energy is plotted against the distance between the sodium and chlorine nuclei, the horizontal line at +1.43 V. from the level 0 is asymptotic to the interaction curve of the gaseous ionic system, I. In the same way the horizontal line at 5.95 V.e. below the level 0 is asymptotic to the interaction curve of the dissolved ionic system.

III. Interaction Curve for the Gaseous Ionic System

The interaction energy between the two gaseous ions is given by

$$\Phi = E_\infty - \frac{e^2}{r} + \frac{B}{r^n} \tag{4}$$

in which E_∞ is the sum of the ionization energy of sodium and of the electroaffinity of chlorine, $-e^2/r$ is the potential energy due to the Coulomb forces

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[1] K. Fredenhagen: Z. physik. Chem., 140, 71 (1929).

and B/r^n is the potential energy due to the Born repulsive forces. At large distances $\Phi = E_\infty$; at moderate distances the term B/r^n is negligible; at very small distances Φ passes through a minimum corresponding to the equilibrium distance between the Na^+ and Cl^- ions.

Taking the derivative of Φ with regard to r and equating it to 0, we find:

$$B = e^2 \cdot \frac{R^{n-1}}{n} \qquad (5)$$

R being the equilibrium distance.

(4) becomes, for r = R:

$$\Phi = E_\infty - \frac{e^2}{R}\left(1 - \frac{1}{n}\right) \qquad (6)$$

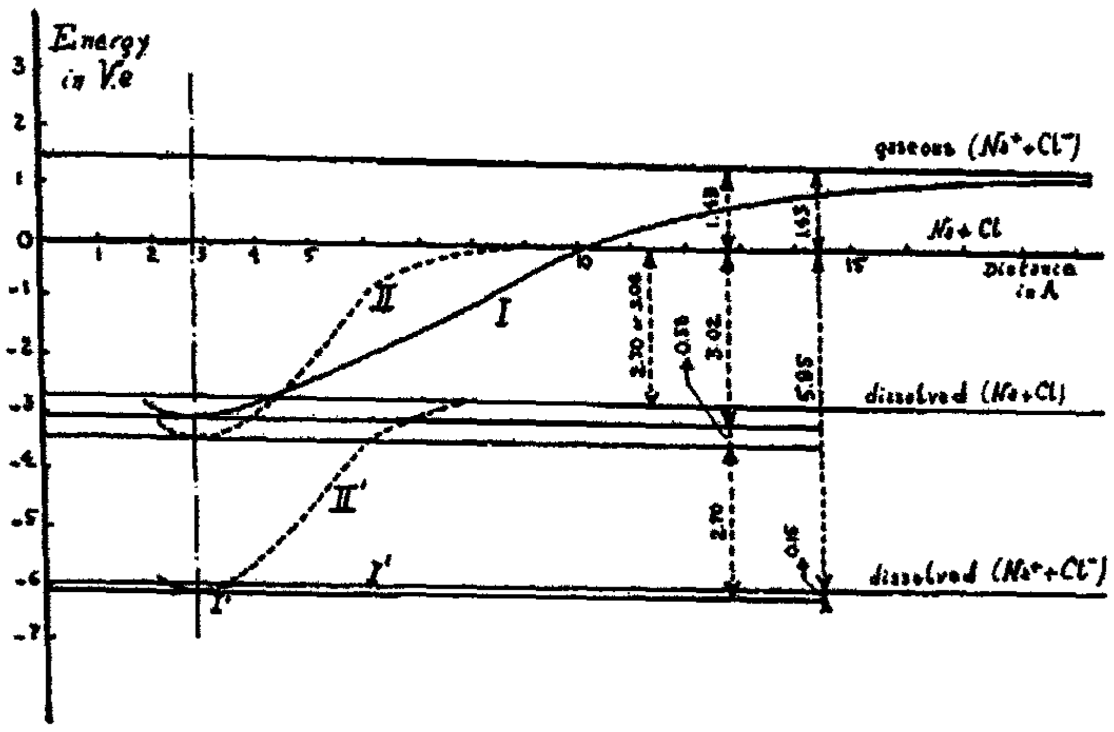

Fig. 3

For sodium chloride, we have as shown in the preceding section $E_\infty = 1.43$ V.e. Taking for R and n the values given by Pauling[1] for the NaCl crystal, i.e. R = 2.81 Å and n = 8, we obtain:

$$\Phi_{\text{min.}} = 1.43 - \frac{14.3}{2.81}\left(1 - \frac{1}{8}\right) = -3.02 \text{ V.e.} \qquad (7)$$

The complete curve for the system (gaseous Na^+ + gaseous Cl^-), I, can then be drawn easily (Fig. 3). It cuts the horizontal axis at r = 10 Å.

Fredenhagen[2] on the basis of numerical data given in the Landolt-Börnstein tables and of computations of von Wartenberg[3] gives for the dissociation energy of gaseous NaCl into gaseous Na and Cl: 78,500 calories which cor-

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[1] L. Pauling: J. Am. Chem. Soc., 49, 765 (1927).

[2] K. Fredenhagen: Z. physik. Chem., 134, 38 (1928).

[3] H. von Wartenberg: Z. anorg. Chem., 151, 328 (1926).

responds to −3.40 V.e. On account of the small accuracy of such a figure, we may consider this value as practically identical with that of the minimum in the interaction of the ionic system (−3.02 V.e.). This result seems to show that the bond in gaseous NaCl is polar. It is unfortunately impossible to compute the interaction curve for neutral atoms of Na and Cl, i.e. the curve corresponding to a hypothetical homopolar bond. We may draw such a curve in an approximate way if we suppose that the minimum in the interaction curve of the gaseous system might correspond to a homopolar bond: the appearance of the curve would be that of the upper dotted line II in Fig. 3.

IV. Interaction Curve for the Dissolved Ionic System

The Coulomb potential in the case of an aqueous solution is very small. It means that the interaction curve for the dissolved Na^+ and Cl^- ions is practically identical with the horizontal line at −5.95 V.e. from the 0 level down to quite small distances.

Let us suppose that, if Na^+ and Cl^- form a neutral molecule or a physical aggregate or cluster in Bjerrum's sense, the equilibrium distance between the two constituents is the same as in the NaCl crystal, i.e., 2.81 Å.

For this particular value of r the interaction curve will present a minimum which we can determine from the value given by Nernst[1] for the dissociation energy of the molecule or physical aggregate NaCl: 3,500 calories per mole. This dissociation energy corresponds to 0.15 V.e. The minimum is then at 0.15 V.e. below the horizontal line of the dissolved Na^+ and Cl^- ions, as shown in Fig. 3, curve I′.

We notice that the two minima, the one corresponding to the gaseous state and the one corresponding to the dissolved NaCl are 2.70.V.e. apart. If we consider the calculated minimum of the upper curve as more accurate, those minima are 3.08 V.e. apart. Supposing that this difference of energy content is the one corresponding to the purely hypothetical process gaseous (Na + Cl) →dissolved (Na + Cl), we may draw an horizontal line at 3.08 V.e. below the 0-level. In case the minimum in the interaction curve of the system dissolved Na^+ + dissolved Cl^- corresponds to a homopolar molecule, the interaction curve for the system dissolved Na+ dissolved Cl has the form of the lower dotted line II′ on Fig. 3.

In aqueous solution, the system ($Na^+ + Cl^-$) corresponds to a much lower energy content than the neutral system: it is the stable one. For small distances between the ions, small amounts of molecules (or physical aggregates?) are formed.

In the case of the gaseous state the curves for the neutral and the ionic systems intersect each other in two points. There is a marked tendency to dissociation of sodium chloride into neutral atoms, a fact which allows us to suppose that the molecule may possess a homopolar character.

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[1] W. Nernst: loc. cit.

V. Summary

1. Current ideas about the structure of compounds of the type of sodium chloride have been reviewed.

2. Curves representing the interaction energy of sodium and chlorine ions and atoms in the gaseous state and in solution in terms of the distance between the nuclei of the two constituents have been drawn.

3. The resulting energy diagram has been discussed.

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THE SURFACE CHEMISTRY OF HYDRATES. I

Aged Hydrous Alumina*

BY V. R. DAMERELL

Introduction

When hydrous aluminum oxide, precipitated with ammonium hydroxide from cold solution, has been allowed to age under water for several months at room temperature, and then dried in the air, a substance of doubtful nature has resulted. It has long been thought that this air-dried product might be a definite hydrate, since it approximately corresponds to a trihydrate in composition;[1] but when examined by the usual methods of hydrate analysis it has failed to show the characteristics of one with any clearness. Thus when dried over various hydrates and desiccants its water content takes a different and nearly always meaningless value for each. The drying curve of Hüttig and von Wittgenstein[2] gives no exact information in the case of their preparation, B_2. Unfortunately they did not take enough low temperature readings to show the course of the curve at the trihydrate stage. Guichard[3] obtained a slight break in the water content-temperature curve when he heated the substance obtained at ordinary temperature, which had dried in the air for six months, using a method of weight change with constantly increasing temperature, but this break is difficult to interpret accurately. Furthermore, he showed that heating had a marked effect on the substance, as shown by the entirely different curve obtained using a preparation that had been boiled in water. For this reason there is doubt whether any of the hydrates claimed by Willstätter[4] are identical with the one in question, since some heating was used in all of his preparations. Also the continuous drying curve of Shidei[5] may have been of another substance, since a hot dialysis was used in the purification of his preparation.

However, by experimenting with precipitates containing particles of different average size, there has been obtained evidence of the true composition of the substance, and of its surface behaviour under different vapor pressures.

Let W_s be the total number of molecules of water, both adsorbed and chemically combined, present for each molecule of aluminum oxide in a small particle precipitate, and W_l be the total number in a large particle precipitate. Let C be the total number of molecules chemically combined,

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* Contribution from the Morley Chemical Laboratory of Western Reserve University.

[1] Tommasi: Compt. rend., 91, 231 (1880); van Bemmelen: Rec. Trav. chim., 7, 75 (1888); cf. J. Chem. Soc., 53A, 1159 (1888).

[2] Z. anorg. Chem., 171, 323 (1928).

[3] Bull., 37, 62 (1925).

[4] Ber., 58, 2448, 2458 (1925); 57, 58, 1082 (1924); 56, 149 (1923).

[5] Mem. Coll. Sci. Kyoto, 9a, 42 (1924); cf. Chem. Abs., 20, 684 (1926).

and A_s and A_l the total number adsorbed in each case. Making the reasonable assumption that C is the same for all sizes of particles, under the same conditions,

$$(1)\quad W_s - C = A_s$$

$$(2)\quad W_l - C = A_l$$

Let S_s and S_l be the total accessible surfaces of the small and large particle precipitates respectively, each of which contains the same number of molecules of aluminum oxide. If the particles are of such size and shape, and are so arranged that the space between does not, as a whole, become congested with water molecules at a given vapor pressure and temperature, then the following should be true, at least as a close approximation.

$$(3)\quad \frac{A_s}{A_l} = \frac{S_s}{S_l} \text{ and,}$$

$$(4)\quad \frac{W_s - C}{W_l - C} = \frac{S_s}{S_l}$$

If two precipitates containing particles of different average size are allowed to stand together over one hydrate until maximum adsorption, or the same fraction of maximum adsorption has taken place in each case, and if this be repeated over a second hydrate, always choosing such vapor pressures that the space between particles does not become congested with water, then if C remains the same for both vapor pressures, the following results from (4)

$$(5)\quad \left[\frac{W_s - C}{W_l - C}\right] \begin{matrix}\text{over first}\\ \text{hydrate}\end{matrix} = \left[\frac{W_s' - C}{W_l' - C}\right] \begin{matrix}\text{over second}\\ \text{hydrate}\end{matrix}$$

since if C remains the same, assuming no change of crystalline form, the total surfaces should not alter. Small temperature changes should not seriously affect this equality, as long as both grades of precipitates are treated just alike regarding these variations, time of standing, and as long as C remains constant.

As a test of this equation (5) it should be possible to obtain values for W experimentally, and then substitute various values for C until an equality resulted. If this value were close to a small whole number, and if a number of pairs of precipitates, each containing a different average size of particle, gave essentially this value, it would constitute good evidence that the substance under investigation was a definite hydrate, that C had remained constant, and that the above assumptions were correct.

The object of this investigation was (a) to determine whether aged hydrous aluminum oxide was a definite hydrate, and (b) to study the surface behaviour of this substance when allowed to stand over compounds having different water vapor pressures, using the method outlined above.

Experimental

Preparation of different grades of precipitates.

A kilogram of recrystallized aluminum sulfate ($Al_2(SO_4)_3.18H_2O$) was dissolved in twenty liters of cold distilled water, and a small excess of a solution of distilled ammonia was added at once with vigorous stirring, the mixing taking place at room temperature. The resulting precipitate was allowed to settle a day or so and then the supernatant liquid was removed by means of a syphon. It was found that a glass tube bent up at the end could be used very effectively for this purpose, with practically no loss of precipitate. After syphoning, distilled water was added with stirring and the precipitate allowed to settle again. It was washed in this way at intervals of one or two days for six weeks, all washings being done at room temperature. Small amounts of ammonia were added occasionally during the first washings, to help in removing the sulfate. At the end of six weeks washing was discontinued, since the precipitate had become peptized. Samples were then dissolved in acid, and tested in the usual qualitative manner for ammonia and sulfate. No sulfate could be detected, and the ratio of equivalents of ammonia to equivalents of alumina was about one to six hundred.

In order to separate this precipitate into portions containing particles of a different average size, it was suspended by vigorous stirring and then allowed to stand for about twenty minutes, when a layer of larger particles settled to the bottom of the container. The suspension above this settled layer was syphoned off to another container and allowed to stand for an hour or so, during which time a layer of smaller particles settled out. This process was repeated a third time in one experiment, several days being allowed for the finest layer to form. These different grades of precipitates were separated from some excess water by filtering on fine-pored filter paper, and were allowed to dry in the air for several weeks. The air-dried precipitates were the starting products for a series of water vapor adsorption experiments. All of the precipitates had stood under water from two to three months before this final separation and air drying took place.

Water Adsorption Experiments.

The precipitates took the form of small, very porous lumps when air dried, and were left this way during the desiccator experiments. They were transferred to large weighing bottles, 2.75 inches in diameter and 1.25 inches deep, with ground glass covers. Large samples were taken (10 to 20 grams) to decrease the experimental error. Two series of water adsorption experiments were completed. In the first, two air-dried precipitates were allowed to stand in succession over phosphorus pentoxide, the partially dehydrated monohydrate of sodium carbonate, and the partially dehydrated heptahydrate of the same substance. The precipitates contained a different average size of particle, and were designated as large and small particle precipitates respectively. (See Pair I, Tables II and III). In the second experiment three precipitates of different average particle size, designated as large, small and very small, respectively, were allowed to stand in succession over the partially dehydrated monohydrate of sodium carbonate, the partially dehydrated heptahydrate, and phosphorus pentoxide. (See Pairs II, III and IV, Tables II and III).

It was not considered necessary to wait for complete constancy of weight at the various vapor pressures, since to obtain absolute equilibrium required considerable time, and maximum gain or loss of water was not particularly desired. When the change in weight became less than one part per thousand, during a period of forty-eight hours, it was assumed that the fraction of maximum gain or loss was essentially the same for each precipitate. The experiments were carried out in a constant temperature room, with an observed temperature of 23° ± 1°C. As proof of the assumption that the fraction of maximum loss or gain of water was essentially the same for each precipitate at the time that weighing was stopped, it was noticed in every case that the ratio between weight gained or lost by each precipitate during the last few weighings was nearly constant, as shown in Table I.

TABLE I

Water lost by air-dried precipitates standing over the partially dehydrated monohydrate of sodium carbonate

grams of air dried precipitate	size of particle	hours between weighing	192	43	49	56	44	48
22.981	large	loss of weight	224	19	16	18	13	4
13.159	small	between each weighing	173	22	15	18	11	3
11.161	very small	in milligrams	187	17	16	19	13	4

Gain or loss of water threatened to take place very rapidly when the desiccators were opened, so the procedure adopted was to put the ground-glass covers on the weighing bottles immediately upon removing the desiccator cover, and then to weigh them as rapidly as possible. Since the gain or loss of weight was slow from the covered weighing bottles, this source of error was small.

The water content of the precipitates was finally determined by transferring them to weighed platinum crucibles and igniting to constant weight. The precipitates, when first dried, after being filtered, left a film on the glass which was difficult to remove quantitatively. For this reason they were not dried originally in the weighing bottles, but on large watch glasses, and were transferred to the weighing bottles after becoming dry. By doing this, it later became easy to transfer the precipitates from the weighing bottles to the crucibles in a quantitative manner.

The water content assumed by each precipitate under different vapor pressures is given in Table II, and the values for C which satisfy equation (5) for the various pairs are given in Table III.

TABLE II

Water content, in parts per 100 parts of aluminum oxide, assumed by each precipitate over phosphorus pentoxide, and the mono and hepta hydrate of sodium carbonate

			over P_2O_5		over $Na_2Co_3 1H_2O$		over $Na_2CO_3 7H_2O$	
Experiment	pair	size of particle	water content	side from which equilibrium was approached	water content	side from which equilibrium was approached	water content	side from which equilibrium was approached
First	I	small	49.44	above	53.83	below	61.18	below
		large	50.98	above	53.63	below	57.64	below
Second	II	very small	50.97	above	56.92	above	60.38	below
		small	51.93	above	56.63	above	59.39	below
"	III	very small	50.97	above	56.92	above	60.38	below
		large	52.74	above	55.92	above	57.85	below
"	IV	small	51.93	above	56.63	above	59.39	below
		large	52.74	above	55.92	above	57.85	below

TABLE III

Values for C which satisfy equation (5) for each pair of precipitates and each pair of vapor pressure sources

Pair	over $\begin{cases} P_2O_5 \\ Na_2CO_3.1H_2O \end{cases}$	over $\begin{cases} Na_2CO_3.1H_2O \\ Na_2CO_3.7H_2O \end{cases}$	over $\begin{cases} P_2O_5 \\ Na_2CO_3.7H_2O \end{cases}$
I	3.02	3.02	3.00
II	3.15	3.15	3.15
III	3.11	3.10	3.11
IV	3.09	3.08	3.09

Discussion of Results

Many modern investigators consider that there is no fundamental difference between the force involved in a chemical bond and in the binding which holds an adsorbed molecule.[6] In discussing the results given above, however, both terms will be retained, since the work largely deals with surfaces. Thus water which is attracted to or leaves the particles in an amount proportional to the surface will be designated as adsorbed water, while water which is present in a stoichiometrical ratio to the amount of aluminum oxide will be designated as chemically bound water.

Since definite values for C were able to be obtained which were close to three, it is concluded that the substance is a definite trihydrate of alumina, and not aluminum oxide and adsorbed water, as Shidei[7] concluded after study of a somewhat similar system. In view of the work of Pascal,[8] on the magnetic

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[6] Cf. Langmuir: J. Am. Chem. Soc., **38**, 2225 (1916).

[7] Mem. Coll. Sci. Kyoto, 9a, 42 (1924); cf. Chem. Abs., **20**, 684 (1926).

[8] Compt. rend., **178**, 481 (1924).

susceptibilities of various alumina preparations, and because of its ready loss of water, the substance will be referred to as a trihydrate and not as aluminum hydroxide.

As the results in Table III show, the average value for C is several per cent higher than that required for the trihydrate. This can be accounted for by assuming the presence of other types of adsorbed water, such as water held jointly by two surfaces, which were not considered in the derivation of (5). The presence of water adsorbed by two or more surfaces is very probable, and should become a factor of more importance as the particle size became smaller.

When the hydrate was allowed to stand over phosphorus pentoxide, an interesting surface phenomenon took place. Part of the water which the positive adsorption experiments had indicated as being chemically bound now apparently behaved as adsorbed water, escaping in proportion to the surface. Thus if the loss be considered as negative adsorption, with the surface of the particles becoming 'pitted', $(W_2-C)/(W_1-C)$ can be calculated for various values of C. When C is larger than W, both parts of the fraction become negative, but the quotient remains positive, and the values can be compared with those for positive adsorption. The values which satisfy equation (5) for various pairs are given in the first and last columns of table III, and it is seen that they are very similar to the values in the middle column from the positive adsorption experiments.

The picture indicated by these results is one of a precipitate containing a great number of very small, probably crystalline particles, whose total surface must be very large. Additional water can be held on the surfaces of these particles, which has the property of adsorbed water, since at a given vapor pressure its quantity varies with the surface. When the vapor pressure becomes low enough, part of the water in the surface of the hydrate particles, which was apparently chemically combined during higher vapor pressures, now behaves as adsorbed water, leaving in an amount proportional to the hydrate surface. The relation between this surface decomposition and the constant vapor pressure decomposition of hydrates is being made the object of further study. It is very probable that this escape of water in proportion to the surface is the initial step in the decomposition mechanism.

Simon and Fischer,[9] in repeating an experiment of Hagiwara,[10] found that the composition of dried hydrargillite was essentially that required for the trihydrate, but that the same substance, ground to a very fine powder with quartz sand, when dried at the same temperature, analyzed to be Al_2O_3 $2.78H_2O$. They attributed their results to local heating during the grinding. From the results obtained in this laboratory, with a substance which is either the same, or closely related to hydrargillite, it is concluded that the difference in water content which Simon and Fischer observed was not due primarily to

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[9] Z. anorg. Chem., **185**, 101 (1929).

[10] Kolloid-Z., **32**, 154 (1923).

local heating, but was probably a natural consequence of the great increase in surface, since similar results were observed by the author with precipitates which had not been subjected to grinding.

Conclusion

1. Experimental evidence has been given showing that hydrous aluminum oxide, when aged under water containing small amounts of ammonia for several months at room temperature, forms a compound with water, which is probably a trihydrate.

2. At room temperature this compound adsorbs water in proportion to its surface when allowed to stand over the partially dehydrated mono and heptahydrate of sodium carbonate.

3. Over phosphorus pentoxide, at room temperature, the hydrate particles lose chemically bound water, which under these conditions behave as adsorbed water and escapes in proportion to the surface.

4. The difference in water content between ground and unground hydrargillite, explained by Simon and Fischer as being due to local heating during the grinding, has been observed in precipitates of a different average size of particle that have not been subjected to grinding, and is probably not primarily due to local heating, but is a natural consequence of the increase in surface.

THE PARTIAL PRESSURES OF VAPOURS OF VOLATILE LIQUIDS IN THE PRESENCE OF INERT GASES[1]

BY W. G. BEARE, G. A. McVICAR AND J. B. FERGUSON[2]

When a volatile liquid is placed in a closed vessel which contains a relatively inert gas and the temperature is kept constant, the partial pressure of the vapour of this liquid is frequently regarded as approximately equal to the difference between the initial gas pressure and the final total pressure; it is considered to differ from this by a negligible amount after corrections are applied for the change in volume of the vapour phase and the loss of permanent gas by solution, provided that the gas phase is a perfect gaseous solution, and that adsorption on the walls of the vessel is not a disturbing factor. The vapour pressure is obtained from the partial pressure by making an allowance for the diminution of the partial pressure caused by the solution of gas in the liquid when this is an appreciable amount.

There does not appear to be any sound theoretical objection to the method outlined for the treatment of the case cited or for similar cases but there is the practical objection, as noted by Dornte,[3] that it is quite at variance with the published results of Regnault[4] and Campbell.[5] Either these results are incorrect or some additional factor must be considered in the theoretical treatment of the case. The matter is of such importance that we felt that the facts in the case should be clearly established. Accordingly, we carried out several series of experiments similar in principle to those of Campbell but essentially different in respect to the apparatus and technique used. Our results, which are given in this paper, do not confirm the results of the earlier experiments.

Materials

Methyl alcohol: Kahlbaum. Dried over freshly prepared lime at room temperature, decanted off and distilled.
D 20/4 0.79232. I.C.T. value 0.7917.
Estimated to be 99.8 percent alcohol.

Ethyl alcohol: Squibbs. Similarly dried.
D 20/4 0.78913. I.C.T. value 0.78934.
Estimated to be pure.

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[1] Presented at the 13th Annual Canadian Chemical Convention held at Ottawa, May 26, 1930.

[2] Measurements by Messrs. Beare and McVicar.

[3] Dornte: J. Phys. Chem., 33, 1312 (1929).

[4] Regnault: Mém. de Paris, 26, 679 (1862).

[5] Campbell: Trans. Faraday Soc., 10, 197 (1914).

Acetone: Kahlbaum, aus der Bisulfit Verbindung. Dried over fused calcium chloride at room temperature, decanted off and distilled.

D 20/4 0.79106. This was not quite dry as the material we prepared last year gave 0.79072.[6]

Ether: Eastman Kodak. This was shaken with clean dry mercury twice, filtered through charcoal, shaken with its own volume of water and the latter operation repeated five times with one-half the quantity of water. The separated product was first dried over fused calcium chloride and then over sodium and distilled.

Air: This was passed through a concentrated aqueous solution of sodium hydroxide, over soda-lime, calcium chloride and phosphorus pentoxide in the order given.

Carbon dioxide: This was prepared by dropping a concentrated aqueous solution of sodium bicarbonate into concentrated sulphuric acid and dried over calcium chloride and phosphorus pentoxide.

Apparatus and Procedure

The apparatus of Ferguson and Funnell[7] as modified by Beare and McVicar[6] together with the additional part, A′, needed for the present work, is shown in Fig. 1. The part, A′, was sealed into the apparatus between the large and the small bulbs in the large air bath. The solenoids of the circulating pump are unfortunately not indicated in their proper positions. Although movable, they were placed close together in actual operation.

A glass container of suitable size was filled with the liquid under investigation, sealed and placed in A′. A trace of lubricant was placed on the ground-glass joint and enough mercury was kept in the glass cap to protect this seal. The apparatus was then evacuated. The air baths were brought up to the desired temperatures, the lower air bath being about four degrees above the temperature at which the vapour pressure was to be determined, the upper about ten degrees above this. If the manometer reading remained constant for several hours or more, the apparatus was considered gas-tight. The gas (air or carbon dioxide) was then admitted until the desired pressure was reached, approximately. Mercury was run into the U tube until it reached a point in the capillary tube just inside of the upper air bath. The temperatures of the air baths were again adjusted, also the height of the mercury column and the pressure reading taken. The container tip was broken with the magnetic hammer; liquid air was placed around the small bulb and the circulating pump started. A small wire heater (not shown) surrounding A′ was turned on and the sample collected in the small bulb. The heater was disconnected, the liquid air removed, the air baths brought up to temperature and cold water circulated through the water bath. When no more of the

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[6] Beare, McVicar and Ferguson: J. Phys. Chem., 34, 1310 (1930).

[7] Ferguson and Funnell: J. Phys. Chem., 33, 1 (1929).

sample remained as liquid in the small bulb the water bath was heated up and maintained at the desired temperature. This temperature was read on a Beckmann thermometer which had been compared with a standard, was kept constant to ± 0.01°C. and known within ±0.02°C. The temperature of the lower air bath was kept constant to ± 0.1°C. and that of the upper to ± 0.5°C. The pump was run at full speed until the pressure became constant. With air, this required approximately 1.5 hours and with carbon dioxide 2.5 hours. The pressure rose gradually until it attained its maximum value. The pump was kept running at full speed for an additional 0.5 hours, the speed was reduced and finally the pump was stopped but observations were continued for an hour after the stoppage. Reducing the pump speed made no appreciable difference in the pressure reading but the final reading was usually 0.2-0.3 mm lower than the readings with pump operating. This difference we attributed to a heat effect.

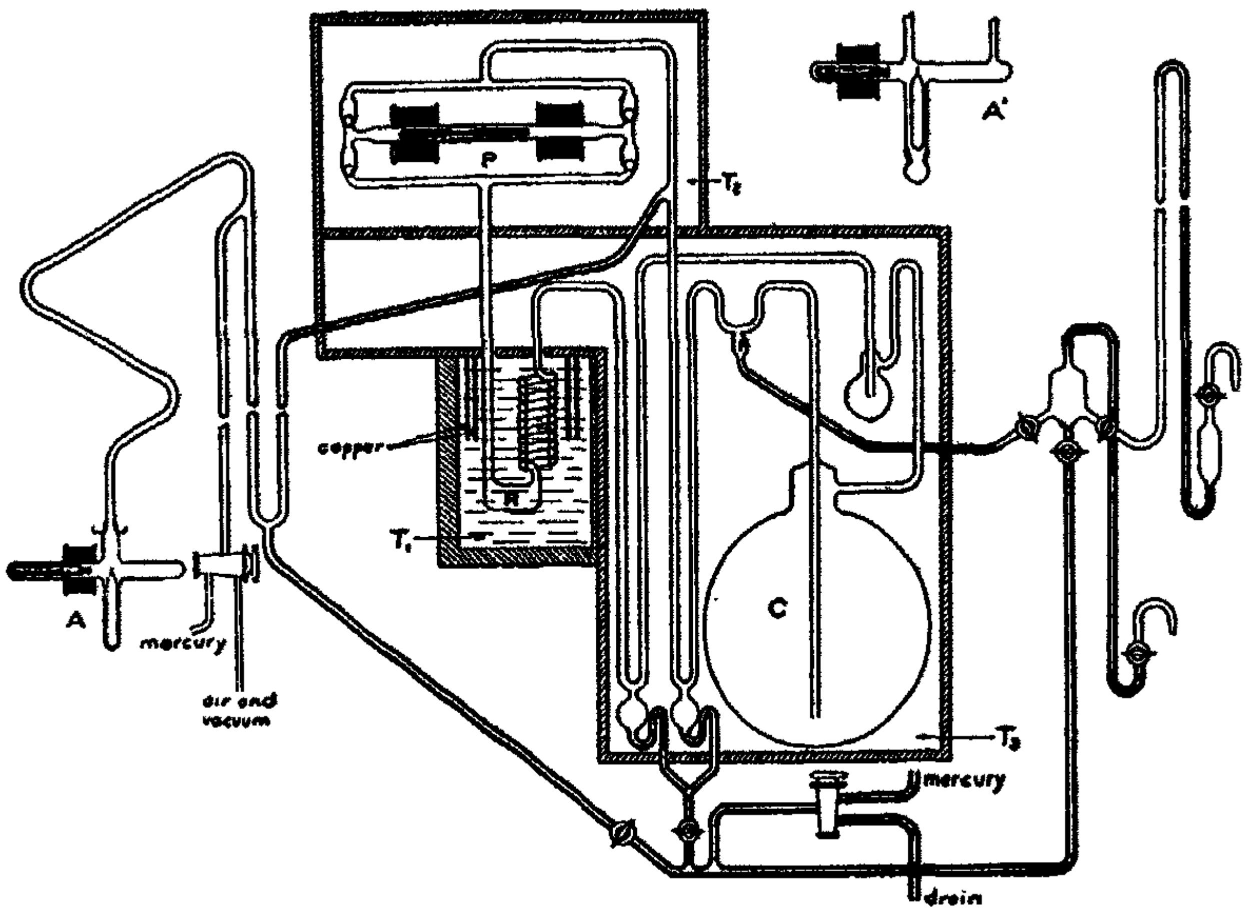

FIG. 1

In experiments, in which air was the inert gas, the small bulb was again cooled with liquid air, the pump operated and the sample collected in this bulb. The apparatus was then evacuated, closed by the mercury column and the vapour pressure of the liquid determined. The details need not be repeated for this operation.

The difference between the initial gas pressure and the final pressure was taken as the approximate partial pressure. All pressure readings were reduced to 0°C. Allowance was then made for the following experimental conditions:

(a). The initial temperature of the reaction chamber which had a volume of 15 cc. was not always identical with its temperature when the final pressure reading was taken.

(b). The evaporation of the liquid increased the volume of the gas phase.

(c). Part of the inert gas dissolved in the liquid phase, the volume of which was approximately 1 cc.

Since the volume of the gas phase was almost 3500 cc, the total pressure was but slightly affected by these conditions.

The results were subject to one source of error, the value of which is unknown but the maximum value of which could be calculated. This arose from the fact that the gas in the container A′ was not circulated and hence may have differed somewhat in composition from the gas in the rest of the apparatus. The maximum error would have occurred if only inert gas were present in A′ and would have amounted to 1 mm in the case of carbon dioxide and ether. The observed differences between the partial pressures and the vapour pressures in the cases of carbon dioxide-ether and carbon-dioxide-acetone might have been due in part to this source of error and in part to a solubility effect although the differences are so small that accidental errors may have been the major factor.

Results and Discussion

The partial pressures and vapour pressures determined by us are given in Table I. The values lying along the same horizontal line were obtained with the same liquid sample. The table also includes a few independent vapour pressure measurements.

The vapour pressure obtained for acetone agrees almost exactly with the value given by Sameshima and is slightly lower than our previously determined value for dry acetone. Our new value supports our previous determination since the specific gravity determination indicated that the original acetone sample was probably the drier of the two. Campbell observed that the partial pressure of methyl alcohol in carbon dioxide at 40°C. was 191 mm whereas the vapour pressure is roughly 260 mm, and offered, as a tentative explanation of this and similar discrepancies, the hypothesis that some sort of adsorption took place at the liquid surface. In our experiments the gas phase was circulated over the liquid phase so that there was ample opportunity for such a phenomenon to occur, if indeed, it were possible. Moreover the stoppage of the circulating pump did not give rise to an increase of pressure but to an almost negligible decrease. We must therefore conclude that such large discrepancies, as have been observed, are due to the particular experimental conditions and are not due to any factor effecting the theoretical principles which have been commonly accepted.

TABLE I

The vapour pressures of volatile liquids and the partial pressures of their vapours in the presence of dry air and dry carbon dioxide

Liquid	t°C.	Air		Carbon Dioxide		True Vapour Pressure	Indep. Vapour Pressure Measurements*	
		Air Pressure	Vapour Partial Pressure	CO$_2$ Pressure	Vapour Partial Pressure		Vapour Pressure	Observer
Methyl Alcohol	25.00					124.3	122.7	Dittmar and Fawsett
	"	268.4	123.6			122.8		
	"	412.0	123.7			123.9		
	"			390.7	124.2			
				198.1	123.7			
	40.00	225.1	259.5			259.9	259.4	Dittmar and Fawsett
	"			295.0	261.1		260.5	Ramsay and Young
Ethyl Alcohol	40.02	300.6	134.5			134.6	134.3	Interpolated from the results of Schmidts
	"			305.2	134.7			
Acetone	30.00	264.2	283.1			282.9	282.7	Sameshima
	"			250.0	281.7		283.7	Beare and McVicar
Ether	20.00	200.1	442.0			441.6	442.4	Ramsay and Young
	"			198.2	439.8			
	"			192.3	440.4			

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* Dittmar and Fawsett: Trans. Roy. Soc. Edin., **33**, II, 509 (1886-7); Ramsay and Young: Phil. Trans., **177**, *1*, *123* (*1886*); **178A**, 57 (1887); Schmidt: Z. physik. Chem., **8**, 628 (1891); Sameshima: J. Am. Chem. Soc., **40**, 1482 (1918); Beare and McVicar: J. Phys. Chem., **34**, 1310 (1930).

Summary

(1). The partial pressures of methyl alcohol, ethyl alcohol, acetone and ether were determined in the presence of dry air and dry carbon dioxide. The determinations in the presence of air were carried out with liquid samples which were subsequently used for the determination of the vapour pressure without removal from the all-glass apparatus.

(2). The differences between the partial pressures and the vapour pressures were usually less than one millimeter. The large discrepancies which had been previously reported, were not observed.

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THE RELATION BETWEEN OBSCURING POWER AND PARTICLE NUMBER AND SIZE OF SCREENING SMOKES

BY P. D. WATSON AND A. L. KIBLER*

Object

The object of the work described in this paper was to check the theoretical assumption that the screening power of smokes and clouds is simply related to their particle number and size and to determine the numerical value of that relationship. In addition to this, data were desired on the absorption of moisture by hygroscopic smoke particles, the composition of smoke particles, the efficiency of dispersion, and the stability of smoke clouds.

Historical

No previous experimental work is known which relates the obscuring power of smokes or clouds with the particle number and size. The fact that such a relationship exists was quite accurately forecast by H. W. Walker[1] on purely theoretical grounds. A closely allied line of work consists in a correlation of particle size (concentration remaining constant) with intensity of the Tyndall beam in aqueous colloidal suspensions. Relevant data include work by Mecklenburg[2] who worked with graduated suspensions of colloidal sulfur particles, and Tolman[3] and his collaborators, who worked with graduated suspensions of silica particles. Tolman extended his work in a qualitative way to rosin smokes. Mecklenburg's work covered the range from 0.05×10^{-5} to 8.4×10^{-5} cm. diameter. Tolman's quantitative work covered the range from 10×10^{-5} to 206×10^{-6} cm. diameter. His qualitative work with smokes covered the range from 0.5×10^{-5} to 10×10^{-6} cm.

Although there is some discrepancy in the results of the two investigators named above the following points seem well established:

1. For particle diameters below that of the wave-lengths of light, the intensity of the Tyndall beam increases with an increase in the size of the particles, concentration remaining constant.

2. For particle diameters above that of the wave-lengths of light, the intensity of the Tyndall beam decreases with increase in the size of the particles, concentration remaining constant.

3. For particle diameters of the order of magnitude of the wave lengths of light, the evidence is conflicting but it is evident that this is the transition range. The range of wave-lengths of visible light is from about 4×10^{-5} to about 7.5×10^{-5} cm. The average wave-length of white light is about 5.7×10^{-5} cm.

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[1] Walker: Ind. Eng. Chem., 17, 1061 (1925).

[2] Mecklenburg, Kolloid-Z., 16, 97 (1925).

[3] Tolman et al.: J. Am. Chem. Soc., 41, 300, 575 (1919).

Theoretical

It is known that the absorption of light by true solutions depends upon the thickness of the layer traversed and on the molecular concentration in that layer.[1] Svedberg has shown that the mechanism of light absorption may be the same for colloidal solutions composed of observable particles and for molecular solutions.[2] Ostwald has also shown that, in many cases, absorption by a colloidal solution of a very high grade of dispersion approximates absorption by the corresponding molecular solutions.[3]

It is by no means certain, however, that the mechanism of screening by smokes is as simple as the absorption of light by the smoke particles. Among other factors which might conceivably affect obscurance are reflection and refraction of light, composition of the smoke particles, relative position of observer, smoke and target, and intensity and location of the light source.

Nature of the Problem.—The relation between the obscuring power of smokes and the number and size of the smoke particles may be expressed specifically as the ratio between the sum of the projections upon the surface of the target for all the smoke particles between the eye and the target, and the area of the target when it is just obscured in the smoke cloud. This ratio is referred to in this paper as the "screening ratio" and designated by the letter R. In order to establish a relation of this kind it is necessary either to use smokes in which the particles are all of the same size, or to know the proportionate number of particles of each size present. We may assume, however, from a study of the Brownian Movement, and from other considerations, that the greater number of particles in any stable smoke are essentially of the same size.

Most of the efficient smokes are hygroscopic in character, absorb large quantities of water, and produce spherical liquid particles. Therefore, the area of a great circle through the sphere may be regarded as the projection of the particle upon the vertical target.

From the above it is obvious that the essential data necessary to establish the desired relationship are the number of smoke particles per unit volume, the average size of these particles and the screening power of the smoke. The number of particles may be found with sufficient accuracy by means of the ultramicroscope. Knowing the number of particles per cubic centimeter, the average diameter of the particles may be calculated from the weight and density of the smoke. This involves sampling and analyzing the smoke from a known volume of air. The obscuring power of the smoke may be determined by noting the distance at which a target just disappears from view while under constant illumination.

Experimental

Experimental work was carried out under accurately controlled conditions in a smoke chamber of approximately 63,000 cubic feet capacity and 1,000 square feet cross-sectional area. It was fairly air-tight and provided with

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[1] Taylor: "Treatise on Physical Chemistry," 2, 1207.

[2] Svedberg: "Colloid Chemistry," 194 (1928).

[3] Ostwald: Kolloidchem. Beihefte, 2, 409 (1910-11).

ventilating ducts and a large circulatory fan for keeping the smoke uniform in concentration throughout. The chamber was also provided with facilities for humidifying and drying the air to any degree of humidity desired.

Obscuring Power. Observations of the obscuring power of the smoke were made through a small window in one end of the chamber upon a circular, black, 10-inch target mounted 4 feet above the floor. The target was mounted upon an iron rod set in a supporting frame directly in line with the observation window. The target was moved back and forth by means of the iron rod which was graduated in feet. The target was illuminated by two rows of overhead lamps, each row containing fourteen 60-watt lamps, set over the target and about 16 feet above it. Visibility readings were taken one or two minutes after the start of each run and at intervals thereafter. These values were plotted in a visibility-time curve and the values used in the work were read from these curves.

Particle Number. Particle number was determined by means of an ultramicroscope arranged upon a shelf on the outer wall of the smoke chamber near the observation window. The smoke was drawn into the cell through a 1/4-inch glass tube about 12 inches long which projected into the smoke chamber. The source of light for the ultramicroscope was a direct current carbon arc. An optical system projected a fine pencil of light into the observation cell. An absorption cell of cupric chloride solution was used to eliminate the short rays and prevent convection currents in the cell. In order to reduce the personal error of the observer to a minimum the illuminating beam was cut off for brief regular intervals by means of a rotating sectored disk placed in its path. The depth of focus of the microscope was 0.0444 mm. A diaphragm with two small circular apertures was inserted in the eyepiece. The apparent diameters of the apertures were 0.150 and 0.120 mm., determined by focusing on a millimeter scale. The average of fifty successive counts was taken. From the particle count, the depth of focus and the diameter of the aperture used, the number of smoke particles per cubic centimeter was calculated.

Smoke Samples. Samples of the smokes were taken by drawing 20 liters of air-smoke mixture through specially prepared filter tubes with filter beds of ground, fritted glass and thin asbestos mats. The filter tubes were weighed immediately before and immediately after the collection of samples. Great care was exercised to keep the tubes at equilibrium with the moisture of the room. The composition of the smoke was determined by analysis for the chief constituent. From the composition of the smoke particles their density was determined either by reference to standard tables or by special experimental work.

Materials. The smokes used were those which, upon dispersion in air of ordinary humidity, will become liquid droplets. For the liquid smoke materials, dispersion was accomplished by means of an efficient spray. White phosphorus was burned in an open pan and zinc chloride was dispersed by means of a smoke candle containing the so-called H.C. smoke mixture. Ammonium chloride was dispersed by atomizing liquid ammonia and 32%

aqueous hydrochloric acid. The several smoke materials used are shown below:

Titanium tetrachloride
Oleum
Chlorsulfonic acid
White phosphorus
Zinc chloride
Ammonium chloride

In the case of most of the smokes generated, upon dispersion in a humid atmosphere, hydration, hydrolysis or deliquescence occurs. The resulting smoke particles are aqueous solutions of the resulting products. In the case of chlorsulfonic acid, analysis of the smoke revealed only traces of hydrochloric acid and it was assumed that this product of hydrolysis escaped from the liquid droplets. The case of titanium tetrachloride presented a difficult problem on account of the complicated chemical reactions which occur between $TiCl_4$ and water. As a consequence of the uncertainty as to the composition of this smoke some special work was done on the densities of titanium compounds. Mixtures were made up containing varying percentages of titanium tetrachloride and water and these mixtures were analyzed for titanium and their densities determined. It was found that when the densities of the titanic acid solutions were plotted against their titanium content, a straight line was obtained. The values for the density of the particles of titanium tetrachloride smoke were taken from this graph.

The several smoke materials used are tabulated below along with the bases to which the analyses of the smoke samples were calculated.

Smoke Material	Analyzed for
Zinc chloride	$ZnCl_2$
White phosphorus	P_2O_5
Titanium tetrachloride	TiO_2
Ammonium chloride	NH_4Cl
Oleum	SO_3
Chlorsulfonic acid	SO_3

Method of Calculation. The radius of a particle is determined from the equation:

$$r = \sqrt[3]{\frac{3M}{4\pi dN}}$$

where

M = total mass of the particles in 1 cc. (g).
d = density of the particles (g./cc.)
N = number of particles (no./cc.)
r = radius of particle (cm.)

The screening ratio, R, is determined from the equation:

$$R = \frac{\pi D^2 NV}{4}$$

where

D = diameter of a smoke particle (cm.)
V = distance between the eye and the target when the target is just obscured (cm.)
R = the screening ratio.

TABLE I

Zinc Chloride

R.H.	Time after dispersion min.	Number particles $N \times 10^{-6}$	Wt. sample from 20 l. mg.	$ZnCl_2$ by anal. mg.	Diam. of part. $D \times 10^4$ cm.	Density of part. d.	Distance of target cm.	Screening ratio R.
90	6	3.50	9.3	3.25	0.547	1.55	153	1.25
	16	1.94	9.5	2.70	0.691	1.42	198	1.44
	26	1.07	8.6	2.17	0.826	1.36	268	1.54
90	6	3.49	14.4	3.94	0.657	1.39	143	1.69
	16	2.24	11.4	2.80	0.711	1.35	192	1.71
	26	1.56	9.3	1.54	0.776	1.22	259	1.91
60	6	3.57	6.5	2.52	0.474	1.63	195	1.23
	16	2.12	4.2	2.25	0.472	1.80	293	1.09
	26	1.15	3.6	2.04	0.550	1.80	390	1.06
60	6	4.16	12.0	3.76	0.570	1.49	198	2.10
	16	2.24	5.1	1.55	0.529	1.47	290	1.43
	26	1.43	4.2	1.36	0.572	1.50	403	1.48
								Ave. 1.49

TABLE II

White Phosphorus

R.H.	Time after dispersion min.	Number particles $N \times 10^{-6}$	Wt. sample from 20 l. mg.	P_2O_5 by anal. mg.	Diam. of part. $D \times 10^4$ cm.	Density of part. d.	Distance of target cm.	Screening ratio R.
90	6	2.68	25.7	3.69	0.938	1.11	198	3.66
	16	1.84	19.7	2.48	0.976	1.10	247	3.40
	26	1.10	15.2	1.93	1.063	1.10	326	3.18
90	6	3.65	35.1	3.71	0.947	1.08	204	5.25
	16	1.89	25.5	2.62	1.061	1.08	250	4.18
	26	0.94	19.2	2.03	1.218	1.08	317	3.47
								Av. 3.86
60	6	2.78	4.9	3.23	0.467	1.65	250	1.19
	16	1.35	3.3	1.96	0.526	1.60	311	0.91
	26	1.10	3.4	1.91	0.573	1.57	412	1.17
60	6	2.78	5.9	3.46	0.502	1.60	275	1.51
	16	1.25	4.0	2.77	0.570	1.65	384	1.22
	26	1.10	3.8	1.73	0.610	1.45	494	1.59
60	6	1.86	8.5	3.46	0.678	1.40	262	1.76
	16	1.89	4.2	1.91	0.527	1.45	357	1.47
	26	1.25	4.2	1.85	0.606	1.44	519	1.87
								Av. 1.41

Experimental Data. The experimental data and the screening ratios calculated therefrom are shown in Tables I to VI. For each smoke tested, runs were made at 60 and 90 per cents relative humidity in order to test the effect of humidity upon particle number and size. The actual humidities were within about one per cent of the humidities desired. Temperatures were recorded but as they had no discernible effect upon the results of the tests they are omitted from the tables. Samples of the smoke were taken and observations were made at 6, 16, and 26 minutes after dispersion of the smokes.

TABLE III

Titanium Tetrachloride

R.H.	Time after dispersion min.	Number particles $N \times 10^{-6}$	Wt. sample from 20 l. mg.	TiO_2 by anal. mg.	Diam. of part. $D \times 10^4$ cm.	Density of part. d.	Distance of target cm.	Screening ratio R.
90	6	4.82	16.8	3.86	0.614	1.44	101	1.44
	16	1.86	7.6	3.04	0.599	1.82	171	0.90
	26	1.40	10.8	2.54	0.796	1.46	250	1.74
90	6	6.17	10.8	1.51	0.513	1.24	134	1.71
	16	2.96	3.8	1.21	0.421	1.64	247	1.02
	26	1.86	2.2	0.95	0.391	1.89	320	0.71
90	6	5.73	16.7	3.22	0.589	1.36	82	1.28
	16	2.86	13.0	3.18	0.664	1.48	146	1.45
	26	2.30	6.4	2.54	0.527	1.82	207	1.04
90	6	3.62	9.6	2.02	0.566	1.40	104	0.95
	16	1.38	4.4	1.68	0.555	1.78	204	0.68
	26	1.02	3.4	1.30	0.563	1.78	320	0.81
60	6	5.85	6.5	4.08	0.358	2.32	186	1.09
	16	2.37	7.3	3.22	0.536	1.91	326	1.74
	26	1.45	3.6	2.42	0.461	2.42	497	1.20
60	6	8.96	10.3	5.00	0.379	2.01	162	1.64
	16	3.60	5.4	3.54	0.391	2.39	302	1.31
	26	1.22	3.5	2.64	0.472	2.61	451	0.96
60	6	5.42	9.9	3.58	0.465	1.74	162	1.49
	16	1.71	6.1	2.78	0.559	1.95	287	1.20
	26	0.87	4.9	1.85	0.672	1.77	448	1.38
60	6	6.21	7.3	3.46	0.384	1.99	162	1.16
	16	3.37	7.9	2.70	0.510	1.69	290	1.99
	26	1.53	3.5	1.95	0.465	2.17	464	1.20
								Av. 1.25

TABLE IV

Ammonium Chloride

R.H.	Time after dispersion min.	Number particles $N \times 10^{-4}$	Wt. sample from 20 l. mg.	NH_4Cl by anal. mg.	Diam. of part. $D \times 10^4$ cm.	Density of part. d.	Distance of target cm.	Screening ratio R.
90	6	5.26	8.1	1.09	0.521	1.04	143	1.60
	16	2.65	—	—	—	—	165	—
	26	1.53	4.4	0.14	0.648	1.01	207	1.04
90	6	4.02	4.2	1.22	0.452	1.08	195	1.26
	16	3.62	—	—	—	—	210	—
	26	2.07	—	—	—	—	241	—
90	6	5.54	10.0	0.95	0.551	1.03	143	1.89
	16	3.04	6.8	0.68	0.592	1.03	156	1.30
	26	2.75	4.8	0.41	0.545	1.03	195	1.25
90	6	4.94	7.3	1.22	0.512	1.05	143	1.46
	16	1.91	2.5	1.09	0.481	1.12	149	0.52
	26	1.35	3.5	0.95	0.612	1.08	189	0.75
90	6	4.66	5.6	0.95	0.478	1.05	180	1.51
	16	2.24	4.9	0.95	0.582	1.06	201	1.20
	26	1.28	2.3	0.41	0.547	1.05	275	0.82
90	6	3.07	1.9	0.68	0.377	1.10	207	0.71
	16	2.19	2.6	0.68	0.472	1.08	217	0.83
	26	1.20	10.4	0.41	0.936	1.01	247	2.04
90	6	2.67	2.5	0.82	0.434	1.09	146	0.58
	16	1.61	3.8	1.22	0.593	1.08	156	0.69
	26	1.30	1.9	0.68	0.502	1.10	192	0.49
75	6	4.34	2.4	1.36	0.356	1.17	650	2.80
	16	1.66	—	0.82	—	—	695	—
	26	0.71	—	0.68	—	—	781	—
75	6	2.91	—	1.22	—	—	592	—
	16	1.10	1.2	0.95	0.436	1.26	708	1.16
	26	1.17	1.9	0.54	0.524	1.08	839	2.11
60	6	3.27	3.0	2.04	0.417	1.21	503	2.24
	16	1.63	1.3	0.82	0.400	1.19	604	1.24
	26	1.15	—	0.54	—	—	750	—
60	6	3.19	—	1.36	—	—	576	—
	16	1.94	2.0	0.68	0.449	1.09	601	1.84
	26	1.17	0.7	0.41	—	—	—	—
60	6	4.34	2.2	1.63	0.340	1.23	461	1.81
	16	2.02	1.0	1.22	0.342	1.18	552	1.03
	26	1.30	0.6	0.68	0.334	1.18	677	0.77
60	6	3.66	3.4	2.18	0.420	1.20	351	1.78
	16	1.96	1.3	2.04	0.377	1.18	439	0.96
	26	0.89	1.9	0.95	0.653	1.14	576	1.28
								Av. 1.30

TABLE V

Oleum

R.H.	Time after dispersion min.	Number particles $N \times 10^{-6}$	Wt. sample from 20 l. mg.	SO_3 by anal. mg.	Diam. of part. $D \times 10^4$ cm.	Density of part. d.	Distance of target cm.	Screening ratio R.
90	6	3.60	5.9	2.0	0.500	1.25	320	2.26
	16	2.70	0.8	0.5	0.265	1.52	326	0.49
	26	1.17	0.9	0.25	0.395	1.19	357	0.51
90	6	8.20	21.4	5.4	0.596	1.18	92	2.08
	16	3.19	15.7	4.2	0.734	1.19	122	1.65
	26	2.07	12.7	3.4	0.790	1.19	165	1.67
90	6	4.18	10.8	3.6	0.582	1.25	104	1.16
	16	2.07	5.6	1.5	0.599	1.20	131	0.77
	26	1.07	7.0	2.2	0.798	1.23	174	0.93
90	6	5.02	11.1	3.9	0.542	1.33	85	0.98
	16	2.27	9.4	2.9	0.687	1.22	116	0.98
	26	1.68	7.0	2.2	0.686	1.23	168	1.04
60	6	6.29	12.9	4.4	0.539	1.25	131	1.88
	16	3.65	5.1	2.8	0.452	1.44	174	1.02
	26	1.45	4.6	2.4	0.599	1.41	238	0.97
60	6	3.27	—	—	—	—	143	—
	16	1.71	7.3	3.7	0.663	1.40	189	1.12
	26	1.40	6.5	2.6	0.699	1.30	247	1.33
60	6	3.90	12.5	6.0	0.607	1.37	119	1.34
	16	1.86	6.7	1.5	0.667	1.16	153	0.99
	26	0.99	5.6	2.6	0.735	1.36	210	0.88
								Av. 1.20

TABLE VI

Chlorsulfonic Acid

R.H.	Time after dispersion min.	Number particles $N\times10^{-4}$	Wt. sample from 20 l. mg.	SO_3 by anal. mg.	Diam of. part $D\times10^4$	Density of part. d.	Distance of target cm.	Screening ratio R.
90	6	—	—	—	—		122	—
	16	1.63	2.1	0.3	0.482	1.10	146	0.43
	26	2.12	3.1	0.1	0.516	1.02	198	0.88
90	6	5.22	6.0	1.1	0.460	1.13	131	1.13
	16	2.70	3.5	—	0.486	1.08	165	0.83
	26	2.83	—	—	—	—	232	—
90	6	5.10	4.6	—	0.430	1.08	131	0.97
	16	2.17	3.0	—	0.496	1.08	156	0.65
	26	1.84	2.8	—	0.512	1.08	201	0.76
60	6	5.26	6.8	1.5	0.474	1.16	232	2.15
	16	2.75	1.3	1.4	0.329	1.27	275	0.64
	26	1.81	2.9	0.6	0.511	1.15	348	1.29
60	6	6.81	4.9	2.1	0.372	1.33	214	1.58
	16	2.17	1.7	1.2	0.359	1.62	241	0.53
	26	1.73	2.8	0.7	0.508	1.18	296	1.04
60	6	5.02	2.7	0.8	0.348	1.22	165	0.79
	16	2.24	0.9	—	0.311	1.27	192	0.33
	26	1.25	0.9	0.3	0.380	1.25	262	0.37
60	6	3.82	4.3	—	0.439	1.27	287	1.66
	16	1.79	3.6	—	0.533	1.27	314	1.25
	26	2.22	—	—	—	—	390	—
								Av. 0.96

Discussion of Data

Screening Ratio. Not including phosphorus smoke at 90% relative humidity the average of the screening ratios is 1.27. If results be omitted which are manifestly out of line, due mainly to very small smoke samples, the average ratio would be somewhat higher than this, in the neighborhood of 1.35. For spheres with uniform packing, the theoretical ratio for complete blocking out of the background is 1.57.

Again excepting phosphorus smoke at 90% relative humidity it will be noted that the diameters of the smoke particles lie substantially between the limits 0.40×10^{-4} cm. and 0.75×10^{-4} cm. which define the range of the wave lengths of visible light. The average diameter of the white phosphorus smoke particles at 90% relative humidity is 1.03×10^{-4} cm. while the average screening ratio is 3.86. The obscuring value of white phosphorus at high humidities is little better than it is at low humidities in spite of the large amount of water absorbed by the particles and their consequently large size.

These data point to the conclusion that for smoke particles whose diameters are within the range of the wave lengths of visible light screening is accomplished by a simple blocking of the light rays. For particles of this size the composition is not a factor. For particles whose diameters are larger than the wave lengths of visible light, screening is accomplished by a different mechanism and the refractive index or other physical properties of the smoke particles may be a factor.

These and other conclusions in this report apply only to white smokes having liquid particles. Some work was also done on a black carbon smoke having solid particles but on account of the irregularity in size and outline the projections of the particles could not be calculated.

It should also be mentioned that the screening ratio named above has been proved to apply only to the experimental conditions which obtain in the smoke chamber used. There is some evidence that smokes are more efficient in screening out of doors than in the smoke chamber. If this is the case, it is probably due to such factors as the relative position of observer, smoke, and target, to the intensity and reflection of light, variation of particle size, and other such causes.

Effect of Humidity. The obscuring power of all the smokes was greater at 90% than at 60% relative humidity, and, in some instances, this was very marked. This was due to the larger size of the particles at the higher humidity caused by the adsorption of moisture. If the absorption of moisture increases the diameter of the particle beyond the wave lengths of light, as in the case of white phosphorus smoke, the increase in screening power is not proportional to the increase in particle size. In the case of ammonium chloride smoke the increase in screening power at 90% relative humidity was very large. By a consideration of the data of Owens[1] with the aid of the vapor pressure of saturated ammonium chloride solutions[2] we were able to show that at 60% relative humidity the ammonium chloride particles were composed of fine crystals, at 90% they were liquid while for the two runs at 75% the particles were just on the border line between liquid and solid. These data check very well with the observed screening power.

The data in the tables give us a means of estimating roughly the amount of water absorbed by the smokes studied. Such an estimate, based on a careful analysis of the data, is shown below. Equilibrium with the moisture in the air is, in all cases but one, reached before 6 minutes and the values shown in the table represent an average of all observations.

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[1] J. S. Owens: Proc. Roy. Soc., **110A**, 738 (1926).

[2] Edgar and Swan: J. Am. Chem. Soc., **44**, 570 (1922).

TABLE VII

Parts of Water absorbed by Smokes

Smoke material	At 90% R.H.	At 60% R.H.
$ZnCl_2$	3	2
P_2O_5	7.5	1
TiO_2	1.5[1]	1
NH_4Cl	5	0.5
SO_3 (from oleum)	2.5	1
SO_3 (from chlorsulfonic acid)	5	2

It is interesting to compare the concentrations represented by the proportions of substance and water shown in the above table with the concentrations of solutions in bulk at equilibrium with air under the conditions of humidity and temperature which obtained in our experiments. In addition to ammonium chloride, which is discussed above, the smokes from phosphorus, oleum, and chlorsulfonic acid lend themselves to such a comparison because for these smokes the composition of the smoke particles is known with a fair degree of accuracy. From the analytical data it is assumed that the smoke from chlorsulfonic acid is composed essentially of sulfuric acid. For sulfuric acid sufficient data exist in the literature for complete vapor pressure curves at any concentration and temperature. For phosphoric acid the data are not so complete. By the aid of the Clausius-Clapeyron equation, however, vapor pressure curves were drawn from the data available for phosphoric acid. A comparison of the theoretical concentrations at equilibrium with the air at the temperatures and relative humidities obtaining in the experiments, with the concentrations represented by the analytical data in tables, is shown below. The comparison is expressed in terms of the ratio of water to SO_3 and P_2O_5, respectively.

TABLE VIII

Comparison between Theoretical and Observed Parts of Water absorbed by Smokes

Smoke	Relative humidity	Ratio H_2O/SO_3 or P_2O_5	
		Theoretical	Experimental
Oleum	90	7	2.5
Oleum	60	2	1
Chlorsulfonic acid	90	8	5
Chlorsulfonic acid	60	2	2
White phosphorus	90	6	7.5
White phosphorus	60	1.4	1.0

The comparison in the above table is as good as could be expected considering the roughly approximate nature of the ratios shown in Table VII. There

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[1] In this case the absorbed water at 6 minutes is distinctly more than at 16 and 26 minutes, and amounts to about 3 parts.

is a tendency for the experimental values to be lower than the theoretical ones. This is probably due primarily to the well known fact that the vapor pressure of small particles is appreciably higher than for the same liquid in bulk, tending to concentrate fine droplets of solutions.

Efficiency of Dispersion and Stability of the Smoke Cloud. The efficiency of the method of dispersion employed may be judged by the amount of smoke material in the air at the end of 6 minutes while the stability of the cloud may be judged by the relative amounts still remaining in the air after 16 and 26 minutes. From the analyses of the samples of smoke collected from 20 liters of air the averages of the amounts of the several original materials found present at the end of 6, 16, and 26 minutes have been calculated and expressed in terms of percentages of the weight of substance originally dispersed. Both humidities have been averaged in together as the recovery was about the same for both. These figures are shown in the following table together with the percentage decrease from 6 to 26 minutes. These last figures represent the stability of the cloud.

TABLE IX

Efficiency of Dispersion and Stability

Substance	Amount found[1] in % of original substance after			Percentage decrease
	6 min.	16 min.	26 min.	6-26 min.
H. C. candle	53.0	37.3	28.3	48
W.P.	68.3	45.4	36.8	46
F.M.	74.0	59.0	44.8	40
Oleum	53.6	28.0	26.0	51
Chlorsulfonic acid	15.2	12.4	4.6	63
NH_4Cl	20.4	16.1	9.0	56

When the percent of smoke still in the air from Table IX are plotted on the logarithmic scale against the time in minutes, on semi-log paper the points define straight lines which are practically parallel. The intersection of these lines on the ordinate representing zero time represents the actual efficiency of dispersion expressed in terms of per cent of the original substance taken. The efficiencies determined in this manner are shown in Table X.

TABLE X

Actual Efficiency of Dispersion of Smokes at Zero Time

Substance	Efficiency as % of original substance
H.C.	65
W.P.	80
F.M.	87
Oleum	66
Chlorsulfonic acid	20
NH_4Cl	32

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[1] Calculated back to the original material dispersed.

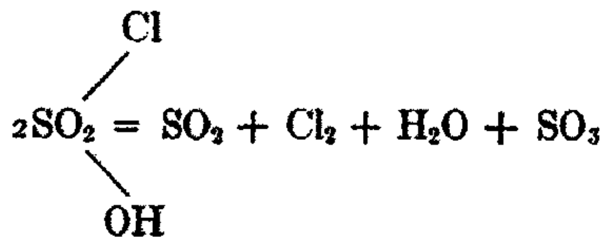
The low efficiencies of dispersion for chlorsulfonic acid and ammonium chloride smokes are probably due to insufficient heat to bring about decomposition in the case of the former and incomplete reaction between NH_3 and HCl in the case of the latter. The stability is about the same for the six smokes studied, chlorsulfonic acid being the most unstable. This again is probably due to inefficiency of the method of dispersion. The average decrease between 6 and 26 minutes is 50%.

On the whole, Table X indicates a much lower efficiency of dispersal than is ordinarily assumed. It should be emphasized that these efficiencies are calculated in a manner which eliminates the effect of precipitation and leakage in the smoke chamber. There is, therefore, no reason to believe that dispersal out of doors, by the same methods, is more efficient than the figures shown in this table.

The stability of a highly non-volatile cloud out of doors is certainly greater than in the smoke chamber. In the main two opposing factors are operative. One of these is the precipitation of smoke particles in the chamber, due to forced ventilation. This occurs particularly around the fan blades and at the bends in the ventilating ducts. (There is also a small but unknown amount of leakage.) The other factor is the increased tendency to evaporation out of doors where the cloud is being continually diluted with fresh air.

Composition of the Smoke Particles. We are justified in the assumption that smokes from the H.C. smoke candle, white phosphorus, oleum, and ammonium chloride consist, respectively, of droplets of $ZnCl_2$, P_2O_5, SO_3 and NH_4Cl with water since there is no likelihood of any further reaction of these constituents.

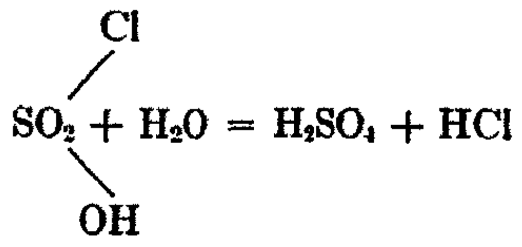
In the case of chlorsulfonic acid it is known that heat is necessary for an efficient dispersal. It is stated in Thorpe's "Dictionary of Applied Chemistry," **5**, 301, that chlorsulfonic acid is decomposed by heat according to the following equation:



$$2SO_2\begin{smallmatrix}\diagup Cl\\ \diagdown OH\end{smallmatrix} = SO_2 + Cl_2 + H_2O + SO_3$$

The reaction is complete when the vapors are heated to 200°C.

Chlorsulfonic acid also reacts with water according to the following equation:



$$SO_2\begin{smallmatrix}\diagup Cl\\ \diagdown OH\end{smallmatrix} + H_2O = H_2SO_4 + HCl$$

If the first reaction takes place before the chlorsulfonic acid is exposed to the moisture of the air, and if the temperature is sufficiently high to bring about complete decomposition, the part of the products represented by $SO_2 + Cl_2$, being gaseous, is lost for the formation of smoke while the part represented by $H_2O + SO_3$ is completely utilized. This latter part represents only 42% of the original molecule. If chlorsulfonic acid is atomized in the cold we might expect a more complete utilization of the original molecule, but the fact that this is not true indicates that the cold chlorsulfonic acid may fall out of suspension before it has a chance to react with the moisture of the air. In the work described in this report chlorsulfonic acid was atomized by means of a rapid current of CO_2. Both the container holding the chlorsulfonic acid and the CO_2 line were heated by steam, the temperature varying from 115 to 135°C. The reaction with heat was, therefore, incomplete. The evidence, therefore, indicates that at least a portion of the original chlorsulfonic acid, not decomposed by heat, fell out of suspension soon after atomization. This theory is strengthened by the fact that analyses of the samples collected from this smoke showed but traces of HCl and also by the very low recovery of this smoke after 6 minutes. This theory indicates that the most efficient method to disperse chlorsulfonic acid is to heat the vapors to a temperature somewhat over 200°C before discharging them into the air, but then only 42% of the original material could be utilized. A somewhat higher efficiency than this might be obtained by a very efficient atomizer, using steam as the atomizing agent. Disregarding the HCl an efficiency of about 70% is theoretically possible by this method. Some work has been done on the use of steam and it has been found that superheated steam gives a good smoke.

The composition of the smoke by either method would be droplets of sulfuric acid, the HCl being driven out by the heat of the reaction.

The case of the composition of the smoke from titanium tetrachloride is more obscure and little seems to be known about the reaction of this substance with water. Consequently, some study was made of the data for this smoke and some additional experimental work was done in an effort to determine its composition. Unfortunately, the samples of smoke taken during the counting experiments were not sufficiently large to analyze for both TiO_2 and HCl. Therefore, additional samples were collected and analyzed for HCl. The data from these analyses admit of only a rather rough estimate of the amount of HCl in these smokes. The percentage of HCl is somewhat more at 90% than at 60% relative humidity. The percentages of HCl present in the smoke at different time intervals and humidities is approximately as follows:

	60% R.H.	90% R.H.
At 6 min.	13	19
At 16 min.	13	17
At 26 min.	8	10

Calculations of the composition of the smoke represented by the data in Table III were made on the basis of the above average contents of HCl. Though the individual variations in composition are quite large, it is probable that average figures are fairly representative of these smokes. The results expressed in percentages of TiO_2, H_2O, and HCl are shown below.

TABLE XI

Composition of Titanium Tetrachloride Smoke in Percentages

Time	60% R.H.			90% R.H.		
	TiO_2	H_2O	HCl	TiO_2	H_2O	HC
6 minutes	49	38	13	19	62	19
16 minutes	47	40	13	28	55	17
26 minutes	59	33	8	36	54	10
Average	52	37	11			

The composition of the smoke at 60% relative humidity appears to be fairly constant from 6 to 26 minutes, and is represented by the following:

$$2\ TiO_2 + 6\ H_2O + HCl$$

or the composition may be written

$$Ti(OH)_4 + H_2O + 1/2\ HCl$$

Under ordinary conditions of moisture, it appears that the compound originally formed, $TiCl_4.5H_2O$, begins at once to hydrolyze, splitting off HCl which escapes from the particles quite readily since most of it is gone in 6 minutes.

At 90% relative humidity the relative proportions of H_2O and HCl change rather rapidly after the first 6 minutes. The compositions at 6, 16, and 26 minutes are represented approximately by the following:

At 6 minutes.................. $Ti(OH)_4 + 12\ H_2O + 2\ HCl$
At 16 minutes................. $Ti(OH)_4 + 7\ H_2O + 1.5\ HCl$
At 26 minutes................. $Ti(OH)_4 + 4\ H_2O + 0.5\ HCl$

The change in composition is due to the loss of both H_2O and HCl. Hydrolysis of the $TiCl_4.5H_2O$, which was probably first formed, is complete before 6 minutes when the composiion of the smoke is a solution of $Ti(OH)_4$ with some HCl dissolved in it.

Limits of Accuracy. The effect of several sources of error in these experiments are briefly discussed below.

The depth of focus of the microscope was utilized in determining the volume of the field containing the particles to be counted. The normal eye is capable of accommodation within limits; consequently, the depth of focus utilized by the observer in viewing the particles may differ from the depth of focus as determined experimentally. It is also not necessarily true that only the particles falling within the depth of focus appear as points of light and not as disks. Particles too small to be detected by the ultramicroscope may have been present, but it is thought that the effect of this error would be negligible. These above-mentioned errors would affect all the results to the same degree. Whytlaw-Gray,[1] in a recent article discusses the errors due to the scattering of light within the cell by the smoke particles.

It was thought possible that the filters might not collect the smallest particles present. A check was made by placing two filters in series, but the second filter showed no increase in weight. If any errors were introduced in this manner they were quite small.

The density of the smokes read from tables and determined experimentally probably does not exactly represent the density of the particles in the cloud, and the errors may be considerable in some cases.

Most of the smokes examined are hygroscopic and hence very sensitive to conditions of humidity and temperature. It was, therefore, important to weigh the samples of smoke immediately after collecting them to avoid errors due to a change in weight due to loss or gain of moisture. The temperature of the observation room was kept as near as possible to that of the smoke chamber but the humidity could not be controlled. When the humidity of the observation room was markedly different from that of the smoke chamber and the smoke being tested was a very hygroscopic one, like phosphorus, the error due to this cause was likely to be considerable.

It is thought that errors in the visibility readings of the target were probably of less importance than many of the other errors. The illumination and the point of observation from the cloud were constant for all smokes, and any divergence in this respect from the true obscuring power would be constant. The chief error would lie in the personal factor of the observer's eyesight.

Conclusions

1. For smokes consisting of spherical particles of diameters within the range of the wave lengths of visible light the average of the screening ratio (ratio of the total cross-sectional areas of the smoke particles to the area of the target) is 1.27. It is indicated that the correct ratio is somewhat higher than this, probably about 1.35. This ratio holds true for the conditions under which the smoke measurements were made in the smoke chamber.

2. For particles of diameters within the range of the wave lengths of visible light (0.40 to 0.75 $\times 10^{-4}$ cm.) the screening power is independent of the composition of the smoke particles and dependent solely upon the number and size of the smoke particles between the eye and the target.

3. Phosphorus smoke at 90% relative humidity consists of particles considerably larger than the wave-lengths of visible light. The average value of the screening ratio for this smoke is 3.86. It is indicated that particles of this size screen by a different law from that applying to particles of diameters equal to the wave-lengths of light. Some light may go through the large phosphoric acid solution particles. It is possible that for particles larger than the wave lengths of light the physical properties of the substance of which the particles are composed, in particular the refractive index, may be a factor.

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[1] Proc. Roy. Soc., **116A**, 540 (1927).

4. For smokes having particle diameters within the range of the wave-lengths of visible light, there is no evidence of any regular change in the value of the screening ratio with the change in size over the comparatively small range within which the particles for these smokes vary.

5. The results suggest that under the conditions obtaining in the smoke chamber, smokes consisting of particles whose diameters are within the range of the wave-lengths of visible light obscure a non-luminous target when the number of particles between the eye and the target are sufficient, when projected, to form a uniform layer of approximately one particle in thickness. The actual average ratio as stated above was 1.27, but it is indicated that the correct ratio is somewhat higher than this. For spheres with uniform packing the theoretical ratio for complete blocking out of the background is 1.57.

6. The obscuring power of efficient smoke-producing materials is to a large extent due to atmospheric moisture which is absorbed from the air by hygroscopic smoke particles. This is the explanation of the superior obscuring power of smokes at high humidities. It is indicated by the case of phosphorus smoke, however, that there is an upper limit beyond which the absorption of water from the air fails to be reflected proportionally in increased obscuring power of the smoke. This limit is reached when the smoke particles exceed in diameter about 0.75×10^{-4} cm.

7. For all the smokes studied the precipitation in the smoke chamber followed a logarithmic law, according to which the logarithm of the amount remaining in the air at any given time was proportional to the time.

THE ADSORPTION OF CERTAIN VAPORS BY ACTIVATED CHARCOAL. III.

BY J. N. PEARCE AND A. L. TAYLOR[1]

All experimental research on adsorption, hitherto, has been directed, for the most part, to the solution of two closely related fundamental problems. These problems involve, (1) the determination of the nature, the extent and range of the forces which are instrumental in producing concentration changes in the gas phase at the solid-gas interface, and (2) the determination of the physical states and of the chemical relationships existing in the adsorption system.

Whenever adsorption is mentioned we naturally think of the monumental work of Langmuir.[2] He has shown that in many cases, especially on plane metallic surfaces, the adsorbed layer is but one molecule thick, often only partially covering the adsorbing surface, and that the adsorbed molecules are highly oriented with respect to the adsorbent. With him adsorption is distinctly a chemical phenomenon.

The whole problem of adsorption becomes much more complicated when the adsorbent presents a rough uneven surface, like amorphous charcoal. Here we not only have the possibility of an increasing preferential adsorption as we pass from surfaces to edges to points,[3] but also the influence of capillarity.

The complete solution of the adsorption problem will require an accurate knowledge not only of the physical properties of the adsorbent, but also of the adsorbate as well. Among the latter are surface tension, capillarity, compressibility, and the heats of condensation, of wetting and adsorption. In case of the highly porous bodies which possess fine capillaries the geometrical configuration of the adsorbed molecules, their size and structure, the chemical and electrical nature of the molecules and of the substituents in these molecules,—all of these must exert a pronounced influence upon the energy and the magnitude of the adsorption of vapors.

In any heterogeneous system in which one phase is rigid and one mobile there will always be, according to Gibbs,[4] a change in concentration of the mobile phase at the interface, if such a change in concentration will result in a decrease in surface energy. Langmuir[5] has shown that in forming films on liquids the molecules of the paraffin hydrocarbons arrange themselves in such a way that the methyl group (CH_3) forms the surface layer. No matter how

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[1] An extract of a thesis presented by A. L. Taylor in partial fulfillment of the requirements for the Ph.D. in Chemistry at the State University of Iowa.

[2] Langmuir: Phys. Rev. (2), 6, 79 (1915); 8, 149 (1916); J. Am. Chem. Soc., 38, 2221 (1916); 40, 1361 (1918).

[3] Taylor: J. Phys. Chem., 30, 145 (1926).

[4] Gibbs: "Scientific Papers," 1, 219 (1906).

[5] Langmuir: Met. Chem. Eng., 15, 468 (1915).

long the chain may be the surface energy of the series from hexane to the molten paraffins is practically the same. The surface energies of the alcohols are practically the same as those of the hydrocarbons. Further, a bulky end group, like "I" or "NO", greatly increases the surface tension of the paraffins just as the substitution of an "OH" group, by orientation, increases the surface energy of benzene. He was able to show conclusively that the molecules are highly oriented in these surface films.

We have been working for some time upon a systematic study of the relation between adsorption magnitudes and the various physical and chemical properties of the vapor molecules. To this end the vapors studied have been taken up in a definite order, viz., the order in which they occur in an homologous series, or in the order of increase in the number of a substituent atom or group in a given molecule, and, finally, from the standpoint of isomeric modifications, involving straight and branched chain compounds.

Our first contribution[6] deals with the adsorption of water, methyl alcohol, ethyl alcohol, ammonia, and methylamine vapors by activated charcoal; the second[7] presents the results of a study of the adsorption of methane and its chlorine derivatives. In these we have assumed that it is the oxygen, the nitrogen, and the chlorine atom, respectively, that is most strongly attracted by the carbon atoms in the surface lattice of the adsorbent. The chlorine derivatives of the hydrocarbons are particularly interesting in the study of adsorption in that the chlorine atom possesses a large number of valence electrons. The force fields about this atom, and hence its residual valence, should be large. Moreover, the chlorine atom is usually considered to be highly electronegative, and hence the substitution of a chlorine atom for hydrogen must increase the electronegativity of the molecule.

The present work presents the results of the study of the adsorption isotherms of two series of vapors. These series are closely related in adsorptive forces and each offers special opportunities for the study of the structure of surface films and of the forces involved in the formation of these films. The isotherms of methyl chloride,[7] ethyl chloride, n-propyl chloride and n-butyl chloride make available data on four alkyl chlorides of an homologous series in which the lengths of the carbon chain of successive members differ by a constant increment, CH_2. By including the study of the vapors of isopropyl chloride and tertiary butyl chloride we have a second series in which one, two and three of the hydrogen atoms of the methyl radicle are replaced by methyl groups. If we remember that these molecules are oriented with the chlorine atom toward the surface of the charcoal, it is evident that we have a series in which the cross-sectional area of the molecule, in a plane parallel to the surface of the adsorbent, is increased by characteristic increments. We may thus produce a crowding effect on the immediate surface, but at some distance from the surface.

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[6] Pearce and Knudson: Proc. Iowa Acad. Sci., 34, 197 (1927).

[7] Pearce and Johnstone: J. Phys. Chem., 34, 1260 (1930).

Materials and Apparatus

The "acid-washed", "acid-free", steam-activated charcoal used in this work was taken from the same large supply as that used in the previous researches[6,7]. It was specially prepared for us from coconut shell by the Carbide and Carbon Chemicals Corporation, under the direction of Dr. N. K. Chaney. The loss in weight on outgassing was found to be 2.5 percent; the density of the outgassed charcoal is 1.80[6]. These values were always employed in calculating the actual weight of the charcoal used and in calculating the volume of the dead "space." All samples of charcoal used were outgassed at 525° until the pressure dropped to about $0.5 \cdot 10^{-4}$ mm. and the charcoal was then allowed to cool to room temperature where the pressure was too small to be measured on a McLeod gage.

The liquid alkyl chlorides used in producing the vapors were of the highest quality obtainable from the Eastman Kodak Co. Each liquid was further purified by careful repeated fractionation. The last three or four fractionations were carried out in an air-free apparatus of such design that the vapor never came in contact with air before it was brought in contact with the charcoal. The boiling points of the purified alkyl chlorides were: ethyl chloride, 12.5° at 755 mm.; n-propyl chloride, 46.5° at 753 mm.; iso-propyl chloride, 34.65° at 748.6 mm.; n-butyl chloride, 77.0°-77.2° at 745 mm; ter-butyl chloride, 50.1° at 740.45 mm.

The apparatus and the experimental procedure was the same as that employed in the work of Pearce and Johnstone.[7] The apparatus was, however, carefully recalibrated. Adsorption equilibrium was assumed when the pressure of the vapor above the charcoal remained constant for at least 30 minutes. In those cases where equilibrium was only slowly attained a much longer time was allowed. Each pressure reading recorded is the mean of at least two or three readings and is corrected to 0°, sea level and 45° latitude. Each isotherm plotted represents at least two different series of measurements on different samples of charcoal. An isotherm was considered as definitely established when the points of successive series were found to lie on the same smooth curve.

To furnish a better basis of comparison the isotherms of the five alkyl chlorides were determined as nearly as possible at the same temperatures. The lowest temperature employed for each vapor was 0°; the highest temperature used depended upon the stability of the vapor in contact with the charcoal. The temperature of each isotherm was frequently checked by raising or lowering the temperature until it corresponded with that of an adjacent isotherm and then by adjusting the volume of vapor in contact with the charcoal so that the point representing equilibrium would fall in the region of high pressures. The equilibrium points thus obtained were in excellent agreement with the isotherm previously determined on a fresh sample of charcoal. Only in one case did we observe any evidence of decomposition. This was for the tertiary butyl chloride at 99.5°.

Natural Isotherms

The adsorption isotherms obtained in this series have the usual characteristic forms. At all temperatures the curves are concave toward the pressure axis throughout the entire pressure range. Attempts to determine the isotherms at temperatures above those for which data were obtained failed because of the occurrence of decomposition as indicated by a progressive increase in pressure over a long period of time. The temperatures at which decomposition of the alkyl chlorides first appeared are: methyl, 236° (rapid); ethyl, 236°; n-propyl, 182°; iso-propyl, 137°; n-butyl, 140°; tertiary butyl, 99.5°. Thus, the stability of the alklyl chlorides in contact with our charcoal decreases with increase in molecular complexity. It is lower for the secondary and tertiary forms than for the corresponding normal compounds.

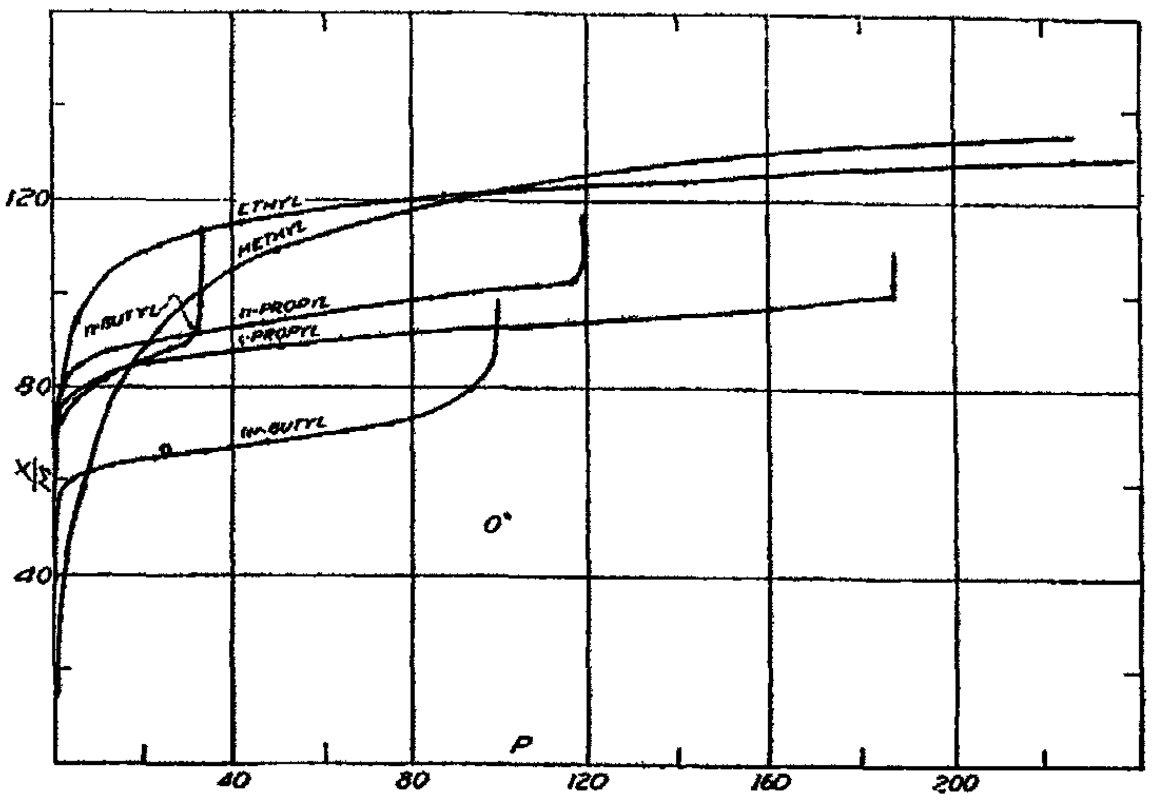

Fig. 1

From the reproducibility of their results Lamb and Coolidge[8] conclude that previous contact with ethyl chloride does not alter the adsorption capacity of activated charcoal for subsequent determinations. Our experience has been exactly the opposite. In no case have we found the activity the same after outgassing at 525°.

The various isotherms for the individual vapors were carefully plotted separately and from these were read the data for the isobars and isosteres. For purposes of illustration we are presenting in Figs. 1-4 the natural isotherms of the alkyl chlorides at 0°, 40°, 77.5° and 99.5°, respectively. The plots of the higher pressures have been purposely omitted to save space. While these temperatures cannot in any way be considered as corresponding adsorption temperatures of the vapors the plots show the characteristic

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[8] Lamb and Coolidge: J. Am. Chem. Soc., 46, 1146 (1920).

trends of the various isotherms. They show also the influence of temperature upon the relative amounts of the different vapors adsorbed at the various pressures.

At 0° the adsorption isotherms break very sharply away from the X/M axis. With rise in temperature the break becomes less pronounced and it should completely disappear in the vicinity of the critical temperature. For a given temperature also the sharpness of the break increases as the boiling point of the liquids increases, but it occurs at lower values of X/M.

The isotherms at 0° (Fig. 1), may be somewhat complicated because of the fact that four of the vapors reach saturation at relatively low pressures.

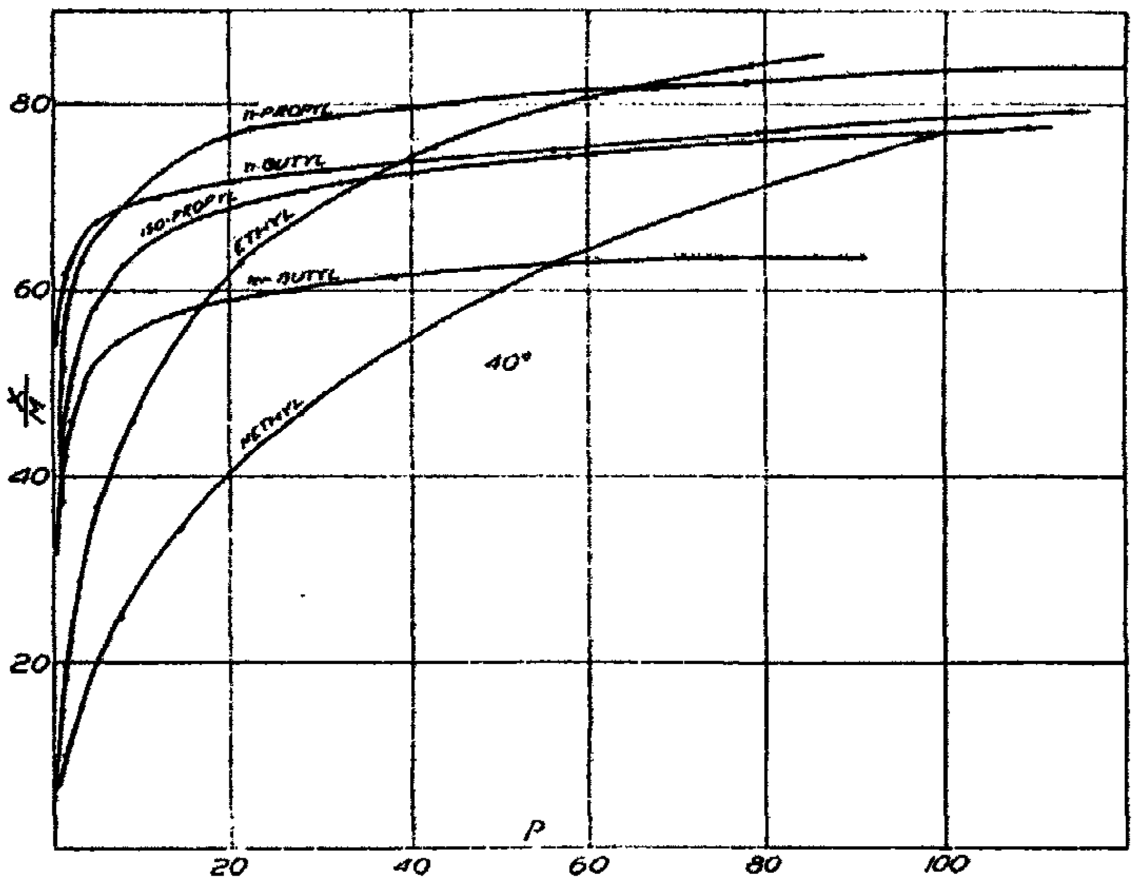

FIG. 2

The tendency for the isotherms to intersect upon variation of pressure is obvious from the plot given. The rapid increase in the adsorption of methyl chloride with increase in pressure is also particularly interesting. For pressures between 10 mm. and 20 mm. the volume of the normal alkyl chloride vapors adsorbed, (cc. per gram), decreases in the order ethyl, n-propyl, n-butyl, methyl. At pressures above 100 mm. the order becomes methyl, ethyl, n-propyl. Above this pressure the magnitude of the adsorption decreases with increase in the length of the carbon chain.

With rise in temperature the tendency for the isotherms to intersect becomes markedly less. For pressures below 60 mm., (Fig. 4) the volumes of vapor adsorbed at 99.5° increases as the length of the normal chain vapor molecule is increased. It is very probable that this relation is completely fulfilled at sufficiently high temperatures. This is also the order of increase in boiling points, critical temperatures and other physical properties of the liquids. At all temperatures the isotherms of the iso-propyl and tertiary butyl chlorides lie below those of the corresponding normal compounds.

The volume of each of the alkyl chloride vapors which had to be admitted to the charcoal at 0° before an equilibrium pressure could be detected is large. The volume of vapor adsorbed at low pressures (below 0.5 mm.), is greater the greater the molecular weight of the vapor. Thus, at 0° and under an equilibrium pressure of 0.45 mm. one gram of charcoal adsorbs 33.65 cc. of the tertiary butyl chloride and 12.99 cc. of ethyl chloride, while at the same temperature, but under 1.39 mm. only 7.85 cc. of methyl chloride are adsorbed.[7] These observations are even more striking when we take into consideration the fact that the total amount of vapor capable of being adsorbed decreases with increasing molecular weight. Further, the amount of vapor adsorbed at 0° under one mm. pressure is equal to or exceeds one-half of the total amount adsorbable at the same temperature under a pressure just short of saturation. This relation holds without exception for the five vapors studied.

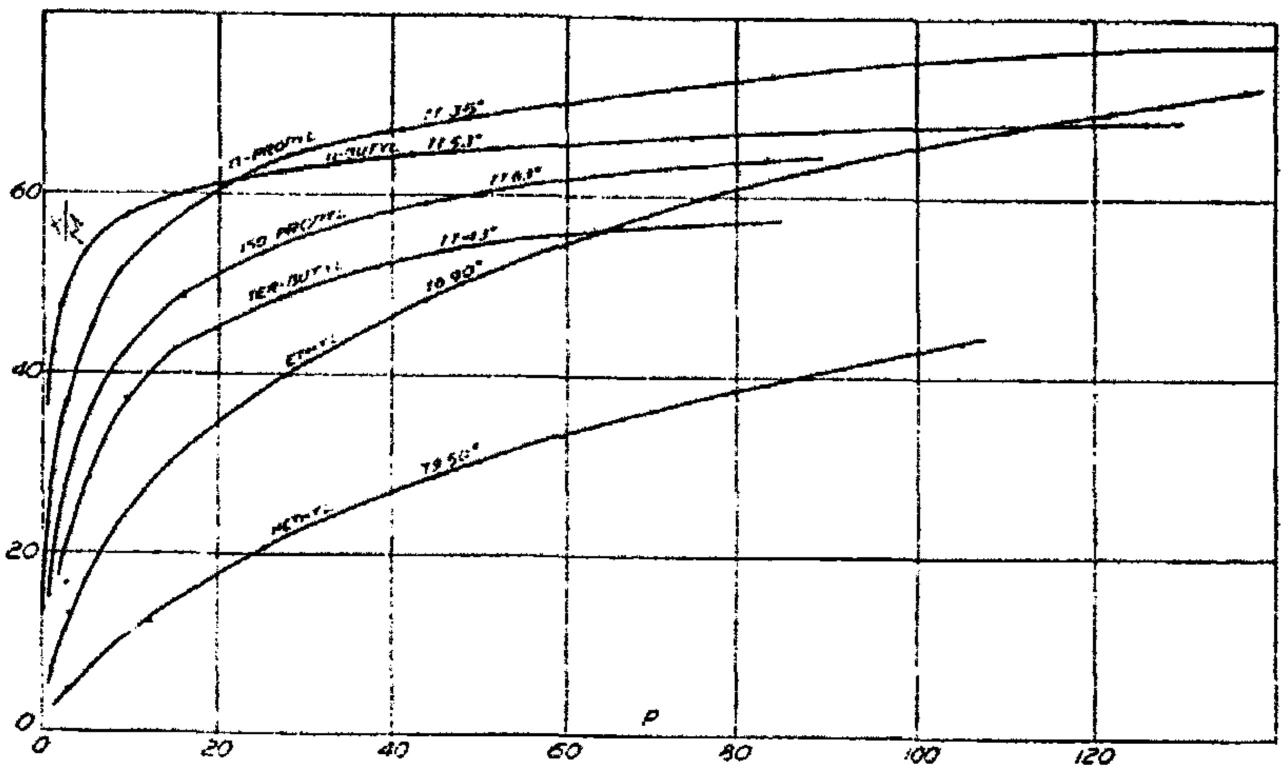

FIG. 3

It has been interesting to observe that the time necessary to attain adsorption equilibrium at a given temperature differs widely corresponding to different points on the isotherm. The time required is greatly increased in the pressure interval including the "break" of the isotherm; it is much greater for the iso-propyl and the tertiary butyl chlorides than for the normal compounds. In fact, it is difficult to reproduce the 0°-isotherm of the tertiary butyl chloride either in the pressure range including the break, or just below condensation. One illustration of the slowness of the pressure variation observed at the break point of the tertiary butyl chloride may not be amiss. Two and one-half hours after the admission of the vapor to the bulb the pressure over the charcoal was 30.65 mm. The pressure decreased slowly and regularly without exhibiting any sign of equilibrium even after 119 hours when the pressure was 19.50 mm. It was observed also that when the adsorption equilibrium was approached from the side of high pressure, especially, if the butyl chloride had been previously condensed on the charcoal, the values of X/M were always too high.

It is evident that the sluggishness in the attainment of adsorption equilibrium in this instance is due to steric hindrance. When the vapor is first admitted to the gas-free surface of the charcoal the molecules will be adsorbed on those points and areas most accessible to the vapor molecules. This will include also the most easily accessible points and areas on the capillary walls.

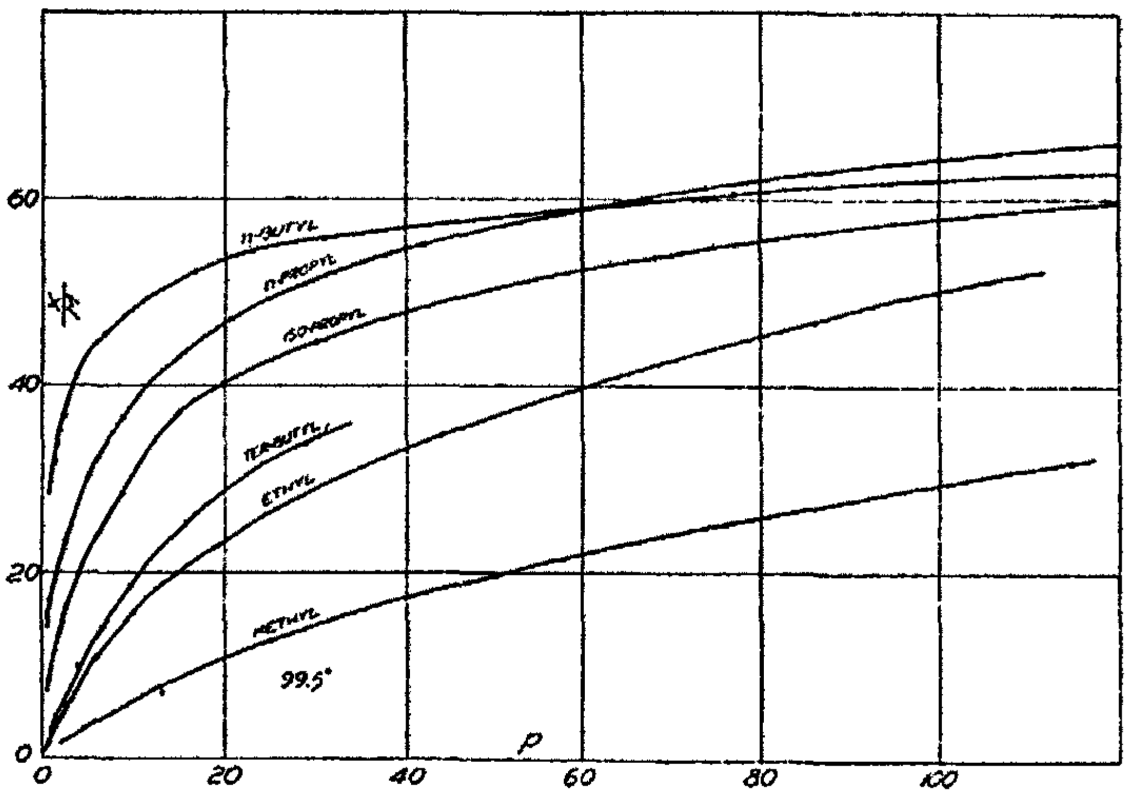

FIG. 4

With increase in the concentration and pressure of the vapor above the adsorbent there will be a crowding and a readjustment of the adsorbed molecules on the surface. These readjustments will require time and they will be most easily made on the more exposed charcoal surfaces; they will be more difficult within the capillaries where the influence of the size and shape of the vapor molecules will be more pronounced. We have then the phenomenon of a "drift," similar to that observed by Cude and Hulett[9] when thoroughly outgassed charcoal is immersed in liquids for long periods of time.

The validity of the Freundlich equation, $X/m = \alpha . p^{1/n}$, requiresa constant value for the exponent 1/n. The plot of the double-log isotherms should, if the equation applies to these vapors, give perfectly straight lines. The behavior of these isotherms is to be seen in Fig. 5. In general, the slopes, 1/n, of these isotherms tend to become more constant the lower the temperature at which they are determined, and to a less pronounced extent also at

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[9] Cude and Hulett: J. Am. Chem. Soc., 42, 391 (1920).

higher pressures. The values of 1/n becomes smaller as the number of carbon atoms in the chain is increased. Further, the flaring of the isotherms, that is the variation of the log X/m values of the chain compounds with decreasing pressures, decreases with increase in the molecular weight of the vapor. This is exactly the same order as that previously observed for methane and its chlorine derivatives[7]. Further discussion of these isotherms will be left for a later paper.

The effect of temperature on the adsorption of the monochlor alkyl derivatives is also shown by their isosteres. If the well-known relation,

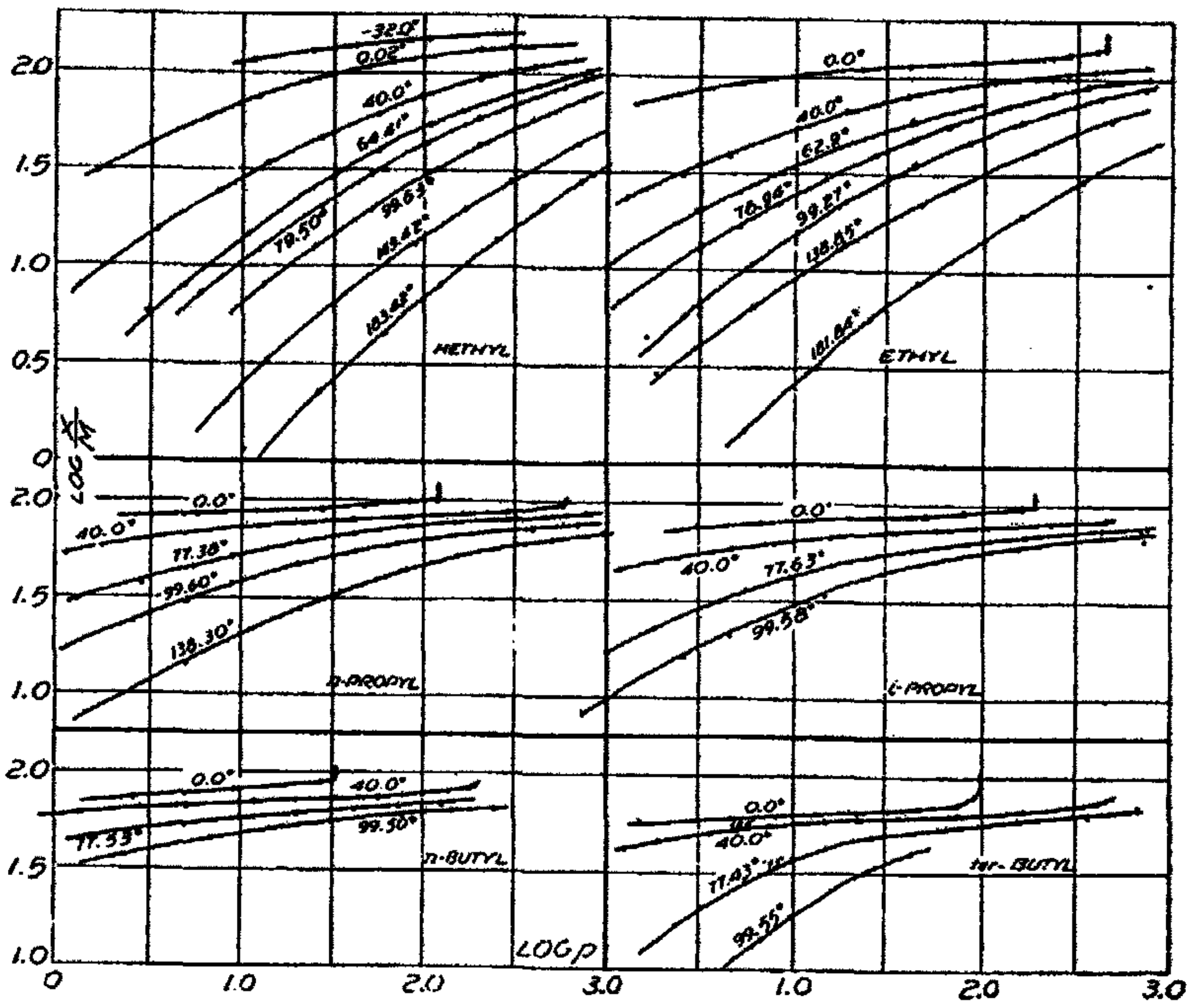

Fig. 5

$$\frac{d \ln p}{d\ 1/T} = -\frac{\Delta H}{R},$$

applies to adsorption phenomena, the slope of these isosteres should be proportional to the negative value of the heat of adsorption. Further, unless the heat of adsorption is dependent upon the temperature the isotherms should be parallel straight lines. Within limits of experimental error the isosteres are both parallel and rectilinear throughout the temperature range. Since they have the usual characteristic form we are omitting the graphs in order to save space. The heats of adsorption calculated from the mean slopes of all of the isosteres of each vapor are given in Table I.

TABLE I

Heats of Adsorption of the Vapors of Alkyl Chlorides on Charcoal

Vapor	ΔH cals.	Vapor	ΔH cals.
CH_3Cl	− 8300	i-C_3H_7Cl	−12250
C_2H_5Cl	−10060	n-C_4H_9Cl	−13400
C_3H_7Cl	−12300	ter-C_4H_9Cl	−11600?

Upon the basis of theoretical considerations Coolidge[10] has justified the use of the Clausius-Clapeyron equation in the calculation of the heat evolved in the adsorption process. However, it has usually been found that the heat effect calculated in this way is lower than that experimentally determined. Pearce and McKinley[11] have determined the heat of adsorption of ethyl chloride and methyl chloride at 25°; the values obtained for ΔH were −15400 and −11600 cals., respectively. The liquids from which they obtained their vapors were those purified for the present work; their charcoal was taken from the same container and subjected to the same treatment in outgassing. The difference between the observed and calculated heats of adsorption may be due in part to the fact that in determining the heats of adsorption experimentally the vapors are not admitted to the charcoal under the equilibrium pressure.

Lamb and Coolidge[6] have shown that the heats of adsorption differ from the heats of vaporization by constant amounts. This they attribute to the compression caused by the adsorption forces. According to the Polanyi theory, however, the surface of the adsorbed layer increases in distance from the surface of the adsorbent as more and more vapor is adsorbed until, finally, it reaches the edge of the adsorption space. The potential and, therefore, the compressive forces decrease very rapidly very near the edge of the adsorption space, and hence the heat of compression must also decrease rapidly. In this range, therefore, the heat of adsorption should change very rapidly with the concentration until it becomes equal to the heat of vaporization.

Application of the Polanyi Theory

In his earlier work Polanyi[12] attempted to explain the forces existing between the adsorbent and adsorbed molecules. He assumed that the adsorption forces act through distances which are large compared with molecular diameters. Also, that the force exerted upon a molecule at a given distance from the surface of the adsorbent is independent of the temperature and independent of whether or not other molecules exist between the molecule and the surface. He has shown that for temperatures below 0.8 $T_{crit.}$ of the vapor the adsorption potential at any point in the adsorption space is given by the relation,

$$\epsilon_i = RT \ln \frac{p_s}{p_x},$$

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[10] Coolidge: J. Am. Chem. Soc., 48, 1795 (1926).

[11] Pearce and McKinley: J. Phys. Chem., 32, 360 (1928).

[12] Polanyi: Ber. deutsch. physik. Ges., 12, 1012 (1924); Verh. deutsch physik. Ges., 18, 55 (1916); Z. Elektrochemie, 26, 370 (1920).

where p_s is the vapor pressure of the liquid in the free state and p_x is the equilibrium pressure in the adsorbed state. The potential ϵ_i is nothing more than the work done in transporting one mole of vapor from the saturation pressure, p_s to the equilibrium pressure p_x.

All points possessing the same adsorption potential, ϵ_i, form an equipotential surface. This and the surface of the adsorbent inclose a definite volume, —the adsorption space, ϕ_i. Assuming the adsorbed substance to have the same density as the free liquid, for temperatures well below the critical temperature, we can calculate the volume of the adsorption space from the relation,

$$\phi_i = x'/\delta,$$

where x' is x/m and δ is the density of the liquid. Thus, for every pair of p_x and x/m values we may calculate a pair of ϵ_i and ϕ_i values, so that

$$\epsilon_i = f(\phi_i).$$

The curves showing the potential distribution with the volume are given in Fig. 6.

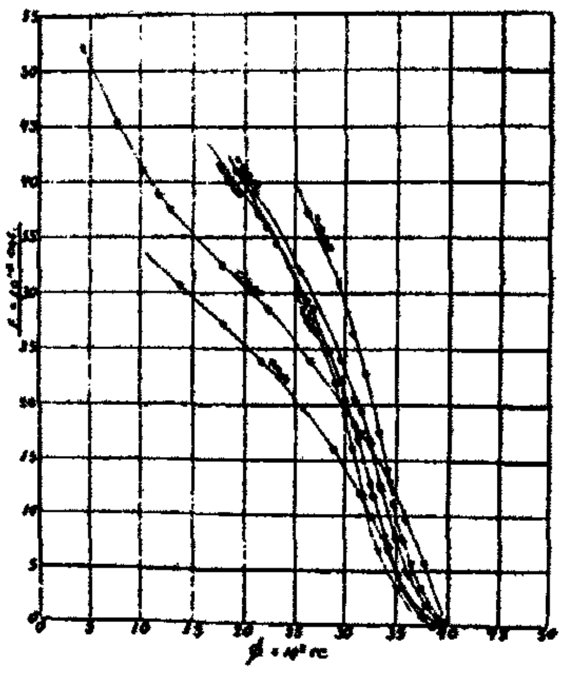

Fig. 6

The (ϵ ϕ)-curve is then a characteristic adsorption curve for a given vapor and adsorbent. If we assume with Polanyi that the temperature coefficient of the adsorption potential is zero, and make the necessary corrections for the volume occupied by the adsorbed substance, the curve should be the same for all temperatures. In the vicinity of and above the critical temperature corrections must be applied for the density of the adsorbed substance. By means of the thermal dilatation formula of the adsorbed substance as a liquid and of its equation of state as a vapor it is possible to calculate the adsorption isotherm at any other temperature from the (ϵ-ϕ)-curve determined for a single isotherm.

We have calculated the (ϵ-ϕ)-curves for propyl chloride and iso-propyl chloride from both the 0° and 40° isotherms. In making these calculations the densities were taken from the "International Critical Tables" and they are corrected for temperature by the dilatation formulas given in the "Physical Chemistry Tables." The curves have been drawn for the 40° isotherms and the points calculated from the 0° isotherms are indicated by double circles. The agreement is all that can be desired. Berenyi[13] has previously applied the method here used to the data of Titoff for the adsorption of carbon dioxide. The agreement in this case is also most excellent.

The relative positions of the (ϵ-ϕ)-curves of the two pairs of isomers is interesting. While they do not coincide the curves for either pair of isomers

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[13] Berenyi: Z. physik. Chem., 94, 628 (1920).

run practically parallel throughout their whole extent. Further, for a given adsorption volume, ϕ, the adsorption potential, ϵ, of the normal compound, is greater than that of its isomer. Conversely, for equal adsorption potentials the adsorption space occupied is always greater for the normal compound. These curves show also the influence of lengthening the hydrocarbon chain by successive increments of CH_2. For relatively high values of ϵ, say ϵ = 3000 cals., the values of ϕ increase regularly from methyl chloride to n-butyl chloride. This relation disappears, however, as we approach saturation.

It is interesting to note also that at the limit of the adsorption space, where the adsorption potential is zero, the adsorption volume, $\phi.10^2$, is practically the same for all of the vapors given, viz., about 39.5. This is almost identically the same value as that obtained by Pearce and Johnstone[7] for the adsorption of the chlorine derivatives of methane on charcoal from the same stock supply. The coincidence is exactly what we should expect, if the Polanyi theory involved is correct. The maximum value of ϕ would not necessarily be the same, however, on another sample of the same charcoal having a different degree of activation.

It is very probable that adsorption relations would be much more significant if comparisons were made at corresponding temperatures rather than at identical temperatures. We have in the 40° isotherms data which is quite suited for such a comparison. The boiling points of propyl chloride and tertiary butyl chloride are 46.6° and 51°, respectively; their isotherms are very similar in shape. We have calculated the ratio of the volumes of the two vapors adsorbed under the same pressure at different pressures throughout the pressure range from 3 mm. to 300 mm. The values of the ratios were found to be practically constant:

$$\frac{\text{cc. of propyl chloride vapor}}{\text{cc. of ter-butyl chloride vapor}} = \frac{1}{0.778} = 1.285$$

The molecular volumes of these chlorides as liquids at 40°, calculated from their values at 20°, are in the ratio

$$\frac{V_l\ \text{(propyl chloride)}}{V_l\ \text{(ter-butyl chloride)}} = \frac{90.7}{112.2} = \frac{0.823}{1}$$

If we now neglect the compressibility of the liquids, the small difference in boiling points, and also any possible blocking effect in the capillaries due to the larger cross-section of the tertiary butyl chloride molecules, we find that the ratio of the actual volumes of the adsorbed substances, considered as liquids, is

$$\frac{V_l\ \text{(propyl chloride)}}{V_l\ \text{(ter-butyl chloride)}} = \frac{1.06}{1.00}$$

Taking into consideration the uncertainty of the density data, this ratio of approximately unity should indicate that the amounts of different vapors, possessing a common orienting atom, adsorbed at identical, or nearly corresponding temperatures, occupy a definite volume for a given equilibrium pressure. It is our intention to study this relation more fully in a forthcoming study of the adsorption of vapors at their boiling points.

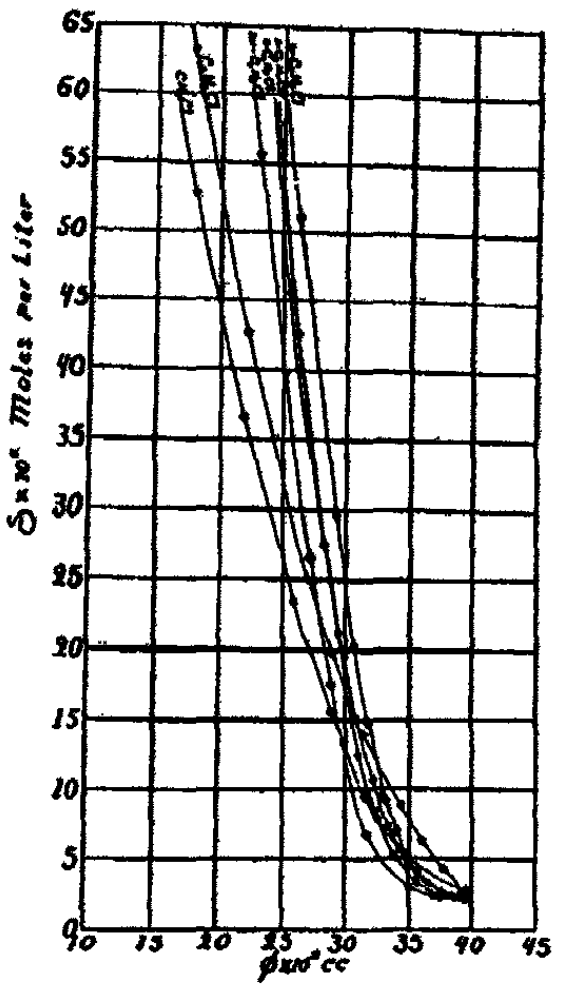

Fig. 7

In his calculations Polanyi has assumed that the density of the adsorbed vapor is the same as that of the free liquid at the same temperature. Above the critical temperature the density of the adsorbed substance is no longer equal to that of the liquid. In order to apply the characteristic (ϵ_i-ϕ_i) curves for the determination of an isotherm, Berenyi[13] has shown that it is necessary to make corrections for the change of density at the various levels in the adsorption space. The relation given by $\epsilon_i = g(\delta_i)$, indicates that for every potential level, ϵ_i, there is a corresponding density, δ_i. Making use of the equation of state of the adsorbed vapor, Berenyi finds that the relation between the density distribution and the potential can be expressed by the equation:

$$\frac{\epsilon_i}{RT} = \ln \frac{RT}{p_x\left(\frac{1}{\delta_i} - b\right)} - \frac{2a\delta_i}{RT} + \frac{1}{1 - b\delta_i} - 1,$$

where a and b are the van der Waal constants and δ_i is the density of the vapor at the potential level, ϵ_i. Neglecting the last three terms on the right will introduce only a negligible error, since $2a\delta_i/RT$ and $b\delta_i$ become vanishingly small at high temperatures. The application of this equation at the temperatures which we have used may introduce error in calculating the density distribution of the vapors studied. The values obtained for the different vapors, however, should be, relatively at least, of the correct order of magnitude. By elimination of ϵ_i between the two functions, $\epsilon_i = f(\phi_i)$ and $\epsilon_i = g(\delta_i)$, we obtain a relation between the density distribution and the volume, viz., $\delta_i = h(\phi_i)$. In making these calculations we have taken the constants a and b of the equations of state of the three lower alkyl chlorides from the Landolt-Börnstein-Roth Tabellen, Ed. 5. The constants for isopropyl chloride and the two butyl chlorides were not available in the literature. They were estimated from the values for similar compounds. The volume-density distribution relations thus obtained are shown graphically in Fig. 7.

Summary

1. The adsorption of the vapors of ethyl, n-propyl, isopropyl, n-butyl and tertiary butyl chlorides by charcoal has been determined at temperatures ranging from 0° to temperatures at which the vapors become unstable when in contact with charcoal. The stability of these alkyl chlorides toward heat decreases with increase in molecular complexity. The iso and tertiary compounds decompose at lower temperatures than do the corresponding normal compounds.

2. At low pressures and for all temperatures the volume of vapor adsorbed in the normal series increases with the molecular weight of the vapor. At 0° the order of adsorbability is completely reversed at sufficiently high pressures. At high temperatures (above 100°) the magnitude of the adsorption at all pressures increases with the length of the carbon chain. The adsorbability of the branch-chain compounds is at all temperatures and pressures less than that of the corresponding normal compounds. The influence of the branching structure of molecules upon the time required for the attainment of pressure equilibrium, especially at the break of the isotherm, is very pronounced.

3. The heats of adsorption of these vapors have been calculated from the slopes of the isosteres and they have been found to be lower than the values experimentally determined.

4. The potential distribution and the density distribution of the vapors in the adsorption space have been calculated according to the method of Polanyi.

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THE STATE OF FORMALDEHYDE IN AQUEOUS SOLUTIONS*

BY FREDERIC WALKER

Our present knowledge of the state of formaldehyde in aqueous solutions is based primarily upon the work of Auerbach and Barschall. As a result of an extensive study of the physical chemistry of such solutions, these investigators came to the conclusion that the solute was in the form of the simple hydrate, $CH_2O.H_2O$, plus a mixture of hydrated polymers having the general formula, $(CH_2O)_n.H_2O$. At concentrations up to approximately 34% they concluded that the only polymer present to any appreciable extent was the hydrated trimer, $(CH_2O)_3.H_2O$.

Auerbach and Barschall believed that the monomolecular hydrate of formaldehyde was methylene glycol, $CH_2(OH)_2$, whose methyl ether, methylal, $CH_2(OCH_3)_2$, is a well-known derivative of formaldehyde. According to this theory, the hydrated polymers of formaldehyde would be polymethylene glycols, having the general formula, $HO.(CH_2O)_n.CH_2OH$, similar to the polyethylene glycols, $(HO.(CH_2.CH_2.O)_n.CH_2.CH_2.OH)$, obtained when ethylene glycol is polymerized. As will be seen later, this view is now supported by the absorption spectra studies of S. A. Schou.

We have found that Auerbach's theories have been substantiated by the findings of later investigators and offer a workable theory for the interpretation of the physical behaviour of formaldehyde solutions. The object of this paper has been to review and correlate the scattered data on this subject. In doing this, we have discovered that the theories and data of Auerbach enable one to arrive at a quantitative explanation of the vapor pressure of formaldehyde in aqueous solutions as recently determined by Ledbury and Blair. We have shown that formaldehyde solutions follow Henry's law in that the partial pressure of the aldehyde vapor is proportional to the concentration of the solute in the simple monomolecular hydrate form. Finally we have been able to show by means of thermochemical calculations that the formaldehyde gas in equilibrium with aqueous solutions is probably the unhydrated monomolecular gas.

In recent years very little has been published on the physical chemistry of formaldehyde solutions. The standard books on formaldehyde scarcely mention it and the classic monograph published by Auerbach and Barschall in 1905 has now gone out of print. Since the use and importance of formaldehyde solutions has increased steadily throughout this period we are of the opinion that this would demand a thorough understanding of the reagent itself. Accordingly we shall begin our paper with a brief review of the research that has already been devoted to this subject.

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* Contribution from the Research Laboratory of The Roessler & Hasslacher Chemical Company.

Tollens and Mayer[1] in 1888 and Eschweiler and Grossmann[2] in 1890 first endeavored to measure the molecular weight of formaldehyde in aqueous solution and noticed a rather surprising anomaly. The apparent molecular weight of formaldehyde in a dilute solution prepared by diluting a more concentrated one was at first something over one and a half times the simple value of 30 required by the theory. If, however, the freezing point of the diluted solution was measured again after a day's standing, the normal value of 30 was obtained. From this evidence they concluded that concentrated formaldehyde solutions contained dissolved polymers which slowly dissociated on dilution.

In 1905 Auerbach and Barschall[3] made an extensive study of this phenomenon and determined the apparent molecular weight of formaldehyde in solutions of all concentrations up to approximately 38%. Their cryoscopic measurements for this work were all made in dilute solutions. This was possible because the change taking place on dilution in the case of most formaldehyde solutions was found to be very slow at 0°C. Accordingly they could dilute a sample of a concentrated formaldehyde solution in a measured volume of cold water and determine the apparent molecular weight of the formaldehyde in the concentrated solution from the freezing point of the dilute solution. Their results are shown in Table I.

TABLE I

The Apparent Molecular Weight of Formaldehyde in Aqueous Solutions at Room Temperature

	Volume Percent of CH_2O	Gms. CH_2O per 1000 gms. H_2O in the solution diluted for measurement	Freezing point lowering at the moment of dilution·	Apparent molecular weight
1	2.39	24.3	1.497	30.0
2	5.99	20.0	1.140	32.5
3	11.54	39.13	1.999	36.2
4	15.81	54.15	2.600	38.5
5	21.36	36.15	1.555	43.0
6	24.20	41.15	1.705	44.6
7	25.76	43.83	1.805	44.9
8	30.60	52.4	2.001	48.45
9	37.38	64.56	2.24	53.3
10	37.71	65.2	2.25	53.6

From these data it may be seen that the apparent molecular weight of the formaldehyde molecules in solution increases with increasing concentration of formaldehyde. Since these measurements were all made under the same

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[1] Ber., 21, 1566, 3503 (1888).

[2] Ann., 258, 103 (1890).

[3] Monograph entitled, "Formaldehyde in wässriger Lösung", from Arbeiten aus d. Kaiserl. Gesundheitsamte, XXII, 3; Zentralblatt, 1905 II, 1081.

conditions and at approximately the same concentration the variation is most probably due to the association of solute molecules as the investigators believed.

Having obtained these figures Auerbach sought for a simple mass action expression which would account for the data. He at first experimented with the equations shown below.

$$
\begin{array}{ll}
2\,CH_2O \rightleftarrows (CH_2O)_2 & \text{(I)} \\
3\,CH_2O \rightleftarrows (CH_2O)_3 & \text{(II)} \\
4\,CH_2O \rightleftarrows (CH_2O)_4 & \text{(III)} \\
6\,CH_2O \rightleftarrows (CH_2O)_6 & \text{(IV)}
\end{array}
$$

The mass action constants based on these equations all showed unsatisfactory trends, the true state of affairs appearing to be something of a mean between equations II and III. For this reason he tried out the following equation in which the formaldehyde and polymer are shown to be hydrated.

$$3\,CH_2(OH)_2 \rightleftarrows CH_2OH.CH_2O.CH_2OH + 2\,H_2O \quad \text{(V)}$$

The values obtained with this equation are shown in Table II compared with those obtained from equations II and III. These constants are here designated as K_{II}, K_{III} and K_V.

TABLE II

	Volume percent CH_2O	Apparent molecular weight	K_{II}	K_{III}	K_V
1	2.39	30.0	—	—	0.029
2	5.99	32.5	72	200	0.023
3	11.54	36.2	71	350	0.025
4	15.81	38.5	75	490	0.030
5	21.36	43.0	55	460	0.028
6	24.20	44.6	52	490	0.028
7	25.76	44.9	56	550	0.032
8	30.60	48.45	43	490	0.027
9	37.38	53.3	29	400	0.022
10	37.71	53.6	28	390	0.021

Average K_V = 0.026

The values for K_V showed no trend and were constant within the limits of the experimental error. Accordingly the investigator was led to the belief that the formaldehyde in aqueous solutions was present as methylene glycol, $CH_2(OH)_2$, and the hydrated trimer, $C_3H_6O_3.H_2O$, in the state of equilibrium shown by the following mass action expression, in which the concentration of the various constituents is measured in terms of mols per liter.

$$K = 0.26 = \frac{(CH_2(OH)_2)^3}{(C_3H_6O_3.H_2O)(H_2O)^2} \qquad (1)$$

At higher concentrations it seemed probable that higher polymers were formed and the low values observed in the last two constants in the table were attributed to this.

Auerbach also showed that when paraformaldehyde was dissolved in cold water, the solute at first showed a high degree of polymerization which disappeared on standing. Apparently the polymerized formaldehyde dissolved as a polymer and then dissociated. Raising the temperature of formaldehyde solutions was found to decrease the polymerization.

M. Delépine[1] as a result of a thermochemical study of formaldehyde solutions in 1897, was led to conclusions that were in complete agreement with those of Auerbach.

Delépine found that on diluting concentrated aqueous solutions of formaldehyde there was an instantaneous evolution of heat followed by a slow absorption of heat. He further discovered that paraformaldehyde has a negative heat of solution. After a quantitative study of these phenomena, he came to the conclusion that the heat developed on diluting formaldehyde solutions was a normal heat of dilution while the heat gradually absorbed on standing was due to some internal change in the solution. The fact that paraformaldehyde possessed a negative heat of solution cast light on the nature of this internal change since paraformaldehyde was known to depolymerize on going into solution. Accordingly Delépine came to the belief that in concentrated formaldehyde solutions, the solute was partially polymerized and on dilution the polymerized molecules slowly dissociated. It is interesting to note that the heat first evolved was found to be practically equal to the heat gradually absorbed.

Delépine[2] also made a study of formaldehyde solutions in chloroform and benzene. In these solvents the compound dissolved but sparingly and the solutions resembled the solutions of permanent gases, whereas in the case of water the solubility is exceedingly high. This investigator measured the heat of solution of the dry gas in water and found it equal to 15 large calories, approaching the heat of formation of the energetic hydrates. This work led him to the conclusion that the aldehyde was hydrated in its aqueous solution.

The recent work of S. A. Schou[3] on the absorption spectra of formaldehyde solutions in water and hexane adds fresh support to these theories. Furthermore, these results show that the monomolecular hydrate of formaldehyde is probably methylene glycol, $CH_2(OH)_2$, and not $CH_2O.H_2O$. The absorption spectra of aqueous solutions of formaldehyde show the band spectra characteristic of the carbonyl group to such a slight extent that Schou was able to estimate that the ratio of CH_2O molecules to molecules of hydrate and polymer is at the most 1 to 1200. In hexane, however, the absorption spectra show that the solute is in the form of CH_2O. Schou checked this work by measurements made on trichloracetaldehyde whose hydrate, chloral, can be isolated.

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[1] Compt. rend. **124**, 816, 1454, 1528 (1897); Bull., (3) **17**, 849 (1897); Ann. Chim., (7) **15**, 554 (1898).

[2] Ann. Chim., (7) **15**, 530 (1898).

[3] J. Chim. phys., **26**, 72-76; Chem. Abs., **23**, 3438 (1929).

The absorption spectra of this compound in water and hexane were qualitatively identical to the formaldehyde spectra. A similar study of acetaldehyde showed that this compound was 26% in the form of $CH_3.CHO$ in aqueous solutions. It is most interesting to note that the heat of solution of acetaldehyde is approximately one third the heat of solution of formaldehyde.

In 1925, Ledbury and Blair[1] determined the vapor pressure of formaldehyde in aqueous solutions at a series of temperatures between 0° and 45°. The investigators published vapor pressure curves and presented an empirical formula for calculating the vapor pressure of formaldehyde in aqueous solutions within the limits of their data.[2] This formula involved two constants, one of which varied with concentration.

The partial pressure of formaldehyde in aqueous solutions as seen in these curves showed a pronounced negative deviation from Raoult's Law. Henry's law for solutions at 20° was followed up to concentrations of approximately 4% after which a negative deviation became increasingly apparent. As will now be shown, a comparison of these data with Auerbach's findings for solutions at room temperature showed that the vapor pressure of formaldehyde was proportional to the mol fraction of methylene glycol. The fact that dissolved formaldehyde is wholly in the methylene glycol form up to concentrations of approximately 4% accounts for the agreement with Henry's law in this range.

Since the solute molecules found in formaldehyde solutions have the general formula, $(CH_2O)_n.H_2O$, the total number of molecules in these solutions does not vary with the concentration. Accordingly if G is taken as equal to the number of grams of formaldehyde in 100 grams of solution, the mol fraction of methylene glycol in dilute solutions may be expressed as follows:

$$x_{CH_2(OH)_2} = \frac{\frac{G}{30}}{\frac{100\text{-}G}{18}} = 0.60\,\frac{G}{100\text{-}G}$$

Now taking γ as equal to the fraction of dissolved formaldehyde in the methylene glycol form, we may write the following expression for the mol fraction of methylene glycol at all concentrations.

$$x_{CH_2(OH_2)} = 0.60\,\frac{\gamma G}{100\text{-}G}$$

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[1] J. Chem. Soc., **127**, 26-40, 2832-2839 (1925).

[2] The formula developed by these investigators is as follows:

$$\log_e P_{CH_2O} = \alpha - 2905/T$$

The value of α varies with the concentration and has the following values:

α 10% = 9.47
α 20% = 9.70
α 30% = 9.81
α 40% = 9.87

We have found that this formula gives approximately correct values for the vapor pressure of formaldehyde up to 100° by comparing the calculated values of the vapor pressure with those found by Auerbach.

Hence if the vapor pressure of formaldehyde in aqueous solutions is proportional to the mol fraction of methylene glycol alone, the following modified Henry's law expression should hold true.

$$P_{CH_2O} = K^1 \frac{\gamma G}{100 \cdot G} \tag{2}$$

Auerbach determined the apparent molecular weight of formaldehyde in solutions of various concentrations from which the corresponding γ values were easily calculated. By inserting these figures together with the values for the partial pressure of formaldehyde obtained from a curve based on the data of Ledbury and Blair for solutions at 20° in which the vapor pressure was plotted as a function of concentration in terms of weight percent, we were able to calculate values of K^1 for the equation.

In the following table are shown values of γ found from Auerbach's data for solutions of various concentrations, and the values of K^1 calculated therefrom. For purposes of comparison we have also included values for the unmodified Henry's law constant, K_H which were calculated by means of the equation shown below.

$$P_{CH_2O} = K_H . X_{CH_2O} = \frac{3G}{500\text{-}2G} \tag{3}$$

TABLE III

Values of K^1 and γ for solution of formaldehyde at 20°C.

G	P_{CH_2O} In millimeters of mercury	γ Observed Calculated from Auerbach's data	K^1	K_H
2.4	0.11	0.98	4.6	7.5
5.9	0.24	0.87	4.4	6.8
11.2	0.39	0.72	4.3	5.6
14.7	0.49	0.64	4.5	5.2
21.1	0.61	0.53	4.3	4.4
22.6	0.67	0.49	4.7	4.5
24.0	0.70	0.48	4.6	4.4
28.2	0.80	0.41	5.0	4.1
33.8	0.93	0.33	5.5	4.0
		Average K^1 =	4.5	

As will be seen the values thus obtained for K^1 are practically constant. They show a slight trend at concentrations over 28%. This may be accounted for as due to the appearance of small quantities of higher polymers at these concentrations. Furthermore the experimental error in the data is greater at the higher concentrations.

The vapor pressure of formaldehyde in aqueous solutions at 100° was determined by Auerbach. At this temperature the solutions still show a negative deviation from Raoult's law but Henry's law is followed up to concentrations of approximately 22%. This is in agreement with Auerbach's finding that when the temperature is raised the equilibrium is shifted in the direction of methylene glycol and the fraction of formaldehyde in the form of hydrated polymers is decreased. With these data we were able to calculate the value of K^1 in equation (2) since at concentrations below 22%, γ is equal to one. Using this value of K^1 we were then able to calculate the γ values for solutions at higher concentrations by substituting in the same equation and solving for γ^1. These results are shown in the following table. The values for $100\text{-}G/G.P_{CH_2O}$ are given which are equal to K^1 at the lower concentrations but fall off as γ decreases.

Table IV

Formaldehyde Solutions at 100°

G	P_{CH_2O} In millimeters of mercury	$100-G/G\,.\,P_{CH_2O}$	γ
7.69	28.3	340	1.00
14.29	56.5	339	1.00
20.00	85.0	340	1.00
22.1	96.0	339	1.00
25.0	106.8	320	0.94
26.8	110.0	300	0.88
29.4	103.0	249	0.73
31.8	94.2	202	0.59
34.4	106.3	199	0.59

K^1 at 100° = 340

We have thus far said nothing about the state of formaldehyde in the vapor phase in equilibrium with aqueous solutions. Some investigators have believed that this vapor consisted of varying proportions of the molecular species CH_2O, $(CH_2O)_n$, $CH_2(OH)_2$ and $(CH_2O)_n.H_2O$. That hydrated polymers should exist in the vapor phase to any extent now seems unlikely since the concentration of these polymers in aqueous solution has no appreciable influence on the vapor pressure. That unhydrated polymers should exist also seems unlikely since Auerbach and Plüddemann[1] found that these were unstable in the presence of water vapor and tended to dissociate under its influence. The only two species of formaldehyde gas which have been studied in a pure state are the monomolecular gas,[2] CH_2O, obtained by the vaporization of the "trioxymethylene" of commerce and a trimeric gas[3] obtained by the vaporization of α-trioxymethylene, a rare polymer obtained only by special procedures. These facts made it seem probable that the formaldehyde gas in equilibrium with aqueous solutions was either the simple monomeric variety or methylene glycol vapor.

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[1] Zentralblatt, **1914**, I, 956.

[2] Trautz and Ufer: J. prakt. Chem., (2) **113**, 105 (1926).

[3] Pratesi: Gazz., **14**, 139 (1884).

Now the constant for the Henry's law expression for formaldehyde would also be the mass action constant for the following equation:

$$CH_2(OH)_2 \text{ (in solution)} \rightleftarrows 1 \text{ mol formaldehyde gas} + \Delta H \qquad (A)$$

Assuming that the formaldehyde gas is CH_2O or $CH_2(OH)_2$ and writing the equation in the opposite direction we obtain the following:

$$CH_2O_{(gas)} \text{ or } CH_2(OH)_{2(gas)} + \text{Aq.} \rightleftarrows CH_2(OH)_{2(\text{in solution})} + \Delta H \qquad (B)$$

Here we can see that ΔH is the heat of solution of the formaldehyde gas that is in equilibrium with aqueous formaldehyde.

Delépine determined this value by measuring the heat evolved when anhydrous formaldehyde gas was dissolved in water. He thus obtained a value of 15,000 calories.[1] H. v. Wartenburg recently determined the heat of formation of anhydrous, gaseous formaldehyde to be 28,700 calories[2] and if this is subtracted from Delépine's figure for the heat of formation of formaldehyde in aqueous solution (40,400 calories[1]), we obtain another value for ΔH. This value is 11,700 calories. Since we knew the Henry's law constants for formaldehyde solutions at 20° and 100°, we were able to calculate an approximate value for ΔH in equation (B). This was done by substituting the T and K values in the following equation in which it is assumed that ΔH does not vary with temperature.

$$\log_e \frac{K_2}{K_1} = \frac{H(T_1-T_2)}{R\,T_1\,T_2} \qquad (4)$$

$$2.30 \log \frac{340}{4.6} = \frac{80\ \Delta H}{216{,}000}$$

$$\Delta H = -\frac{2.30 \times 1.869 \times 216{,}000}{80} = 11{,}600 \text{ calories}$$

As a check on this value we also determined the Henry's law constant for formaldehyde solutions at 45°C. and used it in the calculation of ΔH. The value for the Henry's law constant at 45°C. was obtained from the data of Ledbury in the same manner that the constant for 100° was obtained from the data of Auerbach. The results are shown in Table V in which the vapor pressure values have been obtained from a curve based on Ledbury's data in which the vapor pressure was plotted as a function of formaldehyde concentration in terms of weight percent.

On substituting this value for K^1 in equation (4) together with the value for the 20° constant, we obtained a value for ΔH of $-12{,}300$ calories. Since the two thermochemical values were approximately equal, we concluded that our previous assumption had been correct. ΔH did not vary appreciably

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[1] Delépine: Compt. rend., **124**, 816 (1897).

[2] H. v. Wartenburg: Z. angew, Chem., **38**, 591-2 (1925).

TABLE V

Formaldehyde Solutions at 45°.

G	P_{CH_2O} In millimeters of mercury	$100-G/G \cdot P_{CH_2O}$	γ
2	0.50	24.5	1.00
4	0.97	24.7	1.00
6	1.40	21.9	0.89
8	1.83	21.1	0.86
10.4	2.30	19.8	0.81

K^1 at 45° = 24.6

with temperature and was equal to approximately −12,000 calories. This value of ΔH makes it seem possible that the formaldehyde gas in equilibrium with aqueous solutions consists of monomeric unhydrated molecules. If this gas were a formaldehyde polymer or methylene glycol vapor we should certainly expect a much lower value. ΔH in the latter case would have been a simple heat of solution. The vapor pressure of formaldehyde over its aqueous solutions is probably the decomposition pressure of the dissolved methylene glycol. The extraordinary influence of temperature on the partial pressure of formaldehyde in aqueous solutions adds weight to this conclusion The vapor pressure of water at 100° is 44 times its value at 20° whereas the partial pressure of formaldehyde in a 15% aqueous solution at 100° is 115 times its value at 20°.

In concluding we would point out that the escaping tendency of formaldehyde molecules in aqueous solution is manifested in two ways, by the vapor pressure of gaseous formaldehyde and by the polymerization of the dissolved molecules. The hydrated trimer is fairly soluble but as the polymerization increases the solubility decreases and paraformaldehyde, $(CH_2O)_n.H_2O$, is precipitated. At high temperatures the formaldehyde escapes, as a gas, at low temperatures as a precipitate.

Summary

1. The work of previous investigators has shown that in aqueous solutions of formaldehyde, the solute is probably in the form of the simple hydrate, methylene glycol, $CH_2(OH)_2$, plus a mixture of hydrated polymers having the general formula, $(CH_2O)_n.H_2O$. The evidence upon which this statement is based consists of vapor pressure data, cryoscopic data, thermochemical data and a study of the absorption spectra of formaldehyde solutions.

2. According to Auerbach the only polymer present to any appreciable extent in formaldehyde solutions up to concentrations of approximately 38% is the hydrated trimer, $(CH_2O)_3.H_2O$. The methylene glycol in these solutions is in chemical equilibrium with this hydrated polymer. Raising the temperature of the solution or lowering the concentration of formaldehyde shifts the

equilibrium in the direction of methylene glycol. This statement rests primarily upon the cryoscopic data of Auerbach but the writer has found that it is in agreement with Ledbury's vapor pressure data as seen below.

3. The writer has found that formaldehyde solutions obey Henry's law in that the partial pressure of the aldehyde is proportional to the concentration of the solute in the methylene glycol form. This has been shown to be the case for solutions up to 34%. The data used were Auerbach's cryoscopic data in conjunction with Ledbury's vapor pressure data for formaldehyde solutions at 20°C.

4. According to the writer the formaldehyde in the vapor in equilibrium with aqueous solutions of formaldehyde is probably monomolecular unhydrated formaldehyde gas. The writer came to this conclusion through thermochemical considerations based on a comparison of the thermochemical data of Delépine and thermochemical calculations carried out with the Henry's law constants calculated for aqueous formaldehyde solutions at various temperatures.

OXIDATION OF CARBOHYDRATES AND FATS BY AIR IN PRESENCE OF YELLOW PHOSPHORUS

BY SACHINDRA NATH CHAKRAVARTI AND N. R. DHAR

In previous communications[1] from this laboratory, the phenomenon of induced oxidation has been extensively investigated. It has been shown that solutions of carbohydrates, fats, etc., which cannot be oxidised under ordinary conditions can very easily be oxidised at the laboratory temperature if a current of air is passed through the solution in presence of substances like ferrous hydroxide, cerous hydroxide, manganous hydroxide, sodium sulphite, etc. It has been shown that these easily oxidisable substances in course of their own oxidation by air induce or promote the oxidation of other substances (carbohydrates, fats, etc.) which have the potentiality of being oxidised under ordinary conditions. In a recent paper[2] Dhar has advanced an explanation of the induced reactions based on the generation of ions in chemical changes. It is well known that ions are generated in the oxidation with phosphorus. It is very likely that these ions activate the molecules of oxygen which thus becomes reactive and induce chemical changes which are not possible with molecular oxygen. It is well known that the oxidation of phosphorus can be retarded by various substances. Thénard was the first to observe that the oxidation of phosphorus is considerably decreased by the presence of some organic vapours.[3] Graham[4] observed that alcohol vapour, ether, ethylene, naphtha, sulphuretted hydrogen, etc., protected phosphorus from being acted upon by oxygen. Thus these organic substances act as negative catalysts in the oxidation of phosphorus.

Having investigated a large number of such reactions in which the oxidation of one substance is retarded by the presence of a negative catalyst, Dhar[5] has put forward the view that the phenomenon of negative catalysts is possible when the catalyst itself is likely to be oxidised. Thus in every case of such negative catalysis, the catalyst simultaneously gets oxidised. Though sodium arsenite does not get oxidised under ordinary conditions by passing air through the solution, it can be oxidised under the same conditions only if it is mixed with sodium sulphite or any other reducing agent. At the same time, the oxidation of sodium sulphite is retarded. Hence it was expected that as the oxidation of phosphorus is retarded by the presence of some organic substances, it seems likely that these inhibitors also will get oxidised along with the slow oxidation of phosphorus. The present investigation was undertaken

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[1] J. Chem. Soc., 111, 690 (1917); Z. anorg. Chem., 122, 146 (1922); J. Phys. Chem., 29, 376, 799 (1925); 30, 939 (1926); 32, 1663 (1928).

[2] J. Phys. Chem., 28, 948 (1924).

[3] "Traité de chimie," 1, 236 (1816).

[4] Quarterly Journal of Science, 11, 83 (1829).

[5] Proc. K. Akad. Weten. Amsterdam, 29, 1923 (1921).

with a view to observe whether phosphorus can be used as a suitable inductor like sodium sulphite, ferrous hydroxide, cerous hydroxide, etc. Also, as phosphorus gets oxidised with the generation of ions, it was expected that it would prove a very good inductor. The experimental results recorded in the following pages show that these expectations have been realised to a certain extent.

Experimental

Phosphorus was cut into small bits (each bit being approximately 0.005 gm.) and put in water. The solutions of carbohydrates or the potassium salts of fatty acids were added to it and the volume made up to 100 cc. Dry air free from carbon dioxide was passed through the bottles, care being taken that the air came in contact with the phosphorus surface. A blank experiment was also conducted to see if diffused light of the laboratory had any effect on the oxidation. The fumes of the oxides of phosphorus which were generated from the bottle containing phosphorus, were passed through the same quantity of the solutions of carbohydrates or other substances. The residual carbohydrates were estimated by their reduction of Fehling's solution, the precipitated oxide of copper being dried, ignited, and weighed. The oleate, stearate, and palmitate were estimated by their absorption of iodine monochloride, before and after the experiment. The oxalate and the oxalic acid were estimated by precipitation as calcium oxalate and subsequent titration with potassium permanganate in presence of acetic acid which dissolved the precipitate of calcium phosphite and phosphate. The results are given in Tables I-IV.

TABLE I

Carbohydrates and Bits of Phosphorus

Amount of phosphorus 4.0 gm (Each bit = 0.005 gm)
Amount of carbohydrates 0.1 gm.
Time 5½ hours
Temperature 34°

Carbohydrates	Percentage of oxidation in the diffused light of the laboratory (1)	Percentage of oxidation in presence of Phosphorus (2)	Percentage of oxidation in presence of Phosphorus only (3)	Percentage of oxidation in presence of fumes of Phosphorus (4)	Percentage of oxidation in presence of fumes only (5)
Starch	2.9%	6.1%	3.2%	3.5%	0.6%
Maltrose	2.7%	4.4%	1.7%	3.1%	0.4%
Dextrose	1.9%	4.5%	2.6%	2.5%	0.6%
Glucogen	2.1%	4.9%	2.8%	2.7%	0.6%
Inulin	1.8%	4.4%	2.6%	2.3%	0.5%
Lactose	1.8%	3.9%	2.1%	2.2%	0.4%
Fructose	1.7%	3.9%	2.2%	2.1%	0.4%
Glucose	1.7%	4.2%	2.5%	2.2%	0.5%
Sucrose	1.6%	4.7%	3.1%	2.2%	0.6%
Galactose	1.1%	3.7%	2.6%	1.6%	0.6%
Arabinose	0.8%	3.2%	2.4%	1.3%	0.5%

Table II

Fatty Substances and Bits of Phosphorus
Amount of phosphorus 4.0 gm (Each bit = 0.005 gm)
Amount of fatty substance 0.1 gm
Time 5½ hours
Temperature 34°

Fatty Substances	(1)	(2)	(3)	(4)	(5)
Potassium oleate	2.6%	6.7%	4.1%	3.9%	0.8%
Potassium stearate	2.8%	7.3%	4.5%	3.7%	0.9%
Potassium palmitate	2.1%	6.1%	4.0%	2.9%	0.8%
Potassium oxalate	1.6%	5.6%	4.0%	2.9%	0.8%
Oxalic acid	1.4%	4.9%	3.5%	2.1%	0.7%

Table III

Carbohydrates and Bits of Phosphorus
Amount of phosphorus 4.0 gm (Each bit = 0.005 gm)
Amount of carbohydrates 0.01 gm
Time 11 hours
Temperature 36°

Carbohydrates	(1)	(2)	(3)	(4)	(5)
Starch	5.4%	11.3%	5.9%	6.6%	1.2%
Maltose	5.1%	8.1%	3.0%	5.7%	0.6%
Dextrin	3.8%	8.7%	4.9%	4.8%	1.0%
Glycogen	3.8%	9.2%	5.9%	4.8%	1.0%
Inulin	3.7%	9.0%	5.3%	4.7%	1.0%
Lactose	3.4%	7.4%	4.0%	4.2%	0.8%
Fructose	3.2%	7.2%	4.0%	4.0%	0.8%
Glucose	2.9%	7.7%	4.8%	3.8%	0.9%
Sucrose	2.9%	8.8%	5.9%	4.1%	1.2%
Galactose	2.0%	6.8%	4.8%	3.0%	1.0%
Arabinose	1.4%	5.9%	4.5%	2.3%	0.9%

Table IV

Fatty Substances and Bits of Phosphorus
Amount of phosphorus 4.0 gm (Each bit = 0.005 gm)
Amount of fatty substances 0.1 gm
Time 11 hours
Temperature 34°

Fatty Substances	(1)	(2)	(3)	(4)	(5)
Potassium oleate	4.4%	11.7%	7.3%	5.8%	1.4%
Potassium stearate	5.1%	13.1%	8.0%	6.7%	1.6%
Potassium palmitate	4.0%	10.9%	6.9%	5.4%	1.4%
Potassium oxalate	3.0%	10.0%	7.0%	4.4%	1.4%
Oxalic acid	2.3%	9.1%	6.8%	3.6%	1.3%

A second set of experiments was started in exactly the same way, the only difference being that instead of small bits of phosphorus, colloidal phosphorus was prepared in the following way. About two grams of phosphorus were taken in 25 cc. of absolute alcohol in a small stoppered bottle and warmed in a water bath until the phosphorus melted. The bottle was vigorously shaken and in a short time the phosphorus was divided into very fine particles. The process was repeated several times so that a saturated solution of phosphorus was obtained. The solution was poured into water and a milky white emulsion was formed. In this way, a suspension of about 0.1 gm. of phosphorus was obtained. The next procedure was exactly similar to the previous ones. The oxidation of oleate, stearate, and palmitate could not be investigated in this particular case as the alcohol present interfered with the method of estimation followed in the case of these substances, by absorbing a large quantity of iodine. The oxalate was estimated by adding calcium chloride and dissolving the precipitated phosphates and phosphites by acetic acid and estimating the calcium oxalate with potassium permanganate. The other methods of estimation were similar to the previous ones. The results are tabulated in Tables V-VIII.

TABLE V

Carbohydrates and Colloidal Phosphorus
Amount of phosphorus 0.1 gm
Amount of carbohydrates 0.1 gm
Time 5½ hours
Temperature 36°

Carbohydrates	(1)	(2)	(3)	(4)	(5)
Starch	3.2%	8.8%	5.6%	4.3%	1.1%
Maltose	3.0%	6.3%	3.3%	3.7%	0.7%
Dextrin	2.1%	6.9%	4.4%	3.0%	0.9%
Glucogen	2.2%	7.1%	4.9%	3.2%	1.0%
Inulin	2.1%	6.9%	4.8%	3.1%	1.0%
Lactose	2.0%	6.0%	4.0%	2.8%	0.8%
Fructose	2.0%	6.4%	4.4%	3.1%	1.1%
Glucose	2.0%	6.5%	4.5%	2.9%	0.9%
Sucrose	1.9%	7.4%	5.5%	3.0%	1.1%
Galactose	1.3%	6.0%	4.7%	2.2%	0.9%
Arabinose	1.2%	5.5%	4.3%	2.2%	1.1%

TABLE VI

Oxalates and Colloidal Phosphorus
Amount of phosphorus 0.1 gm
Amount of oxalates 0.1 gm
Time 5½ hours
Temperature 36°

Substances	(1)	(2)	(3)	(4)	(5)
Potassium oxalate	1.9%	7.0%	5.1%	2.9%	1.0%
Oxalic acid	1.6%	6.4%	4.8%	2.5%	0.9%

TABLE VII

Carbohydrates and Colloidal Phosphorus
Amount of phosphorus 0.1 gm
Amount of carbohydrates 0.1 gm
Time 11 hours
Temperature 36°

Carbohydrates	(1)	(2)	(3)	(4)	(5)
Starch	5.4%	11.0%	5.6%	6.6%	1.2%
Maltose	5.2%	8.5%	3.3%	5.9%	1.7%
Dextrin	3.9%	8.8%	4.9%	4.8%	0.9%
Glycogen	3.9%	9.0%	5.1%	4.1%	1.2%
Inulin	3.9%	8.9%	5.0%	4.9%	1.0%
Lactose	3.3%	7.3%	4.0%	4.0%	0.7%
Fructose	3.1%	7.2%	4.1%	3.9%	0.8%
Glucose	3.0%	7.6%	4.6%	4.0%	1.0%
Sucrose	2.8%	8.3%	5.5%	4.0%	1.2%
Galactose	2.2%	7.0%	4.8%	3.2%	1.0%
Arabinose	1.4%	5.8%	4.4%	2.2%	0.8%

TABLE VIII

Oxalates and Colloidal Phosphorus
Amount of phosphorus 0.1 gm
Amount of oxalate 0.1 gm
Time 11 hours
Temperature 36°

Substances	(1)	(2)	(3)	(4)	(5)
Potassium oxalate	3.2%	8.6%	5.2%	4.2%	1.0%
Oxalic acid	2.6%	7.7%	5.1%	3.6%	1.0%

A third set of experiments was conducted under similar conditions but this time finely divided phosphorus (almost powdered) was taken as the inductor. Finely divided phosphorus was prepared in the following way. Two grams of phosphorus were taken in about 30 cc. of water in a stoppered bottle and kept in a water bath until the phosphorus just melted. The bottle was shaken vigorously and in a short time, the phosphorus solidified but in very fine particles—almost to a powdery form. The advantage in working with this form of phosphorus was that on slightly agitating this phosphorus in water, a portion of it remained in a suspended condition temporarily, so when air was passed through such a mixture, a larger volume of air came in contact with the surface of the phosphorus than in the case of small bits of phosphorus.

The next step and the methods of estimation were similar to the other ones. The results are tabulated in Tables IX-XII.

Table IX

Carbohydrates and finely divided Phosphorus
Amount of phosphorus 2.0 gm
Amount of carbohydrates 0.1 gm
Time 5½ hours Temperature 34°

Carbohydrates	(1)	(2)	(3)	(4)	(5)
Starch	3.1%	14.7%	11.6%	5.3%	2.2%
Maltrose	2.8%	9.4%	6.6%	4.1%	1.3%
Dextrin	2.0%	11.0%	9.0%	3.8%	1.8%
Glycogen	2.2%	12.0%	9.8%	4.1%	1.9%
Inulin	2.0%	11.4%	9.4%	3.9%	1.9%
Lactose	1.9%	9.9%	8.0%	3.5%	1.6%
Fructose	1.8%	10.0%	8.2%	3.4%	1.6%
Glucose	1.8%	10.8%	9.0%	3.6%	1.8%
Sucrose	1.8%	12.4%	10.6%	4.0%	2.2%
Galactose	1.2%	10.2%	9.0%	3.0%	1.8%
Arabinose	1.0%	9.6%	8.6%	2.7%	1.7%

Table X

Fatty Substances and finely divided Phosphorus
Amount of phosphorus 2.0 gm
Amount of fatty substances 0.1 gm
Time 5½ hours Temperature 36°

Fatty Substances	(1)	(2)	(3)	(4)	(5)
Potassium oleate	2.4%	11.7%	9.3%	4.2%	1.8%
Potassium stearate	2.8%	13.9%	11.1%	5.0%	2.2%
Potassium palmitate	2.3%	11.2%	8.9%	4.1%	1.8%
Potassium oxalate	1.6%	9.2%	7.5%	3.1%	1.5%
Oxalic acid	1.3%	8.5%	7.2%	2.7%	1.4%

Table XI

Carbohydrates and finely divided Phosphorus
Amount of phosphorus 2.0 gm
Amount of carbohydrates 0.1 gm
Time 11 hours Temperature 34°

Carbohydrates	(1)	(2)	(3)	(4)	(5)
Starch	5.4%	22.2%	16.8%	8.7%	3.3%
Maltose	5.2%	15.1%	9.9%	7.2%	2.0%
Dextrin	3.8%	17.6%	13.8%	6.5%	2.7%
Glycogen	3.8%	18.4%	14.6%	6.7%	2.9%
Inulin	3.8%	18.2%	14.4%	6.7%	2.9%
Lactose	3.3%	15.3%	12.0%	5.7%	2.4%
Fructose	3.2%	15.5%	12.3%	5.7%	2.5%
Glucose	3.0%	16.5%	13.5%	5.7%	2.7%
Sucrose	2.9%	19.4%	16.5%	6.2%	3.3%
Galactose	2.1%	15.9%	13.8%	4.8%	2.7%
Arabinose	1.4%	14.3%	12.9%	4.0%	2.6%

TABLE XII

Fatty Substances and finely divided Phosphorus
Amount of phosphorus 2.0 gm
Amount of fatty substances 0.1 gm
Time 11 hours
Temperature 36°

Fatty Substances	(1)	(2)	(3)	(4)	(5)
Potassium oleate	4.7%	22.1%	17.4%	8.2%	3.5%
Potassium stearate	5.3%	26.5%	21.2%	9.5%	4.2%
Potassium palmitate	4.2%	21.0%	16.8%	7.5%	4.3%
Potassium oxalate	3.0%	17.1%	14.1%	5.8%	2.8%
Oxalic acid	2.4%	16.2%	13.8%	5.1%	2.7%

From the foregoing data it is quite clear that phosphorus can be used as an inductor in the oxidation of carbohydrates and fats. Another interesting fact is observed that even the fumes given off in the oxidation of phosphorus can induce the oxidation of those substances to a slight extent. This probably is caused by particles of phosphorus or phosphorus trioxide which are likely to be carried away by the air. As these experiments were conducted at a time when the intensity of sunlight was very strong, even the diffused light of the laboratory could oxidise a certain portion of the substances. Making allowance for the oxidation in the diffused light without any inductor, we find that phosphorus in the finely divided state induced the oxidation of carbohydrates and fatty substances to the greatest extent. Colloidal phosphorus comes next and then the bits of phosphorus. Of course colloidal phosphorus having the largest surface should have been the most reactive amongst the three varieties but as it was prepared from an alcohloic solution, the alcohol present retarded the oxidation very much. Moreover, as the amount of phosphorus available in the colloidal phosphorus was very small being only about 0.1 gm. per experiment it was oxidised in a very short time. This is the reason why the oxidation of the carbohydrates and the fatty substances in presence of colloidal phosphorus as recorded in the present paper does not show change with time. Thus the amount of oxidation in 10 hours is almost the same as the amount of oxidation in 5 hours. If however, phosphorus could be suspended in water in some other way without introducing any other foreign matter, other than the inductor and the acceptor, it is likely that the percentage of oxidation would be much higher.

From the tables it would be apparent that in each case, starch is oxidised to the highest extent. Curiously enough, in all our previous communications on induced reactions with different carbohydrates we have found that starch can be very easily oxidised. We have shown in a recent communication that in these slow oxidations complete oxidation of carbohydrates, fats and nitrogenous substances to carbon dioxide takes place, without the formation of intermediate products. Hence, it is rather surprising how the complex molecule of starch is so easily susceptible to oxidation, whereas, glucose which is much simpler in structure, can not be so easily oxidised. This much is quite certain that in slow photochemical or induced oxidations, starch does not pass through the stage of glucose before its oxidation to carbon dioxide.

In the oxidation of carbohydrates in presence of diffused light we find that the order in which they are oxidised are as follows:—

Starch > maltose > dextrin > glycogen > inulin > lactose > fructose > glucose > sucrose > galactose > arabinose.

The order is exactly the same as has been recorded in the case of the oxidation in presence of sunlight without any inductor. However, the order is different in the case of the oxidation in presence of phosphorus. The order of the oxidation of carbohydrates in presence of each variety of phosphorus is the same and is as follows:—

Starch > sucrose > glycogen > inulin > dextrin > galactose > glucose > arabinose > fructose > lactose > maltose.

Almost the same order follows in the oxidation in presence of the fumes of phosphorus and phosphorous trioxide.

In the oxidation of the fatty substances, the oxidation follows the same order in all the three types that have been investigated and also the same order as in the diffused light.

Stearate > oleate > palmitate > oxalate > oxalic acid.

It appears also that finely divided phosphorus has the greatest power of inducing the oxidation. The next in order comes colloidal phosphorus in presence of alcohol and last the coarsely divided phosphorus.

In a foregoing paper we have shown that when a mixture of finely divided sulphur and phosphorus are kept under water at the laboratory temperature and air is passed, along with the slow oxidation of phosphorus, sulphur is oxidised to sulphurous and sulphuric acids. We have repeated some of these experiments and we have observed that a mixture of finely divided sulphur mixed with small bits of yellow phosphorus and kept under water at 25° or 30° can be oxidised to sulphurous and sulphuric acids and these can be qualitatively estimated.

Summary

A detailed experimental study has been made to ascertain whether phosphorus can be utilised as an inductor in the oxidation of carbonhydrate, fats and other substances and the following conclusions have been arrived at:—

(1) Finely divided phosphorus in the course of its oxidation has the greatest capacity of oxidising the carbohydrates and the fats, colloidal phosphorus comes second in order and small bits of phosphorus come last.

(2) In all the cases, the oxidation increases with time except in the case of colloidal phosphorus, where it does not vary much. This is due to the fact that the colloidal phosphorus prepared for this investigation is easily oxidised completely within six hours.

(3) The fumes of phosphorus and phosphorus trioxide also induce oxidation of the carbohydrates, fats and other substances to a slight extent.

(4) In the diffused light of the laboratory, carbohydrates, fats etc. are appreciably oxidised by air at the ordinary temperature.

(5) Although colloidal phosphorus should have been the most effective inductor, its apparent ineffectiveness is due to the presence of alcohol which inhibits the reaction.

(6) Under different conditions, amongst the carbohydrates, starch undergoes slow oxidation to the greatest extent.

(7) Sulphur is oxidised to sulphurous and sulphuric acid by simply bubbling air through a mixture of finely divided sulphur and phosphorus kept under water at the ordinary laboratory temperature.

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May 19, 1930.

THE SYSTEM $KCNS-Hg(CNS)_2-H_2O$

BY C. W. MASON AND W. D. FORGENG

The double thiocyanates of mercury have been known since 1838, when Claus[1] published his work on the metal thiocyanates. He prepared a double salt, by mixing $HgCl_2$ with KCNS and water, which he found to have the formula KCNS.2HgCNS.

Phillip[2] in 1867 stated that mercuric thiocyanate crystallized as needles and tablets, and also that when potassium thiocyanate is added to mercuric thiocyanate in warm water until the mercuric thiocyanate barely remains, a substance (no formula given) separates out. This substance is insoluble in cold water, slightly soluble in hot water, and it decomposes in cold water to give mercuric thiocyanate.

In 1872, Nordstroem[3] mentioned $Hg(CNS)_2.KCNS$ as colorless needles, and $Hg(CNS)_2.NH_4CNS$ as colorless prisms.

Fleischer[4] published his work on the double salts of NH_4CNS and Hg(CNS) in 1875. He prepared a double salt by adding yellow oxide of mercury to a boiling solution of NH_4CNS. He found the formula of this salt to be $2Hg(CNS)_2.N_2H_6.H_2O$. The crystals were in the orthorhombic system. Fleischer also prepared $Hg(CNS)_2.2NH_4CNS$ by dissolving $Hg(CNS)_2$ in an aqueous solution of NH_4CNS. By recrystallizing he obtained well-formed monoclinic crystals of this double salt. Drawings and crystal measurements of this double salt were made.

What is probably the most significant work on the double thiocyanates was performed by Rosenheim and Cohn[5] in 1901. They give three series of mercury double thiocyanates:

The monothiocyanates, HgCNSCl, HgCNSBr, and HgCNSOAc are described. Direct physical evidence of the complex cation HgCNS has not been obtained because of the slight solubility of these compounds.

The trithiocyanates, $KHg(CNS)_3$, $NH_4Hg(CNS)_3$, and $Ba[Hg(CNS)_3]$ $.2H_2O$ are well-crystallized salts, insoluble in cold water but easily soluble in hot water, by which they are decomposed into mercuric thiocyanate and the tetrathiocyanates.

Of the tetrathiocyanates, the potassium salt $K_2Hg(CNS)_4$ is obtained by crystallizing a mixture of the constituent salts. It crystallizes as colorless needles [?] and is easily soluble in water and alcohol. The sodium and barium salts are similar. The electrical conductivities of both the trithiocyanates

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[1] Claus: J. prakt. Chem., 15, 409 (1838).

[2] Phillip: Chem. Zentr., 55, 967 (1867).

[3] Nordstroem: Bull. 17, 345 (1872).

[4] Fleischer: Ann., 179, 225 (1875); Bull. 26, 165 (1876).

[5] Rosenheim and Cohn: Z. anorg. Chem., 27, 280 (1901).

and tetrathiocyanates show that they are salts of complex acids as do also their behaviors in Nernst's apparatus for demonstrating the movement of the ions.

Sherrill and Skowronski[1] in 1905, showed by the results of freezing point, solubility, and E. M. F. determinations that the complex salt $K_2Hg(CNS)_4$ is formed in aqueous solution by the reaction of $Hg(CNS)_2$ and KCNS.

H. Grossman[2] in the same year stated that Hg^+ and Hg^{++} thiocyanates dissolve in KCNS to form the complex $K_2Hg(CNS)_4$. Measurements of concentration cells according to Bodländer's method showed that $K_2Hg(CNS)_4$ exists in solution, and in very dilute solutions some $KHg(CNS)_3$ also exists.

Potassium mercuric thiocyanate is of considerable importance as a reagent in microscopic qualitative analysis. Its use was first suggested by Chamot[3] as a substitute for the more deliquescent ammonium salt recommended by Behrens.

Experimental Part

A method of preparation of potassium mercuric thiocyanate is given by Chamot[4]: Freshly precipitated $Hg(CNS)_2$ is added to a cold 5% solution of KCNS, until a slight undissolved excess is present. The saturated solution is filtered and evaporated to crystallization.

The first phase to separate consists of many fine colorless needles, and on further concentration of the solution another type of crystal occurs as well formed monoclinic tablets. The latter phase continues to grow, and the needles dissolve, until eventually the solid phase consists entirely of the monoclinic tablets. The two phases are easily recognized microscopically as different from each other and from the simple mercury and potassium thiocyanates.

The above phenomena alone would seem to point to the fact that there are two double salts formed, but an additional clue is found in the behavior of the monoclinic tablets on dissolving.

To the naked eye the tables appear to dissolve readily in cold water (Rosenheim and Cohn). If, however, the process of solution is followed under the microscope, another phase is seen to separate out in the neighborhood of the dissolving salt. This phase consists of small colorless needles or prismatic crystals, which in turn dissolve slowly in the solution.

When the needle-like crystals (from the first crop obtained in the above method of preparation) are placed in water they dissolve slowly, and another phase [$Hg(CNS)_2$] separates out in the vicinity. Strictly speaking, this is not a decomposition, although it has been stated in the literature on this double salt that the salt decomposes in water to form mercuric thiocyanate and the tetrathiocyanate (Rosenheim and Cohn: *loc. cit.*).

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[1] Sherrill and Skowronski: J. Am. Chem. Soc., 27, 30 (1905).

[2] H. Grossman: Z. anorg. Chem., 43, 356-369 (1905).

[3] "Elementary Chemical Microscopy," p. 353 (1921); Miss R. E. Chipman: Unpublished Thesis, Cornell University, 1917.

[4] Op. cit., p. 450.

The above behavior of the salts suggests that either double salt is capable of existing as a solid phase in the system at a given temperature. The decomposition of the double salts in water indicates that neither salt can be in equilibrium with a saturated solution of its own molecular composition. This is analogous to the behavior of the $KCl-CuCl_2-H_2O$ system and the $KCl-MgCl_2-H_2O$ (Carnallite) system.

The foregoing qualitative evidence points to the ternary system $KCNS-Hg(CNS)_2-H_2O$ being of the type of which the system $(NH_4)_2SO_4-NH_4NO_3-H_2O$ is the best known example.[1]

The present research was undertaken to obtain quantitative confirmation of these assumptions and to establish the chief points on the diagram at room temperature.

Preparation of Potassium Mercuric Thiocyanates

In order to study the effect of the concentrations of KCNS and $Hg(CNS)_2$ in determining the first phase to separate from the solution, and also in order to obtain some crystals of each double salt for analysis, solutions of different compositions were prepared and evaporated in a desiccator. The molecular ratios of $Hg(CNS)_2$ to KCNS were 1:1; 1:2; 1:5; and 1:10.

When equimolecular proportions of $Hg(CNS)_2$ and KCNS were dissolved in water (heating was necessary) and allowed to stand, the first phase to separate out consisted of platy crystals of $Hg(CNS)_2$. Then as the solution evaporated, needle-like crystals [$KHg(CNS)_3$] grew at the expense of the solid $Hg(CNS)_2$. When the solution had gone to dryness, a mass of yellowish needles was left. On recrystallization, the yellow color disappeared.

When the solution containing 2KCNS:1$Hg(CNS)_2$ was evaporated, the first phase to separate was the needle-like crystals [$KHg(CNS)_3$]. These gradually disappeared as the monoclinic tablets [$K_2Hg(CNS)_4$] formed and grew. The final product was a dense mass of poorly formed tabular crystals.

When the solutions of higher proportions of KCNS were allowed to evaporate, the tablets [$K_2Hg(CNS)_4$] were the first phase to separate out, and they were very well formed. Due to the extreme solubility of KCNS it is reasonable to expect that direct evidence of a change from the tablets to KCNS would be difficult to obtain, because in the KCNS range the solutions are very near dryness. Observation verified this.

The tablets or needles were removed from the mother liquor at various stages in the evaporations. They were washed in absolute alcohol because they are not very soluble in it, and therefore the solute in the alcoholic solution which displaces the watery mother liquor is very nearly of the composition of the salt being washed.

Analysis of Double Salts

To analyze either double salt, a known weight of the crystals was dissolved in warm water and a few drops of conc. HNO_3 were added to prevent hydro-

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[1] The properties and the typical diagram of such systems are discussed by Clibbens: "Principles of the Phase Theory," pp. 86-92, 151-152 (1920).

lysis. Some ferric ammonium alum was added, and the solution was titrated with 0.1*N* $Hg(NO_3)_2$ to the disappearance of the red color.[1]

The $Hg(NO_3)_2$ reacts with the KCNS in the mixture, but does not react with the $Hg(CNS)_2$. If KCNS alone is present, the reaction is:

$$2KCNS + Hg(NO_3)_2 \rightarrow \underline{Hg(CNS)_2} + 2KNO_3$$

If the KCNS is present as $K_2Hg(CNS)_4$, the reaction proceeds as follows:

$$K_2Hg(CNS)_4 + Hg(NO_3)_2 \rightarrow \underline{2Hg(CNS)_2} + 2KNO_3$$

and when KCNS is present as $KHg(CNS)_3$:

$$2KHg(CNS)_3 + Hg(NO_3)_2 \rightarrow \underline{3Hg(CNS)_2} + 2KNO_3$$

The mercury in the double salts was determined by precipitation as mercuric sulfide.[2]

The results of the analyses were as follows:

	Tablets		Needles
KCNS	39.4%		23.4%
	39.1		23.5
	39.0		
average	39.2	average	23.45
calculated for $K_2Hg(CNS)_4$-	38.0	calculated for $KHg(CNS)_3$-	23.42
Hg	38.8		48.8
	39.0		49.0
	39.1		
average	39.0	average	48.9
calculated for $K_2Hg(CNS)_4$-	39.2	calculated for $KHg(CNS)_3$-	48.4

A qualitative test for water showed that none was present in either the tablets or the needles. (This test entails heating the salt in a small glass tube which is sealed at one end. A short distance from the salt the inside of the tube is dusted with a water-soluble dye. If water is present in the salt, it is driven off and condenses on the dye and colors the tube. When the tablets were heated, even to decomposition, the test gave negative results.)

From these analyses it was concluded that the crystals having tabular form were the 2:1 double salt $K_2Hg(CNS)_4$, and that the needle-like or prismatic crystals were the 1:1 double salt $KHg(CNS)_3$.

Optical Properties of Double Salts

The needle-like crystals of the double salt $KHg(CNS)_3$ are apparently orthorhombic prisms 110, and pinacoids 100, terminated by domes 011. The terminal angle, between two dome faces, is about 158°.

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[1] Kolthoff and Furman: "Volumetric Analysis," p. 266 (1929).

[2] Treadwell and Hall: "Analytical Chemistry," Vol. II. p. 172 (1928).

All prismatic views exhibit parallel extinction, with very strong double refraction, and anomalous polarization colors which indicate that the double refraction is markedly greater for red than for violet. The axial plane is parallel to 100; the acute bisectrix is parallel to the elongation of the prisms, so interference figures are obtainable only from fragments. The material is biaxial, negative, with $2V$ about 65-70°, $r < v$, marked. Optical orientation: $X = c$, $Y = b$, $Z = a$, $Bx_a = c$. Refractive indices: $\alpha = 1.735 \pm .005$; $\beta = 1.82$; $\gamma = 1.84$ (est).

The tabular crystals of the double salt $K_2Hg(CNS)_4$ are similar in habit to those of the ammonium double salt described by Koch.[1] They are short monoclinic prisms, with basal pinacoid, and when crystallized on a slide lie either on a pinacoid face 001 or a prism face 110. Hemipyramid and clinodome faces are occasionally developed.

As observed perpendicular to 001, the crystals are rhomb shaped in outline, with acute angles of about 80°. Some six- or eight-sided forms are formed, by the truncation of edges by the clinopinacoid 010 and the orthopinacoid 100. The basal view of the crystals shows symmetrical extinction with strong double refraction, the slower component vibrating parallel to the acute diagonal. Interference figures indicating that the "optical normal" is roughly parallel to the *c* axis are observable.

Crystals developed so as to lie on 110 are often markedly flattened, and have plane angles practically the same as those lying on 001, giving a rhomb shaped outline. One or more corners are often obliquely truncated by pyramid faces. This view of the crystals shows no sharp extinction, and its interference figures reveal an optic axis roughly perpendicular to the prism face.

Cliniopinacoidal views of the crystals are rare; they show an angle β of about 74°, and an extinction angle of about 22°. Interference figures are of the obtuse bisectrix type.

The material is biaxial, negative, with $2V$ near 90°, and dispersion very strong, $r > v$. $Bx_o = b$. $Bx_a \wedge a = 22°$. Axial plane $\wedge$ 001 = 22°. Refractive indices: $\alpha = 1.645 \pm 005$; $\beta = 1.80$ (est); $\gamma = 1.9 +$ (est).

Establishment of the Ternary Diagram

As stated above, the microscopical behavior of these double salts when dissolving is direct evidence that the system $KCNS-Hg(CNS)_2-H_2O$ is of the type represented in the diagram shown in Fig. 1.

The most significant points on this diagram are:

A—The solubility of $Hg(CNS)_2$ in water

B—The composition of the invariant solution with which $Hg(CNS)_2$ and $KHg(CNS)_3$ can exist in equilibrium.

C—The composition of the invariant solution with which $KHg(CNS)_3$ and $K_2Hg(CNS)_4$ can exist in equilibrium.

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[1] Fleischer: Ann. 179, 230 (1875).

D—The composition of the invariant solution with which $K_2Hg(CNS)_4$ and KCNS can exist in equilibrium.

E—The solubility of KCNS in water

F and G—The compositions of the two double salts.

The points *A* and *E* are known from the literature: Solubility of $Hg(CNS)_2$ at 25°—0.002 mols per liter, or 0.063% $Hg(CNS)_2$.[1] Solubility of KCNS at 25°—70.5 g. per 100 g. of solution, or 70.5%.[2]

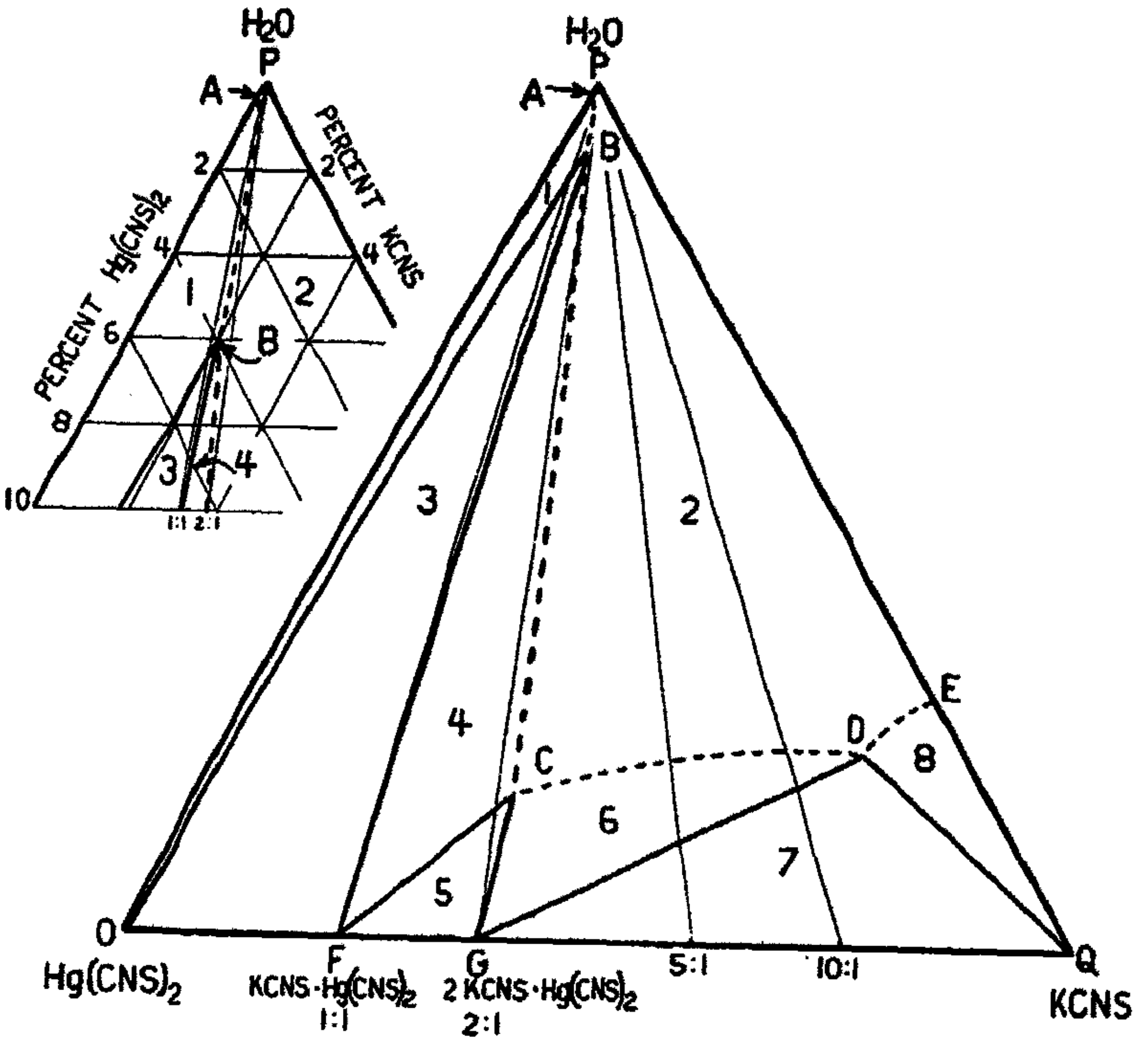

FIG. 1
The System KCNS-$Hg(CNS)_2$-H_2O (weight %-25°)

The points *F* and *G* might be determined by the method of indirect analysis using "tie lines,"[3] but since each of the double salts can be obtained in large well-formed crystals, and can be readily freed from the mother liquor, the analyses of these crystals suffice to furnish the required compositions.

The invariant points *B*, *C*, and *D* were determined by taking advantage of the fact that three phases of the system can coexist at these points. Microscopical examination enabled the identity of the two solid phases present to be established at any stage. This check on the observed constancy of composition

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[1] Comey and Hahn: "Dictionary of Chemical Solubilities," p. 882 (1921).
[2] Seidell: "Dictionary of Solubilities," Vol. I, p. 566 (1919).
[3] Bancroft: J. Phys. Chem., 6, 178; Browne: 287 (1902).

of the solution at each invariant point was particularly useful, on account of the high solubility of KCNS and $K_2Hg(CNS)_4$, which rendered the establishment of equilibrium and subsequent sampling somewhat difficult.

If we add KCNS to a solution of $Hg(CNS)_2$ in contact with excess $Hg(CNS)_2$, the latter will be dissolved and the composition of the solution will vary along the curve *AB* until the invariant point *B* is reached. Here a second solid phase, $KHg(CNS)_3$, makes its appearance. Further addition of KCNS does not alter the composition of the solution, but does increase the amount of the double salt. The $KHg(CNS)_3$ is formed at the expense of the $Hg(CNS)_2$; until all the latter has been thus converted, the solution is saturated with respect to both solid phases and is of constant composition. There is thus a well defined invariant point, the coordinates of which may be determined by analysis of the solution when it becomes constant in composition. The actual solid phases present were also recognized microscopically.

For the point *B*, the composition of the solution is as follows:

KCNS	$Hg(CNS)_2$	H_2O
2.1	4.05	93.9
2.1	3.9	94.0
1.9	4.3	93.8
average 2.05%	average 4.05%	average 93.9%

Likewise, if still more KCNS is added after the point *B* is reached and all the $Hg(CNS)_2$ is used up, the composition of the solution will vary along the line *BC*. At *C* the second double salt $K_2Hg(CNS)_4$ will appear, the solution remaining constant in composition until all the $KHg(CNS)_3$ present has been converted to $K_2Hg(CNS)_4$. Both double salts coexist in contact with the solution, the composition *C* of which is as follows:

KCNS	$Hg(CNS)_2$	H_2O
33.1	49.4	17.8
33.2	49.0	18.0
33.0	48.9	17.6
average 33.1	average 49.1	average 17.8

In a similar manner the point *D* was established. The addition of KCNS to the solution containing an excess of solid $K_2Hg(CNS)_4$ will cause its composition to vary along the line *CD*. At the invariant point *D*, $K_2Hg(CNS)_4$ and KCNS coexist. The composition of the solution at *D* is as follows:

KCNS	$Hg(CNS)_2$	H_2O
66.8	10.8	23.6
66.2	10.2	23.0
66.2	10.2	23.0
average 66.4	average 10.4	average 23.2

The various areas represented in the accompanying diagram are:

(1) *ABO* = $Hg(CNS)_2$ and solution
(2) *ACDEP* = solution
(3) *OFB* = $KHg(CNS)_3$, $Hg(CNS)_2$ and solution
(4) *FCB* = $KHg(CNS)_3$ and solution
(5) *FGC* = $KHg(CNS)_3$, $K_2Hg(CNS)_4$ and solution
(6) *GDC* = $K_2Hg(CNS)_4$ and solution
(7) *GQD* = $K_2Hg(CNS)_4$, KCNS and solution
(8) *DQE* = KCNS and solution

FIG. 2

Evaporation of a 2:1 molar system, within area 5. $K_2Hg(CNS)_4$ (tablet) growing; $KHg(CNS)_3$ (needles) dissolving. 100 ×.

FIG. 3

Addition of water to the 2:1 salt, within area 5. $KHg(CNS)_3$ (needles) growing; $K_2Hg(CNS)_4$ (tablets) dissolving. 50 ×.

The observed behavior, on evaporation, of solutions having various proportions of KCNS to $Hg(CNS)_2$, which has been briefly described above (page 1125) is indicated on the diagram along the lines radiating from *P* and intersecting *OQ* at the respective molecular ratios of 1:1, 2:1, 5:1, and 10:1.

For example, when the 2:1 solution is evaporated at room temperature, its concentration varies along the line *PG* until that line intersects *BC*. The 1:1 double salt $KHg(CNS)_3$, which is relatively slightly soluble in a solution of this composition, then begins to separate. As crystallization proceeds the composition of the mother liquor varies along the line *BC*, becoming relatively richer in KCNS until *C* is reached, at which point tablets of $K_2Hg(CNS)_4$ separate. (Fig. 2).

Crystallization of the 2:1 double salt from a solution of the composition represented by *C* would result in the solution becoming still richer in KCNS. However, any solution to the right of the line *BC* is not in equilibrium with the 1:1 salt, so the latter dissolves as evaporation continues. When the system has gone to dryness, at *G*, only $K_2Hg(CNS)_4$ will remain, provided supersaturation and imperfect diffusion have been avoided.

The observed behavior of the double salt $K_2Hg(CNS)_4$ on the addition of water is also in accordance with the diagram, as followed in the reverse direction along *GP*. Some $KHg(CNS)_3$ separates at once (in the area 5), while $K_2Hg(CNS)_4$ dissolves, and as more water is added the needles of the former entirely replace the tablets of the latter(6). If sufficient water is added the needles finally dissolve completely (2). (See Figs. 4, 5, and 6).

Fig. 4

Fig. 5

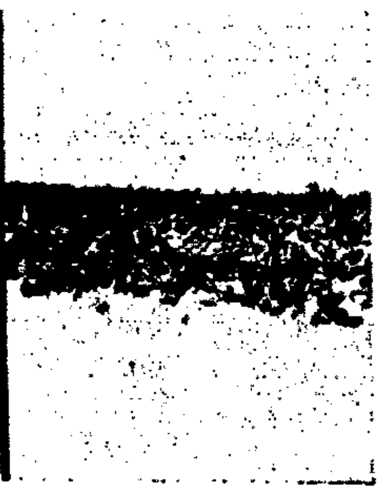

Fig. 6

Fig. 4. Evaporation of a 1:1 molar system, within area 3. $KHg(CNS)_3$(needles) growing; $Hg(CNS)_2$ (small grains) dissolving. 200 ×.

Fig. 5. Addition of water to the 1:1 salt, within area 3. $Hg(CNS)_2$ (tablets) growing; $KHg(CNS)_3$ (coarse needle) dissolving. 200 ×.

Fig. 6. $Hg(CNS)_2$ as a pseudomorph after addition of water to a needle of $KHg(CNS)_3$, in area 3. 100 ×.

In like manner the behavior of a solution containing 1:1 molecular proportions of KCNS and $Hg(CNS)_2$ may be correlated with the diagram. Crystals of $Hg(CNS)_2$ separate first, while the composition of the solution varies along *AB* to *B*. On further evaporation the double salt $KHg(CNS)_3$ grows at their expense, and is the only solid phase remaining when dryness is reached at *F*. When water is added to crystals of $KHg(CNS)_3$ they yield $Hg(CNS)_2$ (3), which remains after they have been dissolved (1), and on further dilution passes into solution (2). (See Figs. 4, 5, and 6).

The following table summarizes the behavior on evaporation of solutions having various molecular compositions.

Solution KCNS:$Hg(CNS)_2$	1st phase	2nd phase
1:1	$Hg(CNS)_2$	$KHg(CNS)_3$
2:1	$KHg(CNS)_3$	$K_2Hg(CNS)_4$
5:1	$K_2Hg(CNS)_4$	KCNS
10:1	$K_2Hg(CNS)_4$	KCNS

Solutions in the *DE* range on the diagram have a great tendency to supersaturate, and it was difficult to determine which phase actually tended to separate first under equilibrium conditions. In all other cases the microscopical observations were in agreement with the predictions from the diagram.

Since only the compositions and behavior of the double salts and the type of the system were sought, the solubility curves of the various solid phases (represented by dotted lines) were not determined experimentally, nor were observations made at other than room temperature (25°C).

The double salt $K_2Hg(CNS)_4$, which on account of its solubility is the one used as a reagent in microscopical qualitative analyses, can be made by either of two procedures:

Fig. 7
$Hg(CNS)_2$ 200 ×.

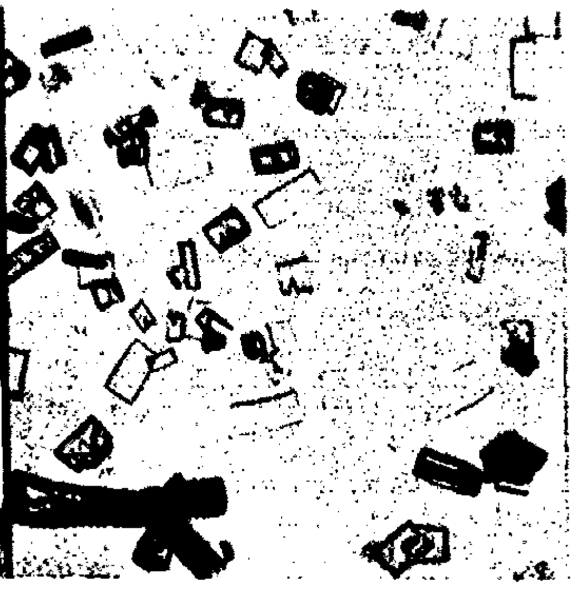

Fig. 8
KCNS 100 ×.

1. Dissolve a known amount of KCNS in water, add the equivalent amount of $Hg(CNS)_2$, and dilute until complete solution is obtained. Evaporate in a desiccator, stirring as dryness is approached.

2. Dissolve KCNS and $Hg(CNS)_2$ in water, in any ratio along the line *CD* (say preferably in molecular ratios between 2.5:1 and 5:1) and evaporate. Collect the first crops of tabular crystals, wash with alcohol, and dry.

Summary

1. At room temperature KCNS and $Hg(CNS)_2$ form two double salts—$KHg(CNS)_3$ and $K_2Hg(CNS)_4$, the optical properties of which are given.

2. Neither of these double salts is stable in contact with a saturated solution having the same molecular ratio of KCNS to $Hg(CNS)_2$ as the solid.

3. A ternary diagram summarizing the behavior of the system at 25° is given.

4. Methods are given for the preparation of $K_2Hg(CNS)_4$ for reagent use in microscopic qualitative analysis.

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CHEMICAL ACTIVITY AND PARTICLE SIZE

The Rate of Solution of Anhydrite below 70 Microns[*]

BY PAUL S. ROLLER[**]

Introduction

In connection with the work of this station on the problem of the utilization of anhydrite in the retardation of Portland cement, it was necessary to measure the rate of solution of anhydrite in water. This substance is generally known to be slowly soluble compared to the fully hydrated form of $CaSO_4$, gypsum, and apparently has a lower solubility. Inasmuch, however, as it is the unstable phase at room temperature[1] it was thought that its really greater solubility might become apparent if fine enough particles were used in the dissolution process. Accordingly the rate of solution of natural anhydrite in water was investigated quantitatively as a function of the particle size, and its saturation solubility determined with fine, rapidly dissolving grains.

Both equilibrium and kinetic effects on increasing the surface energy of a substance by decrease in the particle size have been noted. The thermodynamic consequences were derived in general form by Willard Gibbs[2] in 1876. Hulett[3] found that below 2 microns the solubility of gypsum began to increase and for particles 0.3 micron in size was 19 per cent higher than the normal value. The effects obtained with barium sulphate and mercuric oxide powders were considerably greater. Dundon and Mack[4] also obtained an increase in the solubility of gypsum between 0.2 and 0.5 micron in size, and Dundon extended these observations[5] to other powders, the maximum increase in solubility being 90 per cent. Tzentnershver and Knustinsons[6] found that the vapor pressure of various carbonates showed a decided increase for particles of the order of a micron.

On the kinetic side, no definite theoretical or quantitative experimental results are available on the effect of surface energy on the rate of a reaction. A number of interesting observations have been recorded, however, which indicate a much greater effect than that observed at equilibrium. Reboul[7]

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[*] Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

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[1] van't Hoff et al.: Z. physik. Chem., 45, 257-306 (1905).

[2] Gibbs: "Scientific Papers,".

[3] Hulett: Z. physik. Chem., 37, 385 (1901); 47, 357 (1904).

[4] Dundon and Mack: J. Am. Chem. Soc., 45, 2479 (1923).

[5] Dundon: J. Am. Chem. Soc., 45, 2658 (1923).

[6] Tzentnershver and Knustinsons: Z. physik. Chem., 132, 185-8, (1928); 130, 187-192 (1927).

[7] Reboul: Compt. rend., 155, 1227 (1912); 156; 549 (1913).

observed that the rate of attack on Ag, Cu, and Hg by a number of gases under reduced pressure was greater in proportion to the curvature. He worked with small planes, spheres, cylinders, and ellipsoids of the material.

Sticks of NaOH, $NaNO_3$, etc., partly immersed in water and of Zn, Al, Mg. etc., in dilute acids were observed by Ganguly and Banerji[8] to be rapidly attacked at the air-solution-solid interface, while the remainder of the stick was uniformly and slowly dissolved.

Dehydrated and apparently insoluble Al_2O_3 and ZrO_2, when ground to 0-2.5 microns, were found by Podszus[9] to dissolve appreciably in HCl solution.

Recently, Luce[10] has, by an optical method, determined the attack on various solids by H_2S and halogen, and H_2SO_4 and HNO_3 solutions, and here again the reaction is most active in regions of great curvature.

On the basis of these observations, it was thought that the effect of decreasing particle size on the rate of solution of anhydrite might be considerable, though no noticeable effect on the saturation solubility would be expected since the smallest particle studied had a surface mean diameter of 2 microns.

Materials

A crystalline anhydrite from Midland, Calif., was used for the tests. It contained 0.2% water, less than 0.5% $CaCO_3$, no chlorides, and traces of iron and alumina.

Portions of the powder were fractioned into homogeneous particle size groups. The apparatus used was an air analyzer, to be described in a U. S. Bureau of Mines Technical Paper under the title "The Separation and Size Distribution of Microscopic Particles. An Air Analyzer for Fine Powders."

Microscopic analyses of the various fractions of the anhydrite powder, the diameter of a single particle being taken as the arithmetic mean of the length and breadth, are shown in Table I.

In Table I the distribution of the different sizes in each fraction is given on a weight per cent and a number per cent basis. Sundry particles below the lowest size limit shown here have been omitted; these aggregated in the worst case less than 0.5% by weight, averaging for all the fractions 0.2% by weight. In fraction II, there has been some overlapping with reference to fraction I, due to attrition by the air current of the fine grains during the separation.

Figs. 1-6 are microphotographs of the corresponding fractions in Table I. Figs. 1-4 are at 310 magnification (1 scale division = 3.3 microns); Figs. 5-6 at 70 magnification (1 scale division = 14.3 microns).

The mean diameter or each of the fractions may be defined in a number of ways. The arithmetic mean diameter is defined by the equation where

$$d_m = \Sigma d/n, \qquad (1)$$

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[8] Ganguly and Banerji: Z. anorg. allgem. Chem., 124, 140-2 (1922).

[9] Podszus: Z. physik. Chem., 92, 227-37 (1917).

[10] Luce: Ann. Physik., 11, 167-251 (1929).

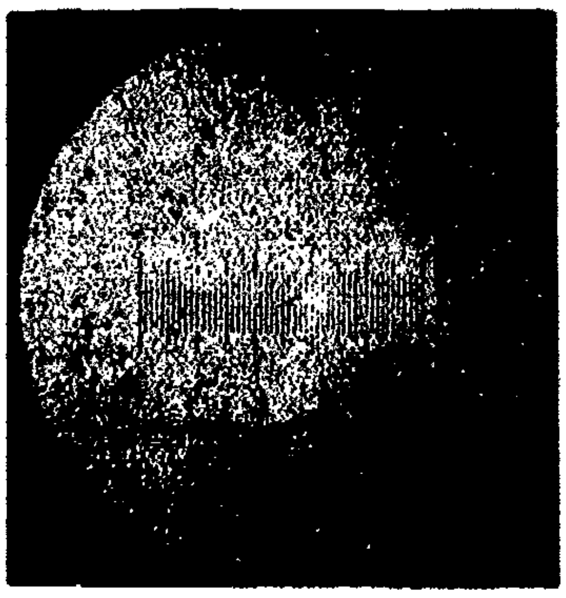

FIG. 1

FIG. 2

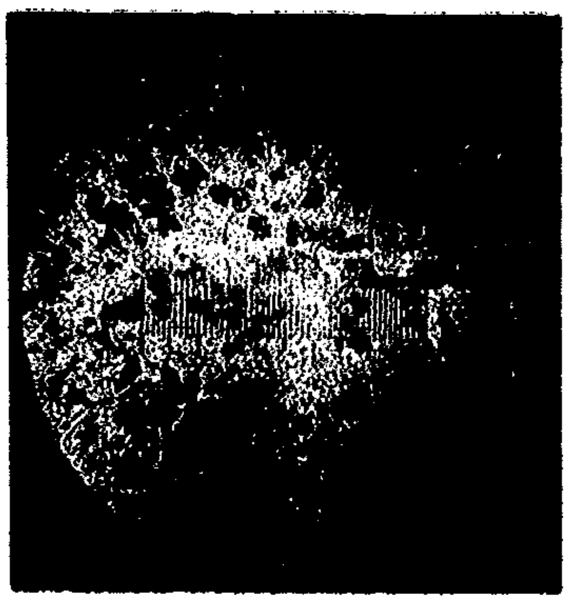

FIG. 3

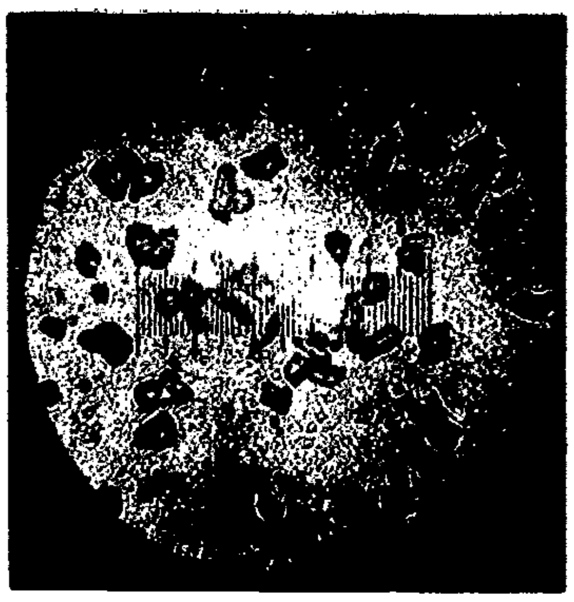

FIG. 4

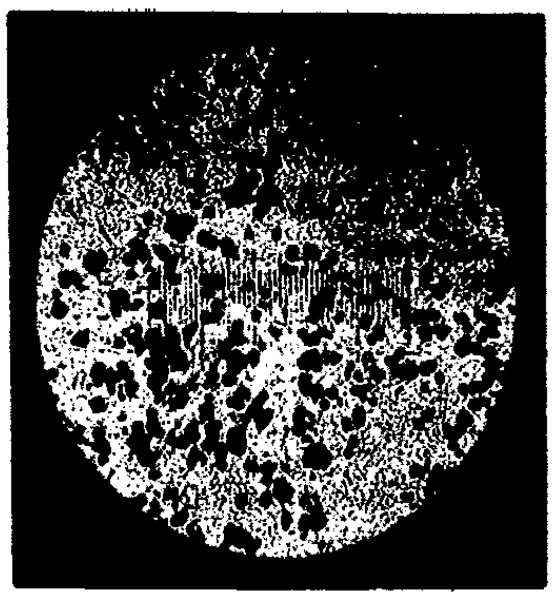

FIG. 5

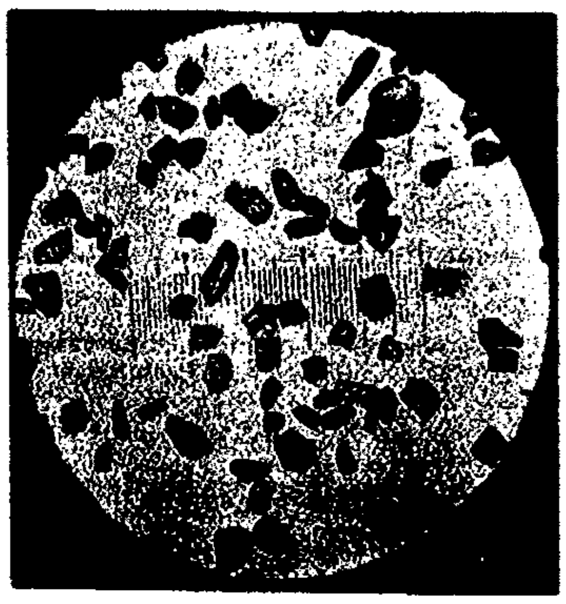

FIG. 6

TABLE I

Microscopic Analyses of Size Fractions of Anhydrite

Fraction No.	0-1	1-2	2-3	3-4				Microns
I	3.4	34.4	44.8	17.4				Weight per cent
	83.0	12.4	4.2	0.4				Number per cent
	0-1	1-2	2-3	3-4	4-5	5-6	6-7	Microns
II	2.3	13.3	31.2	7.9	23.5	21.2	11.3	Weight per cent
	66.0	23.5	7.3	0.9	1.5	0.6	0.2	Number per cent
	3-5	5-7	7-9	9-12				Microns
III	7.6	24.6	39.6	28.2				Weight per cent
	44.4	30.6	19.4	5.6				Number per cent
	7-10	10-15	15-20					Microns
IV	13.8	52.9	33.3					Weight per cent
	38.0	50.0	12.0					Number per cent
	12-15	15-20	20-25	25-35				Microns
V	2.4	13.7	38.0	45.9				Weight per cent
	12.0	24.0	42.0	22.0				Number per cent
	22-30	30-45	45-70	70-100				Microns
VI	0.2	3.5	40.4	55.9				Weight per cent
	6.1	12.2	51.0	30.7				Number per cent

the summation extends over each of the diameters of the n particles measured. However, the arithmetic mean has little weight as an indication of the properties of a powder, as it represents only the diameter of the particle which is numerically most frequent in the mixture of particle sizes.

It is more significant to define the mean diameter of a powder as the diameter of a hypothetical particle whose surface per unit weight is equal to the surface per unit weight of the powder. The quantity thus obtained may appropriately be called the surface mean diameter, d_s, and is defined by the equation

$$d_s = \Sigma d^3/\Sigma d^2 \qquad (2)$$

The surface mean diameter thus defined will be larger than the arithmetic mean in proportion to the range of particle sizes covered by the fraction.

The values of the surface mean diameter of each of the fractions of Table I, calculated by equation (2), are given in Table II. The arithmetic mean diameter calculated from equation (1) is shown in the last column of the table for comparison.

TABLE II

Arithmetic Mean and Surface Mean Diameter of Anhydrite Fractions

Fraction	Surface Mean Diameter (Microns)	Arithmetic Mean Diameter (Microns)
I	1.96	0.63
II	3.17	1.15
III	7.56	5.66
IV	14.1	12.4
V	25.8	23.2
VI	66.9	59.7

The results of Table II are accurate within 3 per cent. In fractions I and II, owing to the preponderance of the very smallest particles, the arithmetic mean is ½ to ⅓ the surface mean diameter. It is the latter, however, which is significant for the calculation connecting surface exposed to the rate of solution, and this is the diameter which will alone be referred to hereafter.

Method and Apparatus

The rates of solution were determined by means of a conductivity bridge. The water used in these experiments had a conductivity of 2×10^{-6} r.o. The conductivity electrodes were two parallel unprotected squares of platinized platinum led into narrow mercury-filled glass tubes which passed through a two-hole stopper. The electrodes and holders were rigidly fastened together. Both the water conductivity and the cell constant of the electrodes were frequently checked between experiments.

The solutions were contained in a tall glass beaker fitted with a hard rubber cover. Through a central hole passed a ⊥ -shaped stirrer made of hollow glass tubing and rotating at 470 r.p.m. The electrodes fitted tightly into a side-hole in the cover.

In making a run, 135 c.c. of water and a sample of the powder, usually 0.7 gram, were brought to temperature in a water bath at 20.00 ±0.03°C. With the stirrer rotating, the powder was rapidly thrown into the solution (by an assistant) and the initial time noted on a stop watch. Readings were thereafter taken at intervals. Curves were checked within 5 per cent by running a duplicate series, and the results averaged.

Specific conductivity readings were converted into concentrations, $CaSO_4$/100 c.c., by means of the empirical formula of Hulett:[11]

$$\frac{\text{mg mol}}{\text{liter}} = -.354 + 5211\ K_{25} + 841{,}400\ K_{25}^2.$$

In order to convert to 20°C., a percentage temperature coefficient, 0.21, was used, this being the average from Hulett's temperature-conductivity data. The resulting equation was:

$$\frac{\text{gr. } CaSO_4}{\text{100 c.c.}} = -\ 0.0048 + 78.37\ K_{20} + 13{,}970\ K_{20}^2. \tag{3}$$

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[11] Hulett: Z. physik. Chem., 42, 581 (1903).

Results

In Table III is shown the concentration in solution against the time in minutes for each of the anhydrite size-fractions of Table II.

TABLE III

Time-Concentration Curves for Anhydrite Size-Fractions

Grams $CaSO_4$/100 c.c.

Min.	Surface		Mean		Diameter		
	1.96	3.17	7.56	14.1	25.8	66.9	Microns
0.15	.002	.003	.000	.004	.004	.002	
0.35	.0550	.0555	.0424	.0297	.0128	.0044	
0.60	.0882	.0911	.0812	.0411	.0168	.0074	
0.85	.1089	.1129	.0986	.0471	.0203	.0094	
1.35	.1352	.1391	.1134	.0555	.0257	.0128	
1.85	.1555	.1550	.1193	.0610	.0302	.0158	
2.85	.1782	.1758	.1278	.0677	.0367	.0198	
4.85	.1995	.1960	.1382	.0773	.0446	.0257	
6.85	.2096	.2059	.1431	.0818	.0486	.0292	
9.85	.2217	.2182	.1476	.0868	.0550	.0352	

The values given in Table III are plotted in Fig. 7. The results may be analyzed into three phases: There is an initial induction of about 0.1 minute. The concentration thereafter rises rapidly for a period, and then in the third phase, falls off to a slow continuous rate.

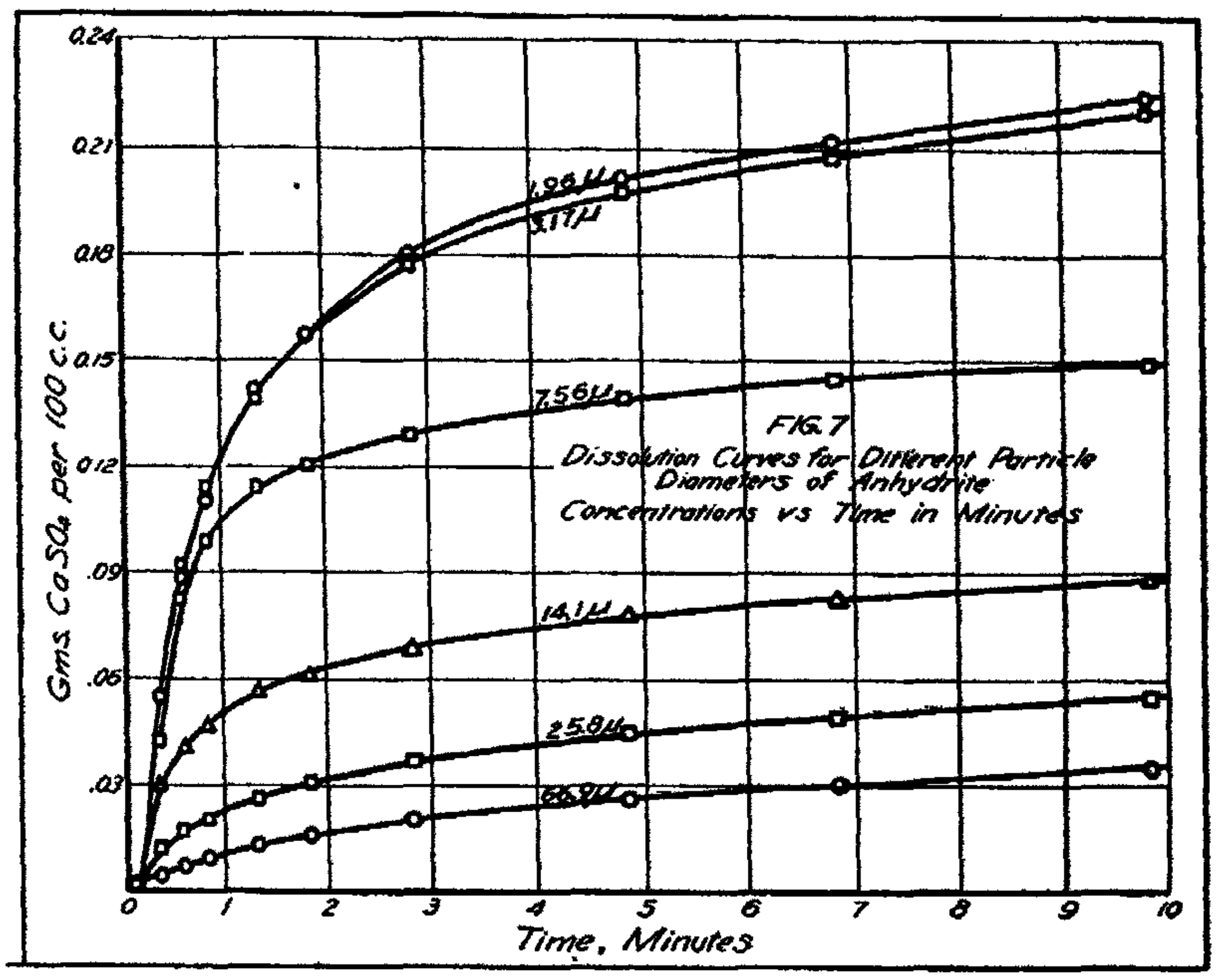

FIG. 7 Dissolution Curves for Different Particle Diameters of Anhydrite Concentrations vs Time in Minutes

The solubility of gypsum at 200°C. is 0.204 gram $CaSO_4$ per 100 c.c.[12] It is seen that at 7 minutes fractions I and II have already surpassed this solubility, the concentration still continuing to rise thereafter.

Rate of Solution vs. Particle Size:

No dissolution velocity constant, either monomolecular or bimolecular, could be calculated for any of the fractions. Owing to the induction period and other disturbances initially present, the relative rates of solution could not be determined by extrapolating the curves of Fig. 7 to zero time. It is necessary to base the determination of the relative rates upon the amount dissolved after a certain period. The procedure adopted for determining the relative velocity of solution of the different fractions was as follows: The fractions were considered in successive pairs, say III and IV. Considering fraction III, the dissolution curves were determined for multiples of the usual weight, 0.7 gram. These curves correspond to different surface exposures of fraction III. At a point 6 (or 3) minutes from the origin, on the slow portion of the dissolution curve, the corresponding ordinates were measured for each of the fractions IV and III, and for the different surface exposures of fraction III. On the assumption that the rate of solution is for a given fraction proportional to the surface exposure, a function connecting the concentration

TABLE IV

Comparison of Concentration Ordinates

Fraction	Surface Mean Diameter	Grams taken	Concentration Ordinate grams per 100 c.c. of solution	
			2.85 min.	5.85 min.
I	1.96	0.7		.2044
II	3.17	0.7		.2010
		1.4		.2434
III	7.56	.7		.1401
		1.4		.1678
		2.8		.1960
IV	14.1	.7	.0679	.0807
		2.8		.1228
		.35	.0436	
		.233	.0346	
V	25.8	.7	.0367	
		.35	.0222	
		.175	.0123	
VI	66.9	.7	.0198	

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[12] Böttger: Z. physik. Chem., 46, 602 (1903).

ordinate with the rate of solution is obtained. By comparison and interpolation of the ordinates, the rate of solution of fraction IV with reference to III is obtained.

The relative specific surface of fraction III to fraction IV is in inverse ratio to the surface mean diameter. Correction was made for the surface reduction due to solution of the powder by subtracting from the initial surface the surface lost by solution up to the point of measurement, this procedure under the conditions being found most accurate. It is readily shown that for small losses the percentage reduction in surface is two-thirds the percentage reduction in weight.

In Table IV is given the results of the comparisons of the concentration ordinates at the end of 2.85 and 5.85 minutes for the different surface exposures of the different fractions.

From the results of Table IV, the ratio of the relative rate of solution against the relative specific surface for the fractions in pairs is obtained as indicated. By taking the relative specific surface and the relative rate of solution of the coarsest fraction equal to unity, the relative rate of solution per unit surface may be calculated for each particle size. For convenience the relative rate of solution per unit surface is called the dissolution factor. In Table V this quantity is calculated against the particle size.

TABLE V

Relative Rate of Solution of Different Particle Sizes of Anhydrite

Surface Mean Diameter	Relative Specific Surface	Relative Rate of Solution	Dissolution Factor
1.96	34.1	382	11.2
3.17	21.1	364	17.2
7.56	8.82	66.7	7.55
14.1	4.74	9.54	2.01
25.8	2.59	2.66	1.03
66.9	1.00	1.00	1.00

In Fig. 8 the results of Table V are plotted on semi-logarithmic paper as the dissolution factor against the surface mean particle diameter.

It is seen that down to a diameter of about 25 microns, the rate of solution per gram for different particles is proportional to the specific surface, and the dissolution factor is a constant, unity. This is the value to be expected if, as in the usual case, the rate of solution is proportional to the surface exposed. Below 25 microns, however, the rate increases more rapidly than the surface exposed up to 2.8 microns at which a maximum is reached. Here the rate of solution of the anhydrite is 17.6 times the proportional increase in surface. Below 2.8 microns the curve descends, but the dissolution factor is still as high as 11.6 at 1.96 microns.

The cause of the enhanced rate of solution of particle sizes of anhydrite below 25 microns, and the appearance of a maximum at 2.8 microns, is due probably to a number of concomitant effects. It is especially to be noted that the range of particle diameters for which the phenomenon occurs is less than the thickness of the diffusion film, 20-50 microns, calculated according to the theory of Noyes and Whitney[13], and Nernst[14], from the monomolecular dissolution rate of a plane surface in water.[15],[16] The initial induction period of about 0.1 second may actually correspond to the formation of a diffusion film of solute around the particle. The maximum at 2.8 microns is possibly due to the electrostatic charge which increases with decrease in particle size below about 20 microns. Further discussion of the cause and significance of these effects will be made in a later paper on the rate of solution of gypsum in its dependence on particle size.

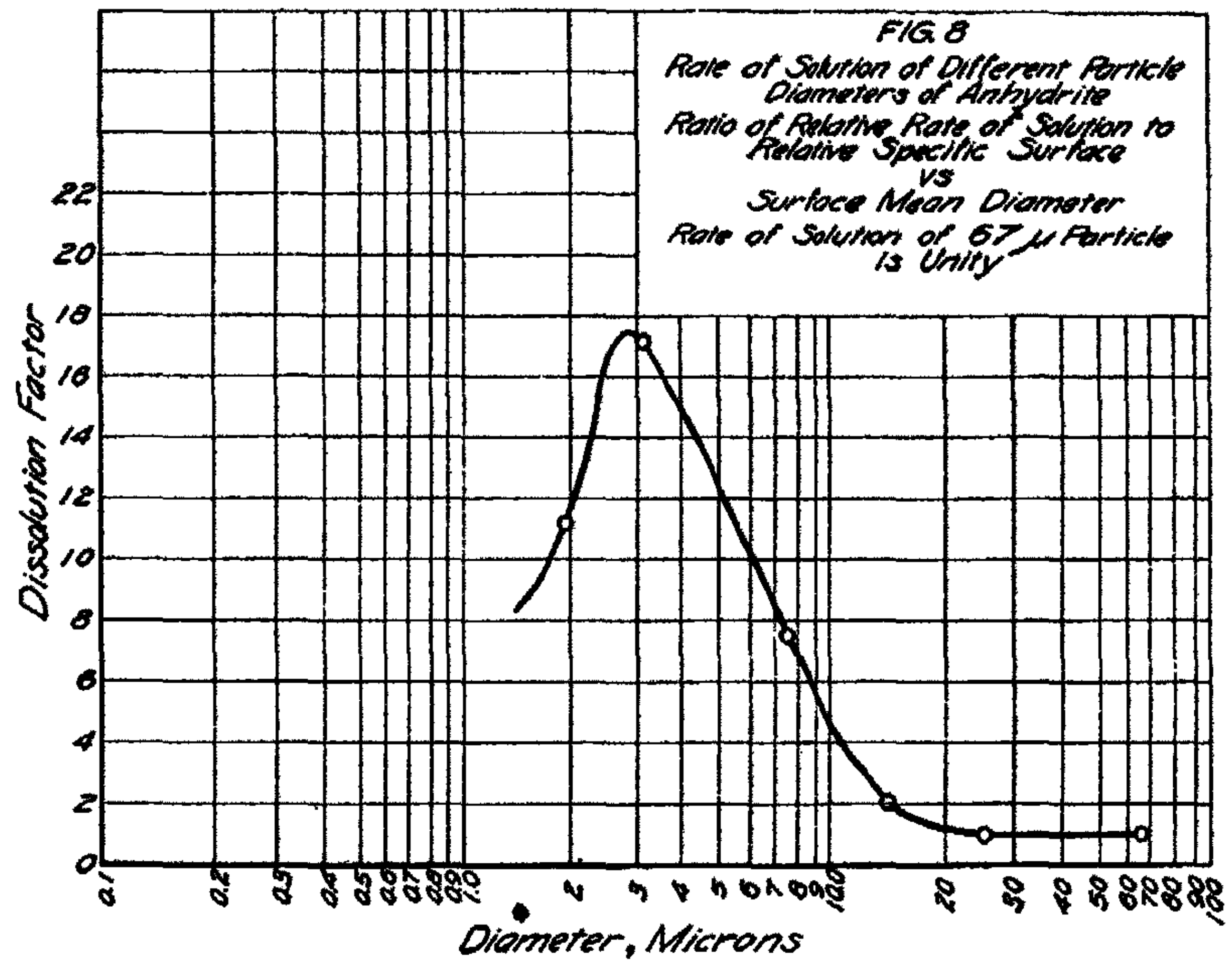
FIG. 8
Rate of Solution of Different Particle Diameters of Anhydrite
Ratio of Relative Rate of Solution to Relative Specific Surface
vs
Surface Mean Diameter
Rate of Solution of 67 μ Particle is Unity

Solubility of Anhydrite:

Anhydrite is the unstable phase of $CaSO_4$ at room temperature. In contact with water it changes into the stable phase, gypsum, but very slowly. The metastable solubility was determined at 20.0°C. by adding a quantity of finely divided powder to water, or to a saturated gypsum solution, and

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[13] Noyes and Whitney: Z. physik. Chem., 23, 689 (1897).

[14] Nerst: Z. physik. Chem., 47, 52 (1904).

[15] Brunner: Z. physik. Chem., 47, 56 (1904).

[16] Wagner: Z. physik. Chem., 71, 434 (1910).

taking conductivity readings until these remained constant over a period of several hours. Thereafter the conductivity would fall, due to hydration of the anhydrite, to the value for gypsum.

1.4 grams of fraction II added to 135 c.c. of water at 20°C. showed a saturation conductivity of 2.602×10^{-3}r.o. 2.1 grams of fraction II in 135 c.c. saturated gypsum solution gave the value 2.600×10^{-3}r.o. 5 grams of a finely ground sample in 135 c.c. of gypsum solution supersaturated by 15% gave 2.622×10^{-3}r.o. The mean of these values is $2.608 \pm .006 \times 10^{-3}$r.o. To determine the concentration at this value we may extrapolate from the empirical equation of Hulett* reduced to 20°C. (equation (3)). Averaging the results, the value obtained for the saturation solubility of anhydrite is then 0.298 gr. $CaSO_4$/100 c.c. solution, or the solubility at 20°C. of natural anhydrite is 1.46 times that of gypsum.

Summary

1. A crystalline anhydrite was fractionated into six homogeneous size groups, ranging from a surface mean diameter of 1.96 microns to 66.9 microns.

2. The dissolution curves of these fractions were determined by conductivity measurements. There is an initial induction period of about .1 minute. In this as well as in general form the curves for the different particle sizes are similar.

3. For the finer particles, the rate of solution was not proportional to the surface exposed. The dissolution factor, i.e., the relative rate of solution per unit surface, is unity for particles above 25 microns. This is in accord with the well known law that the rate is proportional to surface exposed. Below this diameter, however, the dissolution factor increases to a maximum of 17.6 at 2.8 microns and then decreases. At a surface mean diameter of 1.96 microns the dissolution factor is 11.6.

4. The solubility of natural crystalline anhydrite in water was found to be 0.298 gr. $CaSO_4$/100 c.c. at 20°C.

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Rutgers University,
New Brunswick, N. J.

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*Note: Dundon and Mack (Ref. 4) have by comparison shown that an extrapolation of the equation by over 300% is accurate to 1%.

THE OPTICAL ACTIVITY OF ELECTROLYTES

BY NEIL CAMPBELL

Introduction

The optical activity of electrolytes has been studied during the last fifty years in an attempt to throw light upon the nature of electrolytes in solution. The first investigator to provide accurate data was Landolt[1] who in 1873 carried out a detailed investigation on the normal salts of tartaric acid, and showed that they *all* had approximately the same value in 0.5 M solutions. Six years later Oudemans[2] investigated the different salts of the alkaloid quinamine, and found his results to be in harmony with those of Landolt. He accordingly formulated the generalisation known as Oudemans Law, which states that the different salts of an optically active acid or base have the same specific rotation in dilute solutions. Researches by Schneider,[3] Hartmann,[4] Darmois[5] have confirmed this law.

At this time there was no comprehensive theory concerning the nature of electrolytes in solution, and therefore the full significance of the Oudemans Law could not be appreciated. In 1887 however Arrhenius published his first paper on electrolytic dissociation and the value of the theory to account for the variation of the optical activity of electrolytes with change in concentration was soon recognised. In 1893 Hädrich[6] reviewed the work of Landolt and Oudemans in the light of the new theory and in addition determined the rotations of the salts of several optically active strong bases. As a result he extended the Oudemans Law. "The rotations of optically active electrolytes tend towards a definite value as the dilution is increased and this value is independent of the inactive ion." For example in very dilute solutions Hädrich showed that the different salts of the alkaloid quinidine had a molecular rotation of +726°. Hädrich showed that the ionisation theory gave a satisfactory and simple explanation of the Oudemans Law. On this theory changes of rotation of electrolytes with change in concentration are due to variations in the degree of dissociation: in sufficiently dilute solutions however the rotation depends solely on the presence of optically active ions since the degree of dissociation is practically complete.

A more accurate investigation of the Oudemans Law by Walden[7] using the metallic salts of the strong α-bromocamphor-π-sulphonic acid, showed

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[1] Ber., **6**, 1073 (1873).

[2] Ann., **197**, 48 (1879).

[3] Ann., **207**, 257 (1880).

[4] Ber., **21**, 221 (1888).

[5] Ann. phys., **10**, 70 (1928).

[6] Z. physik. Chem., **12**, 476 (1893).

[7] Z. physik. Chem., **15**, 196 (1894).

that in very dilute solutions (1 gm. equivalent per 30 litres) the rotations of the several salts were *exactly* the same. Walden's results therefore served to confirm the correctness of the Oudemans Law, and in consequence were quoted as substantiating the Arrhenius theory. Walden however noted that at the dilution of 30 litres, conductivity measurements indicated that the salts were only 70%-90% dissociated. Noyes[1] pointed out that the rotations of these salts indicated 100% dissociation at the dilution considered; but, in view of the evidence to the contrary, he advanced a reason why this result should differ from that obtained from conductivity measurements. According to Noyes the optical activity of electrolytes depends essentially on the optical activity of ions, whether these ions be "free," or exist as "latent ions" in an undissociated molecule. Recently Walden[2] found that the molecular rotation of the tetra-ethyl-ammonium α-bromocamphor-π-sulphonate in a number of solvents is independent of the concentration at concentrations less than 1 gm. mol. per 17 litres. Walden maintains that there must be undissociated molecules present and explains the non-variation of the molecular rotation on lines similar to those of Noyes. Since Debye and Hückel advanced their theory based on the assumption that strong electrolytes are completely dissociated it is much easier to account for the fact that optical rotatory power measurements—and conductivity measurements—yield different values for the degree of dissociation of any given electrolyte. It is now established that the degree of ionisation of electrolytes is very much greater than that given by the conductivity ratio Λ_o/Λ_∞ and in dilute solutions such as those considered by Walden (1/30 M) the degree of dissociation is probably practically complete. (It is of interest to note that the optical activity measurements of Walden gave the first indication that the degree of ionisation as calculated from conductivity data was incorrect). When moderately concentrated solutions are examined however, it is found that the different salts possess different rotations (e.g. the metallic tartrates); such differences may be explained by assuming the presence of undissociated molecules. (Hädrich). Thus while the optical activity of electrolytes in dilute solutions substantiates the complete ionisation theory, the Arrhenius theory offers a simple explanation of the variations observed at greater concentrations. As a result the optical rotatory power of electrolytes has been quoted both as evidence for the Arrhenius theory and as evidence for the Debye-Hückel theory. (For a discussion on this point a recent paper by Jacobs and King[3] may be consulted).

In view of the uncertain knowledge regarding the nature of electrolytic solutions it is of interest to study further the optical rotation of electrolytes in solution. It is the purpose of this communication to investigate the changes in rotation of the electrolyte ammonium α-bromocamphor-π-sulphonate caused by (1) change of concentration (2) addition of optically inactive electrolytes and non-electrolytes (3) change of solvent.

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[1] Science, 20, 577 (1904).

[2] Monatshefte, 53-54, 14 (1929).

[3] J. Phys. Chem., 34, 1013 (1930).

It may be mentioned at this point that the majority of optically active electrolytes hitherto examined have been hydroxy derivatives of succinic acid, although it has long been recognized that these compounds possess peculiar properties, due to the presence of polar groups. (This point has been stressed in a recent paper by Bancroft[1]). Moreover a number of investigators have examined optically active acids. That their conclusions must be accepted with reserve is obvious since the hydrogen ion is unique in that it has both donor and acceptor properties. It therefore appears unfortunate that so many of the optically active electrolytes examined possess properties not characteristic of electrolytes in general. It must be admitted on the other hand that the alternatives—usually members of the camphor series or alkaloid bases—are open to objection on account of their complex structure. In the present research ammonium α-bromocamphor-π-sulphonate was chosen not only because it is a typical strong electrolyte, but also because it does not possess any group such as the amino or hydroxyl. The present paper deals mainly with the variations in the rotation of this electrolyte.

Experimental

In carrying out this research nearly all the solutions examined contained the same concentration of the active ammonium salt—molecular concentration 0.1. In order that the rotations might be strictly comparable it was necessary that there should always be the same quantity of ammonium salt between the end plates of the polarimeter tube. Careful attention was therefore given to the weights, volumes, and temperatures of the solutions.

The weight of water in each solution was determined from density measurements.

All volume and density measurements were determined at 20°C. The mercury green line was used in all the polarimetric observations.

Apparatus. The polarimeter was a Hilger instrument provided with a Lippich three-shadow polariser and two verniers reading to 0.01°. It was fitted with a direct-vision spectroscope attachment for reading rotations with the mercury green line. The tube was 4 dcm. in length and was provided with a water jacket through which water was pumped from a thermostat by means of an electrically driven water turbine. The temperature of the water in the thermostat was so regulated that the solution in the polarimeter tube was maintained at 20.0°C. (±0.20).

A quartz mercury vapour lamp working at atmospheric pressure was used as a source of light for the mercury green line.

The standard flasks were all calibrated.

The pyknometers were of the usual Ostwald type, with a capacity of about 5 c.c. All densities were referred to water at 20.0°C.

Chemicals. The chemicals were for the most part Analytical Reagents. Each reagent was tested for gross impurities by the standard methods and were purified where necessary. In cases of doubt the reagents were analysed.

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[1] J. Phys. Chem., 34, 897 (1930).

The ammonium α-bromocamphor-π-sulphonate was obtained from the British Drug Houses, Ltd., and was recrystallised from hot water and dried in vacuo over sulphuric acid. The pure salt had a rotation $[M]^{20}_{5461} = +347.2°$: molar conc. of solution = 0.1; cf. the figures of Pope and Read:[1] $[M]^{20}_{5461} = + 346.6°$; molar conc. = 0.2 (approx.).

Accuracy of the Results. Repeated experiments showed that the readings were accurate to 0.02° except in the case of a few solutions such as those containing methyl alcohol. As most of the angles measured were approximately +13° an accuracy of 1 in 500 may legitimately be claimed. Little difficulty was experienced in obtaining weight and volume measurements with this degree of accuracy.

Data and Discussion

Variation of the Molecular Rotation of electrolytes with change of concentration.

In the case of ammonium-α-bromocamphor-π-sulphonate a small but definite increase in the molecular rotation with increase in the concentration was observed.

TABLE I

Molar conc. Amm. Salt	$[M]^{20}_{5461}$	Molar Conc. Amm. Salt	$[M]^{20}_{5461}$
0.02	+345°	0.20	+349.6°
0.04	+345°	0.30	+353.5°
0.10	+347.2°		

These changes are very similar to those observed by Darmois[2] in the case of several tartrates. It appears that below molar concentrations of 0.1 there is little or no variation in the molecular rotations of such salts. This is in agreement with Walden's values for the tetra-ethyl ammonium salt of α-bromo-camphor-π-sulphonic acid—$C_{10}H_{14}BrOSO_3^- + N(Et)_4^+$—in aqueous solution and with the figures quoted by him for several tartrates. It therefore appears that in many cases solutions whose concentrations are less than 0.1 M exhibit no change in rotation with dilution.

A statement by G. N. Lewis[3] on the additive properties of electrolytic solutions may be commented on at this point. "Indeed in all strong electrolytes the partial volume, heat capacity, internal energy, viscosity, refractive index, rotatory power—in fact practically all the significant physical properties of the undissociated part of the electrolyte—seem practically identical with the properties of the constituent ions. If we had no other criterion for the degree of dissociation, these facts would undoubtedly lead one to regard salts up to a concentration of normal or half normal as completely dissociated." So far as results from the study of the optical activity of electrolytes furnish information as to the dissociation of electrolytes this statement by Lewis does not hold for solutions whose concentrations are greater than 0.1M.

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[1] J. Chem. Soc., 97, 2201 (1910).

[2] Loc. cit.

[3] Z. physik. Chem., 70, 214 (1910).

The changes in rotation at higher concentrations may be adequately explained by change in the degree of dissociation of the electrolyte. Recently however Darmois[1] assuming complete dissociation even in concentrated solutions has advanced another theory based on the ionic deformation theory of Fajans. Darmois studied the variation of the rotations of several tartrates and accounts for these changes by the "deformation effect" of the charged cations on the tartrate ions. The work of Fajans[2] shows that in general it is the anions which undergo deformation under the influence of the more compact cations and further that the deformation produced depends on the radius and charge of the cation. Darmois showed that the influence of the cations on the optically active tartrate ions was inversely proportional to the ionic radii as is to be expected from Fajans theory. The deformation theory is not sufficient to account for all the changes in the rotatory power observed and Darmois assumed in addition a "dehydration" process. Stubbs[3] and Patterson and Anderson[4] on the other hand found evidence against such an assumption. Darmois' theory however explains the variations in the rotatory power satisfactorily.

Summarising it may be stated that there are two theories accounting for the variation of the optical rotation of electrolytes with change of concentration. At present there is not enough evidence to enable one to decide which theory is to be preferred.

It is of interest to enquire whether there is any simple relationship between the changes of the optical activity of an electrolyte and the changes in the thermodynamic activity of the electrolyte or its ions. In the present state of our knowledge it is impossible to discuss this matter fully, since the changes in the activity coefficients of ions with concentration cannot be determined except by making certain arbitrary assumptions which may or may not be justified. The activities of electrolytes in aqueous solution have been accurately determined. When the activity coefficients of an electrolyte are plotted against its molecular concentration a characteristic curve is obtained: the curve falling to a minimum and then rising steeply. The nature of the curves obtained by plotting the molecular rotation of an electrolyte against the molar concentration varies. In some cases they assume the form of straight lines and in no case do they give rise to a maximum or minimum, so that there is no obvious correlation between the changes in the optical rotation of an electrolyte and its thermodynamic activity.

Effect on the Molecular Rotation of Electrolytes produced by the Addition of Optically Inactive Electrolytes and Non-Electrolytes.

The effect of adding a fixed weight of potassium chloride to solutions of the ammonium salt was first investigated.

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[1] Loc. cit.; Trans. Faraday Soc., **26**, 384 (1930).

[2] Trans. Faraday Soc., **23**, 357 (1927), etc.

[3] J. Chem. Soc., **99**, 2265 (1911).

[4] J. Chem. Soc., **101**, 1833 (1912).

Rotations of Ammonium Salt in presence of Potassium Chloride.

Molar concentration of KCl = 1.0.

Δ = Increase in the molecular rotation of the ammonium salt in a solution containing KCl 1.0 M, and the molecular rotation in aqueous solution.

Molar Conc. Amm. Salt	$[M]^{20}_{5461}$	Δ	Molar Conc. Amm. Salt	$[M]^{20}_{5461}$	Δ
0.02	+347.9°	2.9°	0.20	353.4°	3.8°
0.04	348.7°	3.7°	0.30	357.5°	3.7°
0.10	349.8°	3.7°			

It is evident that the increase in the molecular rotation of the ammonium salt caused by the addition of a definite weight of potassium chloride is independent of the concentration of the ammonium salt. This is in harmony with the conclusions of Stubbs[1] in regard to the effect of adding salts to l-malic acid "that the influence of the salt on the specific rotation depends mainly on the concentration of the solution with regard to that salt, and not on the concentration of the malic acid present."

An extensive investigation into the influence of different types of electrolytes and non-electrolytes on the rotations of 0.1M solutions of ammonium α-bromocamphor-π-sulphonate was made.

If Damois' view is correct it is to be expected that the addition of inorganic salts to the salt of an optically active acid will result in changes of the molecular rotation of the electrolyte: and further that the following regularities will be observed. The magnitude of the change of rotation will be (1) inversely proportional to the size of the added cation: (2) proportional to the charge of the added cation: (3) dependent on the concentration of the added salt. The effect of adding inorganic salts to optically active electrolytes has been investigated by many workers among whom may be mentioned Stubbs[2], Patterson and Anderson[3], Darmois[4] and Mrs. Liquier-Milward.[5] All these authors succeeded in obtaining interesting regularities. In order to investigate the matter further, many salts of different types were added to solutions of ammonium-α-bromocamphor-π-sulphonate. In addition the effects of acids of different strengths, and non-electrolytes such as alcohol were observed. The changes in rotation produced in this way may be seen in the following table.

Amm. α-bromocamphor-π-sulphonate. Molar Conc. 0.1. Effect on the rotation produced by the addition of various salts, etc.

The molar concentration of the added substance in all cases was 0.5.

Δ = Increase in $[M]^{20}_{5461}$ caused by addition of inactive compound. The probable experimental error ± 0.6°.

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[1] Loc. cit.

[2] Loc. cit.

[3] Loc. cit.

[4] Loc. cit.

[5] Trans. Faraday Soc., 26, 390 (1930).

TABLE II

Added Compound	Δ	Added Compound	Δ
$CH_3.COOH$	0.0°	$CdSO_4$	2.2°
HCl	0.3°	NaI	2.7°
CH_3OH	0.3°	Na_2SO_4	2.9°
NH_4Cl	0.4°	$(NH_4)_2SO_4$	3.1°
$BaCl_2$	0.4°	$CH_2Cl.COOH$	3.4°
LiCl	0.9°	KI	3.4°
Urea	0.9°	$MgSO_4$	3.4°
$CdCl_2$	1.1°	K_2SO_4	4.2°
NaCl	1.4°	K_2CrO_4	4.2°
KBr	1.4°	$CHCl_2.COOH$	5.2°
Glycerol	1.7°	$CCl_3.COOH$	5.2°
KF	2.0°	CdI_2	10.0°
KCl	2.0°	$K_4Fe(CN)_6$	12.0°

Table II serves to show that:—

(1) The change produced by the addition of these substances is small compared with those observed by Darmois and the other workers in this field. For example Darmois found that the specific rotation of a 0.25 M solution of sodium tartrate decreased from + 42.5 to +23.0° in the presence of $BaCl_2$ (0.6M). The greatest change observed in the case of the ammonium α-bromocamphor-π-sulphonate is in the case of potassium ferrocyanide, i.e. the molecular rotation increased from +347.2° to 359.2°.

(2) The magnitude of the change of rotation cannot be correlated with the charges or size of the ions. This is shown more clearly by Tables III and IV.

TABLE III

Molar Conc. of salt = 0.5	Δ
HCl	0.3°
NH_4Cl	0.4°
$BaCl_2$	0.4°
LiCl	0.9°
$CdCl_2$	1.1°
NaCl	1.4°
KCl	2.0°

TABLE IV

Molar Conc. of salt = 0.5	Δ
KBr	1.4°
KF	2.0°
KCl	2.0°
KI	3.4°
K_2SO_4	4.2°
$K_2C_2O_4$	4.2°

Indeed it is obvious that the effect cannot be purely ionic since weak electrolytes such as monochloracetic acid and non-electrolytes like glycerol have greater effects on the rotation than most of the salts mentioned above. It is manifest therefore that in the case of ammonium α-bromocamphor-π-sulphonate no regularities are obtained such as those observed by Darmois in the normal tartrates.

Since according to the modern views the properties of solutions of electrolytes are determined to a large extent by the value of $\sqrt{\Gamma}$ where $\Gamma =$ twice the ionic strength, the molecular rotation of the ammonium salt was plotted against $\sqrt{\Gamma}$. This has already been done by Mrs. J. Liquier-Milward[1] in her study of the effect of neutral salts on the rotation of asparagine, who found from her curves that the salt effect depended on the degree of ionisation of the salt added. Thus salts such as NaCl had the greatest effect, while weakly ionised salts like $CdCl_2$ had the least influence. Salts of the type of $MgSO_4.K_2SO_4$, had intermediate values. The results obtained in the present research are shown in Table V and Fig. 1.

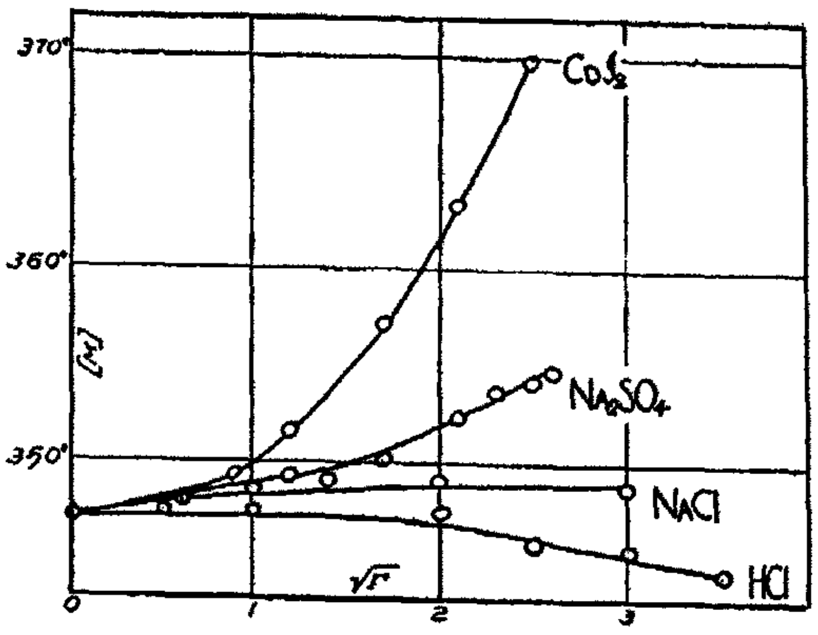

Fig. 1

TABLE V

Conc. of Amm. salt = 0.1M μ = ionic strength $\Gamma = 2\mu$

HCl			NaCl		
Molar Conc.	$\sqrt{\Gamma}$	[M]	Molar Conc.	$\sqrt{\Gamma}$	[M]
—	—	+347.2°			
0.5	1.0	+347.5°	0.2	0.6	+347.6°
1.0	1.4	+347.5°	0.5	1.0	+348.6°
2.0	2.0	+347.5°	1.0	1.4	+349.2°
2.5	2.2	+345.9°	2.0	2.0	+349.2°
3.0	2.5	+345.7°	3.0	2.5	+348.9°
3.5	2.7	+344.2°			
Na_2SO_4	$\sqrt{\Gamma}$		CdI_2	$\sqrt{\Gamma}$	
0.25	1.2	+349.4°	0.125	0.9	+348.9°
0.5	1.7	+350.1°	0.25	1.2	+351.6°
0.75	2.1	+352.4°	0.5	1.7	+357.2°
0.875	2.3	+353.6°	0.75	2.1	+362.9°
1.0	2.5	+354.1°	1.0	2.5	+369.9°
1.125	2.6	+354.6°			

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[1] Loc. cit.

It is clear that the regularities obtained by Mrs. Liquier-Milward have not been obtained in the present instance. Whereas this investigator found that the effect of neutral salts on the rotation of an electrolyte was directly proportional to the degree of ionisation of the salts exactly the reverse is shown by the above figures.

$$CdI_2 > Na_2SO_4 > NaCl.$$

The alternative explanation is that the above changes in rotation are due to repression of the ionisation of the optically active electrolyte caused by the addition of the inorganic salts. It is not easy to test this theory quantitatively since the laws governing the equilibrium of electrolytes are not thoroughly understood. The equilibrium expressions which have been obtained are derived from the isohydric principle which in turn is based on the law of mass action. As strong electrolytes do not obey this law, such expressions are largely of an empiric nature and must be used with caution. It is unlikely however that decrease in the degree of ionisation is the important factor since, as has already been shown, neutral substances like urea influence the rotation to the same extent as many of the salts while weak electrolytes like cadmium iodide and monochloracetic acid have a greater effect.

The above method of treating solutions is open to criticism and indeed the possibility of examining quantitatively equilibria between ions and undissociated molecules has been questioned.[1] Moreover the determination of the ionic concentrations present in solution is attended by great difficulties since the degree of dissociation of electrolytes is not known with certainty. In view of such difficulties the problem of electrolytic solutions has been attacked from the thermodynamic standpoint. The thermodynamic method has proved very fruitful and it is of interest to review the results of the present research from this point of view. From the fact that the thermodynamic activities of salts are conditioned by the type of electrolyte, some relationship might be expected to exist between the salt type and the effect on the optical rotatory power of an electrolyte. As shown in Table VI, however, salts of different types have practically the same effect on the rotation of the optically active salt.

TABLE VI

Molality = 0.1.

Salt	Active Coefficient	Δ
KCl	0.794	2.0°
$BaCl_2$	0.501	0.4°
$MgSO_4$	0.166	1.1°

The thermodynamic activities of the salts and their effects on the optical activity of ammonium α-bromocamphor-π-sulphonate do not seem to be related. This is hardly surprising as the effect may depend essentially on the activities of the positive ions. As already mentioned the activities of ions

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[1] Lewis and Randall: "Thermodynamics," p. 323.

cannot be determined with certainty and therefore no conclusions can be drawn as to whether or not the thermodynamic activity of an ion and its effect on the optical activity of an electrolyte are related.

The effect of adding excess of optically inactive substances was investigated and the results are shown in Table VII and Fig. 2.

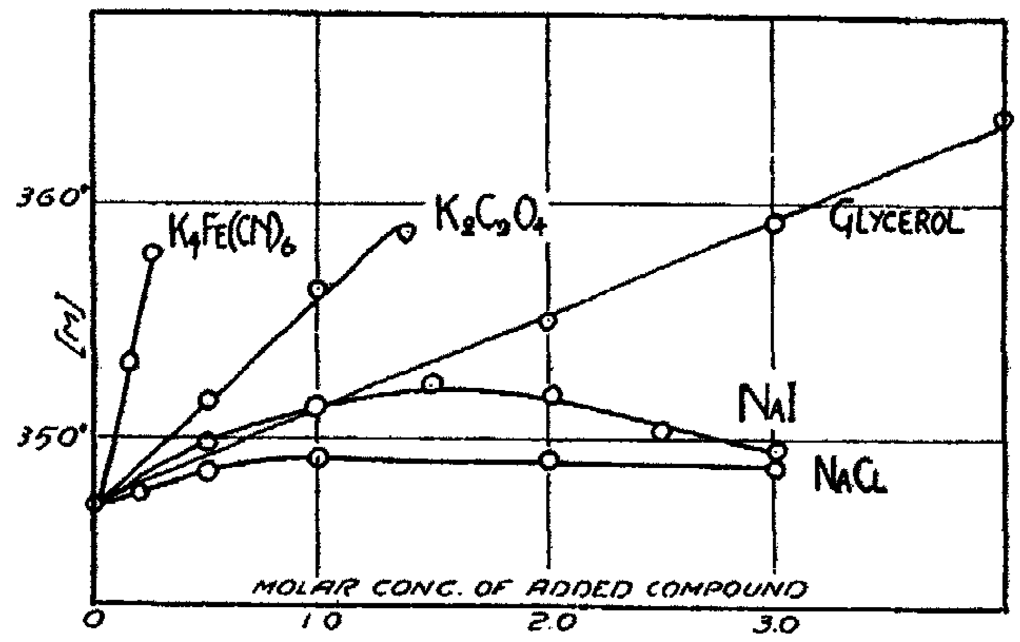

FIG. 2

TABLE VII

Sodium Chloride

Molar Conc.	[M]
—	+347.2°
0.5	+348.6°
1.0	+349.2°
2.0	+349.2°
3.0	+348.9°

Sodium Iodide

Molar Conc.	[M]
0.5	+349.9°
1.0	+351.4°
1.5	+352.4°
2.0	+351.8°
3.0	+349.7°

Potassium Oxalate

Molar Conc.	[M]
0.25	+350.1°
0.5	+351.6°
1.0	+356.3°
1.375	+358.8°

Potassium Ferrocyanide

Molar Conc.	[M]
0.125	+351.1°
0.25	+353.1°

Glycerol

Molar Conc.	[M]
0.5	+348.9°
1.0	+351.1°
2.0	+355.1°
3.0	+359.3°
4.0	+363.9°

For the sake of clarity only the curves of a few salts are given. These are representative and typical. Thus uni-univalent salts give curves similar to that of sodium chloride or sodium iodide while uni-divalent salts have an influence very like potassium oxalate.

The difficulties attending a correlation between the variation of rotation and the known properties of the added compounds are apparent. This is further emphasised by a consideration of Tables VIII and Fig. 3, where the effect of acids and non-electrolytes is shown.

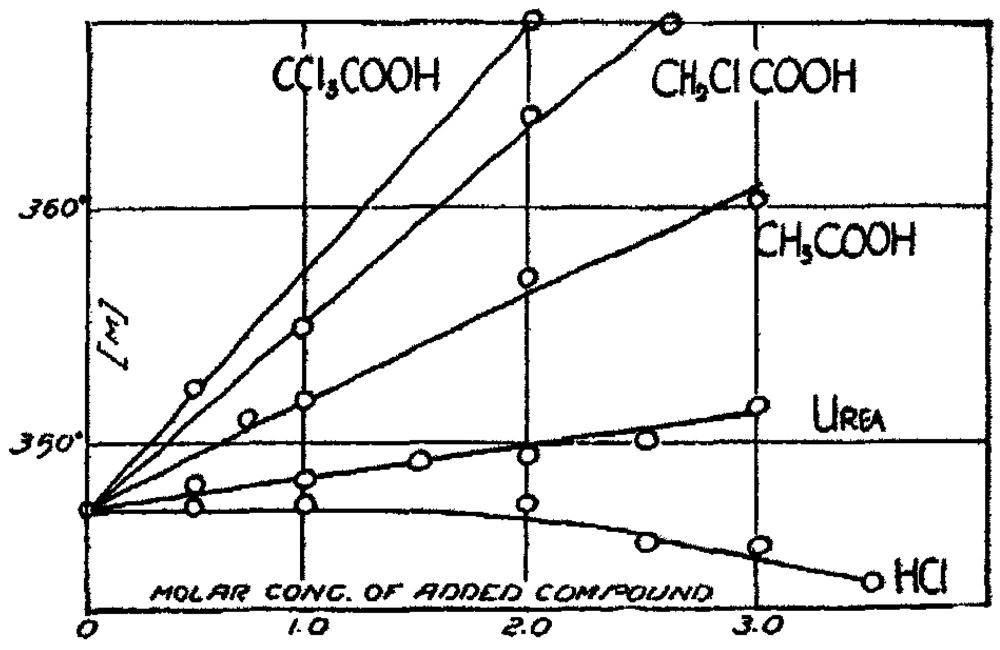

Fig. 3

TABLE VIII

Hydrochloric acid		Acetic acid	
Molar Conc.	[M]	Molar Conc.	[M]
—	+347.2°	—	+347.2°
0.5	+347.5°	0.5	+347.2°
1.0	+347.5°	0.75	+351.1°
2.0	+347.5°	1.0	+351.9°
2.5	+345.9°	2.0	+357.2°
3.0	+345.7°	3.0	+360.5°
Monochloracetic acid		Dichloracetic acid	
—	+346.9°	—	+347.2°
1.0	+354.6°	0.27	+349.4°
2.0	+363.9°	0.53	+352.6°
2.7	+368.6°		
Trichloracetic acid		Urea	
—	+346.9°	—	+347.2°
0.335	+349.7°	0.5	+348.1°
0.5	+352.4°	1.0	+348.3°
2.28	+383.3°	1.5	+349.2°
2.5	+386.4°	2.0	+349.4°
		2.5	+350.3°
		3.0	+351.6°

Two conclusions may be drawn from a study of the above graphs namely, that the influence of electrolytes on the rotation of ammonium α-bromocamphor-π-sulphonic acid is small, and that the effect is not conditioned solely by the ionic nature of the added substance. The theory that the variations of rotation are due essentially to the direct influence of cations on the optically active ion must therefore be considered as incomplete. This is only to be expected in view of the scanty nature of our knowledge of solutions. In considering the optical rotatory power of electrolytes in solution, no account has been taken of the polar nature of the solvent (in most cases water) which results in the solvent dipoles being attracted to the solute molecules or ions. This interaction between solvent and solute molecules may be expected to influence the rotation of the optically active ions and consequently must be taken into account in any discussion on the optical rotatory power of electrolytes. At present the nature of this effect is not fully understood. Further the dielectric constant of the solvent must be taken into consideration. In order to examine the rotations of an electrolyte in solutions of different dielectric constants, aqueous alcohol solutions of ammonium α-bromocamphor-π-sulphonate were investigated.

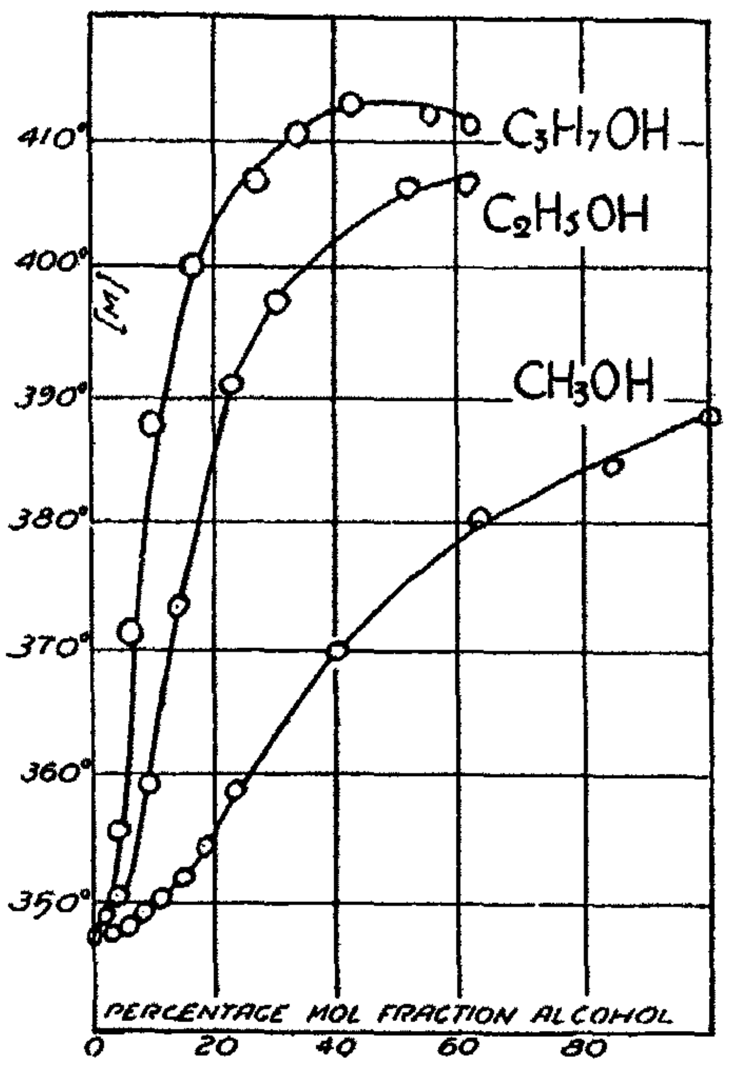

Fig. 4

When the molecular rotation of the ammonium salt is plotted against the mol. fraction of alcohol S-shaped curves are obtained in all cases (Fig. 4). It certainly appears that lowering the dielectric constant of the solvent is accompanied by an increase in the rotation, but the nature of the curves indicates that some other effect or effects must be considered. It would be rash to suggest what these effects are, until more data are provided regarding the optical activity of salts in mixed solvents.

TABLE IX

A = Percentage Mol Fraction Alcohol

A	[M]	A	[M]
	Methyl Alcohol		
—	+347.2°	14.9	+352.2°
0.9	+347.2°	17.5	+354.6°
1.9	+347.2°	23.0	+359.0°
3.8	+347.6°	39.8	+369.9°
5.9	+348.1°	63.2	+380.3°
8.0	+349.4°	84.9	+384.8°
10.2	+349.4°	100.0	+389.0
11.4	+350.3°		
	Ethyl Alcohol		
—	+347.2°	22.8	+391.1°
1.9	+348.1°	29.6	+397.4°
3.9	+350.6°	51.2	+406.8°
8.6	+359.6°	60.6	+406.8°
14.1	+373.5°		
	Propyl Alcohol		
—	+347.2°	26.5	+407.1°
0.9	+348.1°	33.4	+410.9°
1.9	+350.0°	42.3	+413.0°
7.0	+371.4°	57.5	+412.4°
9.3	+387.9°	60.2	+411.8°
16.4	+401.2°		

Summary

1. The work done on the rotatory power of optically active electrolytes is reviewed, and the merits of the theories advanced to account for the variations of the rotations of electrolytes are considered.

2. The rotations of ammonium α-bromocamphor-π-sulphonate have been studied.

In aqueous solutions below molar concentrations of 0.1 there is little or no variation in the value of the molecular rotation. This is in agreement with the results of other investigators on the tartrates, etc. The changes observed at greater concentrations may be adequately explained either by variation in the degree of ionisation, or by Darmois' deformation theory.

The effect of adding optically inactive salts and non-electrolytes has been investigated. The regularities observed by other authors have not been observed. Non-electrolytes have a decided influence.

3. The optical rotatory power of the ammonium salt in aqueous alcohol solutions has been examined.

In conclusion the author has much pleasure in thanking Sir James Walker for his valuable advice and guidance throughout the research.

Edinburgh University,
October 1, 1930.

QUANTITATIVE X-RAY ANALYSIS

Copper-Silver and Copper-Zinc Alloys

BY HENRY TERREY AND ERIC GEORGE VICTORY BARRETT

Introduction

The application of X-ray spectroscopy to chemical analysis may be said to have commenced with the work of Moseley[1] on the relationship between the atomic number of an element and the frequency of its characteristic radiation. In the realm of qualitative analysis, X-ray spectroscopy has demonstrated its use in a wide field, especially in the detection of "missing elements" in the periodic system. Attempts to make the analyses quantitative however have not so far been so successful owing to the complex nature of the phenomena involved.

The general method employed in the quantitative analysis of a substance is the determination of the intensities of corresponding lines of the elements present in the emission spectrum of a sample of the substance, which is made to function as the anticathode in an X-ray tube. In order to determine the relative amounts of the different elements present from the intensity data obtained it is necessary to assume the following: that under equal exciting conditions corresponding lines in the same series of different atomic spectra appear in an intensity ratio corresponding to the atomic concentrations of the sample on the anticathode. The chief sources of error encountered in this emission method are set out in a paper by Glocker and Frohnmayer.[2]

Some previous workers[3] have obtained anomalous values for the intensities of the characteristic radiation measured. These results cannot be explained satisfactorily either by supposing vaporisation of one or more constituents from the anticathode, or by errors arising from the methods employed in the determination of the line intensities. These anomalous intensity ratios would appear to be due to the absorption of the characteristic radiation of one element by another on the anticathode. This absorption effect will occur whenever there are present on the anticathode two elements such that the characteristic radiation of one falls within the absorption region of the other.

Theoretical

It may be assumed that the energy of an X-ray line is proportional to the number of atoms of the corresponding element on the anticathode. This may be written as follows:—

$$E_a = m.c_a$$

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[1] Phil. Mag., 26, 1024 (1913); 27, 703 (1914).

[2] Ann. Physik, 76, 369 (1925).

[3] H. Stintzing: Z. physik. Chem., 108, 51 (1923); Coster and Nishina: Chem. News, 130, 179 (1925); Gunter and Stranski: Z. physik. Chem., 118, 257 (1925); Gunter and Wilke: 119, 219 (1926).

The proportionality between energy and concentration would hold for all kinds of atoms and is a general expression. In the particular case of two atoms adjacent to one another in the periodic system it is possible to carry this relationship a step further. Such atoms would have very similar inner electron systems and consequently the energy relationship for the same lines in their respective spectra, under equal exciting conditions, will be given by:—

$$\frac{E_1}{E_2} = \frac{\text{No. of atoms of 1.}}{\text{No. of atoms of 2.}}$$

The intensity of a line is a measure of the energy of the line. Thus the intensity of a given spectral line is proportional to the atomic concentration of the element emitting the line. In the special case of two elements adjacent in the periodic system the relationship given above will, under equal exciting conditions, hold for the ratio of the intensities.

There remains to be considered the effect of the applied voltage upon the line intensity. Webster and Clark[1] found that the intensity of a given line was proportional to the 3/2 power of the difference between the applied voltage and the critical exciting tension of the series of the element under consideration.

$$I = \text{Constant } (V - V_{\text{min.}})^{3/2}$$

Whether this relationship is general or only applies to the elements investigated by Webster and Clark is open to question.[2]

From the above work however it may be assumed that the intensity is proportional to some function of the difference between the applied voltage and the critical exciting voltage.

$$I \propto f[(V - V_{\text{min.}})]$$

Taking the case of two elements radiating under constant exciting conditions, it is seen that the intensity relationship of the spectral lines in the characteristic radiation of these elements will be constant.

$$\frac{I_1}{I_2} = \frac{K_1.f.(V - V_{\text{min.}})}{K_2.f.(V - V_{\text{min.}})} \text{ or } = \frac{K_1(V - V_{\text{min.}})^n}{K_2(V - V_{\text{min.}})^n}$$

All the expressions in the right hand side of the equation are constant so that

$$\frac{I_1}{I_2} = K.$$

The applied voltage then does not alter the relationship between intensity and concentration, provided that it is kept constant. Thus it is possible to write for any two elements

$$\frac{I_1}{I_2} = K.\frac{C_1}{C_2}$$

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[1] Phys. Rev., (2) 9, 571 (1917).

[2] Cf. Eddy and Laby: Proc. Roy. Soc., 127A, 22 (1930) where reference to other relationships is given.

where I_1 and I_2 are the intensities of the same line in the same series of the characteristic spectra of the two elements. The above is only true when neither of the elements absorbs the characteristic radiation of the other. Whether absorption occurs or not, the most general equation connecting intensity and atomic concentration is the following

$$I_1 = M_1 . C_1$$

In the special case of two elements adjacent to one another in the periodic system, the minimum critical exciting voltages of the two are almost equal. If a sufficiently high voltage be applied to the tube so that the difference between the applied voltage and the critical exciting voltage of either element is large in comparison to the difference between the critical exciting voltages of the elements, then we have

$$\frac{I_1}{I_2} = \frac{K(V-V_{\text{min.}})^n}{K(V-V_{\text{min.}})^n_2} \mathrel{\hat{=}} 1$$

Considering these two elements together on the anticathode, the following intensity concentration relationship would hold for similar lines of their emission spectrum.

$$\frac{I_1}{I_2} = \frac{C_1}{C_2}$$

Of all possible methods of carrying out quantitative analysis by means of X-ray spectra the simplest is the Emission method. This is by a direct measurement of the intensities of the lines of the characteristic radiations of the elements on the anticathode. As has been seen the intensity of a given line in the emission spectrum is proportional to the number of atoms emitting that line. So that if the proportionality factor be known it is possible to determine the number of atoms present.

In the emission method the question of absorption arises. Where there are present on the anticathode two elements, such that the lines in the emission spectrum of one falls within the absorption region of the other then absorption will occur. Also a strengthening of the radiation of the absorbing element will take place owing to the emission of secondary or "fluorescent" radiation.

In the present work alloys of copper and silver and copper and zinc are used, and measurements of the intensities of the Kα radiations made. Taking a mean value for the wavelengths we have the following values

	$K\alpha_{2,1}$
Silver	0.560 A°
Zinc	1.445 A°
Copper	1.539 A°
The absorption limits are as follows:	
Zinc	1.296 A°
Copper	1.379 A°

From these figures it is seen that the $K\alpha_{2,1}$ line of silver falls within the absorption region of copper, as also does the weaker $K\beta$ silver radiation. This silver radiation will be partially absorbed and its intensity suffer diminution. The intensity of the copper radiation however will be strengthened by the addition of the secondary Cu radiation set up by the absorbed Ag radiation. Copper and silver therefore afford a very good example of this absorption effect.

In the case of the copper-zinc alloys no absorption of the $K\alpha_{2,1}$ zinc line occurs, and hence the mixture approximates to the conditions where two elements adjacent to one another in the periodic system are excited to emit radiation. Thus the copper-zinc concentrations can be directly deduced from the intensity ratios, the line intensities being in the same ratio as the atomic concentrations of the respective elements.

Vaporisation yet remains to be considered. This is the most serious difficulty that is to be met with in the emission method. Previous workers have attempted to eliminate this source of error by keeping the current passing through the tube as small as possible, in order to minimise heat effects, and by embedding the analysed substance in a non-volatile medium. By the use of alloys however the trouble of volatilisation is almost entirely eliminated. With long exposures however in the case of the copper-zinc alloys, the well known zinc volatilisation occurs.

All photographic methods used in the determination of the intensities of X-ray spectral lines are, on account of the shape of the blackening curve, liable to introduce error. In the present work this source of error is eliminated by measuring the intensities of the lines by means of the ionisation produced by their passage through a gas. The method however suffers from the drawback that it is not as sensitive as the photographic method, and that it requires a relatively intense beam to produce any marked ionisation effect. For this reason it was found to be impossible to make any measurements, using the ionisation method, on a mixture of oxides or on a mineral.

Another method of measuring the intensities was devised by the authors. It is a photographic method; but it does not depend on the estimation of the blackening of a photographic film. A wedge-shaped piece of aluminium is placed in front of the photographic film in the camera. Lines will be obtained on the film whose height will depend on the thickness of aluminium that each particular beam has been able to penetrate. By a measurement of the height of these lines and a knowledge of the dimensions of the wedge, the thicknesses of aluminium that the various lines have penetrated can be calculated. It must be assumed that where the film has just ceased to be affected, that is at the top of the line, the intensity of any given line radiation is constant. This means that the intensity of a beam of any given wavelength required just to affect a photographic film is a constant quantity for the type of film used.

That is I_λ = Constant.

Then for any given wavelength, applying the well-known absorption equation

$$I = I_0 e^{-\lambda d}.$$

We have

$$I_0 = I_A . e^{+\lambda d} = \text{Constant}. \, e^{+\lambda d}$$

λ is known and d can be calculated from the height of the line obtained. Thus with a knowledge of the constant the line intensity can be calculated.

Considering two lines—for example Cu $K\alpha_2$ and Zn $K\alpha_2$—the ratio of their intensities will be given by the following expression

$$\frac{I_{0Cu}}{I_{0Zn}} = \text{Constant}. \, e^{(\lambda_{Cu} d_{Cu} - \lambda_{Zn} d_{Zn})}$$

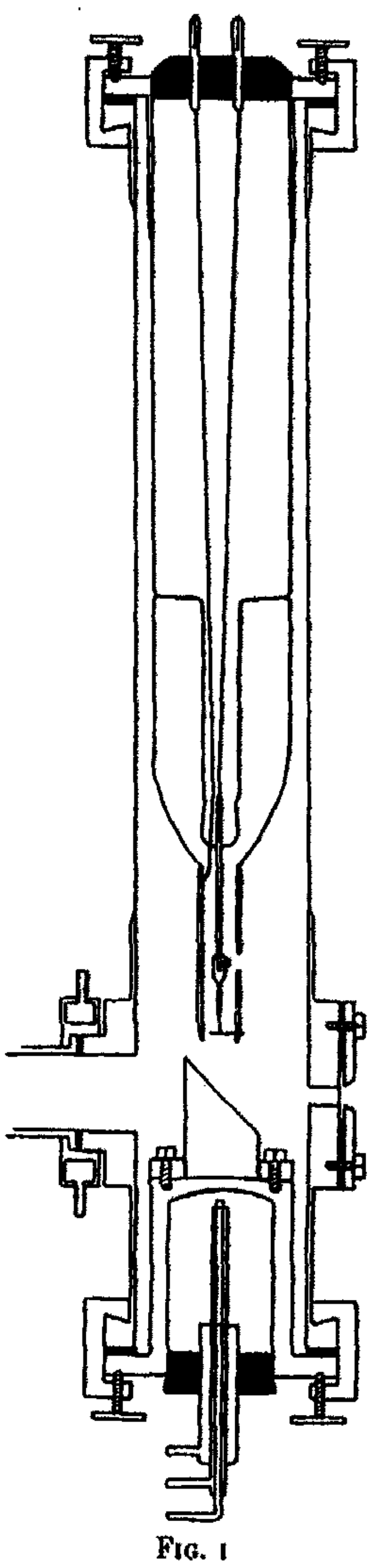

Fig. 1

Apparatus and Experimental Procedure

For this work it is essential to have an X-ray tube that gives a constant output. It is necessary that the potential across the tube remains constant for the whole series of readings, and that during the time taken for a set of readings on a particular alloy the current passing through the tube must also remain constant.

The X-ray tube used in these experiments is a modified form of Seeman Philips tube of the hot cathode or Coolidge type. The body of the tube is constructed of a special steel having the same coefficient of expansion as glass. Connection to the glass walls of the tube is made by direct fusion. Both cathode and anticathode are detachable. Gas-tight joints are made by means of rubber washers between machined faces. The tube is shown diagrammatically in Fig. 1. The anticathode consists of two parts, the body, constructed of bronze and hollow to allow of water cooling, and the cap. This latter is held in position by means of three small bolts. In this way the cap is kept in close contact with the body of the anticathode and does not suffer overheating. The cap consists of two parts, the target constructed out of the alloy under investigation, and the base of brass. The target is screwed into the base allowing good heat conduction. It is essential that the anticathode be efficiently cooled, and for this purpose a special water-cooler was devised. The water is directed in the form of a squirt directly on the underside of the anticathode. With an ordinary flow of water it is almost certain that a cushion of steam will form between the underside of the target and the cooling water. This cushion being a relatively poor conductor of heat will cause overheating of the anticathode with consequent volatilisation, sputtering, and pitting of the surface The present cooling device consists of three concentric tubes The innermost tube is an auxiliary outlet, the volume of water flowing out of which may be controlled by a screw clip, which carries away any steam that may be formed. The middle tube is the water inlet. The difference in diameters of these two tubes is small so that the water is squirted on to the underside of the target. The outer tube is shorter and wider and is the water outlet. The cooler is constructed of brass tubing and held in the anticathode by means of a rubber bung.

The alloys were made by heating together the constituent metals in approximately the correct proportions in a small furnace. A layer of borax was placed on top of the metals to act as a flux and to dissolve out any oxide formed. When the mixture was molten it was well stirred with a carbon rod and cast into a piece of steel tube that had been covered internally with graphite. The cylinders of alloys so obtained were turned down to the required dimensions and cut at 45°. Since the X-ray analysis does not give a high degree of accuracy it was considered sufficient to analyse for one constituent only of the alloys. The copper-silver alloys were analysed for silver by means of a gravimetric estimation of silver chloride. The copper-zinc alloys were analysed for copper electrolytically.

The X-ray tube was continuously evacuated by means of a Leybolt three-stage mercury diffusion pump, backed by a two stage large capacity rotary oil pump. An estimate of the state of the vacuum was obtained by means of a McLeod gauge in the system. The requisite potential for working the tube was generated by an induction coil. One side of the secondary of the coil was earthed, the other connection to the cathode of the tube. The anticathode was earthed, and an alternate spark gap connected across the tube. An energy input of 0.77 kilowatts was supplied to the coil, and the exciting voltage of the tube was 40,000 volts. The filament was heated by an insulated bank of accumulators of large capacity giving a total of 16 volts. The filament current was 4.6 amperes. The filament current was found to be very critical.

The spectrometer used in these experiments was a standard Bragg type supplied by Messrs Pye. A calcite crystal was used and the angles of the crystal table and ionisation chamber calculated from the wavelength and lattice constant data. Measurements were made on the first order Kα radiations, the α_2 and α_1 not being resolvable. A modified type of Tilting Electroscope was used to measure the ionisation produced, a description of which is given in a paper by H. A. Bumstead.[1] The ionisation chamber was charged to a potential of +200 volts, and the two plates of the electroscope to +200 and −200 volts. Under these conditions and using a gold leaf of

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[1] Am. J. Sci., December (1911).

width not greater than 0.05 cm. a sensitivity of 25 scale divisions for 0.1 v. was obtained. The gas used in the ionisation chamber was dry sulphur dioxide. This was obtained from a siphon and passed over P_2O_5 before use. In practice it was found necessary to recharge the chamber with gas for every set of readings. The electroscope leaf was timed, by means of a metronome, over 10 or 30 scale divisions depending on the intensity of the beam and the sensitivity of the electroscope. The metronome was set to 100 beats per minute. Care had to be taken to earth shield the electroscope and connections against stray electrical effects.

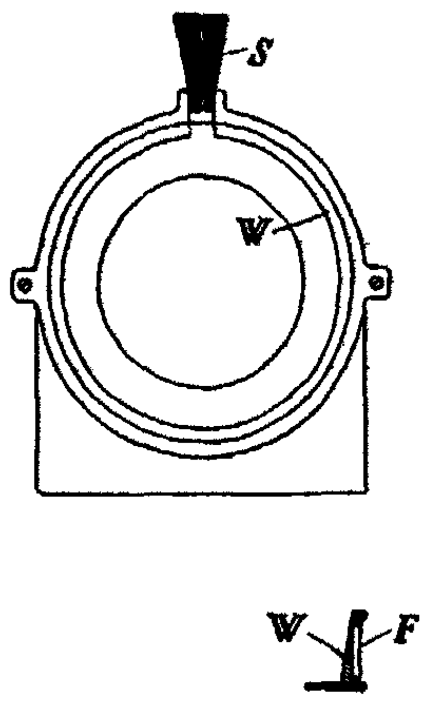


FIG. 2

The wedge camera consists of a Debye camera of diameter 10 cms. fitted with an aluminium wedge around its circumference. This is best seen by reference to Fig. 2. The wedge (W) is made by driving to fit inside the circular film holder. The dimensions of the wedge will depend on the wavelength of the radiation used. For copper K radiation it was made 0.15 cms. at the base tapering off to zero at the top—the height of the wedge being 1.81 cms. These dimensions gave lines of the correct magnitude with an exposure of 4 hours. The slit (S) is a line slit, extending the height of the film in order to obtain an even intensity distribution throughout each reflected beam. The wedge camera was used in a Müller spectrograph. A calcite crystal rocked through a small angle was used to analyse the beam.

Experimental Results

1. *Copper-Silver Alloys.*

Intensity measurements by ionisation method. In order to obtain the correct values for the intensity ratios of the copper and silver lines it is necessary to

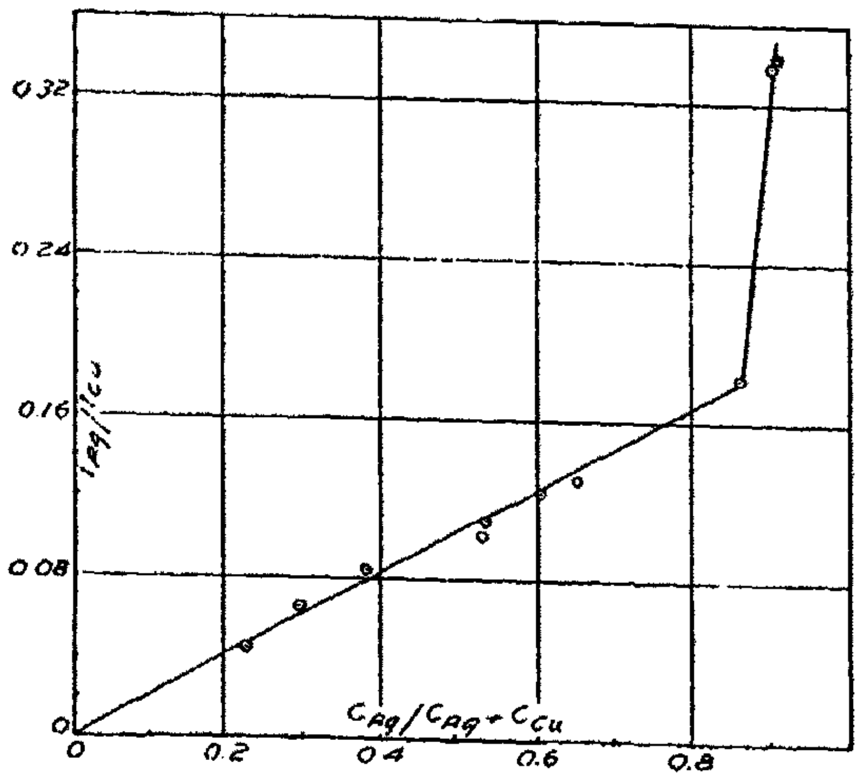
TABLE I

% Composition		Measured Intensity Ratio		Corrected Intensity Ratio		$\frac{C_{Ag}^*}{C_{Ag}+C_{Cu}}$	$\frac{I_{Ag}}{I_{Cu}}$
Ag	Cu	Ag	Cu	Ag	Cu		
94.5	5.5	1	1.52	1	2.90	0.908	0.345
93.9	6.1	1	1.58	1	2.94	0.903	0.340
91.8	8.2	1	2.95	1	5.50	0.865	0.182
76.3	23.7	1	4.10	1	7.63	0.655	0.137
72.2	27.8	1	4.35	1	8.10	0.605	0.124
66.2	33.8	1	4.84	1	9.02	0.535	0.111
65.9	34.1	1	5.25	1	9.78	0.532	0.102
50.2	49.8	1	6.30	1	11.7	0.380	0.0853
41.6	58.4	1	8.06	1	15.0	0.296	0.0666
32.7	67.3	1	11.85	1	22.1	0.227	0.0453

* C_{Ag} = Concentration silver in gm. mols.
C_{Cu} = Concentration copper in gm. mols.

correct the observed intensity values for absorption in the aluminium windows of the X-ray tube and ionisation chamber, and also for absorption in the air space between the X-ray tube and the chamber.

The total thickness of aluminium passed through is 0.0051 cms., and the length of air traversed is 30 cms. This gives a correction factor of × 1.37 for the aluminium, and × 1.36 for the air.



GRAPH I
Copper-Silver Alloys

As is seen from the graph the following relationship between relative intensity and atomic concentration holds over a large concentration range

$$\frac{I_{Ag}}{I_{Cu}} = \frac{M.C_{Ag}}{C_{Ag} + C_{Cu}}$$

2. *Copper-Zinc Alloys.*

Intensity measurements by ionisation method. As in the case of the copper-silver alloys a correction must be applied for the absorption that occurs in the aluminium windows. In this case however the wavelength difference is sufficiently small that the different absorptive powers of the air traversed in the spectrometer can be neglected. The correction factor of the aluminium is × 1.12.

TABLE II

% Composition		Measured Intensity Ratio		Corrected Intensity Ratio		Composition in Gm. Mols	
Zn	Cu	Zn	Cu	Zn	Cu	Zn	Cu
40.15	59.85	1	1.48	1	1.66	1	1.53
48.15	51.85	1	0.84	1	0.94	1	1.11

Intensity measurements by wedge camera method. In the circular camera the top of the wedge is masked by the top flange of the camera for a distance of 0.25 cm. This length therefore must be added to the measured lengths of the lines in order to obtain the correct length. The thickness of the aluminium window of the X-ray tube (0.0025 cm.) is added to the thickness of aluminium penetrated calculated from the height of the lines.

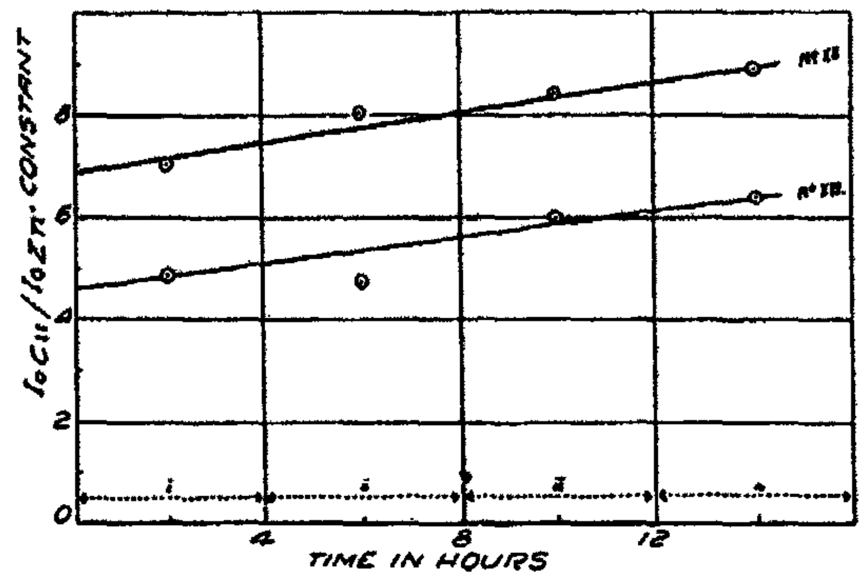
TABLE III

Alloy No. XII 40.15% Zn 59.85% Cu
Alloy No. XIII 48.15% Zn 51.85% Cu

Four exposures each of four hours' duration were made with each alloy.

Exposure	Line Measured	Measured Length of Line on Film		Calculated Thickness Al Penetrated		$\lambda_{Cu}d_{Cu}-\lambda_{Zn}d_{Zn}$	$\frac{K.I_{oCu}}{I_{oZn}}$
		Cu	Zn	Cu	Zn		
				Alloy XII			
1.	$K\alpha_2$	0.295	0.200	0.048	0.040	1.924	6.9
	$K\alpha_1$	0.260	0.150	0.045	0.036	1.960	7.1
2.	$K\alpha_2$	0.300	0.200	0.049	0.040	2.05	7.8
	$K\alpha_1$	0.290	0.175	0.048	0.038	2.12	8.3
3.	$K\alpha_2$	0.300	0.200	0.049	0.040	2.05	7.8
	$K\alpha_1$	0.280	0.150	0.047	0.036	2.20	9.0
4.	$K\alpha_2$	0.310	0.175	0.049	0.038	2.27	9.6
	$K\alpha_1$	0.280	0.160	0.047	0.037	2.11	8.2
				Alloy XIII			
1.	$K\alpha_2$	0.275	0.225	0.047	0.042	1.58	4.85
	$K\alpha_1$	0.250		0.045	——	——	——
2.	$K\alpha_2$	0.300	0.250	0.049	0.045	1.52	4.56
	$K\alpha_1$	0.275	0.230	0.047	0.042	1.58	4.85
3.	$K\alpha_2$	0.275	0.200	0.047	0.040	1.79	5.99
	$K\alpha_1$	0.275		0.047			
4.	$K\alpha_2$	0.200	0.100	0.040	0.031	1.85	6.37
	$K\alpha_1$	0.200		0.040			

During the measurements it was noticed from the condition of the X-ray tube that a certain amount of zinc volatilisation was taking place. From the experimental results it is seen that a progressive amount has taken place, causing, in both cases, a steady increase in the concentration of the copper and hence an increase in the intensity ratio. In order to correct for this progressive increase and to obtain the intensity ratio given by the alloy before volatilisation occurred, the intensity ratios were plotted against the time of exposure. For a four hour exposure the resulting intensity ratio is the average of the intensity ratios over that period. The intensity ratios therefore were plotted at 2 hrs., 6 hrs., 10 hrs., and 14 hrs. Extrapolating these values back to zero time gives the correct intensity ratio. It was necessary to assume a linear relationship between volatilisation and time of exposure.



GRAPH II

Copper-Zinc Alloys. Extrapolation of Intensity Ratios

Extrapolated Intensity Ratios from Graph.

Alloy No.	$K.I_oCu/I_oZn$
XII.	6.9
XIII.	4.6

Putting 4.35 for the value of the constant K, we have the following values for the intensity ratios

XII.	1.59
XIII.	1.06

TABLE IV

% Composition		Composition in Gm. Mols		Intensity Ratio Ionisation Method		Intensity Ratio Wedge Camera Method	
Zn.	Cu.	Zn.	Cu.	Zn.	Cu.	Zn.	Cu.
40.15	59.85	1	1.53	1	1.66	1	1.59
48.15	51.85	1	1.11	1	0.94	1	1.06

Conclusions

The results obtained demonstrate two different phenomena that are to be met in the direct emission method of quantitative X-ray analysis. The copper-silver alloys offer a good example of two elements that are such that one absorbs the radiation of the other. The copper-zinc alloys exhibit no such absorption, and are an example of the simpler type where one is dealing with two elements adjacent to one another in the periodic system.

Considering firstly the results obtained from the measurements of the copper-silver alloys. It is seen that the intensity ratio is directly proportional to the ratio of the silver concentration expressed in gm. mols. to the total number of gm. mols. of silver and copper present.

This may be expressed

$$I_{Ag}/I_{Cu} = M.C_{Ag}/C_{Ag}+C_{Cu}$$

The wavelength of the line of shortest wavelength in the K series of copper is greater than the wavelength of the $K\alpha_2$ line of silver, so that the energy of the $K\alpha_2$ line is greater than the energy required to excite the K series of copper. Hence in accordance with Stokes law secondary or fluorescent radiation will be produced. The absorbed silver radiation will give rise to secondary K radiation of copper. Thus the silver intensity, diminished by absorption, will be some function of the silver concentration, whilst the copper intensity, augmented by secondary Cu radiation, will be a function of both the copper and the silver concentrations.

The high values obtained with very low concentrations of copper may be accounted for by assuming that the number of copper atoms present are insufficient to absorb the optimum quantity of the emitted silver radiation.

The copper-zinc alloys behave in a normal manner and demonstrate the possibility of quantitative X-ray analysis of metallic alloys. The conditions that must be observed in order that the composition of a mixture may be directly determined quantitatively from the intensities of the lines in its emission spectrum are then the following:

The elements are adjacent to one another in the periodic system.

The emission spectrum of any constituent element must not fall within the absorption region of any other.

The measurement of the relative intensities of the lines in the emission spectra by means of the ionisation of a gas overcomes many of the difficulties inherent in any photographic method, especially that of estimating the blackening produced. The ionisation method however suffers from the disadvantage that it requires a relatively intense X-ray beam.

From the results obtained with the "wedge" camera the following conclusions can be drawn.

The relative intensities of similar lines in emission spectra can be determined by a measurement of their penetration of a wedge of aluminium, the depth of penetration being given by the length line received on a photographic film behind the wedge.

When dealing with lines of different wavelength it is necessary to introduce a constant to correct for change of photographic effect with wavelength.

Summary

1. The relative intensities of the K lines in the characteristic X-ray emission spectra of copper-silver alloys have been determined by measurement of their ionising powers.

The following relationship between intensity and atomic concentration has been found to hold:

$$\frac{I_{Ag}}{I_{Cu}} = \frac{M.C_{Ag}}{C_{Ag} + C_{Cu}}$$

The silver radiation suffers partial absorption in the copper and gives rise thereby to secondary copper radiation, thus diminishing the silver radiation and augmenting the copper.

2. Copper-zinc alloys have been similarly investigated. A linear relationship between relative intensity and atomic concentration has been found to hold.

3. A method for the determination of relative intensities of lines in an X-ray spectrum, dependent on the measurement of their penetration of an aluminium wedge, has been devised. The copper-zinc alloys were also investigated by this method.

The Sir William Ramsay Laboratories of Inorganic
and Physical Chemistry,
University College, London.
September 8, 1930.

THE "THERMO-SENESCENCE EFFECT" EXHIBITED BY GOLD SOLS AT ELEVATED TEMPERATURES, AND "AGEING" AT ROOM TEMPERATURE*

BY EMLYN JONES AND W. C. M. LEWIS

Introduction

The present investigation has been carried out with the object of investigating further the change in behaviour—with respect to the rate of coagulation—which is exhibited by gold sols as a consequence of the sol having been maintained at a high temperature, namely 80°C., before addition of the coagulating agent.

The maintenance of the sol at 80°C. for approximately three hours has been shown by previous workers in this Laboratory (Miss A. Davies,[1] P. J. R. Butler[2]) to give rise to a sol which has reached a colloid equilibrium or steady state. The process of attainment of this state has been termed thermo-senescence. It is only with material which has undergone preliminary treatment of this kind that reproducible values for the Smoluchowski coagulation coefficient can be obtained. The value of this coefficient can therefore be employed, other conditions being maintained constant, as a precise means of determining to what extent the thermo-senescence process has been controlled.

It will be convenient at this point to recall the definition of the coefficient as it appears in Smoluchowski's[3] theory of coagulation of colloids by an electrolyte.

For the case in which the coagulation is "rapid," that is, the rate is independent of further increase in concentration of coagulating electrolyte. Smoluchowski's theory leads to the expression

$$\nu_1 = \frac{\nu_0}{(1 + \beta_0 t)^2}$$

where β_0 is the coefficient for the conditions referred to, ν_0 = the initial number of primary particles, and ν_1 = the number of primary particles remaining after time "t."

$$\beta_0 = 4 \pi D \rho \nu_0$$

where ρ = the radius of the sphere of attraction of a primary particle, and D = the diffusion constant as given by Einstein's equation, viz.

$$D = \frac{RT}{N} \cdot \frac{1}{6\pi\eta r},$$

where r = the radius of the particle and η = the viscosity of the medium.

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* From the Muspratt Laboratory of Physical and Electro-chemistry, University of Liverpool.

[1] A. Davies: J. Phys. Chem., 33, 274 (1929).

[2] Butler: J. Phys. Chem., 34, 656 (1930).

[3] Smoluchowski: Z. physik. Chem., 92, 129 (1917).

Smoluchowski attempted to modify his theory so as to include the case where the coagulation velocity is dependent upon the concentration of electrolyte, i.e. the slow region of coagulation. In this region owing to incomplete neutralisation of the electric charge on the particles the attractive forces are not at their maximum. Thus every collision does not lead to a permanent aggregation but only a certain fraction of them. A probability factor ξ was, therefore, introduced to allow for this, the resulting equation being

$$\nu_1 = \frac{\nu_0}{(1 + \xi\,\beta_0\,t)^2}$$

ξ, being a function of the residual net charge on the particle, will be constant throughout the course of the coagulation only on the assumption that the particles are equally charged, an assumption apparently not justified in practice, cf. Miss Garner.[1] Setting $\xi\,\beta_0 = \beta$ we obtain, for the region of slow coagulation

$$\nu_1 = \frac{\nu_0}{(1 + \beta t)^2} \text{ or } \beta = \frac{1}{t}\left(\sqrt{\frac{\nu_0}{\nu_1}} - 1\right)$$

β is therefore the rate of variation of $\left(\sqrt{\frac{\nu_0}{\nu_1}} - 1\right)$ with time, and if this expression be plotted against the time "t," β at any instant will be given by the tangent to the resulting curve.

If β be a true constant the relation should be linear with its origin at zero time. Miss Garner, *loc. cit.*, using gold sols which had undergone the preliminary thermo-senescence treatment, found that the relation was linear over a considerable portion of the time interval employed, but that, on being extrapolated backwards, the line did not pass through the origin. This "zero discrepancy" as it has been termed by Miss Garner, is due to the fact that, although over a major portion of the reaction the velocity coefficient of coagulation is constant, during a short initial period the velocity is enhanced. In other words a fraction of the primaries coagulate much more rapidly than do the majority of the particles. This has been explained as being due to the particles of the sol being unequally charged to begin with.

To return to the thermo-senescence phenomenon itself. This effect was first recognised in the case of colloidal material coagulated under slow conditions. The effect was always in the direction of a decrease in the value of β as compared with material which had not undergone thermal treatment. In other words thermo-senescence *increases* the stability of the sol. This has been ascribed by Miss Davies, *loc. cit.*, to an actual contraction of the initial particles with the result that the charge density increases and the rate of coagulation (in the slow region) is rendered still slower.

More recently, Butler, *loc. cit.*, has found the phenomenon to exist when the concentration of electrolyte is such as to ensure rapid conditions. Com-

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[1] Garner: J. Phys. Chem., 30, 1410 (1926).

bining the results of both investigators the most probable explanation is that high temperature causes a contraction in the size of the primaries. In the case of slow coagulation this causes an increase in charge density which would give rise to a slower rate of coagulation. In the case of the rapid region the particles are completely discharged and the contraction of the particle acts to give rise to a decrease in ρ, the radius of attraction of the particle, which in turn decreases the probability of collision between the uncharged particles, thereby leading to a less rapid rate of coagulation.

Although the theory advanced to account for thermo-senescence, namely contraction of the particle, is logical enough, it is clear that other explanations might be put forward. The most obvious of these would be to attribute the influence of temperature to removal of impurities, themselves electrically charged. It was the main purpose of the experiments described in the present paper to test this possibility by endeavouring to get rid of such impurities by dialysis prolonged far beyond the usual 3 to 4 days normally given to "remove impurities," and then to see if the thermo-senescence phenomenon was modified thereby.

Experimental

The gold sol was prepared by the "Acetone" reduction method adopted by Miss Davies, *loc. cit.* The method consists in adding to 480 ccs. of redistilled water, 5 ccs. of a 1.2 percent solution of gold chloride together with 14 ccs. of a 0.18 N potassium carbonate solution, and 3 ccs. of acetone. On warming the mixture a pinkish tinge appears which deepens as the temperature rises. The solution is allowed to boil vigorously for about three minutes. A clear ruby-red sol results. A number of these preparations were made and mixed to form one large volume of sol.

All vessels and containers with which the sols come in contact were of quartz. These were thoroughly cleaned before use with alkali, alcohol-nitric acid mixture, distilled water, and finally steamed out for five minutes with steam from redistilled water. In the present investigation the sol was diluted with redistilled water. The original sol contained about 56 mgs. of gold per litre. The dilution employed was 1 part of sol to 1 part of water.

The apparatus employed for the continuous dialysis of the gold sol simply consisted of a series of collodion sacs containing the gold sol. These were surrounded by a continuous stream of distilled water. The collodion sacs, having a capacity of over 300 ccs. were mounted on wide rubber bungs and were made air-tight. A stream of nitrogen was passed periodically through the whole series of sacs. Such an arrangement ensured that the sol was never in contact with the air during the dialysis. Samples of the sol were syphoned out at various time intervals by means of a syphon tube leading in to each sac. A sheet of wood covered each of the beakers containing the distilled water. In this sheet, holes were bored of sufficient size to allow of the support of the sacs and the entrance and exit of the distilled water which passed through the whole series of beakers by means of a series of syphon tubes. The water was, therefore, kept free from dust and metallic particles which may have been present in the atmosphere. From the last beaker of the series the water passed to another vessel from which there was an overflow and the level of the distilled water throughout the apparatus was regulated by varying the level of this outlet. The dialysis operation was carried out at room temperature.

In order to find the mean rate of coagulation in the slow region the technique employed by Butler, *loc. cit.*, was used as it ensures greater reproducibility and more controllable conditions than were possible in the methods employed by other workers.

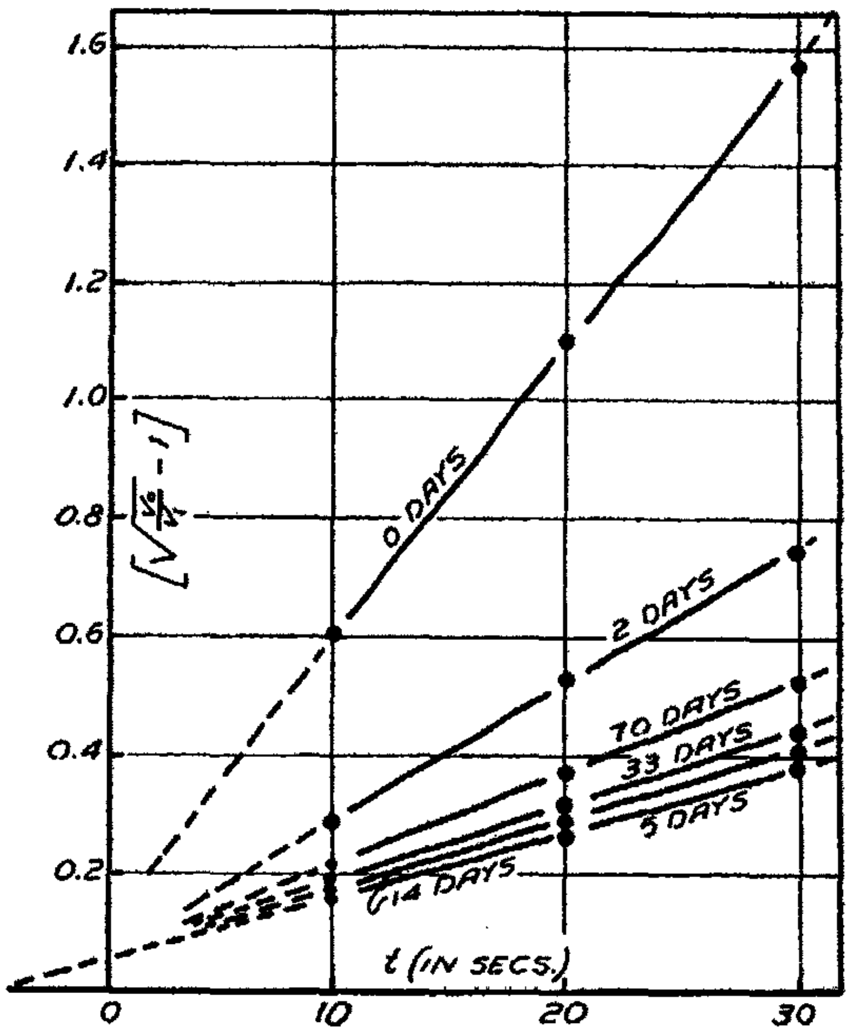

FIG. 1

50 ccs. samples of the sol were syphoned out at various time intervals during the dialysis. Each sample was then made up to 100 ccs. with redistilled water. The samples were then raised to and maintained at 80°C. In order to initiate the actual coagulation process (carried out at 80°C.) 2 ccs. of a 0.0664 N $BaCl_2$ was added. This on addition to the sol gave a concentration of 0.00133 N which concentration gave a slow rate of coagulation. The coagulation was arrested by adding 2 ccs. of a 2% gelatin solution and shaking. It has been found that the flasks containing the sol sample have to be immersed in the thermostat at 80°C. for half an hour before they attain this temperature and this was taken as the zero time for the "duration of heat treatment." The sol samples were then maintained at this temperature for 1 hour and 3 hours respectively before initiating the coagulating process.

In the present investigation the extent of coagulation was determined after 10, 20, and 30 secs. respectively. The Hatschek[1] wedge method as modified by Butler, *loc. cit.*, was employed.

Table I summarises the results obtained. The "duration of heat treatment" refers to the time during which the sol is maintained at 80°C. prior to the initiation of the coagulation process at 80°C. The β values are obtained from the slope of the curve as previously described. The accompanying graph serves to illustrate some of the results obtained, namely those obtained for the various periods of dialysis after three hours heat treatment.

TABLE I

Period of Dialysis	Duration of heat treatment	β
0 Days	1 Hour	0.0352
"	3 Hours	0.0493
2 Days	1 Hour	0.0234
"	3 Hours	0.0217
5 Days	1 Hour	0.0149
"	3 Hours	0.0112
14 Days	1 Hour	0.0152
"	3 Hours	0.0122
33 Days	1 Hour	0.0154
"	3 Hours	0.0128
70 Days	1 Hour	0.0186
"	3 Hours	0.0157

Discussion of Results

The results given in the table demonstrate the existence of two distinct phenomena.

In the first place on comparing the β values obtained after heat treatment for 1 hour and 3 hours respectively, it will be observed that in all cases (except the case in which the sol was completely undialysed) there is a diminution in the coagulation coefficient, the value recorded after 3 hours heat treatment being, in fact, an equilibrium or limiting value. This behaviour is exhibited by material which has been dialysed (at room temperature) over very different periods of time, from two days to as much as seventy days. This phenomenon, namely, a *fall* in β to a limiting value, as a result of heat treatment, is the true thermo-senescence phenomenon, i.e. an increased stability. In the second place the results show that dialysis, when

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[1] Hatschek: Trans. Faraday Soc., **17**, 499 (1921).

prolonged, has the effect of *increasing* β. This effect manifests itself after a dialysis of 5 days duration and goes on increasing up to 70 days, the farthest point investigated. In other words, after a few days dialysis at room temperature further treatment is accompanied by a decrease in the stability of the sol. This phenomenon most closely resembles that to which the term "ageing" has very generally been given.

It may be recalled that the earlier work from this laboratory led to the conclusion that thermo-senescence is due essentially to a contraction of the individual sol particle whereby its range of attraction is diminished and, if it be charged at all, its charge density is increased. On the other hand, it is generally assumed that the decreased stability associated with ageing (at ordinary temperature) has its origin in a redistribution of adsorption effects on the part of the electrolytic "impurities" present in the sol system.

Until the results just given had been obtained, it was not clear whether heat treatment led in the same direction as the effect of mere passage of time. It now appears that the two effects do not necessarily operate in the same direction. In the light of this conclusion the term thermo-senescence is perhaps not particularly suitable but we have retained its use as it is unlikely to lead to ambiguity.

As a practical point the results obtained lead to the conclusion that in general no sol is in a suitable state for examination until it has been dialysed for about 4-5 days and has then been subjected to about 3 hours heat treatment.

Summary

Instead of the usual three to four days dialysis, gold sol has been subjected to prolonged dialysis (up to 70 days) and examined for the thermo-senescence phenomenon. This was found to be exhibited in all cases as a real and definite phenomenon, which fact renders the view that thermo-senescence may be attributed to the further removal of impurities, invalid. The conclusion already arrived at that thermo-senescence is due to contraction of the sol particles as a result of raising the temperature seems still to be the most probable explanation of the phenomenon. Incidentally the investigation has served to demonstrate the existence of the ordinary ageing effect at room temperature. The ageing effect decreases the stability of the sol as shown by the increase in the coefficient β. The ageing effect may well be attributed to ionic adsorptions and desorptions. The thermo-senescence effect on the other hand decreases β, that is increases the stability of the sol. The two phenomena, namely thermo-senescence, and slow ageing at ordinary temperatures, are therefore distinct phenomena.

The authors desire to express their thanks to Imperial Chemical Industries, Ltd. for a Grant to the Department of Physical Chemistry of this University.

Liverpool,
October, 1930.

ON PHENYLACETALDEHYDE AND ITS POLYMERISATION

BY JAMES ROBERT POUND

It is known that phenylacetaldehyde polymerises easily, especially on contact with air and light. Enklaar[1] kept a specimen in the dark for six months and found it had then polymerised to the extent of nearly one-half; finally he obtained a crystalline solid, melting at 33°. A sample of phenylacetaldehyde was obtained by the writer from L. Givaudan and Co., France. The manufacturers state that storage in a stoppered bottle in a dark place reduces polymerisation and that the alcoholic solution keeps almost indefinitely. Our sample of phenylacetaldehyde was a colourless, sweet-smelling and fairly viscous liquid; it was kept corked in a dark cupboard and gradually became more viscous, and after 17 months small crystals appeared in the body of the liquid, though some crystals had formed above the liquid some months previously. The refractive index of the liquid increased with age, as well as its density and viscosity; these changes have been studied at room temperatures (7°-20°) and at 30°.

Some experiments were carried out with phenylacetaldehyde on watch-glasses, which were weighed from time to time. Though phenylacetaldehyde boils at about 200° and has a vapour pressure of 5 mm at 74.5° (Givaudan), it is sufficiently volatile to lose weight continuously when kept at room temperatures on watch-glasses in air or in closed vessels over sulphuric acid or calcium chloride or water. In all these experiments the decrease in weight falls off with age. When kept over sulphuric acid or calcium chloride, the phenylacetaldehyde vaporised is picked up by these reagents. In air and over sulphuric acid and calcium chloride, the phenylacetaldehyde becomes in time slightly yellow, covered with a skin or viscous surface-layer, develops crystals, and finally becomes a hard glassy mass: these changes proceed more rapidly over the desiccating agents; but the rate of loss of weight is approximately the same in all cases. When kept in a closed vessel over water, the phenylacetaldehyde does not become glassy hard or full of crystals, but it remains somewhat fluid and becomes opalescent with age: the loss of weight however is the same as before. This loss of weight depends on the room temperature and is due to simple evaporation. One sample, kept in the open air at an average temperature of 20°, lost in 150 days 14 per cent of its original weight: minute crystals were present in the liquid at the start of the experiment, were numerous after 30 days, and constituted the bulk of the mass, which was then slightly straw-coloured, after 90 days. Another sample of phenylacetaldehyde was placed in a flask and attached to a Lunge nitrometer containing mercury: after several days no absorption of oxygen was noticed. The flask was opened, a tube of calcium carbide was enclosed, and the whole

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[1] J. Chem. Soc. Abs. A, 1926, 614.

system joined up again: after several weeks the volume of the gas in the system was unaltered. Thus no absorption of oxygen and no evolution of water vapour occurred.

The acidities of samples of the phenylacetaldehyde were determined by dissolving known weights in alcohol and titrating with carbonate-free alkali, using phenolphthalein as indicator: the end-points were sharp, and the acid was calculated as phenylacetic acid. The stock phenylacetaldehyde showed 1.1% acid. A sample dissolved in alcohol had air aspirated through it for 20 hours at 7° and then showed 1.8% acid. Another sample after exposure to air on a watch-glass for 56 days showed 2.3% acid; and that sample exposed to air for 150 days showed finally 2.0% acid: but the residues from the other watch-glass experiments (see above) showed lower '% acid'. A sample, III (see later), after keeping at 30° for 30 days showed 1.35% acid. Thus phenylacetaldehyde does not oxidise appreciably on exposure to the air.

The refractive index, *n*, was determined at 20° by a Hilger-Abbe refractometer, which gave results to the fourth decimal place for $n_{\mathrm{D}}^{20^\circ}$. For the stock sample of phenylacetaldehyde, S, kept at room temperature, about 15°, the refractive index increased with age at a diminishing rate; but after crystals had formed, the refractive index of the liquid varied little: with this and other samples n actually diminished a little after crystals had separated, —indicating supersaturation: also just before crystals appeared, the 'line' in the refractometer was blurred, as it is with suspensions,—indicating incipient (liquid?) crystals. The refractive index is the most convenient property to indicate the age of phenylacetaldehyde; and crystals are about to form, polymerisation having progressed thus far, when $n_{\mathrm{D}}^{20^\circ} = 1.570$ approximately. Some results for the stock sample, S, were:—

Age of sample (days)	0[x]	145	343	364	413[y]	563[z]	692
n_{D}^{20}	1.5564	1.5631	1.5700	1.5706	1.5709	1.5703	1.5730

Notes: [x] On first opening the stock bottle, 4 months after arrival in Ballarat.

[y] After small crystals had appeared.

[z] From only a thin layer of liquid above a paste of crystals. Between dates y and z, n lay between these values.

Part of the stock sample was distilled under reduced pressure, the B.P. rising somewhat throughout: the distillate, sample I, was kept at room temperature, say about 15°, for 85 days and the refractive index was determined from time to time, see Table and Graph. The refractive index increased throughout, and this sample never reached crystal-formation. The refractive index, like the density and the viscosity, changes somewhat abnormally with the fresh sample for the first few hours.

Another part of the stock sample was distilled under 79 mm pressure: a first fraction was discarded, and then was collected the main sample, III, boiling from 125° to 141°. This sample was divided into three lots which were kept at 30° for eighteen days and more. One lot was kept in a specific-gravity bottle, in which its density was determined at intervals, the bottle being filled up as required from the third lot. The second lot was kept in an Ostwald viscometer, closed with calcium chloride tubes, and the time of flow was found at intervals; from the contemporaneous values of the density the viscosities were calculated. After eighteen days the density of the liquid from the viscometer was 1.0855, while that in the specific gravity bottle was 1.0912 (both at 30°). The increases in density of the two lots were therefore not quite equal; but as the viscosity increases in this time to over twelve times its initial value, the errors introduced by taking the densities of the viscometer liquid as equal to those of the specific-gravity bottle liquid are negligible. For these reasons however the densities are only quoted to four decimal places and the viscosities to the third significant figure. From the third lot of the liquid the specific gravity bottle was filled up from time to time and samples were withdrawn for the refractive index determinations. In these samples kept at 30° crystals appeared in thirty days.

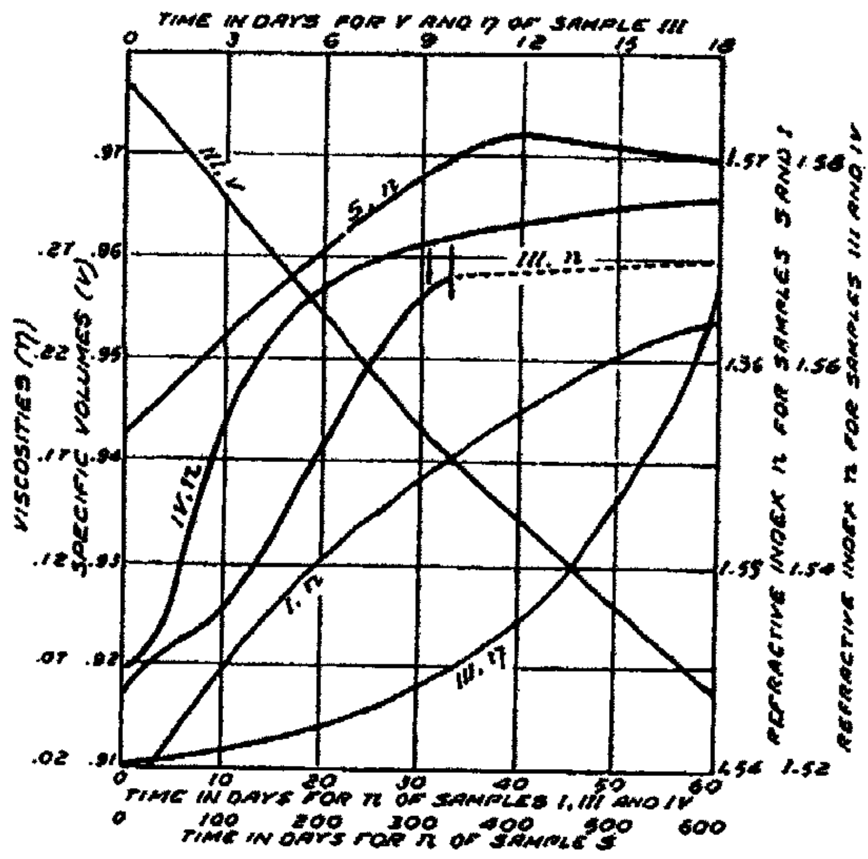

Fig. 1

Graph showing variation of properties of phenylacetaldehyde with lime

That part of samples I and III which remained after the experiments therewith, was redistilled and gave a sample IV of similar boiling point to III. Sample IV was kept at 30°, in two lots, for eighteen days, the density and refractive index being determined at intervals as before. The results obtained with the samples I, III and IV are given in the table and are plotted in the graph.

TABLE I

Table showing the Change of Properties of Phenylacetaldehyde with Time

Age of Sample	Sample I (kept at room temps)	Sample III (kept at 30°)			Sample IV (kept at 30°)	
	$n_D^{20°}$	$n_D^{20°}$	$D_{4°}^{30°}$	$\eta^{30°}$	$n_D^{20°}$	$D_{4°}^{30°}$
1 hour	1.5370	1.5272	1.0242	—	1.5295	—
5 hours	—	1.5282	—	.02044	1.5296	1.5275
1 day	—	1.5291	1.0274	.0220	—	—
3 days	1.5402	1.5310	1.0357	.0279	1.5339	1.0347
4 "	1.5411	1.5319	1.0398	.0313	—	—
6 "	1.5422	1.5329	1.0481	.0403	1.5431	1.0419
9 "	1.5444	1.5351	1.0597	.0603	1.5519	1.0488
12 "	1.5466	1.5390	1.0698	.0937	1.5578	1.0586
15 "	1.5481	1.5440	1.0783	.1503	1.5618	1.0716
17 "	1.5488	—	—	—	1.5649	1.0792
18 "	1.5492	1.5482	1.0912	.248	1.5654	—
20 "	1.0502	1.5510	1.0969	—	1.5670	
29 "	1.5540	1.5651	—	—	1.5713	
30 "	1.5543	1.5663	1.1160[x]	—	1.5716	
32 "	1.5550	1.5678[x]	—		1.5722	
40 "	1.5575	*1.5689[x]			1.5736	
47 "	1.5593	*1.5692[x]			1.5743[x]	
79 "	1.5658	*1.5723[x]			1.5762[x]	
85 "	1.5667	—			1.5767[x]	

[x] Crystals had formed here.

* This part of sample III was kept at room temperatures, say 20°, from the 32nd day.

The density increases linearly with the time and the specific-volume decreases linearly with the time; the density of sample IV increases less rapidly than that of sample III; and the mean density at time zero, $D_{4°}^{30°}$, is 1.026, and the density seems to rise less rapidly for the first few hours than it does afterwards. The fluidity-time curve is linear for the first few days, indicating $f_0 = 50.15$ or $\eta_0 = 0.01994$, and then the curve becomes convex to the time-axis. The viscosity-time curve is convex to the time-axis and becomes steeper with time. The (logarithm of the viscosity)-time curve is nearly linear; it is slightly convex to the time-axis, and when the time is large the ratio $\frac{\log \eta}{\text{time}}$ approaches a constant value. In general the refractive index-time curve is linear. However the refractive index, n, tends to rise abnormally rapidly at the start, that is just after the distillation of the sample. And the various n/time curves at last become concave to the time axis or the rate of increase of n slackens with the age of the specimen and becomes much less after crystals have formed. With sample III crystals appeared before the thirty-second day, when the n was 1.5678. The average rate of increase of n is 0.0015 at 30° and 0.00043 at 15°. It may also be concluded that the specific refractive power, $(n-1)/d$, does not vary much with the age of the sample.

The above results seem to indicate that the rate of formation of the polymerised phenylacetaldehyde is constant at the one temperature, and finally the crystalline polymer separates from the liquid. For the specific volumes of simple liquid mixtures are additive; and the refractive index is also an additive property. And many observers have concluded that the logarithm of the viscosity is an additive property,—see Arrhenius (1887) and Kendall and Monroe (1917). The rate of formation of the polymer is approximately three to four times faster at 30° than at 15°, which is about the normal result for a chemical change. But by distillation the unpolymerised liquid is again obtained. The rate of formation of the polymer doubtless is influenced too by the impurities in the liquid, such as traces of moisture and of acid and of other substances which were present to some extent in our samples, as well as by exposure to the light. In conclusion there seems little reason to doubt that the rate of formation of the polymer is constant under constant conditions.

The crystals of the polymerised phenylacetaldehyde were much less soluble in alcohol than the unchanged liquid. Thus the stock sample of phenylacetaldehyde, containing much polymer, was treated with alcohol and the residual crystals were washed with alcohol on a glass filter until they were free of the viscous mother-liquid, and then the crystals were dried in a desiccator over sulphuric acid. Two separate lots of the polymer, a white opaque, granular powder, were thus prepared: they proved to have identical properties. This polymer melted sharply at 104°: no water vapour was evolved on melting, and the fused mass cooled to a glassy hard solid. This polymer was soluble in hot alcohol or in excess of cold alcohol, insoluble in cold or boiling water, and was more or less soluble in petrol (gasoline; B.P. = 82°-98°), carbon tetrachloride, chlorobenzene, benzene, bromoform, ethylene chloride, ethylene bromide, acetophenone and benzophenone. From the carbon tetrachloride and the benzene (and possibly from other solvents) the solid polymer was obtained again as the solvent evaporated.

Combustion analyses of this polymer gave for lot (1), %H = 6.67 and %C = 79.75, and for lot (2), %H = 6.71 and %C = 80.0; while the calculated values from the formula $(C_8H_8O)_n$ are %H = 6.72 and %C = 80.0.

The molecular weight of the polymer was found from cryoscopic measurements. In solution in bromoform the depression of the freezing-point for a solution of 1 gram of polymer in 100 grams of solvent was 0.1895°, and the molecular weight = 144/0.1895 = 760; whence n is 6. (The molecular weight of $(C_8H_8O)_n$ is 120.n) But compounds like $(C_8H_8O, CHBr_3)_2$, M.W. = 746, are possible. In carefully purified benzene the depression of freezing point for a solution of one gram of polymer in 100 grams of solvent was 0.142°; whence the molecular weight was 51/0.142 = 359; and thus n is 3. (Raoult's cryoscopic constant for benzene is quoted from 49 to 52, and we suppose that similar or larger errors are probable for the 'Raoult's constant' given for the other liquids used.) In ethylene dibromide (K = 118) the molecular weight of the polymer was 383; in benzophenone (M.P. = 47° and K = 98) the molecular weight was 400 approximately; in acetophenone (K = 56.5) the molecular weight was 349; in cyclohexanol (K = 383) the molecular weight was 330; and in paraldehyde (K = 70.5) the molecular weight was 403. Thus in the last six solvents the polymer dissolved as $(C_8H_8O)_3$ and in bromoform as $(C_8H_8O)_6$. The crystal unit of the solid polymer is therefore $(C_8H_8O)_{3n}$.

Summary

1. Phenylacetaldehyde polymerises with time.

2. Any sample becomes with age more viscous, denser, and of higher refractive index, until finally there separate crystals of the polymer. The density and the refractive index increase, in general, linearly with the time, but the viscosity increases much more rapidly.

3. The refractive index is a very convenient property by which to determine the age of a specimen of phenylacetaldehyde.

4. Phenylacetaldehyde does not oxidise appreciably in air at ordinary temperatures.

5. In most solvents the polymer dissolves as $(C_8H_8O)_3$, but in bromoform as $(C_8H_8O)_6$.

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NEW BOOKS

An Introduction to Chemistry. *By John A. Timm. 20 × 14 cm; xviii + 561. New York and London: McGraw-Hill Book Company, 1930. Price: $3.60.* In the foreword John Johnston says: "Since the war, and probably by reason of the emphasis then placed upon chemical knowledge, there has been a growing dissatisfaction with the kind of introductory course in chemistry commonly given in college, particularly when this is the only chemistry course taken by many of the students. Believing in the desirability of a discipline planned specifically for the considerable group of students who will take no other course in physical science, the Faculty of Yale College about four years ago inaugurated such a course, which, since its inception, has been taught each year to a larger number of students; and the present book is the outcome.

"The general purpose is to give the student some acquaintance with the subject as a whole—with the general philosophy of physical science and with its manifold bearing upon the life of each one of us. The syllabus is based on a belief in the cultural value of the philosophy of a subject as compared with that of mere information, and hence it aims to emphasize that what we are dealing with is a series of related phenomena rather than a host of separate facts. In other words, this course endeavors, not to give the student a temporary command of assorted facts, relating to restricted classes of substances, but to correlate and to explain in simpler terms, some of the chemical and physical phenomena which he encounters every day. The subject of chemistry is regarded as a living tree, with roots becoming always better established and with new branches appearing and growing, rather than as a finished array of ordered facts; for much more remains to be discovered than is now known, and the process of discovery is as romantic and as joyful as is the exploration of any new region.

"It was intended that the range of topics discussed would be limited to those which can, in the time available, be treated thoroughly; that every effort would be made to interest the student by reference to familiar things for instance, to the automobile, which illustrates a great variety of chemical processes and physical phenomena; and that there would be considerable collateral reading of good biographies of scientists and of other books dealing generally with physical science," p. xiv.

The scope of the book is shown by the titles of the chapters: introduction; the nature of matter; the nature of gases; the nature of liquids and solids; changes of state; molecules; atoms; the shorthand of chemistry; the nature of chemical reactions; rate of chemical reactions; the atmosphere; the nature of combustion; our fuel resources; the metals; iron and steel; the periodic law; sub-atomic phenomena; the structure of the atom; the planetary electrons; radioactivity; the nature of energy; the nature of heat; radiation; the complete spectrum; the emission and absorption of radiant energy; water; solutions; alloys; electrolytic dissociation; electrolytes; reactions of electrolytes; the acid heavy chemicals; the basic heavy chemicals; electrolysis and the electrochemical industries; electrochemical cells; colloids; plant food; organic chemistry; carbohydrates, fats, and proteins; coal tar.

"In Chap. VIII you were introduced to chemical shorthand; to the mysteries of chemical symbols and formulae. You will now be introduced to a more complex form of chemical shorthand—the chemical equation. You have probably heard of this instrument of intellectual torture before from others who have struggled with elementary chemistry; but do not become unduly alarmed for we shall consider it here as a great convenience, the meaning of which you must understand, but shall not subject you to a drill in writing them for the purpose of giving you facility in their use. Such a drill is necessary in the training of a chemist as he must be able to handle the tools of his profession but it is neither necessary nor desirable that your time be wasted in this way," p. 87.

"Not all of the effects of ultraviolet light are harmful, however. Too much of a good thing is always bad. Rickets has always been a distressing disease of childhood. It is a defect in the mechanism by which the body controls the development of bone. Children with rickets suffer from a delayed and abnormal bone development which results in a warpage of the body contours. The teeth also are affected. It is a disease of the temperate zones only. Practically no cases are known in the arctic and tropical climates. It has been suspected for at least a few hundred years that sunlight was a preventive. Children who live in tropical climates wear little if any clothing and hence escape rickets. In the temperate zone, however, during the long winter months children are kept indoors most of the time and so are screened by window glass from the ultraviolet light of the sun. Also these are the relatively dark months of the year, hence rickets develops almost exclusively in the winter time. A striking illustration of the efficacy of sunlight in preventing this disease was brought out by Hutchinson and Shole in their study of rickets among the children of India. The children of the laboring class which run naked in the streets never develop rickets but those of the high-caste Hindus generally develop severe cases because of the fact that their mothers must be kept in seclusion due to the religious custom of purdah. This naturally results in the children being kept in dark rooms with their mothers," p. 293. One rather wishes that the author had mentioned why people do not have rickets in the polar regions. While he did not wish to discuss vitamines then, a reference to food would have been helpful.

The paragraph on p. 309 indicates Einstein as a guesser and not an accumulator. "In 1905 Einstein enlarged this theory. He proposed the theory that not only do atoms absorb and emit light in fixed finite quantities but also that these quanta of radiant energy preserve their identity as they travel through space. At the time he had little proof as to the truth of his proposal but he expected that in time evidence would accumulate to prove its correctness. This has been the case,".

"When we look more closely into the nature of the organic compounds of which plants are composed to discover why these elements are essential, we find that most of these can be divided into three classes; the carbohydrates, which class includes the sugars, starches, and cellulose; the fats; and the proteins. Carbohydrates and fats are compounds of carbon, hydrogen, and oxygen, and the proteins in addition to these three elements contain nitrogen and sulfur. Certain compounds within the nuclei of the plant cells contain phosphorus; and that most important compound, chlorophyl, the green coloring matter in the leaves which serves as the link by which the radiant energy of the sun is made available to all living organisms, contains magnesium. Potassium is indubitably essential to plants, and yet it does not appear in the molecules of the organic compounds of which they are composed. It seems to aid in some way in the synthesis of the starches and sugars and helps to keep up the vigor of the plant, making it more resistant to disease. The need of iron is in some way connected with the synthesis of chlorophyl, and calcium, in a manner that is little understood, aids in the formation of the cell-wall material, or woody fibre," p. 486.

"Ethylene is now used extensively to color green oranges and lemons. Citrus fruit becomes ripe before its skin loses the green color. It can be shipped in this condition with little danger of spoilage and then brought to full color by ethylene gas after it has arrived at its destination. In as low a concentration as one part of ethylene per 3,000 parts of air, 25 cu. ft. of this gas can color a carload of oranges in 5 days. Ethylene is also used as a general anaesthetic in medicine. The story of the discovery of its use for this purpose is interesting. About 1908 a Chicago florist discovered that several shipments of carnations promptly closed up their petals and went to sleep when placed in a certain corner of his greenhouse. He called Dr. Crocker, a botanist in the University of Chicago, into consultation. The latter discovered that a leaky gas pipe was doing the damage. Since illuminating gas is a mixture of various substances (p. 141), he tried the action of each of these on carnations and found ethylene to be the offender. Finally, in 1922, Professor Luckhardt, also of the University of Chicago, with the aid of Mr. Carter, found that rats in an atmosphere of 80 per cent ethylene curled up and went to sleep and in this way its anaesthetic properties were discovered," p. 507.

"In 1909 Friedländer succeeded in establishing the structure of Tyrian purple and, oddly enough, found out that it had already been synthesized five years before by Sachs but had been rejected as an inferior dyestuff! It was a dibrom-indigo," p. 542.

The reviewer would have liked to have seen one chapter on qualitative and quantitative analysis and one on medicine. The first would be easy to write and the second difficult. There are some things which should be changed in the second edition. The statement of the generalized gas equation, p. 25, is right but nobody will recognize it. It would be better to connect it with the form PV = RT. On p. 46 it would be better to give the normal boiling, in Ecuador or on Pike's Peak, rather than to say that it is lower than at sea-level. There is nothing to show the magnitude of the change and that is what one is interested in. The reviewer may be wrong; but he thinks that helium has been liquefied at the Bureau of Standards, p. 54. On p. 56 the word "liquefier" is spelled wrongly in the diagram. The reviewer does not like the spelling of "liquidous" and "solidous", p. 354.

On p. 124 we read that resuscitation from carbon monoxide poisoning "involves the administration of a mixture of 95 percent oxygen and 5 percent carbon dioxide to the victim. The carbon dioxide is needed to stimulate respiration as experiments by Yandell Henderson of Yale have shown." One would like to know why carbon dioxide is needed to stimulate respiration. The reviewer feels that it would be better to start with the flames containing incandescent solids rather than with the statement, p. 129, that "a flame is produced whenever an exothermic reaction between gases takes place so rapidly that they become luminous." Nothing is said about wood-fires, candles, oil lamps, acetylene burners, or magnesium flash-lights.

The reviewer questions the wisdom of saying, p. 337, that sugar lowers the vapor pressure of water because it decreases the surface concentration of water. If that were true, we should get different vapor pressure relations for solutes which raised or lowered the surface tension and there is no experimental evidence for this as yet. Also, this point of view is absolutely inconsistent with the behavior of three-component systems.

As is apparently inevitable nowadays, there is a good deal of careless proof reading. The author is probably responsible for writing Sir Humphry Davy's Christian name as Humphrey.

We had hoped to put in a course in pandemic chemistry at Cornell; but conditions were not favorable, and Yale is the first of the larger universities to do so. Apparently it has been a success there, as it ought to be. Last year there were two hundred and fifty students taking it, and this text was written for their benefit. It should also make possible the giving of similar, much-needed, courses elsewhere.

The principle involved has been discussed unfavorably by McPherson in his presidential address before the American Chemical Society, published in Science. This was before he had seen Timm's text. "There has been much discussion as to whether chemistry viewed in this way as a constituent of the course in liberal arts should not have a different treatment from the course arranged for our future chemists. We have, at least, a name [pandemic] for such a course; but, in the main, the discussions have had little influence on the character of the course.

"Two methods of procedure are open to us. (1) We may separate our students into two classes, according to whether or not they expect to make chemistry their life work, and give to each class courses differing fundamentally in character; or (2) we may so shape our introductory course that it will serve the aims of education and be of value to all students alike. The first of these methods is open to the very serious objection that the course offered to the general student is likely to resolve itself into a collection of facts pertaining to chemistry, interesting undoubtedly, but serving neither the aims of education nor those of science—enjoyable bed-time reading but out of place in serious college work. Equally true, the technical course might miss many of the suggested and cultural values. It would seem entirely possible to frame a course that would be of value to all alike, providing a foundation knowledge of the science of chemistry but stressing acquaintance with fundamental laws and principles; also habits of clear thinking and independent judgment such as contribute to constructive ability and ultimately to good living as well. Many a liberal arts student, not supposing himself interested in science, through such a course has had awakened the profound intellectual passion of his life."

By a suitable juggling of the premises one can arrive at any desired conclusion. McPherson slips in the phrase about making chemistry their life work and thereby shunts the prospective engineers, medical men, and biologists into the pandemic course, which nobody else has suggested doing. While a pandemic course might conceivably be a collection of bed-time stories, no one could classify Timm's text under that head, nor that of Findlay. McPherson ignores the question whether a course which leads up to analytical chemistry, organic chemistry, physical chemistry, etc., can possibly cover the ground which should be covered by the pandemic course. Having eliminated arbitrarily the good points of one and the weak points of the other, McPherson concludes triumphantly that there is no room for two courses. His conclusion will not be accepted by anybody who has given any careful thought to the subject. *Wilder D. Bancroft*

Band Spectra and Molecular Structure. *By R. de L. Kronig. 22 × 14 cm; pp. x + 163. New York: The Macmillan Company; Cambridge: The University Press; 1930. Price: $3.50; 10 shillings, 6 pence.* This book takes its origin in a course of lectures given at Cambridge about eighteen months ago. It is scarcely necessary therefore to add that it is an accurate and authoritative presentation of the subject on its theoretical side. Prof. Kronig has himself made notable contributions to this subject and we are indebted to him for the present excellent little book. It is essentially concerned with the theoretical developments: specific spectra and experimental matters are not dealt with. The reader is plunged without delay into the application of wave mechanics to the diatomic molecule: a knowledge of the necessary mathematical technique is assumed. The major problems of the electronic, vibrational, and rotational energy levels are dealt with in this fashion. In the next chapter the more detailed problems of multiplet structure and fine structure generally are treated by the perturbation methods of quantum mechanics. A further chapter deals with selection rules and intensities in diatomic molecules: it is a particularly good summary of these and kindred matters. Under the heading of Macroscopic Properties of Molecular Gases the author has touched on light-scattering, dispersion, the Kerr and Faraday effects, dielectric constants, magnetic susceptibilities and specific heats. Finally there is a short chapter on the problems of molecule formation and chemical binding. There is a valuable bibliography of over three hundred and fifty papers grouped appropriately under the above headings: this very greatly enriches the book.

To the mathematical physicist and those interested in the diverse fields of application of the new quantum theory the book can be highly commended. It brings together a great variety of information, otherwise scattered too widely through the Journals of Learned Societies and other publications. We imagine however that the book may be found difficult in large part by those without considerable mathematical equipment. *R. C. Johnson*

Photochemistry. *By D. W. G. Style. 18 × 11 cm; pp. vii + 96. London: Methuen and Co., 1930. Price: 2 shillings, 6 pence.* Dr. Style's little book on Photochemistry provides a welcome introduction to a branch of physical chemistry which of recent years has undergone a very extensive development. This development is one of general importance and interest, and a book of this nature should therefore appeal to a wide circle of readers. This is particularly the case in the present instance, since while the principal results and conceptions of photochemistry, such as the law of photochemical equivalence, or chain reaction mechanism, are clear cut and well-defined, the large amount of work which has gone to their establishment is detailed and technical. It involves a close quantitative study of a large number of photochemical reactions and their critical comparison with the results of spectroscopic study; and while the more specialised student has been catered for by at least two admirable text-books in the English language, the general reader has probably up to the present found it difficult to assimilate the fundamental facts and principles without an undue amount of labour.

To this end, Dr. Style's book is of great assistance; it aims at giving a concise account of the main aspects of photochemistry without a burdensome amount of detail, and altogether forms a well-balanced whole. At the same time the author has been at pains to introduce the reader to the spirit of the subject by discussing in some detail a limited number of well-chosen examples.

The introductory chapter deals in main with the subject of light absorption, brief reference being made to the quantum theory of band spectra and its bearing on photochemical processes. This is somewhat further developed in the second chapter, which discusses the nature of the primary photochemical change effected in the molecule. In Chapter III the secondary "dark" reactions which follow the primary processes of molecular dissociation or activation are considered, and it is shown how the varying types of photochemical change may ge generalised by the conception of the reaction chain. Many of the concepts of Chapters II and III are developed in greater detail in the fourth chapter, which deals with the dependence of quantum yield on temperature and wave-length. The book closes with a short chapter on experimental methods. There are a short bibliography, a table of references, and an index.

The reviewer can only express his admiration at the large amount of useful information that has been collected in a small space, and can recommend this little work to those interested as a representative taste of a very interesting subject.

R. G. W. Norrish

Recent Advances in Physical and Inorganic Chemistry. *By Alfred W. Stewart. 22 × 14 cm; pp. x + 387. London: Longmans, Green and Co., 1930. Price: 18 shillings.* The fact that this is the sixth edition of this book is sufficient testimony that the author is able successfully to summarise the more important advances made in chemistry in a way which appeals not only to the aspirant for an honours degree, but also to those who desire to keep in touch with the trend of modern work.

In the present volume, which contains seventy-five more pages than its predecessor, the author's main topics consist of the advances made in our knowledge of spectra—including line, X-ray, positive-ray, band, emission and Tesla-luminescence spectra—and of radio-activity. Subjects arising from these, as, for example, the structure of the atom, isotopes, isobares, the discovery of hafnium, etc., are given due consideration. In addition, there are given chapters dealing with the various hydrides of metals and non-metals, which have assumed theoretical importance in recent years, with certain flame reactions and with the Donnan equilibrium.

Generally speaking, the subject matter is right up-to-date, but in the chapter on the Donnan equilibrium, which deals with a subject which seems to be somewhat alien to the rest of the book, the latest reference to gelatin is dated 1918.

The author is neither so outspoken in his antipathies nor so dogmatic in his statements as he has been at times in former editions, and the present volume is well worth the study of those who desire a readable and corrected account of recent advances.

T. Slater Price

Messungen elektromotorischer Kräfte galvanischer Ketten mit wässerigen Elektrolyten. *By Carl Drucker. 24 × 17 cm; pp. xx + 234. Berlin: Verlag Chemie, 1929. Price: 24 marks.* This is No. 10 of the *Abhandlungen der deutschen Bunsengesellschaft* and is a supplementary volume to No. 5. It contains chiefly data which appeared from 1914 to 1927 both inclusive. Cells in which non-electrolytes have been added are also included. The book is invaluable for reference purposes.

Wilder D. Bancroft.

THE COLLOID CHEMISTRY OF THE NERVOUS SYSTEMS. I*

Sodium Thiocyanate Therapy. I

BY WILDER D. BANCROFT AND J. E. RUTZLER, JR.**

Fifty-six years after his work was published we find Bancroft and Richter[1] honoring the great physiologist and prophet, Claude Bernard, by showing that his theory of anesthesia[2] explains correctly the facts that are met with in the process of the loss of consciousness by the agencies of man. We find further tribute to Bernard's far-sightedness when we consider the fact that his works were first published[3] only five years after Graham differentiated colloidal suspensions from true solutions by means of his famous dialyzer.

The theory of anesthesia having been definitely settled, it can become more solidly intrenched in direct proportion to its ability to serve as a basis for accurate and sweeping prediction as to the effect that various chemicals will have upon animals under anesthetics. In other words, how often can one predict accurately the effect of adding drug B to an animal under the influence of anesthetic A?

The thesis of this paper is, then, to show how, with Claude Bernard's theory of anesthesia as developed by Bancroft and Richter as a basis, the state of anesthesia is affected by certain chemicals, particularly sodium thiocyanate. As the story unfolds, we will consider sodium thiocyanate in its relation to narcoses by means of ether, "amytal," morphine, "nembutal," and alcohol. Then, using the same type of theoretical considerations, the effect of sodium thiocyanate upon the action of histamine, strychnine, and anaphylactic shock will be described and explained.

In order to start with a clear idea of the phenomenon of anesthesia we will first quote the Claude Bernard theory as put forth by Bancroft and Richter: "If the colloids of a cell are reversibly coagulated (anesthesia will result, if the cells are those of the sensory nerves) and the agent (the anesthetic) that caused the flocculation is displaced by a substance of weaker flocculation capacity for the given concentration, naturally the bio-colloids are peptized again by the electrolytes. Concurrent with this peptization there will be a return of irritability and consciousness. Now (in the normal case of a person recovering from an anesthetic) the agents that are responsible for the peptization are the electrolytes within the cells." This, briefly, is the theory of anesthesia as it stands today.

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*This work is part of the programme now being carried out at Cornell University under a grant from the Heckscher Foundation for the Advancement of Research, established at Cornell University by August Heckscher.

**Eli Lilly Research Fellow.

[1] J. Phys. Chem., 35, 215 (1931).

[2] "Leçons sur les anesthésiques et sur l'asphyxie" (1875).

[3] "L'Anesthésie," Union med., Paris, 8, 109 (1867).

The authors say, in another part of their paper: "Consider the simplest possible theoretical case, in which the drug is affecting only one substrate. The possible methods of elimination of the drug have already been discussed in the paragraph on recovery; suppose that these methods of elimination are slow and we desire to hasten it. Another substance is given which will be adsorbed upon the same substrate and displace some or all of the original material, thus increasing its effective concentration so that it may undergo the reactions of detoxication faster or diffuse out more rapidly. This method is very effective, provided that the antagonist does not complicate the situation by its own action. It can be seen that the drug has been displaced by another whose physiological action is less but whose adsorption is greater. The extent of the adsorption is determined by the concentration, so there will be antagonizing concentrations below which this effect will be very small. Also if the elimination of the drug is not hastened by the displacement the effect of the antagonist will only be transient."

In another paper Bancroft and Richter[1] draw the following conclusions:

"1. Claude Bernard was right in postulating that reversible coagulation of the colloids of the sensory nerves produces or accompanies anesthesia.

"2. Decreasing stability of the nerve colloids means increasing irritability up to the point of incipient coagulation.

"3. Claude Bernard's theory affords an apparently adequate explanation of the difference between a general and local anesthetic.

"4. Claude Bernard's theory accounts for the effects observed when morphine is used together with chloroform or ether.

"5. Claude Bernard's theory offers an apparently adequate explanation for the difference between a true anesthetic and a habit-forming drug.

"6. Claude Bernard's theory accounts for the phenomena observed in the action of mercuric chloride on bacteria, of strychnine on frogs and dogs, and of hydrocyanic acid on the eggs of citrus scale.

"7. Decreasing stability of a suitable colloid or group of colloids—accompanied by increasing irritability up to a certain point—and then reversible coagulation will apparently account for the law, accepted as universal by biologists, physiologists, and bacteriologists, that all depressor substances exert a stimulating effect when used at an appropriate dilution.

"8. Claude Bernard's theory offers a clue to a scientific method of counteracting habit-forming drugs.

"9. Nitrous oxide and acetylene are not true anesthetics in the sense that ether and chloroform are. These two gases cause reversible coagulations of the colloids of the sensory nerves indirectly, and not directly as ether and chloroform do.

"10. Claude Bernard's theory dealt with the colloids of sensory nerves. There is, therefore, nothing to prevent reversible coagulation of other materials besides proteins from being important in connection with anesthesia. It seems wise, however, to see how much can be explained solely by reversible

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[1] Proc. Nat. Acad. Sci., **16**, 573 (1930).

coagulation of the proteins. We then have the behavior of the other colloids in reserve to be called into play when and as needed.

"11. The Overton-Meyer theory accounts satisfactorily for many, though not for all, cases of cell permeability; but it is not true that all substances which enter the cells produce narcosis, and consequently the Overton-Meyer theory is a theory of permeability and not in any proper sense a theory of narcosis at all."

These considerations, then, form the basis of the work reported in this paper.

In the same paper the authors postulated tentatively that the colloids of the sensory nerves are albumin-like in nature. This immediately gives us a foothold; for it becomes obvious that here also the lyotropic series of the anions must play a dominant role. Höber[1] and also Pauli[2] have shown that albumin on the alkaline side of an $(H^+) = 1 \times 10^{-7}$ is peptized by anions in the order $CNS > I > Br > NO_3 > Cl > CH_3COO$; the sulphate, tartrate, and citrate ions[3] can be added in that order to make the series more complete. At the same time the order of the cations is[4] $Cs > Rb > K > Na > Li$. So long as one does not work with living things, it does not make any vital difference which one of the alkali metal cations is used; the cations having higher valences tend to precipitate natural egg albumin. Upon making a natural egg albumin sol acid, it becomes charged positively,[5] then both of the ion series are completely reversed; the ions that peptize the negatively charged albumin the most effectively now coagulate it most strongly.

Now, the sensory-nerve colloids, if they are albumin-like, or less hydrophilic and globulin-like, should adsorb the thiocyanate ion strongly and as a result become peptized and more finely dispersed. We know that coagulated egg white can be peptized by the thiocyanate ion.[6] The next two steps immediately become obvious; first we must choose a cation to go with the thiocyanate radical, and then apply the compound chosen to the peptization of reversibly-coagulated sensory-nerve proteins, thus bringing animals out of anesthesia.

For the cation, chemical considerations and the lyotropic series tell us that we are limited to those that will give us a respectably soluble salt and one that will not interfere with the peptizing action of the thiocyanate ion. This leads to the choice of one of the alkali metals. The natural choice, then, lies between potassium and sodium. Some care must be exercised in deciding whether to use sodium or potassium thiocyanate in living things to peptize reversibly coagulated colloids. Lusanna[7] found, on studying the effects of different metal chlorides upon frog muscle in faradic excitation, that lithium does

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[1] Hofmeister's Beitr., 11, 35 (1907).

[2] Hofmeister's Beitr., 5, 27 1903; Biochem. Z., 47, 269 (1912).

[3] Freundlich: "Colloid and Capillary Chemistry" (1922).

[4] See also, Robertson: "Physical Chemistry of the Proteins," 120 (1918).

[5] Hardy: J. Physiol. 24, 288 (1899).

[6] Bancroft and Rutzler: J. Phys. Chem., 35, 144 (1931).

[7] Bull. Soc. Med., No. 4 (1907).

not affect the contractility, but depresses respiration; potassium destroys the contractility but does not affect respiration; and sodium affects neither the contractility nor the respiration.

Gellhorn[1] showed that potassium contraction in both smooth and striated muscle is favored most by the thiocyanate ion; the order of the ions in this respect is $SO_4 > Cl > Br > I > CNS$. Menten,[2] working on the sciatic nerves from the brachial plexus supplying the fore-paws in dogs, found that, with the exception of potassium citrate, acetate, oxalate, and tartrate, many salts of potassium produce a loss of irritability. He states that the salts of sodium do not have this anesthetic effect.

Potassium contracts voluntary muscles,[3] whereas sodium does not exhibit this effect. Potassium is a powerful cardiac poison,[4] rubidium and caesium act the same way, but to a much less extent. Spiegel[5] says: "Therefore, contrary to the original formulation of Blake, but in accordance with the demands of the periodic system, potassium shows properties in common with the other alkali metals (excepting sodium)."

Kahn[6] has studied the effect of injections of various amounts of potassium thiocyanate (which was cyanide free) into the dorsal lymph sacs of frogs. Depending upon the dose of potassium thiocyanate used, he found that the heart was stopped in systole, and violent strychnine convulsions, tetanic contractions, opisthotonus, and hypersensitiveness occurred. Doses up to 0.24 milligrams per gram resulted in the survival of the frog, whereas a dose of 0.35 milligrams per gram was lethal. Somewhere in between one would expect to find the M. L. D. (minimum lethal dose). Kahn then worked with guinea pigs and observed that here again the potassium thiocyanate caused violent tetanic convulsions. The dose that the guinea pig could stand was somewhat less than the M. L. D. for frogs. In conclusion Kahn says: "Potassium sulphocyanate is toxic to both plants and animals. Its toxicity is so marked that indiscriminate dispensation of the substance to patients is dangerous."

There is food for thought in the fact that a completely non-toxic substance has been prepared[7] that consists of thiocyanate adsorbed upon albumin; it is called "rhodalzid."

So much for the potassium salt, as it is evidently distinctly toxic to animal life. We are thus forced to choose sodium thiocyanate as the compound most likely to peptize efficiently the reversibly-coagulated colloids of the sensory nervous system under the influence of an anesthetic. One objection that might be raised thoughtlessly to the use of sodium thiocyanate is that in the body it might be converted into cyanides. There are several reasons why this

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[1] Archiv ges. Physiol. (Pflüger's), 219, 761 (1928).
[2] Am. J. Physiol., 31, No. 2, 85 (1913).
[3] Spiegel: "Chemical Constitution and Physiological Action," 27 (1915).
[4] Astolfoni: Archiv intern. Pharmacodyn., 11, 381 (1903).
[5] "Chemical Constitution and Physiological Action," 27 (1915).
[6] "Biochemical Studies of Sulphocyanates," Columbia University Dissertation, 74 (1912).
[7] Diena: Biochem. Z., 39, 13 (1912).

possible objection should be overthrown immediately; in the first place the thiocyanates are chemically more stable than the cyanides; in the presence of sulphur or oxygen, cyanides tend to go to thiocyanates and cyanates respectively upon the least provocation. Secondly,[1] "the cyanide of potassium is liable, during putrefaction, to be converted into sulphocyanide (KCNS)." Taylor continues: "A case of poisoning occurred to Dr. Letheby in September, 1864, in which sulphocyanide of potassium and carbonate of potash were found in the stomach in place of the poison actually taken." The potassium atom, of course, plays no significant part in these changes, so that the same reactions would hold for sodium thiocyanate. Thirdly, Grober[2] found that feeding small quantities of prussic acid increased the output of potassium thiocyanate. So it seems probable that cyanides go to thiocyanates in the body. McGuigan,[3] Bodansky,[4] and Franz[5] dispose of all doubt concerning the possibility that thiocyanates go to cyanides in the body; they all say either that cyanides go to thiocyanates in the body, or else that cyanides are not formed from thiocyanates *in vivo*.

Experimental Study

1. Ether

A young rabbit weighing approximately 600 grams was selected for this work. The bottom of a 500 cc. beaker was covered with cotton; ten cc. of peroxide-free ether was poured on the cotton, and the beaker placed tightly over the head of the rabbit. At first the animal struggled violently; this was the well-known excitatory stage during which the sensory-nerve colloids are on the verge of reversible coagulation. The administration of the anesthetic was continued until the lid reflex disappeared. This corresponds to a very deep anesthesia, for Gwathmey[6] states that the lid reflex is weakly present in surgical anesthesia. It took three minutes 20 seconds to reach this stage, as timed by a stop-watch. Four and one-half minutes after the mask was removed there was a slight lid reflex; the animal was completely out of the anesthesia six and one half minutes after the administration was stopped. This return to normal was judged by the fact that the rabbit sat up of its own accord. The excitatory stage upon recovery was not pronounced.

The animal was then allowed several hours in which to come back completely to normal, although no abnormal symptoms were noticed after it arose from the narcosis. Then it was again anesthetized exactly as before (body position and everything being the same) except that the anesthetic was administered for a period of four minutes ten seconds. During the last minute that the ether was given, 0.9 cc. of a 10% solution of sodium thiocyanate

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[1] Taylor: "A Treatise on Poisons," 601 (1875).

[2] Deutsch. Archiv Clin. Med., 69, 243 (1901).

[3] "A Textbook of Pharmacology and Therapeutics," 102 (1928).

[4] J. Pharmacol., 37, 463 (1929).

[5] J. Chem. Soc., 102 II, 668 (1912).

[6] "Anesthesia," 194 (1914).

was injected into the marginal vein of the ear. As before, the lid reflex disappeared in three minutes 20 seconds. Thus, the period of administration of the anesthetic was 25% longer in the experiment where the sodium thiocyanate was given. The lid reflex this time returned 50 seconds after the mask was removed, or 540% more rapidly. The animal arose of its own accord four and one-half minutes after the mask was removed, or 44% faster. Although the animal arose of its own accord, it was very intoxicated. The intoxication wore off quickly. Thus, in this case, the period of irritability upon recovery was considerably more marked. Apart from the gross action of the thiocyanate ion, which was to repeptize the reversibly-ether-coagulated sensory-nerve proteins, what does the quicker recovery and resultant intoxication mean?

It merely means that both the ether and the thiocyanate ion were courting the sensory nerve colloids. Obviously the thiocyanate ion won, but not without a struggle; for the observed period of intoxication was the excitation upon recovery during which time the presence of the ether with its coagulating effect prevented the thiocyanate ion from restoring the nerve colloids of the rabbit completely to normal. Had the animal waked up the second time in six and one half minutes (a condition obviously impossible of fulfillment) there would have been no intoxication. The intoxication (excitation) was, therefore, a natural consequence of the treatment.

The next question that might be brought up is, why did the lid reflex return 540% faster with the help of sodium thiocyanate, while it caused the rabbit to arise only 44% faster?

Here again the answer is not difficult. The rate of adsorption is greater just after adsorption starts than it is after it has been in progress for some time. So, the greatest evident peptizing effect is at the start, and as time progresses the adsorption makes itself much less evident. Suppose we take a cloudy egg albumin sol. Upon adding a solution of sodium thiocyanate to this we see an immediate and large decrease in the degree of turbidity but certainly all of the thiocyanate ion that can be adsorbed is not adsorbed immediately. Still the amount that the sol clears up in the next few hours is almost imperceptible.

One might say that in this experiment the rabbit was shocked out of the anesthesia by the injection. There is no trouble encountered in refuting this argument; it should be remembered that the injection was made while the ether was being administered. Animals can stand the severe shock of surgery, so there is no evident reason why they should be bothered by the mere injection of a small amount of sodium thiocyanate. Cases are on record[1] in which 1,000 to 2,000 cc. of "normal saline solution" were injected intravenously into patients under oil-ether colonic anesthesia without any mention being made of their having been roused from the narcosis. So, the shock objection is overruled.

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[1] Gwathmey: "Anesthesia," 462, 463 (1914).

In the case of ether anesthesia the respiratory center in the brain is only slightly affected in comparison to other centers.[1] The importance of this will become evident as this paper progresses.

Concerning the toxicity of the sodium thiocyanate, it is interesting to note that in this case the dose of salt was equivalent to 150 milligrams per kilogram, whereas Kahn[2] found that potassium thiocyanate in a dose of 150 milligrams per kilogram is fatal to guinea pigs. Thus, a dose at least equal to the dose of potassium thiocyanate can be used with impunity when one employs the sodium salt.

It is almost a shame to perform such an experiment as that which we have described, for, granting a normal animal and a careful technique, the case is so clear-cut that the experiment almost assuredly could have done naught but succeed.

2. "Amytal"

Ether being easily and quickly eliminated, and requiring a high concentration[3] (150 milligrams per 100 cc. of blood immediately after cessation of the inhalation) to be effective, is not very strongly adsorbed by the sensory nerve colloids. For that reason the task of displacement and subsequent peptization to which the thiocyanate ion was assigned was not a very difficult one.

In casting about for an anesthetic capable of exerting the thiocyanate ion into a demonstration of its efficacy it was decided that there are several reasons why "Amytal" (iso-amylethyl barbituric acid, the sodium salt is used in anesthesia) should be such. Reference to a paper by Clowes[4] on anesthesia by means of sodium "amytal" brings forth several facts. "Amytal," being a solid, is not eliminated through the lungs; small doses, 40 to 50 milligrams per kilogram injected intravenously into dogs, bring about a deep narcosis. The compound is not eliminated quickly, for one of its chief disadvantages as an anesthetic is that "following anesthesia (deep surgical anesthesia lasts for a period of one to three hours) there is a somewhat prolonged period of post-operative sleep." Thus, it may be safely assumed that "amytal" is, compared to ether, very strongly adsorbed by the sensory nerve colloids. This, of course, results in their reversible coagulation. It would be a boon to the general use of "amytal" for the induction of anesthesia if the post-anesthetic sleep could be "antidoted" by other means than by the use of ephedrine sulphate and caffeine sodium benzoate.

A solution of 0.03 grams of the acid "amytal" was prepared by gently warming it in distilled water[5] and slowly and carefully adding sodium carbonate until the "amytal" was completely dissolved. Following the method

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[1] Crile: "A Bipolar Theory of Living Processes," 101 (1926).

[2] "Biochemical Studies of Sulphocyanates," Columbia University Dissertation, 76 (1912).

[3] Gwathmey: "Anesthesia," 196 (1914).

[4] Clowes et al: Proc. Soc. Exp. Biol. Med., **26**, 399 (1929).

[5] The authors wish to thank Dr. G. H. A. Clowes of Eli Lilly and Co. for generously supplying them with sodium "amytal."

of Clowes, this solution was injected slowly into the marginal vein of the ear of a young rabbit weighing about 600 grams. Before the injection was completed the animal was entirely limp and the lid reflex had disappeared. This rabbit was used as the control. Thirty-nine minutes after the "amytal" was administered, a hypodermic needle was thrust gently under the skin; the rabbit showed no signs of feeling this. The respiration was only 14 per minute after 42 minutes; it was 18 per minute after one hour 16 minutes. This shows that the colloids of the respiratory center were affected by the anesthetic. Two hours after the anesthetic was given there was no sign that the lid reflex had returned; the animal was still unconscious 14 minutes later. In two hours 20 minutes there was a very weak lid reflex; eight minutes later the rabbit began to stir; consciousness was fast returning. One minute later the animal was definitely conscious, but could not sit up; it was still unable to sit up after three hours 14 minutes. The rabbit was up and about four hours 14 minutes after the induction of anesthesia. It showed no desire to eat at this time.

At the same time a litter-mate of the rabbit described in the above experiment (weight the same) was anesthetized in an identical manner with the same compound. However, instead of allowing the animal to sleep peacefully, four minutes after the "amytal" was administered, 1 cc. of a 10% solution of sodium thiocyanate was injected intravenously, using the marginal vein of the ear. The injection was made slowly; and the rabbit raised its head and worked its legs before it was finished. Fifteen minutes later the lid reflex had returned definitely; this was 19 minutes after the anesthetic was injected. When 25 minutes had elapsed 0.5 cc. of the same sodium thiocyanate solution was injected subcutaneously. During the injection the rabbit struggled very hard to arise, and it very distinctly felt the needle when it was inserted. It will be remembered that the control rabbit exhibited no response to the insertion of the needle under the skin. When the injection was completed, the animal arose of its own accord, and there was a very strong lid reflex. This phenomenon was followed quite shortly by a relapse of strength which was, however, not accompanied by the loss of the lid reflex. The respiration was 32 per minute after 33 minutes of the narcosis, as compared to a respiration rate of 14 per minute in the control after 42 minutes of the narcosis. This is striking, for the rate of respiration in the case where the sodium thiocyanate was used was practically 130% greater. Fifty-eight minutes after the "amytal" was given 0.5 cc. more of the sodium thiocyanate solution were injected subcutaneously. The effect of this second subcutaneous injection was the same as the first time it was done; only it was much more striking, and the rabbit so far as one could judge largely overthrew the effects of the anesthetic. The animal had a great deal of strength after this injection; there was not a noticeable relapse of any kind from this time on. Meanwhile the control rabbit slept on without even a sign of the return of the lid reflex. The respiration rate was 35 per minute after one hour seven minutes. When one hour 42 minutes had elapsed 0.2 cc. more of the thiocyanate solution was injected subcutaneously; this induced the animal to crawl around, although it was still somewhat weak. The hind legs were not completely normal, because the rabbit walked rather than hopped. So, after one hour 53 minutes, 0.3 cc. more of the sodium thiocyanate solution was introduced by the subcutaneous route. This caused the hind legs to become normal, and the rabbit hopped five or six yards. It was somewhat intoxicated at this stage. The reason for this is the same as for the rabbit emerging from the ether narcosis. After two hours and ten minutes 0.2 cc. more of the sodium thiocyanate was injected subcutaneously. The rabbit held up its ears this time and hopped around, after first crawling a short distance. Every time that the sodium thiocyanate was administered after and including the injection at one hour and 42 minutes, the rabbit crawled around. From 58 minutes after the anesthetic was administered onward the animal was able to sit up of its own accord and did so. The animal passed considerable water after three hours and five minutes; it ate heartily after four hours five minutes and was quite happy so far as one could judge. Both of these rabbits were males.

It is interesting to note that the total dose of sodium thiocyanate in this case amounted to 450 milligrams per kilogram, or more than twice the dose that Kahn found was lethal to guinea pigs when using potassium thiocyanate.

These experiments show several interesting things; in the first place, they show the unusual degree of accuracy with which, with the developed Claude Bernard theory as the background, one is able to predict what will happen when a strong peptizing agent is introduced into a narcotized animal. Now, were the striking fact of the much accelerated recovery of the animal by the use of sodium thiocyanate entirely stricken from the experiment, there still remains a valuable observation. The rate of respiration of the rabbit that was subjected to the sodium thiocyanate treatment was more than twice as great as that of the control rabbit. What is the meaning of this? The lowered rate of respiration in the case of anesthesia is due to the effect of the anesthetic on the respiratory center in the brain; this effect is in all probability at least in part due to the coagulation of the colloids of the respiratory center. The displacement and peptizing action of the thiocyanate ion upon this center is, thus, quite marked. The result is that the respiratory center tends to regain normality very quickly as is shown by the data on the above experiments The value of this fact in preserving life is obvious.

The above rabbit which received the sodium thiocyanate injections was intoxicated for the same reason that the rabbit upon emergence from the ether narcosis hastened by thiocyanate ions was intoxicated. This intoxication affected the hind legs to a large extent in each of the two cases; and in the case of the controls they slipped through the excitation stage in each case too rapidly for it to be observed.

Thus, another and more powerful anesthetic has been found to yield with celerity to the displacing and peptizing effect of the thiocyanate ion upon the reversibly coagulated colloids of the sensory nerves of the central nervous system.

3. Morphine

This brings us to a study of the effect of sodium thiocyanate on that insidious alkaloid morphine. Morphine is, of course, a habit-forming drug; so, in this therapy there may be a clue to the solution of the problem of drug addition.

Taylor[1] says that morphine is probably slowly detoxicated, for it has been found unchanged in cadavers months after death as a result of an overdose. Spiegel[2] says that the site of the destruction of morphine in the body is mainly the brain. This also means that morphine is strongly adsorbed by the brain. Morphine slows down the rate of the heart beat; and one of the first effects of the drug in the body, in large doses is the paralysis of the respiratory center.[3] It is a matter of common knowledge that morphine affects various animals in different ways. For instance, the cat goes wild under its influence; it narcotizes some horses and with others it acts more as it does with the cat; rabbits require an unusually large dose to produce an effect;[4] whereas, a small dose will produce sleep in white people. These differences are undoubtedly due to varying degrees of adsorption on the nerve colloids of the various animals.

From these facts concerning morphine, what can be predicted concerning the action of sodium thiocyanate upon animals narcotized by means of it? Although the obstacles appear to be formidable, there are two experimental results that help to give us a clue as to what will happen in this case. Taylor[5] says that injections of starch have been found to be beneficial when there are signs of recovery from morphine poisoning; while Rother[6] found that starch can be used to prevent egg albumin from coagulating, even in boiling water. This means that the starch is adsorbed by, and acts as a protective colloid for, the egg albumin. The inference is obvious; in the case of morphine poisoning the starch probably displaces the morphine from the nerve colloids of the brain and then peptizes them. The other possibility that the starch adsorbs the morphine more strongly than do the brain colloids does not, however, become untenable, because of these facts. If starch peptizes the reversibly-coagulated nerve colloids of the brain in the presence of morphine it is decidedly not too much to expect that the thiocyanate ion will do the same. Since the respiratory center is affected by morphine (it has been shown that sodium thiocyanate tends to repeptize that center when the nerve colloids are reversibly coagulated by "amytal"), it is to be classed in the category of an entirely reasonable supposition that sodium thiocyanate will be of aid in relieving respiratory difficulties. Too much cannot be expected of sodium thiocyanate by way of rousing an animal out of morphine narcosis because the morphine is at least strongly adsorbed in the brain. The displace-

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[1] "A Treatise on Poisons," 48 (1875).

[2] "Chemical Constitution and Physiological Action" 119 (1915).

[3] Gwathmey: "Anesthesia," 372, 643 (1914); see also Spiegel: loc. cit., p. 123.

[4] Crile: "A Bipolar Theory of Living Processes," 317, 320 (1926).

[5] "A Treatise on Poisons," 538 (1875).

[6] Kingzett: "Animal Chemistry," 380 (1878).

ment of the drug from the nerve colloids of the brain by the adsorbed thiocyanate ions would not, therefore, make for any great increase in the rate of elimination of the drug.

Morphine hydrochloride was used[1] in the experiments about to be described; it will be characterized as morphine. The first experiment that was made was done as a control. A water solution of morphine containing 0.12 grams of the drug was injected subcutaneously into a 2300 gram rabbit. The animal became dull in four minutes and was asleep in 12 minutes. The rabbit began to stir in 41 minutes; and it tried to rise after 59 minutes. It was not able to sit up after one hour and 14 minutes; at this time the animal lapsed back into a deep narcosis. The respiration was 12 per minute after three hours eight minutes. Shaking the rabbit produced no visible effect upon the narcosis. After three hours and 56 minutes the rabbit was turned over on its back; it stayed that way with its head thrown back and all of its legs stretched out at different angles for ten minutes. It was then laid over on its side again. Up to this time the animal had neither defecated nor urinated. The rabbit showed practically no resistance to severe mauling after four hours and 26 minutes; it kicked once upon being lifted by the ears. After five hours the respiration was only 18 per minute. The animal was left at two o'clock in the morning. At nine o'clock it appeared to be normal but somewhat washed out.

At the start of the above experiment, the companion rabbit to the one just described, weighing 2500 grams, was narcotized by morphine by a subcutaneous injection of 0.123 grams of morphine in water solution. The animal became dull in six minutes, and was asleep in ten minutes. When the narcosis became deep and definite, and the respiration was very low, (about 15 minutes after the morphine was administered) 3.8 cc. of a 10% solution of sodium thiocyanate was injected by the intravenous route. Eight minutes later the rabbit appeared to become conscious; it was able to sit up without trouble. The animal seemed to be in a dull stupor. One hour and three minutes after the injection of the morphine it seemed to lose strength somewhat; for that reason 3 cc. more of the sodium thiocyanate was injected intravenously. This procedure brought the rabbit back quickly. The respiration was 22 per minute after two hours and 35 minutes, as compared to 12 per minute for the control. Throughout the experiment the rate of respiration of the animal with sodium thiocyanate in it was twice as great as the respiration rate of the control. The rabbit was turned over on its back after three hours and 27 minutes; it kicked hard and turned over on its side. Repetition of the procedure brought the same result; finally the rabbit was put on its back and soothed (properly stroked, rabbits often go to sleep when in this position). Despite this the animal kicked very hard and determinedly until it was freed; then it turned over. Up to this time this rabbit had defecated quite a few times; whereas the control had not done so at all. This ratio was increased several fold at the time that the two animals were left. After four hours this

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[1] The authors wish to thank Prof. J. B. Sumner of the Biochemistry Department of the Cornell Medical College for supplying us with morphine hydrochloride.

rabbit strongly resisted mauling as compared to no resistance by the control. The animal kicked violently upon being lifted up by the ears four and one-half hours after the start of the experiment; at this time the respiration rate was 38 per minute as compared to 18 per minute for the control. The depth of narcosis that this animal was in was on the very border-line of consciousness from the time that the first injection of sodium thiocyanate was made; consciousness is elusive when one tries to define it for animals. Certainly the depth of narcosis of this rabbit was considerably less than that of the control. The animal appeared to be normal, but somewhat washed out when next seen at nine o'clock in the morning.

The most evident conclusion that one can draw from these two experiments is that the thiocyanate ion tends to repeptize the reversibly coagulated nerve colloids of the respiratory center, for the respiration was much better in the case of the rabbit with sodium thiocyanate in it. Furthermore the state of narcosis produced by the morphine was visibly lessened by the presence of the sodium thiocyanate. So, the prediction that the thiocyanate ion would lessen the degree of narcosis and aid respiratory difficulties has been realized experimentally.

If one goes to the opposite end of the lyotropic series from the thiocyanate ion, the peptizing action of the anions there is nil. It is then that the cations become effective, and, as they are positively charged, they will tend to act as coagulants for a negatively charged protein sol. Therefore, one would expect that sodium tartrate (see the lyotropic series) would tend to act in the same direction as morphine; in other words it should prolong a morphine narcosis when injected into a rabbit.

The two rabbits that were used in the above experiments were prepared for the following experiments by feeding them heartily for a week and keeping them in the fresh air.

An intravenous injection of 5 cc. of a 10% solution of sodium tartrate was made on the 2300 gram rabbit. There was no visible ill effects from this treatment. Nine minutes later 0.10 gm. of morphine in distilled water was injected subcutaneously. Three minutes later the rabbit was strong and determined, but the rate of respiration was slowing down rapidly. After 15 minutes there was a distinct depression; the respiration rate was still falling rapidly, after 19 minutes it was very slow. This was accompanied by the exudation of saliva. Twenty-four minutes after the morphine was injected a good narcosis was observable. The rate of respiration was 30 per minute after 38 minutes; in one hour eight minutes the rabbit seemed to be in much better shape. The animal began to stir after one hour 39 minutes; it crawled around a bit after two hours. Ten minutes later it appeared to be approaching normal, but the rate of respiration was still down. The animal came a cropper, for it was extremely disinterested after four hours. After five hours the respiration rate was only ten per minute, as compared to 18 per minute after five hours when the animal had 0.128 gm. of morphine in it, and it was still in a narcosis. The rabbit appeared to be a little more nearly normal in five hours 33 minutes, but it was still in a poor condition after six hours 33 minutes.

From the above detailed description it would seem that this animal underwent a narcosis which was not quite so deep in its general aspect but which was as prolonged as when it was under the influence of 0.12 gm. of morphine, or a 16.7% greater amount of the drug. This can be ascribed to the action of the sodium ion as was predicted. So far as the respiratory center is concerned, it has been pointed out that there was a noteworthy improvement when using sodium thiocyanate.

In order to be more certain that the sodium tartrate had its own sensory-nerve coagulating effect the above rabbit was conditioned for a control experiment. After eight or nine days in the open air with plenty of food, the animal was injected subcutaneously with 0.1 gram of morphine in water solution. A slight depression was noticed within five minutes. After 18 minutes the rabbit was able to move its head unaided, but the morphine was beginning to have a profound effect. The breathing was very bad and irregular after 22 minutes. The animal refused to lie on its back after one hour and 40 minutes; its strength had returned, and it appeared to be quite conscious. The respiration rate was 18 per minute at this time. Four minutes later the animal arose of its own accord. In two hours 50 minutes it was strong, and completely conscious so far as could be judged; but it was unable to hop around. The animal was quite full of life after four hours and five minutes; it crawled around after four hours and 40 minutes. After five hours it was impossible to misjudge the fact that the rabbit was definitely and completely out of the narcosis; it was not very strong but it got around with ease and facility.

Comparing these last two experiments, it becomes evident that the animal came out of the morphine narcosis more quickly when there was no sodium tartrate in it. The narcosis was somewhat less deep and the period of recovery more sharp when the sodium tartrate was not present. So it seems that it has been clearly, although not strikingly, demonstrated that the sodium tartrate exerts its own narcotic effect which enhances the effect of the morphine. That the difference is not greater is very likely due to the sodium ion not being very strongly adsorbed as compared to the morphine.

At the time that the above rabbit was treated with sodium tartrate and morphine, the companion rabbit was treated with sodium thiocyanate and morphine. The 2500 gram rabbit was injected intravenously with 5 cc. of a 20% solution of sodium thiocyanate; this is roughly an equimolar amount with the sodium tartrate that was injected into the other rabbit at the same time. This caused a depression and rather queer pedal difficulties. The pedal idiosyncrasy was characterized by the fact that in attempting to move forward, about 50% of the time the net result was that the animal moved backward. This phenomenon is analogous to the effect of a subcutaneous injection of sodium thiocyanate into a normal rabbit when the rabbit hops into the air going forward at times and other times backwards. Fifteen minutes after the sodium thiocyanate was injected a subcutaneous injection was made of 0.1 gram of morphine in water solution. In two minutes the depression was greater; and in five minutes the animal was limp. During this time the usual large drop in respiration rate did not become manifest for the respiration remained rapid. So far as we could judge there was no loss of consciousness. The rate of respiration was 80 per minute 44 minutes after the morphine was administered; the animal still appeared to be conscious. At this time it was placed on its back, but it turned over of its own accord and proceeded to stretch. The animal was still conscious after one hour and 12 minutes. After one hour and 42 minutes a severe twitching of the neck, jaw, and head muscles was noticed. In a short time the twitching ran through the whole body. The animal acted as though it had chills. The convulsions became progressively more severe; the rabbit threw its head back and died after two hours and 17 minutes. There did not appear to be any tetanus and the animal seemingly never lost consciousness. As the rabbit was about to die peculiar ripples ran up and down its back on either side of the spinal column.

There are two obvious conclusions that can be drawn from this experiment; in the first place, the effect of morphine on the respiratory center can be very greatly diminished by the action of the thiocyanate ion upon the nerve colloids of that center. Witness the fact that the respiration rate did not decline before the above rabbit died, and in the case of the rabbit under the influence of morphine and sodium tartrate it was at one time only ten per minute as compared to 80 per minute for the above animal.

The experiment was a success but the rabbit died. Why? The symptoms were not those of morphine poisoning because so far as could be observed there was no loss of consciousness, and there was certainly no coma; furthermore the slow, deep breathing characteristic of the rabbit under a large dose of morphine was absent. There is ample support for the view that in the presence of the morphine the large amount of sodium introduced into the animal caused its death, the mechanism being a decrease in the amount of thiocyanate ions adsorbed, due to the coagulating effect of the morphine, with a consequent rise in the amount of sodium ions adsorbed, which ions work in the same direction as the morphine. Rabuteau[1] points out that potassium thiocyanate is a muscular poison, paralysis and death often being preceded by convulsions, but that the other salts of potassium are poisons and cause the same symptoms as potassium thiocyanate. In other words the poisonous action of this salt is due to the potassium: "On sût bientôt que le sulfocyanure de potassium agissait moins en qualité de sulfocyanure qu'en qualité de sel de potassium." He goes on to say that upon replacing the potassium atom by the sodium atom the effect in animals is very much less. In *high enough concentrations* sodium should act as a poison much like potassium. The presence of the morphine could conceivably cause the sodium to behave as though it were present in even higher concentrations than it was. On these grounds rests the case for the present.

The bearing of these experiments upon the problem of drug addiction is an inviting thesis. It is a natural corollary of this theory of anesthesia that

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[1] "Éléments de Toxicologie," 498, 543-545, 547, 549 (1887).

the habitual user of drugs for the purpose of removing himself from the natural spheres of human society must, as a result, possess a brain in which the colloids of the sensory nerves are qualitatively constantly in a state of partial coagulation. Were these colloids peptized by a non-toxic dispersing agent so that they return either to their normal degree of dispersion or very close to it, normal brain function should ensue. The normal person is generally not a drug addict. Therefore, peptizing the nerve colloids of the brain should displace the drug, return the drug addict to a normal condition, relieve the desire for more, and result in a cure. It is not a necessary condition that sodium thiocyanate is the only compound that will produce these results, or that it will cure drug addicts at all. But, it is an enticing thought that perhaps it will; and almost certainly peptization therapy is the correct lead to follow, regardless of what compound is used. The compound that would be, according to this theory, useful in combating drug addiction should be water-soluble, strongly adsorbed by the brain and sensory nerve colloids, a good peptizing agent for protein sols, non-toxic, stable, not too quickly eliminated from the body, and preferable organic in nature.

In the light of our present knowledge of the action of morphine and sodium thiocyanate, it is entirely possible for the colloid chemist to make a good guess as to how one should go about treating drug addiction by means of sodium thiocyanate. Were addiction to drugs a psychological phenomenon, whatever that may mean, rather than a physiological colloidal change practically the same treatment would apply. The starting point for the treatment theoretically can be when the patient is in any one of the several conditions that one observes in addicts. Were the patient in imminent danger of death from morphine poisoning the first dose of sodium thiocyanate could be administered intravenously. McGuigan[1] states that intravenously 0.08 gm. of sodium thiocyanate per kilogram of body weight produces no toxic symptoms. Following this, the sodium thiocyanate could be given in small doses by mouth, progressively increasing the amount of the compound administered until a condition is obtained[2] in which there is, "disorientation, hallucinations of sight and hearing, mania, and ideas of persecution singly or in combination." This condition disappears shortly after the administration of the drug is discontinued. This, as will be shown in a later paper by Bancroft and Richter is the production of a neurotic condition by peptization of the brain colloids to a state greater than normal; that is, the colloidal micellae become smaller in size.

Dr. Norman S. Moore of Ithaca has brought to our attention the fact that the symptoms encountered upon withdrawal of morphine (apart from craving) from addicts resemble very closely those symptoms stated by Borg to be the result of prolonged administration of fairly large amounts of sodium thiocyanate. The normal state of the nerve colloids of the drug addict during the time that he is addicted is one of greater aggregation than that of the person

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[1] "A Textbook of Pharmacology and Therapeutics," 102 (1928).

[2] Borg: Minnesota Med., 13, 293 (1930).

who does not use morphine. Upon withdrawing morphine the natural peptizing agents of the body begin to work to break up the aggregates. There is thus a peptizing action which is in the direction of return to the state of an ordinary human being, and away from the state of partial aggregation that was normal during the time that morphine was used. Thereupon the mental symptoms appear. Sodium bromide, which is near the thiocyanate end of the lyotropic series, will relieve mental disturbances which are due to coagulation symptoms. Slight agglomeration or slight peptization of certain of the brain colloids cause much the same mental symptoms. Bancroft and Richter will discuss mental conditions more completely in a later paper.

At the same time the quantity of morphine allowed the addict should be progressively decreased. If possible it would be well to discontinue the administration of morphine well before the neurotic symptoms due to the thiocyanate ion become manifest. Then as the neurotic symptoms disappear the sodium thiocyanate should again be commenced in small doses, for a short while, at the same time abstinence from the drug should be complete. The same sort of treatment should apply were the starting point the drug addict who is not in a state of coma.

As a result of such a treatment as this the brain colloids will theoretically be returned to their normal degree of peptization as a result of the action of the thiocyanate ion; that is after the neurotic condition has been attained and the thiocyanate treatment has been discontinued, this condition should obtain. The beauty of the direct employment of this therapy in humans is that the drug is fed slowly and at any signs of real distress the administration can be stopped before any permanent damage can be done. It will be increasingly apparent, as the story unfolds, that the danger involved in the proposed treatment is, barring outside complications, slight if not nonexistent. The only difficulty that can be foreseen is that due to the possible lowering of the blood pressure by the sodium thiocyanate. Perhaps ephedrine will circumvent this condition, should it arise, without interfering with the peptizing action of the thiocyanate ion.

4. Strychnine

"Strychnine[1] stimulates the spinal cord, increasing its reflex excitability, but it has little effect on the centers above the medulla. It stimulates the respiratory center, increasing the rate of respiration, but the effect is only temporary. Toxic doses raise the blood pressure by stimulating the vasoconstrictory center; it has little direct action on the heart. Poisonous doses cause tetanus, but the trismus is not marked. Between the attacks there is usually complete relaxation of the affected muscles. The convulsions are of spinal origin. Death may occur, during a convulsion, from fixation of the chest by spasm of the respiratory muscles or during the interval from respiratory paralysis."

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[1] Hatcher and Eggleston: "Useful Drugs," 139 (1926).

Now, if a given peptizing agent for proteins can make its way to the spinal cord, and provided it is adsorbed more strongly there than is strychnine, it will, according to this theory, displace the alkaloid, peptize the protein, and thereby tend to return that part of the nervous system to normal. Thus, sodium thiocyanate is obviously the first choice, on the basis of this theory, as the causative agent of a relief for strychnine poisoning. Accordingly a strychnine sulphate solution containing 0.03 grams per 100 cc. of distilled water was prepared. An 860-gram rabbit was injected intravenously with 0.86 cc. of this solution. Severe tetanic convulsions occurred almost immediately. In two and one-half minutes the rabbit was laid out by the convulsions. The animal exhibited severe dyspnea; it squealed loudly while in the convulsed state. The rabbit died in a great spasm eight minutes after the strychnine was administered. This was, of course, the control experiment. A litter-mate of the above rabbit, weighing 1000 grams, was injected intravenously with 1.1 cc. of a 10% solution of sodium thiocyanate. After seven minutes had elapsed one cc. of the above strychnine solution was injected intravenously. Tetanic stimulation came on immediately; this time it was not nearly so severe, and was spasmodic rather than continuous as in the control. No dyspnea was manifest; the breathing was regular. The tetanic stimulation ceased in three or four minutes; and in nine minutes strong clonic movements were observed. After 17 minutes from the time that the strychnine was administered, the clonic movements suddenly landed the rabbit erect on its feet. Three minutes later the animal appeared to be almost normal. At this time it partook of water when it was offered, and nibbled lightly at grass. This animal did not squeal at all. The rabbit was well and happy 24 hours later.

Thus, another portion of the central nervous system is brought into accord with the general theory. Since strychnine can also be made to act as an anesthetic,[1] it requires no stretching of the imagination to see that strychnine acts upon the sensory nerve colloids in such a manner as to cause coagulation. The theory is vindicated by the action of one more drug.

Chloroform and some other general anesthetics are well known as antagonists for strychnine poisoning. This may be cited as evidence against the validity of this theory of the colloidal behavior of the central nervous system, for chloroform is also a coagulant. The answer is easy. Chloroform must be more strongly adsorbed by the proteins of the sensory nerves than is strychnine. As a result the strychnine is displaced by the chloroform which, although it is more strongly adsorbed, is not so good a coagulant, and eliminated by the body. The chloroform is then, in its turn, also eliminated. The more strongly adsorbed substance is not necessarily the better coagulating agent, for the rate and amount of coagulation are functions of the degree that electrokinetic potential of the charged micellae is lowered by the coagulating substance.

One finds[2] that potassium thiocyanate precipitates strychnine from solutions of its salts when the concentrations are right, by forming an in-

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[1] Bancroft and Richter: Proc. Nat. Acad. Sci., **16**, 574 (1930).

[2] Wormley: "Micro-chemistry of Poisons," 575 (1885).

soluble strychnine thiocyanate. However, it is fairly certain that this is not the mechanism of the experimental results reported here; for with a solution such as was used, one fails to observe a precipitation upon adding an equal volume of a 10% sodium thiocyanate solution.

5. Alcohol

This brings us to a study of the effect of sodium thiocyanate upon the action of ethyl alcohol. As one ordinarily observes the action of alcohol, the period of stimulation is distinctly greater than with the ordinary anesthetics. With fish it can be demonstrated that under comparable conditions the period of stimulation in an alcohol solution is longer than in an ether solution. May[1] states that, "the chief action of ethyl alcohol is on the nervous system, the narcotic effect being preceded by a loss of control of the higher centers, an effect which has led to the mistaken belief that alcohol in small quantities acts as a stimulant." While holding no brief for the medicinal use of alcohol as a stimulant, it does seem somewhat useless to argue that stimulation is not one of the physiological effects; certainly there may be vocal stimulation. May becomes more interesting on page 49. "The action of certain substances, such as alcohol cannot be explained by the foregoing theories [Meyer-Overton, and others]. Alcohol is miscible with water in all proportions, and is only slightly soluble in fats, but this need occasion no surprise when it is borne in mind that alcohol does not really belong to the same class of substances as sulphonal and inert bodies of that type, as it exerts some action on proteins and is oxidized in the body. The action of alcohol is, therefore, probably specific, and of a different kind from that of sulphonal, etc."

From the general considerations of the case there does not appear to be any outstanding reason why sodium thiocyanate should not exert some antagonistic effect upon the action of alcohol.

The first experiment[2] was performed on a young 8.0 kg. female dog. Approximately 14 cc. of 95% alcohol was diluted with about three times its volume of water and administered per os. The alcohol took effect in nine to ten minutes. Ten minutes after the alcohol was administered 15 cc. of a 10% solution of sodium thiocyanate was injected intravenously at the approximate rate of one cc. per minute. During the injection, which was done under a local anesthetic, the dog's head hung over the side of the operating table. By the time that the injection was finished the animal showed more interest in life. Twenty minutes after the injection the dog was sober again. No depression was noted at any time after the injection.

As a result of experiments with rabbits, it would appear that both by the intravenous injection and inhalation methods it takes a great deal of ethyl alcohol to produce anesthesia. A 2100 gram rabbit was kept for four hours in a closed space in an atmosphere containing alcohol vapor. This did not seem

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[1] "Synthetic Drugs," 23 (1921).

[2] Our thanks are gratefully extended to Dr. H. C. Stephenson, Professor of Materia Medica in the New York State Veterinary College at Cornell University for performing this and other experiments at our request.

to affect the animal; so it was removed and placed in a much smaller closed space containing what to a human being would be almost a suffocating concentration of alcohol vapor. After one and one-half hours in the strong atmosphere the animal was removed. It was quite intoxicated; that is, it could hardly hop, and when placed on its side was content to remain so. These observations consumed about five minutes. The rabbit was then put back into the alcohol chamber into which more alcohol vapor was introduced. Fifteen minutes thereafter the rabbit was removed and two cc. of a 10% solution of sodium thiocyanate was administered intravenously. This was followed immediately by a subcutaneous injection of six cc. of the same solution. The rabbit remained intoxicated, but hopped around a great deal. It would not repose upon its side when so placed.

Two persons volunteered to become intoxicated and then take sodium thiocyanate.[1] One of the volunteers ingested the equivalent of approximately 275 cc. of alcohol; while the other consumed the equivalent of approximately 175 cc. of alcohol. In the space of three quarters of an hour the two persons took respectively four and three grams of sodium thiocyanate in water solution, a gram at a time.

The general results of this experiment were several. In the first place, the dilatation of the pupils of the eyes had decreased noticeably fifteen minutes after the sodium thiocyanate was taken; shortly after this there was a marked decrease in the apathetic euphoria in both cases. Over a period of 70 minutes the pulse rate went steadily down from 92 to 72 and from 76 to 70 respectively. The two persons were kept quiet throughout, and neither lost consciousness. The rate of respiration tended to rise slightly in each case.

Thus, with ethyl alcohol there were no very striking results observed. But, that there was some antagonism between the sodium thiocyanate and the alcohol seems certain, although quantitatively it was not very much. It does not appear, on the surface, that it should be very difficult to demonstrate in a somewhat more dramatic manner the antagonism between these two compounds. We are working on this problem at present.

6. "Nembutal"

"Nembutal," sodium ethyl (1-methyl butyl) barbiturate, is an isomer of "Sodium Amytal." One would naturally predict that since "amytal" yields to sodium thiocyanate therapy, "nembutal" might also fall in line. The results of a brief study indicate that this is not quite the case. Dr. Stephenson tried an experiment upon a dog such as those reported under "Amytal" which was not successful. Unsuccessful experiments upon rabbits and goldfish have also been made.

The apparent reason for the failure of sodium thiocyanate in this case is that the "nembutal" is more strongly adsorbed than is "amytal." As a result it would be more difficult for the thiocyanate ion to displace the adsorbed

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[1] The authors extend their sincere thanks to Barton F. Hauenstein, M.D., Tompkins County Pathologist, who so kindly conducted these experiments. They also duly thank the volunteers.

anesthetic. More reasonableness is lent to this view when one considers that 40 to 50 mg. of "sodium amytal" per kilogram of body weight injected intravenously produces in dogs a surgical anesthesia which lasts for from one to three hours,[1] whereas, Dr. H. C. Stephenson[2] says that 25 mg. of "nembutal" per kilogram of body weight, injected intraperitoreally, will produce in dogs a surgical anesthesia which lasts for from one to three hours. Since "nembutal" requires only one-half the amount that "amytal" does to produce surgical anesthesia in dogs, one seems to have as the best explanation on the basis of this theory that alternative which we have chosen.

7. Anaphylaxis

The case of anaphylaxis involves a shift from the central nervous system to the sympathetic nervous system. One is impressed by the multitude of different reactions found under the general headings of anaphylaxis, anaphylactoid reaction, and allergy with their various symptomatological manifestations. So wide is the field that Wells[3] has been lead to define true anaphylaxis rather rigidly. On the other hand, we find the statement[4] that, "the symptomatology of the reactions following the introduction of any serum, vaccine, protein substance and colloid is always the same: it is the symptomatology of colloid or humoral shock." Lumière[5] says: "Our colloidal theory of life and disease enables us readily to understand this community of symptoms. All these pathogenic agents, however they may differ have one property in common: they determine the flocculation of certain humoral colloids whose coagulation produces the pathological symptoms." Despite the fact that anaphylaxis is not due to a humoral reaction,[6] the flocculation and peptization structure of the statements of Kopaczewski and Lumière appear to hold for the case in hand.

While in anaphylaxis and the various forms of allergy one notes certain symptoms in common, they are not necessarily quantitatively alike, nor are all of the symptoms of one affection present in the cases of all of the other affections. This is hardly to be wondered at when one considers that the efferent sympathetic nervous system has communication with and is distributed in the eyes, mucous membranes of the nose, the palate, the parotids, the heart, the larynx, the trachea, the bronchii, the lungs, the esophagus, the stomach, abdominal blood vessels, the liver and ducts, the pancreas, the adrenals, both intestines, the kidneys, the bladder, etc.[7] Thus, purely on the grounds of chance a silver sol, for instance, would be more strongly adsorbed on some of these substrates than on others, and also, it probably would be adsorbed quantitatively differently from an albumin sol. Even though the

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[1] Clowes, et al: Proc. Soc. Exp. Biol. Med., 26, 399 (1929).

[2] Private communication concerning a long series of experimental results.

[3] "The Chemical Aspects of Immunity," 228 (1929).

[4] Kopaczewski: Alexander's "Colloid Chemistry," 2, 968 (1928).

[5] Alexander's "Colloid Chemistry," 2, 688 (1928).

[6] "The Chemical Aspects of Immunity," 234 (1928).

[7] Gray: "Anatomy of the Human Body," 967 (1930).

sympathetic nerve colloids in all parts of the body were chemically the same, their physico-chemical conditions could be different, due to being bathed in different amounts of different electrolytes.

If, as seems probable, anaphylaxis is intimately associated with the flocculation or peptization of the colloidal proteins of the sympathetic nervous system, it is not too much to expect that sodium thiocyanate will either relieve or aggravate the condition markedly. Especially is this so when one considers that the sympathetic nerves are exposed.

An 800 gram rabbit was sensitized by injecting one cc. of a sterile 22% egg while sol (22 cc. of fresh egg white mixed with 78 cc. of distilled water) subcutaneously.[1] Twenty-one days later 0.8 cc. of a 10% solution of sodium thiocyanate was injected intravenously. Twenty minutes later two cc. of a sterile 22% egg white sol was administered by the same route. None of the symptoms of anaphylaxis were observed in this rabbit.

The control rabbit was a litter-mate of the above; they were both sensitized at the same time with the same amount of the same 22% egg white sol. The antigen was introduced into this animal a few hours before the above rabbit was injected. The technique and amount were identical. A typical but mild shock was observed, from which the rabbit apparently recovered in about three quarters of an hour.

A third litter-mate of the above rabbits that was sensitized at the same time in the same way was injected intravenously with 2 cc. of a 22% egg white sol mixed with 0.8 cc. of a 10% sodium thiocyanate solution. There was severe dyspnea and probably tetanic convulsions (they could not be seen because the body was inclosed during the injection); the animal died within a minute after injection. The following symptoms were observed: marked depression, body limp, increasingly weaker heart beat, irregular respiration with dyspnea, protruding eyes which became fixed. No defecation or urination was noticed during the minute that the rabbit lived. Upon picking the dead rabbit up it became obvious that contraction of the bladder and intestines had taken place. A post-mortem examination revealed that both intestines were constricted. Also the sigmoid colon, rectum, gall bladder, bladder, and the abdominal arteries were constricted. The left ventricle was in systole; there were no apparent signs of disease.

These experiments, in addition to two others in which rabbits, apparently about to die from anaphylaxis, were rapidly revived by the use of sodium thiocyanate, leave little doubt that here again it is a question of coagulation and peptization. Exactly what phenomena take place, and their order of occurrence are questions that are reserved for a later paper on the mechanism of anaphylactic shock.

Karsner[2] says: "Drugs which depress smooth muscle excitability, those which depress nerve activity generally [note the parallelism to Claude Bernard's theory of narcosis], in the group of narcotics and anesthetics, those which tend

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[1] The authors wish to thank Mr. William B. Stocking for his assistance with this work.

[2] Karsner, in Jordan and Falk: "The Newer Knowledge of Bacteriology and Immunology," 978 (1928).

to maintain blood pressure, are pharmacologically adapted to the inhibition or even prevention of shock. Thus atropin, adrenalin, chloral hydrate, ether, alcohol, atoxyl, and numerous other drugs have been employed."

These drugs are of course diametrically opposite in their action to sodium thiocyanate, provided the adsorption of the thiocyanate is upon negatively charged sympathetic nerve colloids, and provided the lyotropic series for the active protein is the same as it is for egg albumin. Still it is conceivable that anaphylaxis can be prevented either by peptization or coagulation.

8. Histamine

Histamine causes a reaction very much like that of anaphylaxis.[1] "Not only does histamine cause bronchial spasm in guinea pigs, obstruction to pulmonary circulation in rabbits, and fall of blood pressure in dogs, but applied to the skin or mucous membranes, it causes marked local urticaria resembling closely that of skin reactions in sensitized persons, and it does all these things in extremely minute dosage, comparable with the dosage of proteins used in anaphylactic reactions."

Delbet[2] says that histamine acts upon the same substrates as does a protein in causing anaphylaxis. However, in true anaphylaxis there is a distinct decrease in the coagulability of the blood; this change[3] is not apparent in the case of histamine shock.[4]

So, histamine, acting on the colloids of the sympathetic nervous system, probably has a more direct and less complicated colloidal effect, not being in colloidal suspension itself, than is met with in the antigen-antibody actions. Assuming, therefore, that histamine is either directly or indirectly responsible for the coagulation, and the possible complicating circumstances, of sympathetic nerve colloids, one can predict the effect of sodium thiocyanate upon its action. Depending upon the type of colloid met with in the case of the sympathetic nerve proteins, sodium thiocyanate should either increase or decrease the action of histamine. That is, were the colloids with which we are dealing positively charged the action of the histamine should be intensified; whereas were they negative, and were the lyotropic series not reversed, the sodium thiocyanate should decrease or inhibit the action of histamine.

One cc. of a solution of histamine dihydrochloride containing three milligrams per cc. was injected intravenously into a rabbit weighing 930 grams. The effect was very rapid, for the rabbit was dead in about four minutes. The obvious symptom was severe convulsions.

A 790 gram rabbit was given 1.1 cc. of a 10% solution of sodium thiocyanate intravenously. Fourteen minutes later, 0.85 cc. of the same histamine solution was injected by the same route. This time, instead of the rapid

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[1] Wells: "The Chemical Aspects of Immunity," 240 (1929).

[2] Rev. Chir., 57, 309 (1919); Wells: "The Chemical Aspects of Immunity," 241 (1929).

[3] Achard and Aynaud: Compt. rend. Soç. Biol., 67, 83 (1909); Lee and Vincent: J. Med. Res., 32, 445 (1915); Pepper and Krumbhaar: J. Infect. Dis., 14, 476 (1914).

[4] Smith: J. Immunol., 5, 239 (1920).

appearance of violent convulsions, the striking thing was that no outward symptoms of shock appeared; no symptoms of any kind were observed.

This is even more striking when one considers that sodium thiocyanate has been shown to act upon nerve colloids in the opposite way to anesthetics. The drama of the situation is increased when one takes into account the fact that a litter-mate of the above rabbits weighing about 790 grams died quickly from the effect of 0.2 cc. of the above histamine solution.

Thus it is that histamine falls into line with the general theory that protein coagulation is the cause of various changes in living tissue, whereas, protein peptization is the cause of the reversal of these changes. Since the exposed sympathetic nerves are said not to be coated by lipoids, these experiments deal a sharp blow to the idea that lipoid disturbance plays a significant part in anesthesia.

9. Some Experiments in Vitro

If one works with things known to have little or no secondary or by-effects there seems to be no real theoretical reason why many, if not all, of the drug actions falling into classes of those reported in this paper should not be studied *in vitro*. The ground has been broken for this type of study. It has been shown[1] that a slightly acidified albumin sol, to which sodium sulphate has been added, flocculated upon the addition of small amounts of an alcohol or chloral hydrate. Edestin, under similar conditions, was not sensitized as much as albumin. Likewise, calcium chloride sensitized an albumin sol to alcohol. "This shows that this sensitization is specific both for different narcotics and substrates and is in line with the fact that all narcotics do not affect the same tissues equally."

Bancroft and Richter continue: "In the experiments where the protein sols were sensitized by ether to electrolytes it was found that at the beginning of the decrease in dispersion the phenomenon was reversible. That is, if the ether is removed by blowing a stream of air through the solution, the turbidity is decreased. At a later stage when the albumin has been precipitated, the precipitate can be removed by filtration and partially repeptized in a solution of the same composition as the original except that the ether is absent. This peptization becomes increasingly difficult if the ether is allowed to act for longer lengths of time."

An albumin sol sensitized by electrolytes and partially coagulated by ether cleared up again when sodium thiocyanate was added to the system.

Binz[2] has shown that sections of the brain cortex of rabbits coagulate when immersed in a 1% solution of morphine hydrochloride. If the coagulation was not allowed to proceed too far, peptization was accomplished by merely washing out the morphine.

By layering one liquid against the other, as in the precipitin test, it was found that histamine dihydrochloride caused a sterile horse serum sol to precipitate at the liquid-liquid interface. This was not due to the absence of

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[1] Bancroft and Richter: J. Phys. Chem., 35, 227 (1931).

[2] Gwathmey: "Anesthesia," 34 (1914).

the proper amounts of electrolytes with the resultant possible precipitation of globulin for when pure water was layered against the sol there was no precipitation. Likewise a negatively charged silver sol gave a very heavy precipitate with sterile horse serum.

Such studies as these give us a clue to the anaphylactoid reaction due to "Electrargol" and "Collargol." By reducing a solution of silver nitrate with ferrous sulphate in the presence of citric acid a negatively charged silver sol is formed; when one cc. of such a sol (after dialysis) was injected intravenously into a rabbit weighing about 900 grams, it immediately caused convulsions, clonic movements, and dyspnea. Thus, an anaphylactoid reaction is observed. The particular role that this experiment plays in the general line-up is that it shows that the reactions of "Electrargol" and "Collargol" are not necessarily due to protein products adsorbed thereon. In cases such as this, the reaction may be to a large extent of a humoral nature; for when one adds such a silver sol as the above to sterile horse serum a great deal of visible coagulation takes place.

Urethane, which is an anesthetic, caused a slightly sensitized egg albumin sol to precipitate; on the other hand, it lowered the temperature of jelly formation of a 10% gelatin jelly. This raises the strong suspicion that anesthesia of the sensory nerves does not depend upon colloids of the gelatin type where the water equilibrium plays a dominant part in determining the degree of dispersion of the sol.

It is not claimed, as a result of these experiments, that a colloidal system has been found that will respond to coagulation and peptization in a manner analogous to that of the sensory nerve colloids. For instance in the cases of the artificially sensitized albumin sols, the systems were slightly acid; in such cases sodium thiocyanate itself is a coagulating agent for the sol. The important thing is that by choosing a protein sol that is coagulated to a greater or lesser extent by anesthetics in general, and which is peptized strongly by the thiocyanate ion, one should be able to study quite thoroughly the quantitative side of anesthesia, the theoretical side of which is now on a firm basis.

General Considerations

Lest misunderstandings arise, it is well to consider what the purpose of this paper is. The prime motive is to establish even more firmly by experiments *in vivo* that the colloidal coagulation theory of narcosis is the correct explanation of the direct facts met with in anesthesia and certain other physiological conditions. No effort is made to show that in any given case sodium thiocyanate will alleviate the conditions dealt with at any *given* greater rate than would normally obtain. For instance, it makes little or no difference theoretically whether sodium thiocyanate causes a rabbit to come out of "amytal" anesthesia 100% sooner than normal or 1% sooner than it ordinarily would. The main thing is that it does cause the animal to return to consciousness in a shorter period of time than when no peptizing agent is present. In other words the quantitative side is not important, but the presence of a colloidal antagonism is. A drug is not being offered for immediate clinical use, although there are indications that it may be of value in certain conditions other than hypertension. This thesis will be more fully considered in the next paper.

A plea is made for peptization therapy as being the correct theoretical line to follow in the case of some specified physiological conditions. If sodium thiocyanate is not an efficient enough peptizing agent for employment in clinical practice there do not seem to be any great barriers to the preparation of a non-toxic organic compound which is better in that respect, although in any case the appearance of transient toxic psychoses should not be wondered at. In the ordinary course of events this task should not necessarily be up to the physical chemist.

Since this paper is not concerned with an exhaustive study of the pharmacological properties of sodium thiocyanate, it has been deemed sufficient to perform one control experiment along with each experiment on antagonism. The question of biological variation does not, therefore, logically enter into the situation. The strength of the case that has been built up lies to a appreciable extent in the completeness with which a variety of drugs behave toward sodium thiocyanate as one would predict in advance that they should. At the same time, it should be pointed out that if a given drug is not antagonized by sodium thiocyanate, that fact is not a proof that the drug does not act by coagulation. In other words, lack of antagonism to a given drug by sodium thiocyanate does not characterize the action of that drug. All that it shows is that the drug is so strongly adsorbed by the nerve colloids that the thiocyanate ion is not able to displace it effectively, or else the drug does not have a direct action; yet again the drug might be acting upon substrates that are inaccessible to the sodium thiocyanate. A drug may bring about irreversible coagulation; in such a case antagonism by sodium thiocyanate is a paradox. However, each drug that is known to act upon the nervous system which is antagonized by sodium thiocyanate is just one more building block on the superstructure of this theory of anesthesia.

It is not amiss to point out again that in all probability we are not dealing with coagulation that can be observed with the unaided eye; in such cases coalescence is likely to intervene and cause a coagulation the reversal of which would demand drastic means. In the cases such as we are dealing with the nerve protein colloids probably only agglomerate forming slightly larger particles.

The trail has been blazed; let those follow who will.

The general conclusions supported by this paper are as follows:

1. *In vivo* application of Claude Bernard's theory of narcosis as developed by Bancroft and Richter has been made successfully.

2. Sodium thiocyanate has been found to be a valuable antagonist for the study of ether, "amytal," and morphine narcoses, strychnine and histamine poisoning, and anaphylaxis.

3. Sodium thiocyanate relieves to greater or lesser extents the effects of these drugs.

4. The action of the sodium thiocyanate is due to the thiocyanate ion.

5. The thiocyanate ion peptizes the colloids that are coagulated by the above-mentioned drugs.

6. The cycle, stimulation, anesthesia, stimulation, normal condition has been observed experimentally.

7. The period of stimulation upon forced recovery due to the thiocyanate ion is somewhat exaggerated; this phenomenon is explained on the coagulation and peptization theory. It is a natural consequence of the existing state of affairs in the recovering animal.

8. The way has been opened for the relief of the long post-operative anesthesia due to "amytal."

9. "Nembutal" is probably more strongly adsorbed by the protein colloids of the sensory nerves than is "amytal."

10. Sodium thiocyanate apparently peptizes the colloids of the respiratory center.

11. A theory, and a treatment based thereon, for the relief of drug addiction has been proposed. The theory is based on peptization of coagulated protein colloids of the brain.

12. Sodium thiocyanate may give relief to drug addicts. If this is not the case, the properties of a compound that will so do (based on the general theory of anesthesia) have been elucidated.

13. There is apparently a lyotropic series of ions, as there should be, connected with the peptization of the colloids that are coagulated by morphine. This is supported by the fact that sodium tartrate augments the action of morphine whereas sodium thiocyanate tends to antagonize it.

14. The use of too much sodium thiocyanate in the presence of a strong narotic may cause sodium poisoning.

15. Sodium and potassium are not interchangeable, when administering drugs.

16. Alcohol appears to be antagonized only slightly by sodium thiocyanate.

17. Under ordinary conditions there is no noticeable antagonism to "nembutal" by sodium thiocyanate.

18. The intensity of strychnine poisoning is lessened markedly by the thiocyanate ion.

19. Complete protection against a large dose of histamine has been observed.

20. Sodium thiocyanate has been found to protect rabbits against anaphylactic shock. A peptizing agent as well as coagulating agents (anesthetics) therefore counteracts anaphylaxis.

21. The thiocyanate ion has been shown to act upon the protein colloids of the central nervous system including the brain and spinal cord, and the sympathetic nervous system.

22. The value of experiments with proteins *in vitro* with compounds affecting the nervous systems and with peptizing agents has been pointed out. Examples of the actions have been given.

23. The possible therapeutic value of sodium thiocyanate in treating coagulated conditions of the nervous systems has been pointed out, although no extended pharmacological investigation of the compound has been made.

24. No evidence has been found or adduced that the lipoids play a dominant role in the phenomena studied.

25. Claude Bernard's theory of anesthesia as developed by Bancroft and Richter has been found to be inescapable.

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THE INFLUENCE OF THE PROXIMITY OF A SOLID WALL ON THE CONSISTENCY OF VISCOUS AND PLASTIC MATERIALS. III

BY R. K. SCHOFIELD AND G. W. SCOTT BLAIR*

It has been recognized for some time that, if a paste of clay or soil in water is forced through a narrow tube, there are certain limits of pressure between which the flow is telescopic. Within this range the rate of increase of extrusion with increase of pressure is constant within the present limits of experimental accuracy. Except in the case of very thin pastes the straight line obtained by plotting the volume V extruded in unit time against the pressure P does not on extrapolation pass through the origin, but makes a positive intercept on the pressure axis. Nevertheless, according to the treatment of Bingham[1] as amended by Buckingham[2] and independently by Reiner[3] the slope of this line should give the mobility of the material, a constant of which the reciprocal is closely analogous to the viscosity of a true fluid and has therefore been called the pseudo-viscosity.

In an investigation described in the first paper of this series[4] it was found that with many pastes the value obtained for the mobility from Bingham's equation depended upon the diameter of the tube used. It was shown that this result could only be accounted for by supposing a layer of material near the wall of the tube to have a mobility different from that of the bulk of the paste passing through the centre of the tube. It appeared sufficient for the purpose of obtaining this true mobility to assume that the thickness of the modified layer is small in comparison with the radius of the tube. Since the discrepancies are often considerable, it is desirable to obtain assurance on this point, or failing this, to form an estimate of the error that may be introduced in cases where the modified layer forms an appreciable fraction of the radius of the tube.

An attack was made on this in a second paper.[5] The method used, though direct, was rather cumbersome and was not quite complete.** The following treatment is more concise and enables the implications to be more clearly set out.

Imagine that a material of mobility μ_ω is flowing through a tube of radius R, and that the line ACB in Fig. 1 represents, by the distance above AB, the velocity distribution within the tube. This curve is of course a section of a surface which can be traced within the tube, and the volume enclosed between this surface and the cross-section at AB is a measure of the volume extruded in unit time. If now it be supposed that, instead of a constant mobility across

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**In giving an expression for the velocity of a point within the bulk of the material, the velocity given was that relative to the boundary distant δ from the wall (the symbol r' was used in the earlier paper). There should also have been a term in addition to allow for the velocity of the boundary relative to the wall of the tube.

the tube, the value μ_ω only holds between the wall and an imaginary cylindrical boundary distant δ from it, and that within this boundary the mobility is μ_0, the surface within the boundary will have a section represented by the line ADB. The total extrusion will, in this case, be less than that in the first case by an amount given by the volume enclosed between the two curved surfaces. This volume may be taken to represent an extrusion through a tube of radius $(R - \delta)$.

Within the pressure range over which the flow curves are straight, its slope dV/dP has, for the case where the mobility is μ_ω over the whole cross-section, a value

$$dV/dP = \frac{\pi R^4}{8L}\mu_\omega$$

L being the length of the tube which is long in comparison with its radius R.

To obtain the slope of the flow curve in the second case an amount must be subtracted equal to the rate of change with P of the volume enclosed between the two curved surfaces of Fig. 1. This is

$$\frac{\pi(R - \delta)^4}{8L}(\mu_\omega - \mu_0)$$

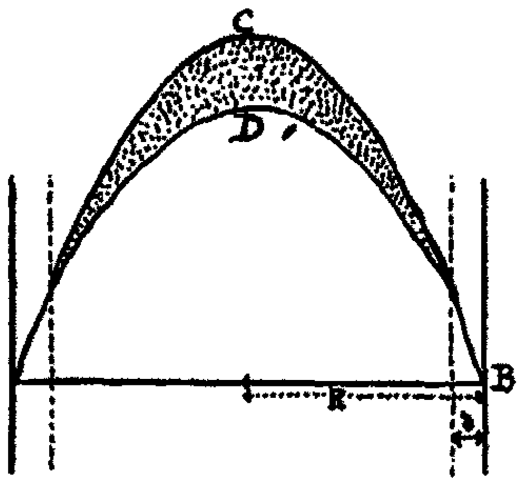

FIG. 1

Thus in the second case

$$dV/dP = \frac{\pi R^4}{8L}\mu_\omega - \frac{\pi(R - \delta)^4}{8L}(\mu_\omega - \mu_0)$$

The slope σ of the graph of mean velocity of extrusion $(V/\pi R^2)$ against stress on the wall of the tube $(PR/2L)$, used in the earlier papers, is readily obtained by multiplying both sides by $2L/\pi R^3$

$$\text{thus } \sigma = \frac{d(V/\pi R^2)}{d(PR/2L)} = \frac{2L}{\pi R^3}\cdot\frac{dV}{dP} = \tfrac{1}{4}R\mu_\omega - \tfrac{1}{4}\frac{(R - \delta)^4}{R^3}(\mu_\omega - \mu_0)$$

If now we suppose that the change from μ_ω to μ_0 does not take place abruptly at a fixed distance δ, but that the mobility at a point in the tube is a function of its distance δ from the wall (but not of R), the expression for σ becomes

$$\sigma = \tfrac{1}{4}R\mu_\omega - \tfrac{1}{4}\int_{\mu_\omega}^{\mu_0}\frac{(R - \delta)^4}{R^3}d\mu$$

provided that μ reaches the constant value μ_0 before δ reaches R. On expansion this becomes

$$\sigma = \tfrac{1}{4}R\mu_\omega - \tfrac{1}{4}\int_{\mu_\omega}^{\mu_0}R\,d\mu + \int_{\mu_\omega}^{\mu_0}\delta\,d\mu - \tfrac{3}{2}\int_{\mu_\omega}^{\mu_0}\frac{\delta^2}{R}d\mu + \text{etc.}$$

$$= \tfrac{1}{4}\,\mathrm{R}\mu_0 + \int_{\mu_\omega}^{\mu_0} \delta d\mu - \frac{3}{2\mathrm{R}}\int_{\mu_\omega}^{\mu_0} \delta^2 d\mu + \text{etc.}$$

According to this expression the graph σ against R should be of the type shown by the full line in Fig. 2. At high values of R, the curve approaches an assymptote which has a slope $\frac{1}{4}\mu_0$ and which is represented by the broken line. The departure of the actual curve from this assymptote depends on the relative magnitudes of R and $\bar{\delta} = \int \delta^2 d\mu / \int \delta d\mu$. Although no sharp boundary has been assumed to exist between the bulk of the material and the modified layer, nevertheless $\bar{\delta}$ is a kind of effective thickness of the modified layer near the wall. The assymptote was drawn in by inspection to give a convenient intercept on the σ axis. The position of the curve was then calculated assuming a value for $\bar{\delta}$ equal to 8×10^{-3} cm. (being 20 per cent of the radius of the smallest tube used in the experimental work). The experimental points are for the Broadbalk field subsoil for which the full data were given in the first paper. It is evident that although a straight line could fairly be drawn through the points, as was done in the earlier paper, the experimental uncertainty is such that the possibility of a slight curvature is not ruled out. Actually a number of curves could be drawn each of which would pass sufficiently near the points so that the position of the assymptote is to some extent arbitrary.

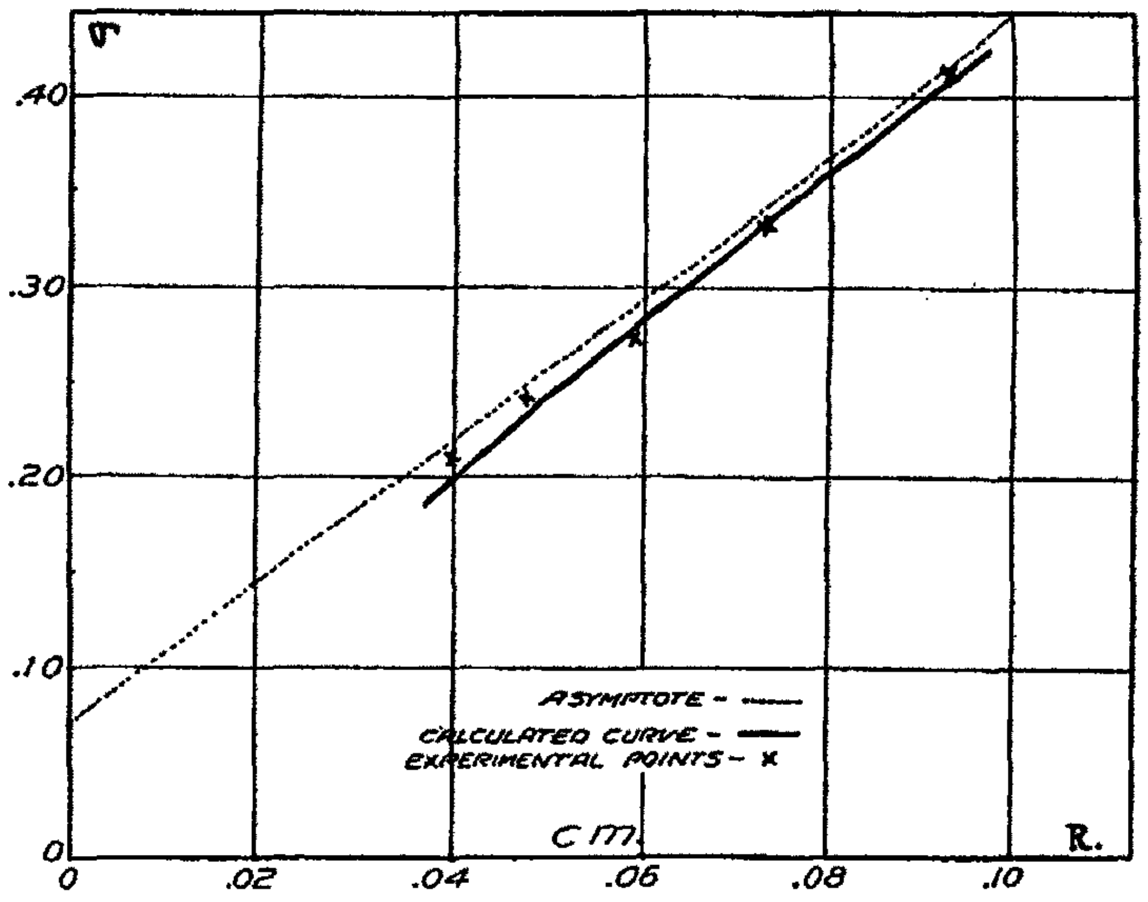

FIG. 2

Conclusions

An examination of all our data shows that no reliable estimate can be made of the curvature of the $\sigma - R$ graphs and thus no evaluation of $\bar{\delta}$ is yet possible. At the same time it is apparent that a value of $\bar{\delta}$ amounting to 8×10^{-3} cm. could escape detection owing to present experimental uncertainties.

Were it possible to draw the true assymptote, its intercept on the σ axis would, according to the forgoing analysis, give the value of $\int_{\mu_\omega}^{\mu_0} \delta d\mu$. The intercept made by the best straight line through the points, which we have called σ_0 is evidently somewhat less than this.

With regard to the value of μ_0, the mobility of the material in bulk, we may conclude that although a determination based on the slope of the best straight line drawn through experimental points on the $\sigma - R$ diagram is more accurate than any value calculated by the Bingham formula for a single tube, the value may still be a little too low owing to a finite thickness of the modified layer.

Summary

Evidence was obtained in an earlier paper that, when a clay or soil paste is forced through a narrow tube, a layer of material next to the wall has a consistency different from that of the bulk of the material. It was first assumed, for simplicity of treatment, that the modified layer is very thin compared with the radius of the tube; but later an attempt was made to remove this restriction.

A simpler and more complete treatment is now given, and it is concluded that a solid wall may modify the consistency of the material at an appreciable distance from it, but that the accuracy of the available data is insufficient to enable any reliable estimate to be made of the thickness of the modified layer. It is shown that, even when its effective thickness is as much as 20 per cent of the radius of the tube, the construction proposed in the first paper for determining the mobility of the material in bulk gives a close approximation to the true value. A full application of the extended treatment must await the development of more accurate experimental methods.

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THE APPLICATION OF X-RAYS TO CHEMICAL PROBLEMS*

BY MAURICE L. HUGGINS

The great importance of x-rays in medicine and surgery is well known to nearly everyone, and most of us are at least vaguely familiar with the use of x-rays in arriving at the arrangements of atoms and molecules in crystals. The many ways in which x-rays can be of service to chemists, however, are little realized. What seem to the writer the most important of these will be sketched in this paper.

Let us start by considering the usefulness of analyses of crystal structures. In the first place they furnish evidence regarding the structures of the component atoms, for it is these structures which determine the type of arrangement in the crystal. For instance, iodine crystals contain diatomic groups, each atom adjacent to but one other; selenium and tellurium crystals contain strings of atoms, each atom having two neighbors; arsenic, antimony and bismuth crystallize in puckered layers, in which each atom is equidistant from three others; while in the diamond structure each atom is surrounded by four others. These facts furnish strong evidence for the existence of 7, 6, 5, and 4 valence electrons, respectively, per atom in these various types and for the tendency of electronegative atoms to share pairs of valence electrons until each has a complete octet around its atomic kernel, as postulated by Lewis.[1]

Let me give a second example. By applying the proper corrections to a large number of intensities of x-ray reflection from a given crystal or crystal powder, taking the square root and using these structure factors (as they are called) as coefficients in a suitable Fourier Series, and then summing the series in the proper manner, it is possible in certain cases to obtain the time average distribution of scattering power (called, for short, the "electron density distribution") in a crystal.[2] Doing this for points along the centerline between adjacent atoms in the diamond, the curve shown in Fig. 1 has been obtained.[3] The small peak midway between the peaks representing the atoms of carbon is probably due to the electron pair serving as the bond holding the atoms together. In calcium fluoride we have found similar peaks, but before we can be sure of this interpretation it will be necessary to apply the method to a number of other crystals.

As a third example may be mentioned the evidence regarding atomic structures and interatomic forces which can be gained from a study of the relative distances between atoms in different structures. One can both compare the sizes of different kinds of atoms in similar environments and study the effect of different environments on the apparent size.

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* Presented at the Pacific Coast Intersectional Meeting of the American Chemical Society at Eugene, Oregon, June 19, 1930. Contribution from the Chemistry Department of Stanford University.

Crystal structure studies also give interesting and important information regarding the arrangement of atoms in molecules and ions. Only one example will be given here.

Tetramethylammonium chloroplatinate has a structure in which the $N(CH_3)_4^+$ and the $PtCl_6^{--}$ ions are distributed as are the F^- and Ca^{++} ions in the CaF_2 structure. (See Fig. 3 of the following paper.) Each nitrogen is surrounded tetrahedrally by four equivalent carbon atoms and each platinum octahedrally by six equivalent chlorine atoms. This and results with other ammonium derivatives studied with x-rays show very definitely that the fifth valence of nitrogen represents an electron transfer, producing a positive and a negative ion rather than a shared pair of electrons.[5] The equivalence of the six chlorine atoms around the platinum shows that a secondary valence bond, once formed, is not different from a primary valence bond. A consideration of this and many other similar structures shows most conclusively that secondary valence can be completely accounted for by assuming that both electrons of a secondary valence bond originate in the same atom, while the two electrons of a primary valence bond came from different atoms.[6]

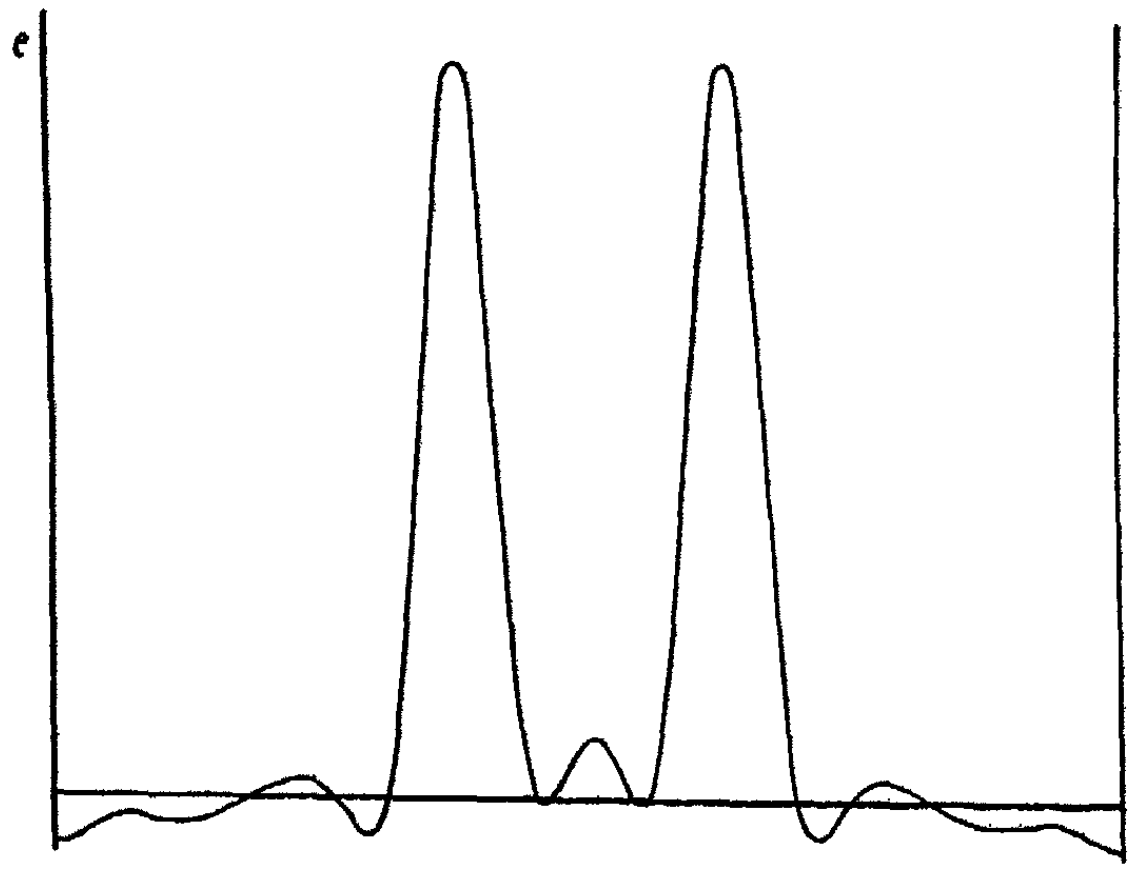

FIG. 1

The distribution of "electron density," as calculated from x-ray reflections, along the diagonal of the unit cube in the diamond. The large peaks show the positions of the carbon kernels.

By combining what is known about atoms and molecules from various other sources with the results of crystal structure analysis, one can now deduce certain basic principles governing the existence and stability of different types of arrangement, these principles accounting both for the empirical formulas of the compounds observed and for the actual arrangements of atoms in the structures.[7] Knowing these principles one can even predict with considerable success the structures of many crystals without experimental x-ray data.

The properties of solid matter depend to a large extent on just two things, —the structures of the component atoms and their arrangement in space. In the writer's opinion one of the most important aims of crystal structure analysis is the study of these relationships. Although little has been done along this line, much is possible. One can often relate brittleness and ready cleavage[8] to layer-like arrangements in which the distances between layers are relatively large and the forces between them weak, as indicated in Fig. 2, representing a two-dimensional crystal analogous to a crystal of arsenic, antimony or bismuth. Malleability and ductility can be attributed to the existence of "slip planes" (Fig. 3), the part of the crystal on one side of such a plane slipping readily with respect to the part on the other side.[9] The resulting arrangement, except on the surface, is exactly like that before the shift. Tensile strength and solubility can be readily interpreted, in simple cases at least, in terms of structure, especially when electrostatic potential theory is carefully applied. Optical properties (such as index of refraction) are also closely related to structure and the correlation has been studied in a few instances.

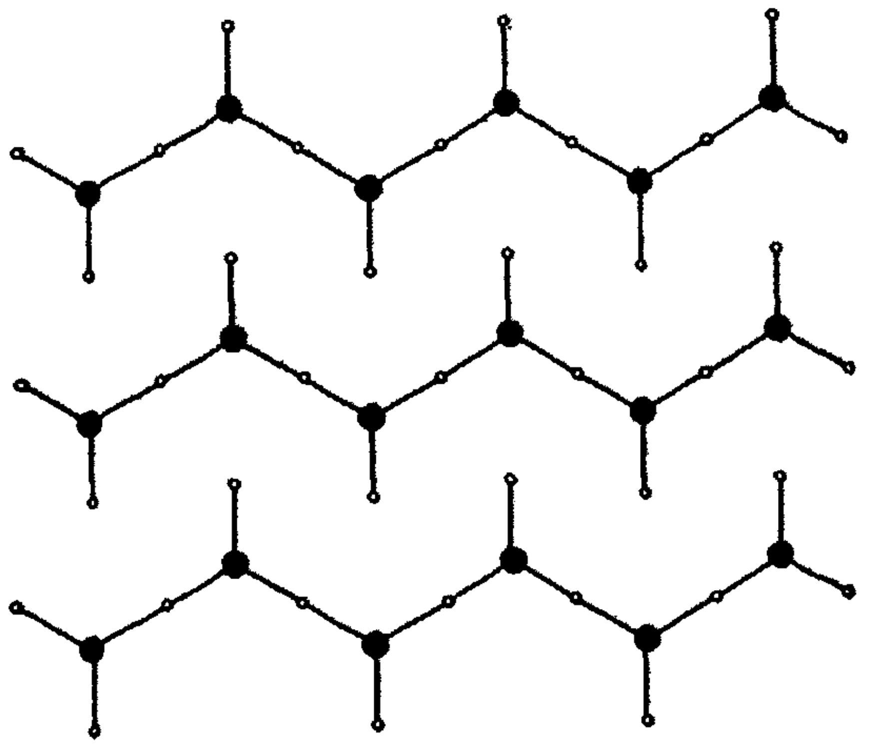

FIG. 2

A representation of a two-dimensional structure analogous to that of arsenic, antimony and bismuth.

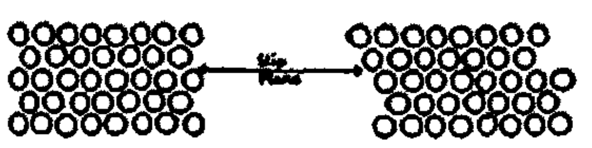

FIG. 3

Illustrating "slip planes." The interior of the crystal is the same after slipping as before.

The last few years have seen such a great development in methods and technique that it is now possible to study with success very complicated structures, provided one has the experimental facilities and knows the methods thoroughly. The theory of x-ray intensities is at last on a firm, satisfactory basis, making it possible to take full advantage of accurate, quantitative measurements. The results of the theory of space groups have been put in such form as to facilitate the analyses greatly; moreover, in cases in which a complete solution of the structure in terms of atomic positions is impossible, unimportant or too laborious, this theory frequently gives important information regarding the symmetry of the component atoms or molecules. Various graphical aids have been developed to simplify the process of interpreting the x-ray data. For example, the writer has made considerable use of a pivoted ruler, with which, from a rotating crystal photograph, one can readily make a projection and determine from that projection the size of the unit cell, the crystallographic indices of the reflections, and other useful information. Another rather new but extremely powerful aid to structure analysis is the method of calculating "electron densities" by Fourier Series summations,[2] already mentioned. A perhaps even more important development in crystal structure methods is the use, along with x-ray data, of principles and generalities derived from studies of known structures, considerations of potential theory, etc. For instance Professor W. L. Bragg has used the conception of close-packing of oxygens, considered as spheres, in working on the silicates; Pauling has made much use of coordination numbers (4 for silicon, 6 for aluminum, etc.) in similar work; while the writer has found the Lewis conception of valence very valuable in working out structures in which electronegative atoms are adjacent to each other. Considerations of the relative values of atomic dimensions, as obtained from other structures, are also frequently of great service.

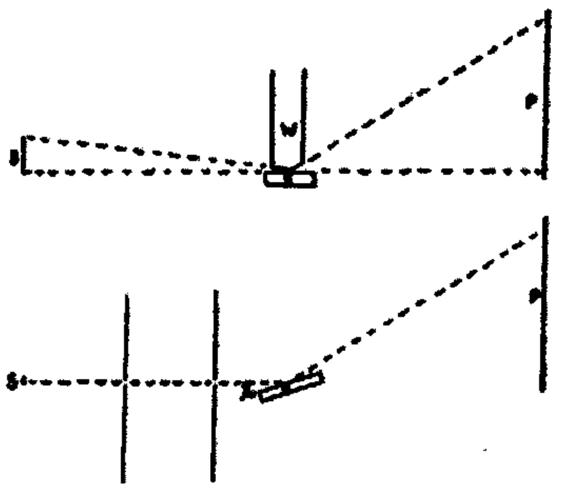

FIG. 4

Illustrating (upper) the Seemann wedge method and (lower) the oscillating crystal method of x-ray crystal photography. S = source of x-rays. C = crystal. W = wedge. P = photographic plate or film.

Before leaving the subject of crystal structures certain developments in apparatus should be noted. In particular, the progress made in high-vacuum technique makes feasible the use of demountable x-ray tubes with interchangeable targets and cathodes. The sample crystal or powder can now be placed within a few centimeters of a strong source of x-rays, with only a thin aluminum window and a slit system (if desired) between, thus shortening enormously the required time of exposure. By employing a "line focus" cathode giving an elongated focal spot, one can use a convergent beam, fixed crystal method (Fig. 4) due to Seemann[10] and obtain useful photographs, similar to oscillating crystal photographs, in a small fraction of a second. With this method the crystal gives many reflections at once during the whole time of exposure, while with the oscillating crystal method each reflection is taking place only a very small fraction of the time. An analogous method with powders, (Fig. 5) developed independently by Seemann[11] and by Bohlin,[12] cuts down the length of exposure required for that type of photograph to somewhat less than a minute, a great advance over the 6 to 48 hours required if sealed-up glass x-ray tubes and a narrow incident beam are used. This type of apparatus should also prove very useful in studying needle-like crystals and fibrous structures. In cutting down the time in this way one cuts down proportionately the difficulties due to a background of scattered radiation obscuring the fainter lines.

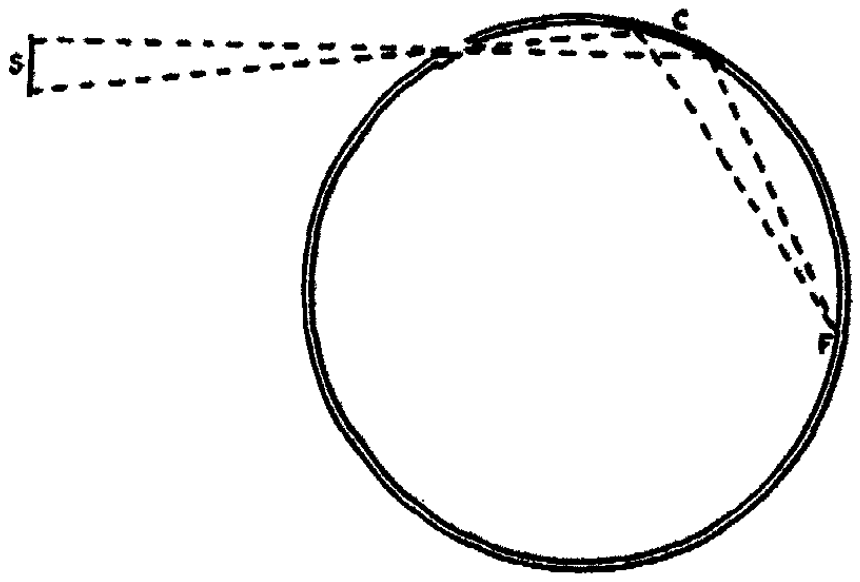

Fig. 5
Illustrating the Seemann-Bohlin method of x-ray powder photography. S = source of x-rays. C = crystal powder or metal foil. F = photographic film.

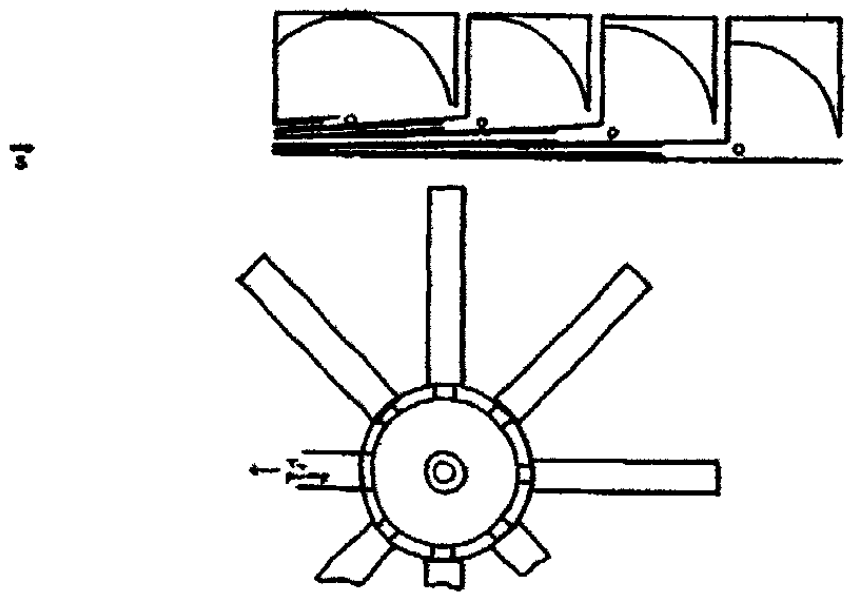

Fig. 6
(Upper) Cross-section of cassette for taking four x-ray photographs at once.
(Lower) Method of arranging seven such cassettes around a cylindrical x-ray tube, making it possible to take 28 photographs at once.

Another way of saving time is to use an x-ray tube and cameras designed to make possible a number of photographs at once. One scheme for doing this is diagrammatically shown in Fig. 6.

The interpretation of photographs obtained by reflection from a crystal or powder of the characterisitc radiation—of wave-lengths characteristic of the element composing the target—is complicated by the fact that this radiation is not strictly monochromatic. Besides the Kα_1 and Kα_2 lines (which are very close together and can usually be treated as a single line) there is a Kβ line of somewhat shorter wave-length,—much fainter, it is true, but still strong enough to increase considerably the difficulty of unambiguous interpretation of the photographs in some cases (See Fig. 7). A filter[13] containing an element of slightly lower atomic number than the element of the target will cut out most of the Kβ intensity without diminishing very greatly the intensity of the Kα lines. However, because there is still some of the β left to cause trouble by confusion with faint Kα reflections (often the most useful in certain parts of the structure analysis) and because of the diminution in intensity of the Kα lines, it is perhaps preferable merely to make identification of the Kβ lines certain by placing the filter over only half of the slit or half of the sample. The beta lines are then those half of which are very markedly stronger than the other half. Probably a still better way, because it cuts out both the beta radiation and the general or white radiation, is to reflect the x-rays first from a crystal of calcite or some other good reflector. By grinding the crystal so that the reflected rays just graze the surface a reflected beam practically as intense as a direct beam of the same cross-section can be obtained. (Fig. 8).

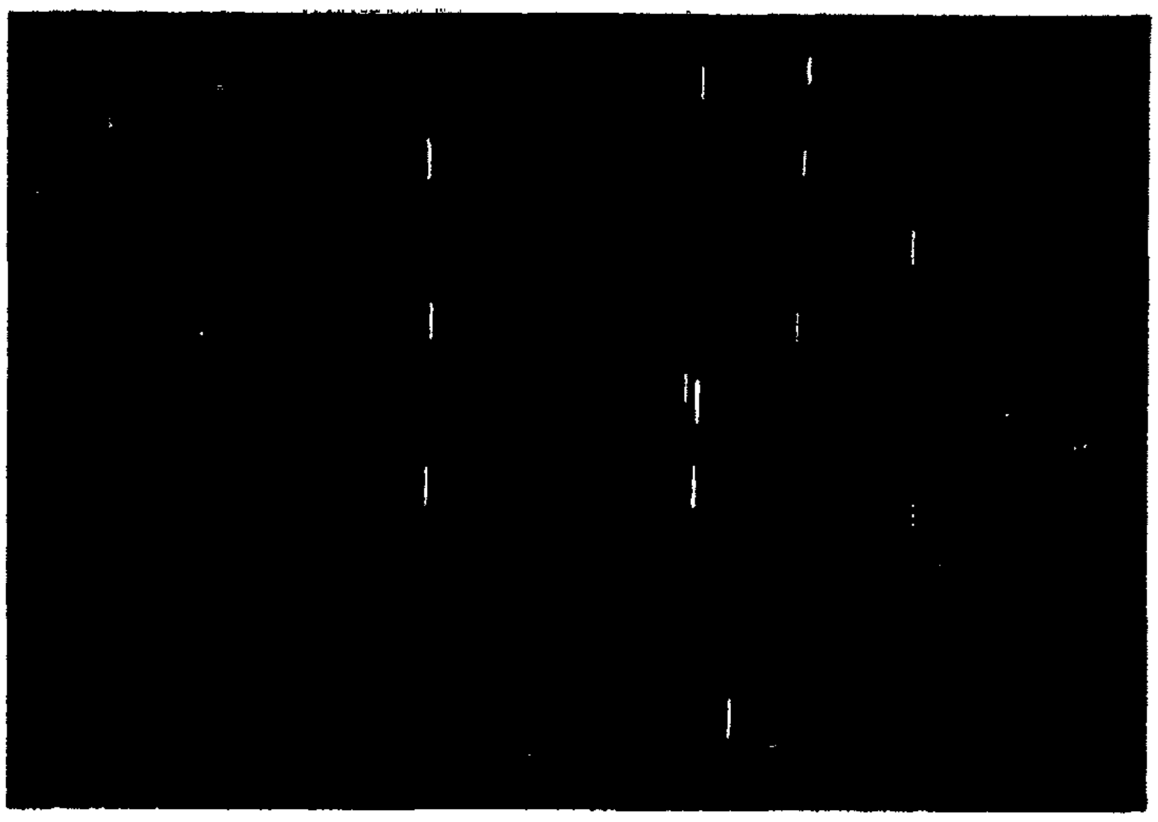

FIG. 7

An oscillating crystal x-ray photograph. Note that for nearly every strong reflection there is a fainter reflection slightly closer to the image of the undeflected beam. The former are the Kα, the latter the Kβ reflections from the same atomic planes in the crystal.

The assumption that the structure of the interior of a crystal extends in unmodified form to the crystal surfaces, although not strictly true, is at least approximately so and the nature and amount of the distortions can be estimated. One can then relate in a qualitative and semi-quantitative way the surface structure to rates of reaction, including the rates of growth and solution of the crystal, and to adsorption and catalysis. Experiments on these things, using crystals of known structure grown or cleaved under the proper conditions, would in the author's opinion be well worth doing, but so far as he knows none have yet been attempted. Another method of attack on surface problems is suggested by the fact that certain substances, such as urea, will, if dissolved in a solution from which sodium chloride is crystallizing, change the habit of the crystals, producing octahedra instead of cubes.[14] If methyl chloride, for instance, would do the same thing, one might reasonably assume the crystal surface to be a nearly monomolecular layer of methyl chloride molecules in a regular arrangement,—perhaps the same as the arrangement of chloride ions in a layer parallel to the surface—and all oriented in the same way,—with the methyl groups extending away from the crystal.[15] The use of such approximately known surfaces in catalysis experiments might to a large extent eliminate one of the usually unknown variables.

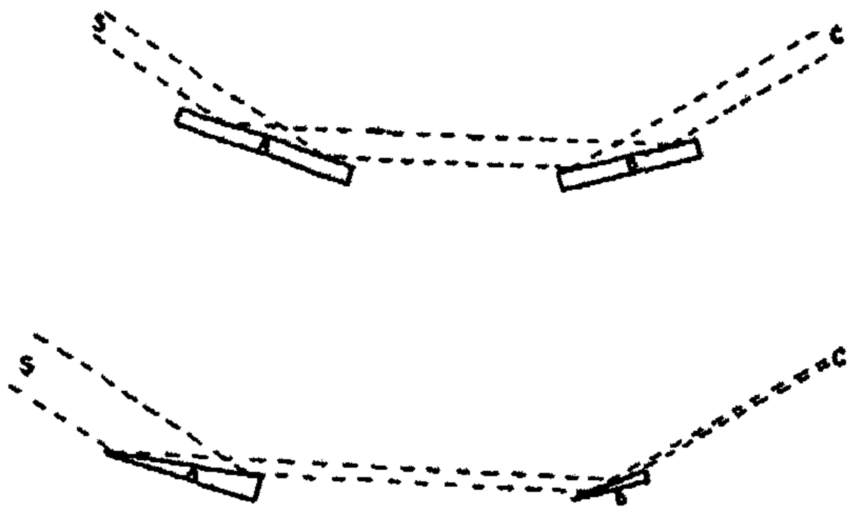

Fig. 8

Illustrating a method of obtaining a fairly intense monochromatic x-ray beam, using a broad incident beam reflected from a crystal ground so that the surface makes but a small angle with the reflected beam.

One very important field of x-ray research which has only begun to be explored[16] is that of studies of liquids and solutions. Diffraction effects are observed similar to those from crystal powders, but much more diffuse. There is some disagreement about the interpretation of the results obtained, but further experimental work will undoubtedly clear that up. What is most needed just now seems to be quantitative work using truly monochromatic x-rays and studying liquids or solutions of simple substances whose structures and interatomic distances are already quite accurately known from crystal structure or band spectra results. Studies of gases with x-rays[17] have been just sufficient to show that this is a most promising method of attack on some molecular structure problems. Complications due to intermolecular interference are negligible. The chief experimental difficulty is that of obtaining sufficient intensity, but there are ways of accomplishing that.

Other promising fields of x-ray work are studies of liquid crystals, in which there is probably only one- or two-dimensional regularity; studies of fibers, which may be considered as aggregates of needle-like crystals with their long axes approximately parallel but with random orientation otherwise; studies of particle size, from the width of spectrum lines; studies of the effect of mechanical and heat treatment or impurities on type of structure, distortions, particle size, etc. In this connection, phase rule studies using x-rays seem to give more definite results than other methods and with suitable refinements of technique they can be carried out with greater speed. With suitable equipment x-ray studies at low and high temperatures can readily be made and for such problems as those just mentioned are of inestimable value.

The study of photochemical reactions produced by x-rays might increase considerably our knowledge of such fundamental processes.[18] A monochromatic source of fairly high intensity and a method for measuring the absolute amount of energy absorbed are the chief requirements, and these can be met without much trouble.

The use of x-rays for qualitative and quantitative analysis will next be considered. One can analyze either for the chemical elememts present or for particular compounds. Analyzing for compounds is usually done by obtaining x-ray photographs of powders just as if one were to attempt a structure analysis. Each crystalline species,—compound or free element,—is identified by means of a characteristic set of lines on the photograph, a mixture giving the lines corresponding to all the types of crystal present. It is usually necessary to have a similar photograph of a pure sample of each compound (or free element) being looked for. The presence of a set of lines in the correct relative positions and with the correct relative intensities is practically proof of the presence of the corresponding compound, but the method as at present carried out is not very sensitive to small amounts of impurities; nor is more than a rough quantitative analysis possible without comparison photographs of knowns of similar composition. By using Seemann-Bohlin focussing cameras or by designing camera and x-ray tube so as to take a number of photographs at once, with the samples as close as possible to the source of x-rays, the time element can be largely eliminated. Another difficulty in the case of complex mixtures is removed if one either labels or eliminates entirely the $K\beta$ radiation by one of the methods which have been suggested, thus effectively halving the complexity of the photograph being studied.

In analyzing for elements[19] one can place the sample to be studied either (a) on the target of the x-ray tube, studying the primary emission spectra, (b) near the cathode within the tube, studying the secondary or fluorescent emission spectra or outside of the tube, studying either (c) the secondary emission spectra or (d) the absorption spectra. The most sensitive method is the first, 1 part in 10^6 or 10^7 being detectable in favorable cases.[20] It has the disadvantages that a volatile sample cannot be used and that quantitative estimates are quite unreliable, except in certain specific cases as when the spectra of metals of nearly equal atomic number are excited under equivalent conditions.[21] Both first and second methods are unsuited for rapid analyses, as the x-ray tube must be taken apart, breaking the vacuum, to change the sample. The second and third methods require exposures of considerable duration, for the fluorescent radiation is relatively weak; nor are the results quantitatively very accurate, (although more accurate than those obtained by the first method[22]), unless one takes blanks at the same time or under identical conditions with knowns of similar composition. The last method mentioned[23] seems to the author most favorable for rapid, quantitative analysis. For many analyses one could use a fixed crystal, convergent beam method, cutting the exposure time per analysis probably to a minute or two. What are measured are the different positions of the absorption limits in the spectra, to get the kinds of elements present in the sample, and the relative intensities on the two sides of each absorption limit, to get the amount of each element in the path of the beam. Densitometer measurements of photographs can be used, or, what would perhaps be a more accurate method, the x-ray intensity differences could be measured with the aid of an ionization chamber-electrometer outfit. One might expect to get accuracies of a fraction of a per cent in this way, using suitable blanks and comparison standards. Without using a vacuum spectrograph this method is suitable for all elements having atomic numbers greater than about 24 (chromium) or 25 (manganese). With vacuum apparatus one can analyze for somewhat lighter elements, at least down to silicon, atomic number 14. There seems to be little hope at present of easy, accurate x-ray analysis for such light elements as carbon, nitrogen or oxygen, but x-ray methods bid fair to replace all others before long in analysis for the heavier elements.

The wave-length and so the position in the spectrum of the x-ray absorption limit of an element placed in the path of a beam of x-rays depends but little on the state of chemical combination of that element, for the wave-length is determined by the energy necessary to remove an electron from one of the inner electron shells in the atom and this is little affected by the number or arrangement of surrounding atoms. Studies with a vacuum spectrograph of the K absorption limits for such elements as phosphorus, sulfur or chlorine, however, show slight differences for different compounds.[24] For instance, all chlorides have practically the same limit; all chlorates have nearly the same limit (but a different one from that for chlorides); perchlorates are still different, etc. If one could increase the resolving power somewhat it would be possible to measure significant differences between different chlorine compounds within each class, thus obtaining an experimental measure of the electropositiveness or electronegativeness of the atom attached to the chlorine. Using organic compounds one could thus classify various radicals according to their pull on the electron pair bonding them to chlorine,—a most useful series in organic chemistry. Also one could take an unknown and determine not only whether or not it contains chlorine but the nature of the atom or group to which the chlorine is attached. Similarly for sulfur and phosphorus and some other elements. The effect of change of state, solvation and adsorption on the wave-lengths would also make most interesting studies.

Greater resolving power without loss of intensity can be obtained by reflecting the x-rays from two crystals,[25] set up as shown in Fig. 9. A broad incident beam is used. Crystal A remains fixed in position while crystal B is rotated, different positions of B sending different wave-lengths into an ionization chamber at C. Only one wave-length will be reflected by both crystals in a given pair of positions. Others, if reflected by A, will not strike B at the proper angle for reflection. Ross has suggested using a *horizontal* slit at S and putting a photographic plate at C. With both crystals fixed in position, different *heights* at C would then represent very slightly different wave-lengths. Such a scheme could be made more sensitive to weak radiations by grinding the crystals so as to concentrate all of the doubly reflected rays into a narrow beam. An arrangement of this sort in vacuum would greatly improve the sensitivity of absorption edge measurements and in all probability would make possible such distinctions between different compounds as mentioned above.

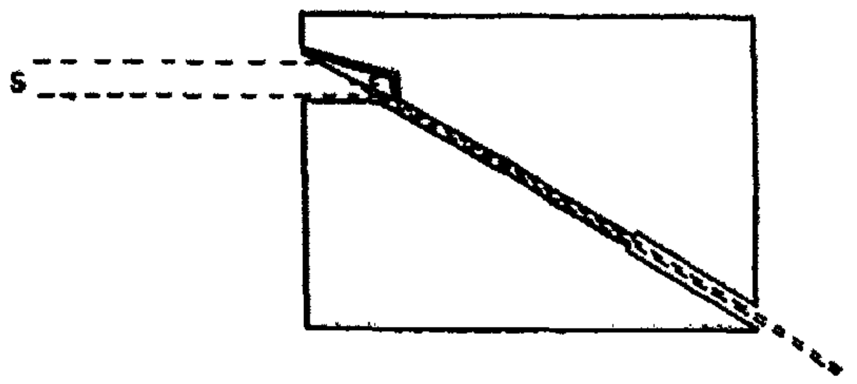

Fig. 9
Illustrating double crystal reflection, with and without the crystal surfaces ground nearly parallel to the reflected beam.

In the foregoing, reference has been made chiefly to photographic methods of obtaining data, but it should be mentioned that with good equipment and technique it is possible to observe many diffraction effects *visually* on a fluorescent screen. When the best conditions have been found, it is quite possible that visual observations will prove of great value, for instance in analyzing for elements of compounds and in following structural changes accompanying thermal or mechanical treatment.

In conclusion the writer wishes to emphasize the fact that although enough has been done along the various lines mentioned to indicate in a general way what are the possibilities and limitations of this new scientific tool, the best design of apparatus for each purpose, the best conditions of operation, etc., will be known only after more research.

Stanford University.

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A CONDUCTIVITY METHOD FOR THE ANALYSIS OF BINARY MIXTURES OF THE VOLATILE FATTY ACIDS*

BY ELLIS I. FULMER, E. E. MOORE AND R. L. FOSTER

Practically all of the methods for the analysis of mixtures of the volatile fatty acids are based upon separation by distillation, that is they are modifications of the original Duclaux procedure. The various methods for the analysis of these compounds were reviewed by Moore and Fulmer[1] who proposed a method for the analysis of mixtures of formic and acetic acids based upon a conductometric titration with ammonium hydroxide. Werkman[2] has developed a procedure based upon the distribution of the acids between water and an immiscible solvent.

In the paper here presented are given data leading to a simple conductivity procedure for the analysis of binary mixtures of the volatile fatty acids a preliminary report of which was made by Moore, Fulmer and Foster.[3]

Procedure

The equipment used consisted of a Vreeland Oscillator, Kohlrausch bridge and telephone receiver with standard adjuncts. The apparatus was appropriately shielded. The Washburn pipette type of cell was used. The cell constant was determined by the use of KCl solutions at the same ranges of specific conductivities as the solutions to be tested. The cell constant was likewise determined for the various bridge readings, a necessary precaution as emphasized by Wark.[4] The conductivities were measured at 25°.

The acids were the purest obtainable on the market and were redistilled, the middle fractions only being used in the preparation of the standard solutions.[5,6]

Experimental Results

The data for the specific conductivities for 0.0100 N solutions of formic-acetic, formic-propionic, formic-n-butyric, and acetic-propionic acids are given in Table I.

Discussion of Results

The specific conductivity of the mixtures is obviously not a linear function of the percentage composition. However, the antilogarithm of $10^3 \times$ specific conductivity is a linear function, within reasonable limits for analytical purposes, of the percentage composition, or if,

S'_{AB} = Antilogarithm of $10^3 \times$ specific conductivity of mixture of acids *A* and *B* at a given normality.

S'_{A} = Antilogarithm of $10^3 \times$ specific conductivity of acid *A* at the same normality as the mixture.

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* A Contribution from the Laboratory of Biophysical Chemistry, Iowa State College, Ames, Iowa.

Table I

Specific Conductivities of Binary Mixtures of Formic, Acetic, Propionic and Butyric Acids at 0.01 N.

C_A = % of first acid in mixture; S_{AB} = specific conductivity × 10^3;
S' = antilogs

C_A	Formic-Acetic C_A (calc.)	 % diff.	 S_{AB}	 S'	Formic-Propionic C_A (calc.)	 % diff.	 S_{AB}	 S'
0	0.01	+0.01	0.1579	1.4380	−0.05	−0.05	0.1366	1.3698
20.00	19.52	−0.48	0.2477	1.7688	18.91	−1.09	0.2321	1.7067
33.33	—	—	—	—	—	—	—	—
40.00	40.27	+0.27	0.3625	2.1028	40.39	+0.39	0.3198	2.0884
50.00	—	—	—	—	—	—	—	—
60.00	60.70	+0.70	0.3923	2.4673	61.77	+1.77	0.3859	2.4683
66.67	—	—	—	—	—	—	—	—
80.00	79.67	−0.33	0.4456	2.7891	79.71	−0.29	0.4437	2.7902
100.00	99.84	−0.16	0.4960	3.1311	99.08	−0.92	0.4960	3.1311

Formic-Acetic:

$$S' = 0.01696\, C_A + 1.4378$$

$$C_A = \frac{S'_{AB} - 1.4378}{3.1338 - 1.4378} \times 100$$

Av. % diff. = +0.0017

Formic-Propionic:

$$S' = 0.01776\, C_A + 1.3707$$

$$C_A = \frac{S'_{AB} - 1.3707}{3.1474 - 1.3707} \times 100$$

Av. % diff. = −0.05

TABLE I (continued)

C_A	Formic-Butyric				Acetic-Propionic			
	C_A (calc.)	% diff.	S_{AB}	S'	C_A (calc.)	% diff.	S_{AB}	S'
0	−0.90	−0.90	0.1447	1.3985	+1.15	+1.15	0.1366	1.3698
20.00	—	—	—	—	19.04	−0.96	0.1405	1.3822
33.33	33.42	+0.09	0.2971	1.9880	—	—	—	—
40.00	—	—	—	—	40.11	+0.11	0.1451	1.3968
50.00	49.67	−0.33	0.3556	2.2684	—	—	—	—
60.00	—	—	—	—	60.89	−0.89	0.1496	1.4112
66.67	66.60	−0.07	0.4086	2.5604	—	—	—	—
80.00	—	—	—	—	79.53	−0.47	0.1539	1.4254
100.00	99.91	−0.09	0.4960	3.1311	99.56	−0.44	0.1579	1.4380

Formic-Butyric:

$$S' = 0.01725\,C_A + 1.4114$$

$$C_A = \frac{S'_{AB} - 1.4114}{3.1366 - 1.4114} \times 100$$

Av. % diff. = −0.256

Acetic-Propionic:

$$S' = 0.0006985\,C_A + 1.36906$$

$$C_A = \frac{S'_{AB} - 1.36906}{1.4383 - 1.36906} \times 100$$

Av. % diff. = +0.047

S'_B = Antilogarithm of $10^3 \times$ specific conductivity of acid *B* at the same normality as the mixture.

C_A and C_B = percent of each acid present at the given normality.

$C_A + C_B = 100$

(1) $S'_{AB} = mC_A + S'_B$

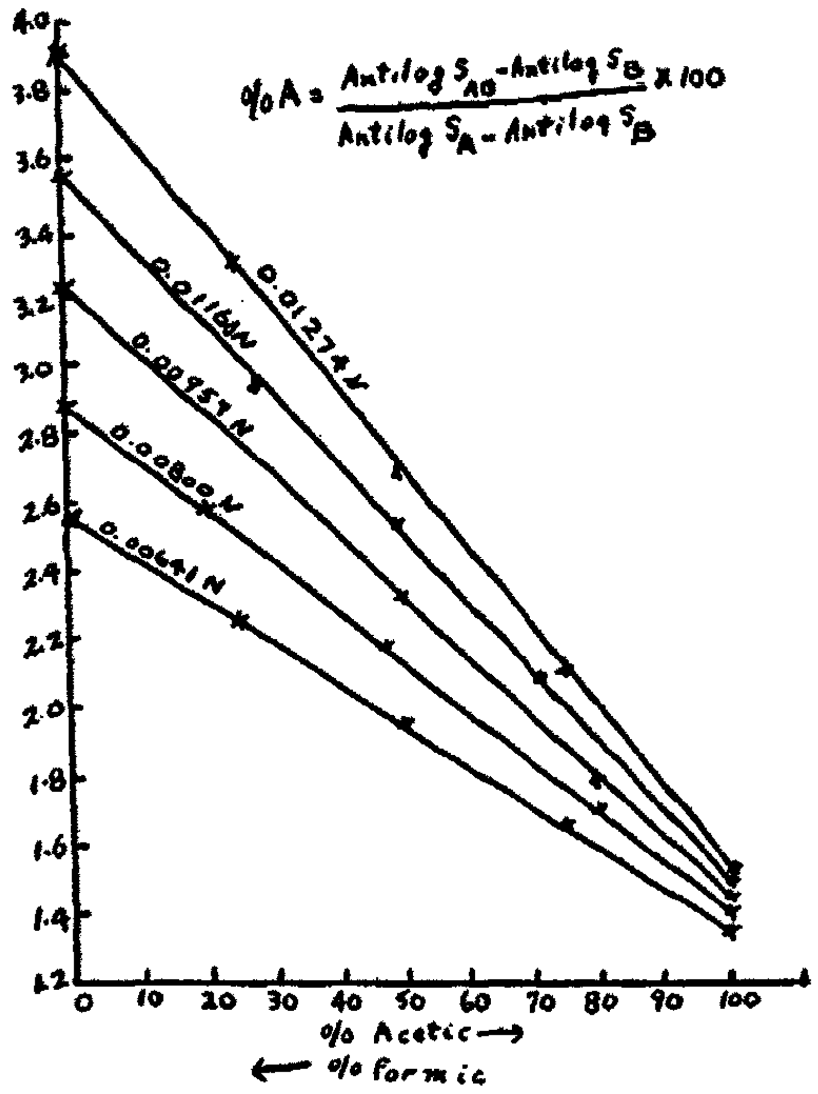

Fig. 1

and

(2) $$S'_{AB} = \frac{(S'_A - S'_B)\, C_A}{100} + S'_B$$

and

(3) $$C_A = \frac{S'_{AB} - S'_B}{S'_A - S'_B} \times 100$$

In the table the equations for the various mixtures are given as calculated by the method of least squares permitting the establishment of standard values for S'_A and S'_B. Calculated values are also given for C_A for each mixture. The linear relation between the antilogarithm of $10^3 \times$ specific conductivity and the percentage composition was found to hold for mixtures of formic and acetic acids for the following normalities, 0.00641 N, 0.00800 N, 0.00959 N, 0.0116 N and 0.0127 N. These data are graphed on Fig. 1.

Summary

It has been shown that the antilogarithms of $10^4 \times$ specific conductivities of binary mixtures of formic, acetic, propionic, and n-butyric acids are a linear function of the percent composition of the solutions. The above relation is proposed as a basis for the analysis of such binary mixtures.

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THE SYSTEM P_2O_5–CaO–H_2O AND THE RECRYSTALLIZATION OF MONOCALCIUM PHOSPHATE*

BY NORMAN ASHWELL CLARK

Primary or monocalcium phosphate is employed to a considerable extent in nutrient media; it is of general use for the growth of green plants in inorganic solutions[1] and is specified for solutions numbers 3 and 4 in the plan for cooperative research of the National Research Council.[2] The salt is frequently referred to as the soluble calcium phosphate, and is of interest from the standpoint of soils in that it is the chief component of the commercial 'acid phosphate' fertilizers. The behavior of the salt in solution and its purity when used in experiments are therefore of more than usual importance.

Small quantities of water readily decompose monocalcium phosphate. Stoklasa[3] gives one part of salt to 200 parts of water for solution without decomposition. He states further that the pure salt decomposes very slowly in a closed vessel, setting free H_3PO_4. Cameron and Seidell[4] also found a considerable amount of free acid in a sample of Kahlbaum's manufacture, and they pointed out that it is impracticable to obtain the monocalcium phosphate without an excess of acid.

Because of this decomposition by water, it is necessary to recrystallize from acid solution in order to purify the salt, but the optimum conditions for precipitation set out in the literature are indefinite. Abegg's Handbuch[5] states that the monocalcium phosphate crystallizes by evaporation of strongly acid solutions of the other calcium phosphates. Stoklasa used 31 per cent H_3PO_4 and dicalcium phosphate to obtain the primary salt. Pointet[6] investigated the commercial monocalcium phosphate and found a very large excess of acid in the amorphous salt. He suggested pressing out some of the acid or adding dibasic calcium phosphate to the solution to produce crystallization—an indication that too great a concentration of acid might prevent precipitation of the salt. Causse[7] reported that if he added di- or tricalcium phosphate with more than 30 grams of H_3PO_4 in 100 cc. the mono salt precipitated. Prunier and Jouve[8] placed a mixture of phosphoric acid and dicalcium phosphate in molecular proportions in a quantity of water equal to the weight of the two (approximately 30 per cent acid) and found that by

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* Contribution from the Department of Chemistry, Iowa State College.

[1] Clark: J. Phys. Chem., **29**, 935 (1925).

[2] Livingston: Plan for cooperative research. Johns Hopkins Univ. (1919).

[3] Listy Chem. **13**, Abstracted in J. Chem. Soc., **58**, 695 (1890).

[4] J. Am. Chem. Soc., **26**, 1454 (1904).

[5] "Handbuch anorg. Chemie", 2 II, 151 (1905).

[6] Bull., (3) **5**, 254 (1891).

[7] Compt. rend., **114**, 414 (1892).

[8] J. Pharm. Chim., (6) **10**, 529 (1899).

rapid evaporation they obtained dicalcium phosphate or a mixture of this with mono phosphate, but by very slow evaporation the mono salt precipitated.

Cameron and Seidell in 1904[4] and in 1905[9] made the first systematic attempt to clear up the difficulties. They determined the isotherm at 25 C. for the system P_2O_5-CaO-H_2O and at a concentration of 77 grams CaO and 317 grams P_2O_5 per liter found both the solid phases, monocalcium phosphate and dicalcium phosphate, in equilibrium with the solution. They also noted that there was a region of meta-stable equilibrium for the monocalcium phosphate where that salt would exist in contact with a solution containing less P_2O_5 than required by the triple point, until agitation, standing or rise of temperature caused the precipitation of the dicalcium phosphate.

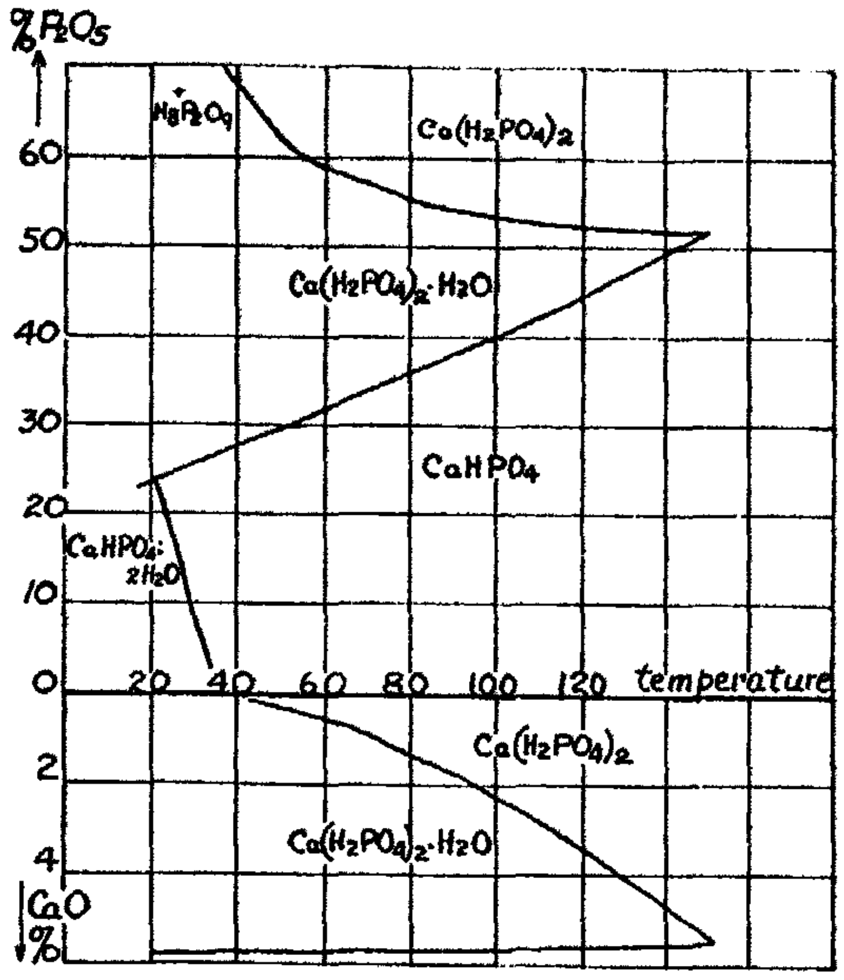

FIG. 1

Projection of part of space model of the system CaO-P_2O_5-H_2O. (After Bassett).

H. Bassett in 1908[10] made an extensive study of the system CaO-P_2O_5-H_2O in order to get the main points of the space model. He determined the isotherms at 50.7°, 40° and 25°, and fixed a number of the quintuple points. Fig. 1 is a projection of part of this model and shows the area for $Ca(H_2PO_4)_2 \cdot H_2O$.

When these isotherms are plotted with an amount of water which is constant over the diagram, it is possible to draw further conclusions as to the

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[9] J. Am. Chem. Soc., 27, 1503 (1905).

[10] Z. anorg. Chem., 59, 1 (1908).

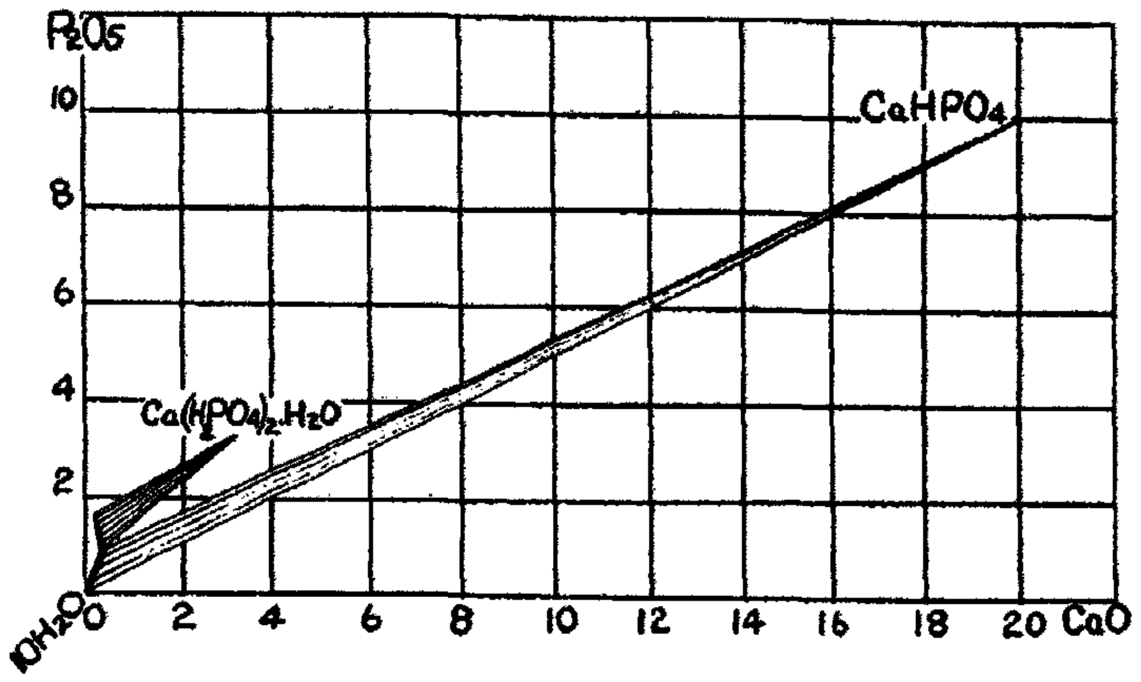

FIG. 2
Isotherm at 100° showing position of $CaHPO_4$ and $Ca(H_2PO_4)_2.H_2O$. Quantities in moles. $10H_2O$ over diagram.

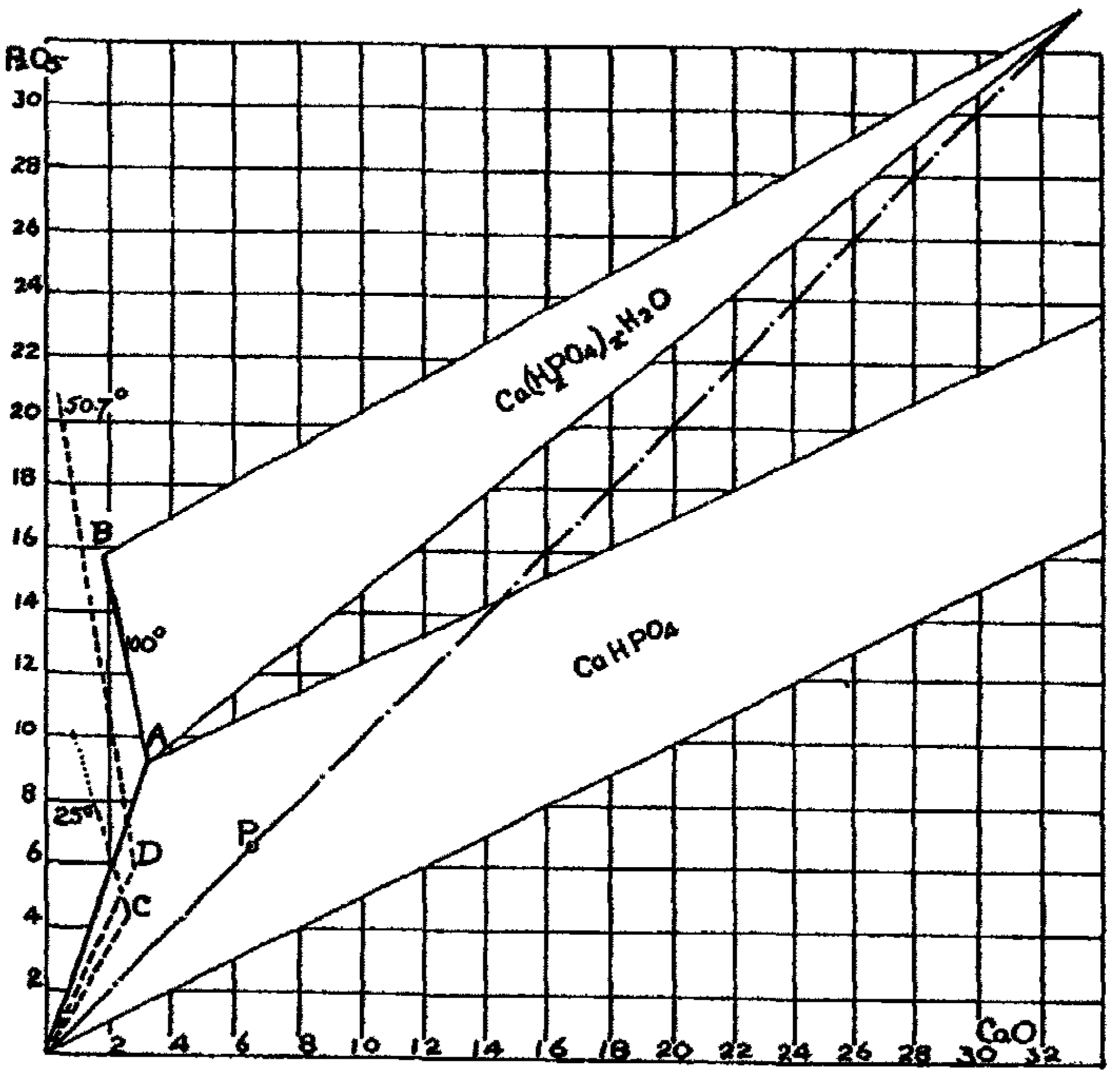

FIG. 3
Isotherms at 100°, 50.7°, and 25°. Quantities in moles. 100 H_2O over diagram.

behavior of the system. Fig. 2 shows the approximate position of the isotherm at 100°, the position of the monocalcium phosphate with one H_2O and that of the anhydrous dicalcium phosphate, and has 10 moles of water over the diagram. The 'tie-lines' join the salts to the isotherm. Fig. 3 gives the same points but is on a larger scale with 100 moles of water. The dotted lines show the isotherms for 50.7° and 25°. On these scales the curves can be represented as straight lines which would intersect at the origin if no other phases existed.

An examination of these figures indicates the limits of the triangles within which there is equilibrium between one of the solid phases and a solution on the isotherm. For systems at 100° a solution within the triangle bounded by that isotherm and $Ca(H_2PO_4)_2.H_2O$ is unstable and will precipitate that salt, while solutions within the triangle bounded by the isotherm and $CaHPO_4$ will precipitate the dicalcium phosphate. It will be seen that both curves lie outside the triangle formed by H_2O at the origin and the points marked $Ca(H_2PO_4)_2.H_2O$ and $CaHPO_4$ (Fig. 2); that is, the solution at A (Fig. 3) is incongruent[11] and with $CaHPO_4$ can form water and $Ca(H_2PO_4)_2.H_2O$, or if A is evaporated at 100° in the presence of the dicalcium phosphate, that salt will dissolve and the monocalcium phosphate will precipitate, while the composition of the solution remains as at A until all the dicalcium salt has disappeared. If no dicalcium phosphate is present and the solution represented at A is evaporated at 100°, monocalcium salt precipitates and the solution increases in P_2O_5 content, the successive compositions being represented by the points on the isotherm. At B both the hydrated and dehydrated monocalcium phosphates are in equilibrium with the solution.

A solution of composition represented by the point A was made up of 25.2 per cent of the recrystallized monocalcium phosphate, 35.6 per cent of H_3PO_4 crystals prepared from the acid solution by the method outlined by Ross[12] and by Clark[13] centrifuged in glass containers and dried over P_2O_5, and 39.2 per cent of water. The clear solution was evaporated in an oven at 100° with the beaker almost covered. This caused the crystals to be formed under the liquid; if evaporated without the cover the crystals form on the surface as a skin and may fall or may need to be pushed to the bottom. After crystallization has proceeded for some time the liquid was poured off into weighing bottles and analysed.

The method adopted for analysis of calcium was that studied by McCrudden[14] and recommended for use when phosphorus is present. The calcium was weighed as CaO. For phosphorus, the Bureau of Standards 'Standard' method of double precipitation with magnesia mixture[15] was found excellent. The analyses reported are the average of two closely agreeing determinations.

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[11] Meyerhoffer: Ber., 30, 1804 (1897).

[12] Ind. Eng. Chem., 17, 1081 (1925).

[13] Proc. First Int. Cong. Soil Sci., 3, 300 (1927).

[14] J. Biol. Chem., 10, 187 (1911).

[15] Epperson: J. Am. Chem. Soc., 50, 321 (1928).

The composition of the solution after separation from the crystals was 43.12 per cent P_2O_5 and 5.12 per cent CaO. This is 10.5 moles P_2O_5, 3.2 CaO and 100 H_2O, and the point falls almost on the isotherm as drawn.

A solution given by the point D is in equilibrium with both the mono and dicalcium salts at 50.7°. If evaporated at 50.7° $Ca(H_2PO_4)_2 . H_2O$ is precipitated and the solutions obtained are represented by the dotted isotherm (Fig. 3). If evaporated at a higher temperature (e.g. 100°) it can be seen from the figure that the solution at D will precipitate the dicalcium salt at first and its concentration will reach the point A. On the other hand if the solution at D is cooled, it falls within the mono salt area and $Ca(H_2PO_4)_2 . H_2O$ is precipitated.

A solution was made up of 23.5 per cent of recrystallized monocalcium phosphate, 23.7 per cent H_3PO_4 crystals and 52.8 per cent water, which is approximately the concentration at the point D. It was then evaporated at 50°-51° while slowly stirring. Crystallization started in 45 minutes and after 7 hours a sample was filtered through a jacketed funnel and analysed after rejecting the first few cc of the filtrate. The liquid contained 5.00 per cent CaO and 35.4 per cent P_2O_5 which corresponds to 2.7 moles CaO, 7.6 moles P_2O_5 and 100 H_2O, a point which is almost on the isotherm. After further evaporation the solution was again analysed and found to contain 2.5 CaO, 8.3 P_2O_5 and 100 H_2O, which falls on the curve.

The point P represents 30 per cent P_2O_5 and 12 per cent CaO. This is the composition of one of the mixtures of Prunier and Jouve[8], and it is clear that at 100° there is equilibrium in the system between the dicalcium solid phase and a solution on the isotherm. We should expect, therefore, that boiling, violent shaking or long standing would cause the dicalcium phosphate to precipitate —as Prunier and Jouve found actually occurred through quick evaporation. Very slow evaporation, however, gave them the monocalcium phosphate. This salt would be formed as soon as the composition of the solution reached A, where any dicalcium phosphate which had solidified would tend to dissolve and the monocalcium to precipitate. The farther the evaporation was carried the more monocalcium phosphate would result. As the point P is on the line joining the origin to the $Ca(H_2PO_4)_2 . H_2O$, there would always be a trace of $CaHPO_4$ present. When the point giving the composition used falls to the left of the dotted line, theoretically all the dicalcium phosphate should dissolve, but practically it is almost impossible to obtain this because of the slowness with which the dicalcium phosphate reacts in a matrix of primary crystals. This will be referred to later.

A solution with composition represented at C (Fig. 3), when evaporated at 25° produces the mono salt, while the solution increases in concentration of the P_2O_5. Birnbaum[16] obtained crystals without raising the temperature by drying over concentrated sulphuric acid. Neither Cameron nor Bassett determined exactly how far the 25° isotherm should be carried, and that

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[16] Z. Chem., 1871; Gmelin-Kraut: "Handbuch", 2 II, 302 (1909).

corner of the space model has yet to be investigated, but it can be seen from Fig. 1 that the solution does not come into equilibrium with the anhydrous monophosphate as it would if evaporated at 100°.

A solution of the composition at C, when tested by evaporation over concentrated sulphuric crystallized very slowly—after some three weeks over the acid at room temperature (near 25°) the composition of the solution centrifuged from the crystals was 1.5 moles CaO, 7.8 P_2O_5 and 100 H_2O, which lies near the 25° curve. A series was also run at room temperature over concentrated sulphuric with from 33 to 40 grams of the salt per 100 cc of acid, 15 to 18 per cent H_3PO_4, giving concentrations near the point C; ten days elapsed before crystallization commenced and for some weeks the crystallization continued. The time required might be somewhat shortened but as a method of recrystallization it is very slow.

A quicker way to purify the monocalcium phosphate is to make up a solution at 100°, evaporate at that temperature or slightly below until crystallization is well started, (it is advisable to prevent the crystals forming a thick layer on the surface), then to cool to 50° and to centrifuge; the amount of acid originally present in the solution may vary within limits, but it will be seen from the curves that there is no point in making the acid concentration very small as it will increase to A or beyond. The composition of the original system must not fall to the right of the line joining the origin to $Ca(H_2PO_4)_2.H_2O$ (Fig. 3), as the system would then precipitate more $CaHPO_4$ than would dissolve; the solution at A would dry up and leave a mixture of the two salts.

A similar mixture of the two salts may be formed if the composition of the system to be evaporated falls to the left of the line joining the origin to $Ca(H_2PO_4)_2.H_2O$ but within the $CaHPO_4$ triangle. Here the dicalcium salt precipitates first, but should dissolve when the solution concentration reaches A and pure monophosphate result. Even with regular stirring it seems to be difficult to remove all the dicalcium salt, and if the solution is left to evaporate undisturbed, most of the dicalcium fails to dissolve and the two forms of crystals will exist together for a long period of time.

This slowness in attaining equilibrium was commented upon both by Cameron and Seidell and by Bassett. The theoretical percentages of P_2O_5 and CaO in the monocalcium phosphate are 56.35 and 22.22; Bassett[10] reported usually a high CaO content, a condition he attributed to the presence of small amounts of $CaHPO_4$ in the crystals. In this laboratory, systems with a concentration near point C, even when evaporated with stirring at 100° have shown this high CaO content, which tends to confirm Bassett's explanation, although no traces of the dicalcium salt could be seen.

Solutions with concentrations which fall within the triangle made by the origin and the isotherm AB, when evaporated at 100°, will be clear of the dicalcium phosphate and will precipitate the primary salt; for recrystallization, therefore, it is better to have the system fall within these limits. Crystals produced in this way and analysed after centrifuging did not show a high CaO content; the ratio of P_2O_5 to CaO was slightly higher than the theoretical. This increase in the P_2O_5 may have been due to the presence of some of the acid from which the crystals were not completely separated. Similarly, crystals obtained at 25°, by evaporation over sulphuric acid, showed a ratio of P_2O_5 to CaO a fraction higher than theoretical but lower than those from evaporation at 100°, and as these were produced in a lower concentration of acid, this smaller ratio would tend to support that conclusion.

Two precautions are necessary when crystals are obtained by evaporating solutions whose composition falls within the triangle formed by the origin and the isotherm AB. If the air above the solution is much cooler than the solution itself, crystals form on the surface as a skin and may persist there giving rise to local conditions which cause white spots to appear. This can be prevented by pushing the crystals below the surface or by evaporating in an oven at 100°. Secondly, if the solution is suddenly chilled when it has a concentration near the 100° isotherm, a voluminous white precipitate forms which is exceedingly soluble in water and very difficult to separate from the solution. Slow cooling to 50° prevents the appearance of this precipitate. It is a simple matter to make up a solution represented by the point A, or with slightly more water and acid, evaporate until 10 to 20 per cent of the total weight is lost (crystallization will be well started), cool slowly to 50° and centrifuge.

By the use of recrystallized phosphoric acid a very pure sample of monophosphate can be prepared by recrystallizing the primary calcium salt as described above. It is difficult to remove every trace of excess H_3PO_4 from the crystals. Stoklasa[3] suggested removing the excess acid by washing with alcohol and ether. Samples treated in this way should be used with caution, as some gave a strong tarry odor after a few weeks in stoppered bottles, and there was also some indications that water of crystallization had been removed. The exact theoretical content of water of crystallization was not attained and this is being further investigated, but crystals without the excess of CaO can be produced quickly by the method outlined.

Summary

1. An examination has been made of parts of the space model for the system $CaO-P_2O_5-H_2O$ as drawn by Bassett, and the indicated behavior of mono and dicalcium phosphates in solution has been investigated.

2. Methods for the recrystallization of the monocalcium phosphate have been given.

THE REDUCTION OF NITRIC OXIDE[*]

BY M. L. NICHOLS AND C. W. MORSE

A theory for the mechanism of the reduction of nitric acid has been proposed and developed in previous papers[1] from this laboratory. These studies required a knowledge of the reactions between the reducing agents and the reduced nitrogen compounds formed from the acid. In the case of nitric oxide the published results[2] were only qualitative and often contradictory. The purpose of the present investigation was the quantitative determination of the effect upon the reduction products of nitric oxide caused by the variation of the temperature, the acidity, and the concentration of some strong reducing agents.

Experimental

Quantitative Experiments

The methods for the preparation and the analysis of the reagents and the reduction products used in this work were those described in detail by Milligan.[3] A brief outline of these methods is given below and any deviation from Milligan's procedure is described.

Nitric Oxide. The nitric oxide was prepared by the action of 2 cc. of dilute nitric acid and 15 cc. of concentrated sulphuric acid upon the mercury in the nitrometer, A, Fig. 1.

The nitric oxide content of the gas mixtures was determined by measuring the decrease in volume that resulted from the treatment of the gas with two 25 cc. portions of a mixture of 2 cc. of concentrated nitric acid with 100 cc. of concentrated sulphuric acid. It was found that 25 cc. of this acid mixture would completely dissolve 100 cc. of pure nitric oxide and that no gas could be pumped from this solution. In the apparatus used by Milligan it was not possible to measure the decrease in volume directly and the nitrosylsulfuric acid formed was determined by titration with a solution of potassium permanganate. The nitric oxide was considered to be pure if 50 cc. of it was completely absorbed by 25 cc. of the mixed acid.

Nitrous Oxide. The nitrous oxide was prepared by allowing a concentrated solution of pure sodium nitrite to drop slowly into a concentrated solution of hydroxylamine sulphate.

The nitrous oxide was determined after the removal of the nitric oxide by measuring the decrease in volume that occurred when the gas mixture was

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[*] Contribution from the Baker Laboratory of Chemistry at Cornell University.

[1] Bancroft: J. Phys. Chem., 28, 475; Milligan: 544; Milligan and Gillette: 744 (1924); Coblens and Bernstein: 29, 750 (1925); Nichols and Derbigny: 30, 491; Joss: 1222 (1926).

[2] Ludwig and Hein: Ber., 2, 671 (1869); Maumené: Compt. rend., 70, 147 (1870); Dumreicher: Monatsheft, 1, 724 (1880); Divers and Haga: J. Chem. Soc., 47, 623 (1885); Gay: Ann. Chim. Phys., (6), 5, 145 (1885); Chesneau: Compt. rend., 129, 100 (1889); Kohlschütter: Ber., 37, 3053 (1904).

[3] J. Phys. Chem., 28, 544 (1924).

burned with an excess of hydrogen over a red-hot platinum spiral in a slow combustion pipette. The solubility of nitrous oxide under the conditions of these experiments in the mixed acid used for the absorption of the nitric oxide, was found to be 2.06 cc., at 0°C, 760 mm. and dry.

Nitrogen. The incombustible gas left after the burning of the nitrous oxide was considered to be nitrogen.

Hydroxylamine. The hydroxylamine was determined by reducing it to ammonia with an excess of a 20 percent solution of titanous chloride and distilling the ammonia as described below. Since there was no nitric acid present, it was not necessary to carry out the reduction in a solution buffered with sodium dihydrogen phosphate. The presence of stannous chloride has no effect upon the accuracy of this determination.

Ammonia. The ammonia was determined by distillation with steam, after the reducing salts had been oxidized by a solution of copper sulphate and an excess of a syrupy solution of sodium hydroxide had been added. The distillate was collected in an excess of standard 0.033 N. hydrochloric acid. The excess acid was titrated with standard 0.033 N. sodium hydroxide, using methyl red as indicator. In the middle of the distillation, a sufficient amount of a solution of sodium sulphide was added to precipitate all of the heavy metals as sulphides.

Stannous Chloride. The concentrated solutions of stannous chloride were saturated at room temperature with respect to $SnCl_2.2H_2O$. They were prepared by boiling hydrochloric acid with an excess of pure tin or by dissolving crystallized stannous chloride (Kahlbaum's *For Analysis*) in distilled water. When the latter method was used, it was necessary to add a small quantity of hydrochloric acid and boil with tin for a few minutes to reduce the small quantity of stannic tin which was present. No difference in behavior of the solutions prepared by the two methods could be detected. Dilute solutions of stannous chloride were made by adding the necessary amount of the saturated solution to freshly boiled and cooled distilled water. The strength of the dilute solutions of stannous chloride was determined by adding a known volume to an excess of a standard solution of iodine and titrating the excess iodine with a standard solution of sodium thiosulphate.

Titanous Chloride. The concentrated solution of titanous chloride used in these experiments was the Titanous Chloride, 20 percent, (Standardized) the LaMotte Chemical Products Company. The dilute solutions were made with freshly boiled and cooled distilled water. The titanous content of the dilute solutions was determined by adding a measured volume to an excess of a solution of ferric alum and then titrating the ferrous iron with a standard solution of potassium permanganate in the presence of manganous sulphate and phosphoric acid.

It was originally planned to study the reduction of nitric oxide in a manner similar to that used by one of us[1] in the work on nitrous oxide. In this method, however, the gas is always mixed with a large amount of carbon dioxide and

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[1] Nichols and Derbigny: J. Phys. Chem., 30, 491 (1926).

the solution of the reducing agent is saturated with carbon dioxide. Thus the exact partial pressure of the oxide of nitrogen is known only at the beginning of an experiment and decreases to some unknown smaller value as the reduction removes the reacting gas, which introduces an uncontrollable variable. Also the previous work on the reduction of both nitric oxide and nitrous oxide indicated that the reduction products were solids, ammonium or hydroxylamine compounds, or a relatively insoluble gas, nitrogen, and it was probable that these same products would be obtained in the present experiments so a simpler apparatus, as shown in Fig. 1, was used.

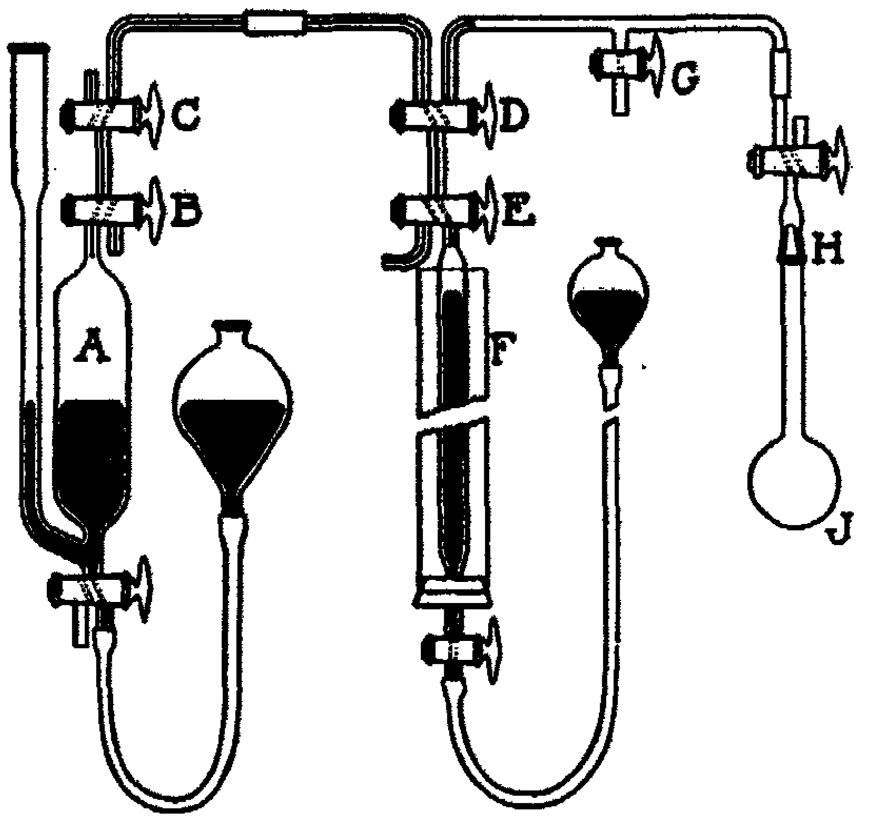

Fig. 1

Apparatus. The apparatus was made up of three parts, the nitrometer A, the burette F and the reaction bulb J. The nitrometer was modeled after the one described by Dennis[1] but differed from this in that the upper stopcock B was permanently sealed to the bulb and a second two-way stopcock C was sealed to B. One outlet of C was open to the air, the other was suitably bent for attaching to a burette by means of rubber tubing. For convenience of manipulation, two two-way stopcocks, D and E, were sealed to the top of the burette, This allowed either the nitrometer or the reaction bulb to communicate with either the burette or the air. The burette was of 50 cc. capacity and was calibrated with mercury from the bottom of the upper stopcock D. A water jacket, in which the water was constantly agitated by a slow stream of air, was used to keep the temperature uniform. The reaction bulb J was spherical in shape and had a capacity of 60 cc. It was connected to the burette by a ground glass slip-joint, H, and by a piece of enameled rubber tubing cemented in place. The tubing was sufficiently flexible to permit the shaking of the reaction bulb. A connection, G, for a water suction pump was inserted between the bulb and the burette.

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[1] Dennis and Nichols: "Gas Analysis", 428 (1929).

The apparatus was tested by filling the reaction bulb with distilled water, evacuating and then shaking the water with a measured volume of nitric oxide for one-half hour. The gas was then pumped off, measured and analyzed. There was no decrease in volume of gas and the gas was found to be completely soluble in the mixed acid.

Procedure. A measuring flask, calibrated to hold four times the volume delivered by a 25 cc. pipette, was filled with a solution of the reducing agent. Two 25 cc. portions, measured with the pipette used to calibrate the flask, were put into the reaction bulb J. A third 25 cc. portion was used for a blank hydroxylamine determination. The volume remaining in the flask was washed out with distilled water and was used for a blank ammonia determination.

The reaction bulb, containing the reducing agent, was attached to the apparatus by the slip-joint H. The apparatus was then evacuated, most of the air being removed through stopcock G with a water suction pump, the rest by using the burette F as a pump. During the evacuation, the bulb was shaken vigorously and the pumping was continued until all of the uncondensible gas was removed. This condition was indicated by a sharp click as the mercury struck the lower side of stopcock D, when the pressure in the burette was brought to atmospheric.

The nitrometer A, containing about 125 cc. of nitric oxide was connected as shown. The air was driven from the connecting system through the small jet on stopcock B by raising the level-bulb attached to the burette. Slightly less than 50 cc. of nitric oxide was run into the burette, stopcock C was closed and the gas was allowed to stand a few minutes to become saturated with water vapor at the temperature of the water jacket. The volume at atmospheric pressure, the temperature of the water jacket and the barometric pressure were recorded. Stopcock D was reversed and the gas was run into the bulb J until the pressure in the system was atmospheric. Atmospheric pressure was maintained by keeping the mercury in the level-bulb at the same height as the mercury in the burette. The bulb was shaken throughout the time of reaction and if all of the gas was absorbed before the end of the reaction, additional portions of the gas were measured and added in the same way. Before the end of the period of the reaction, the nitrometer, without being detached, was cleaned of acid and mercurous sulphate and washed with distilled water. It was then filled with mercury to stopcock C.

At the end of the reaction, the gas remaining in the burette was forced into the nitrometer and the gas in the bulb J was pumped out and also stored in the nitrometer. When the bulb was completely evacuated, all the gas in the connecting system was driven into the nitrometer and stopcock B was turned through 180° to preserve the gas for analysis. Bulb J was detached and, using the same pipette as before, 25 cc. of the solution was withdrawn for the determination of hydroxylamine. The remaining solution was washed out with distilled water and analyzed for ammonia.

25 cc. of mixed acid, for the absorption of nitric oxide, was put in bulb J and the system was again evacuated. The gas from the nitrometer was run into the burette, its volume and temperature determined, and then

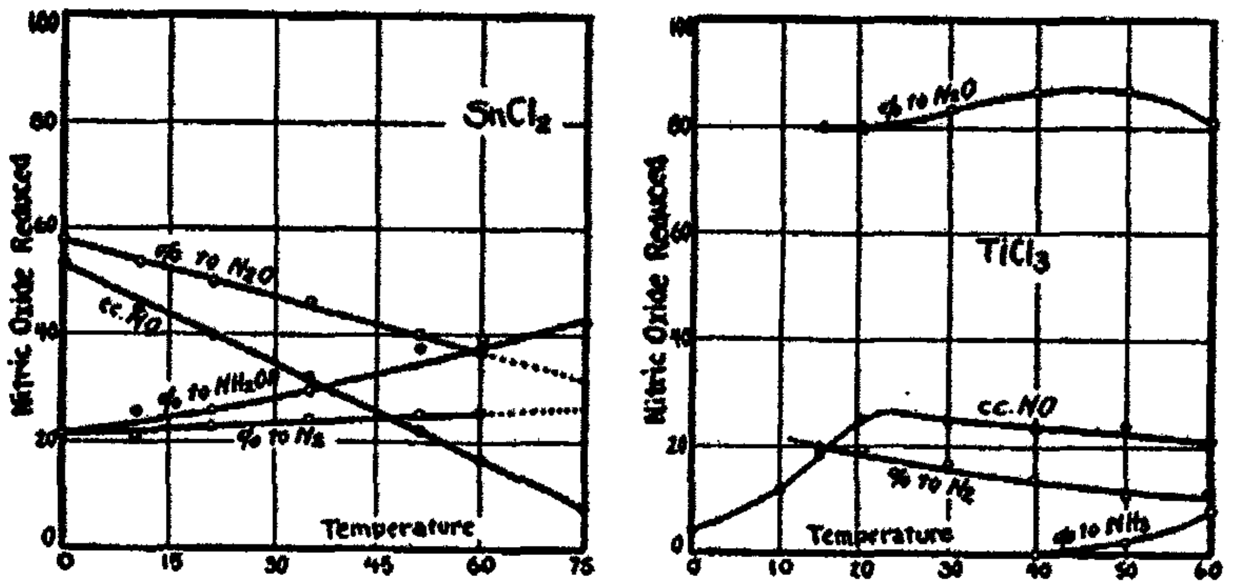

FIG. 2

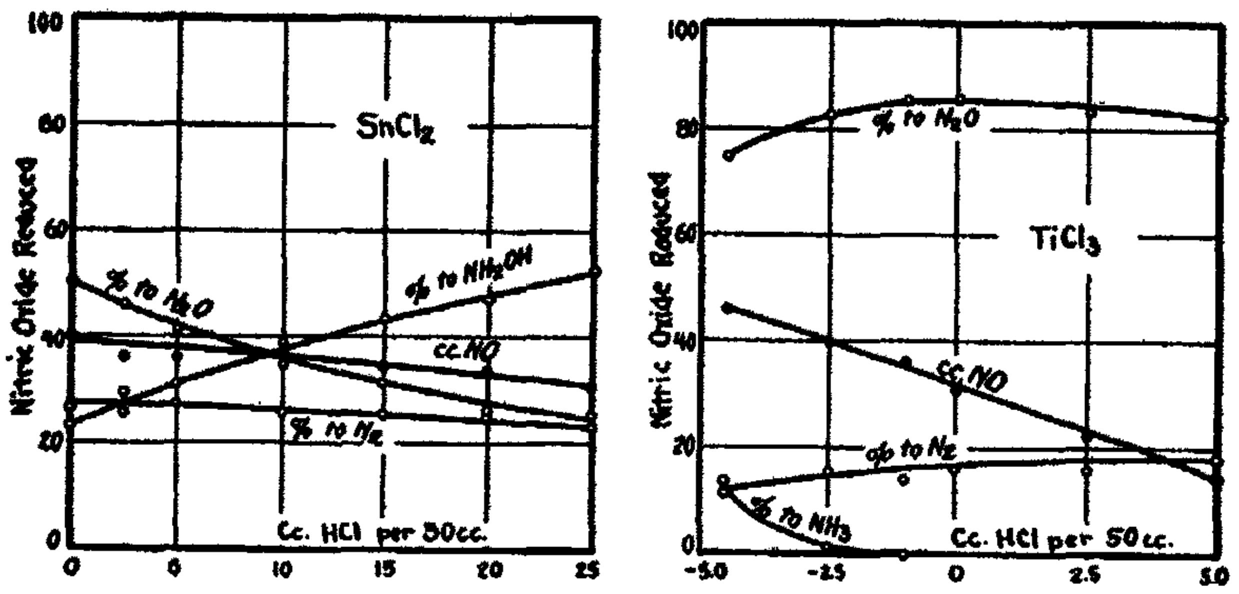

FIG. 3

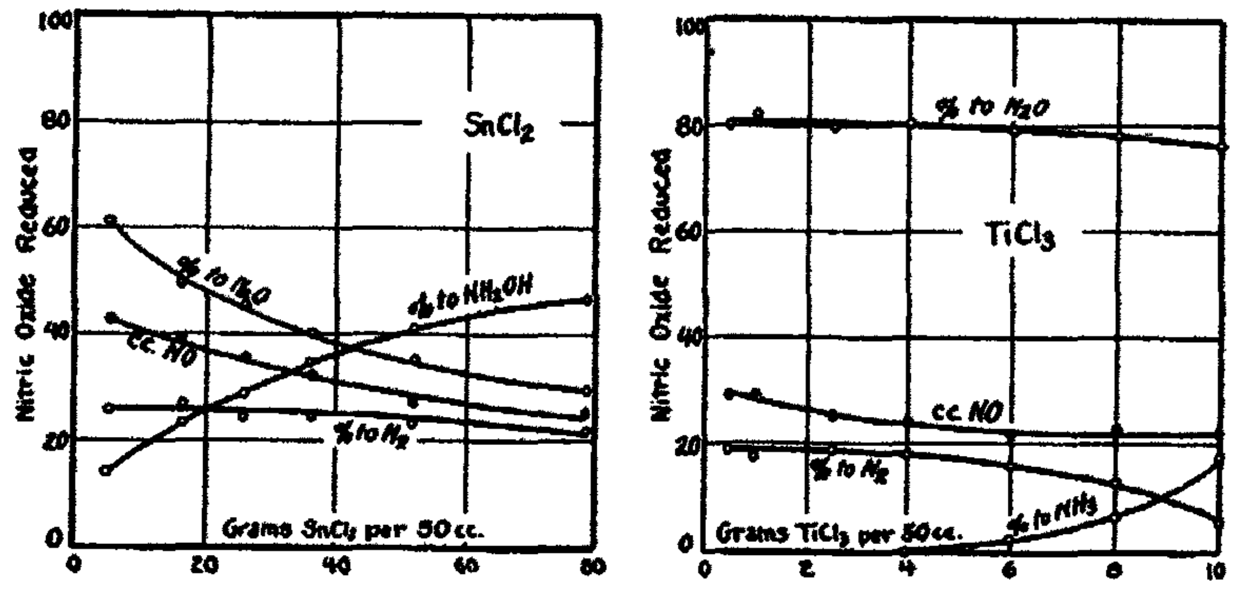

FIG. 4

transferred to the bulb. After five minutes contact, the gas was pumped out and stored in the nitrometer while a fresh 25 cc. portion of acid was put into the bulb. The absorption was repeated. After this second treatment, the volume and temperature of the residual gas were determined and the gas was again stored in the nitrometer. A second gas burette was attached to the free tube of stopcock E. The mercury from this burette was run through the connecting tube to stopcock B and a sample of the gas was withdrawn from the nitrometer. The burette, containing the sample, was detached and then connected to a slow combustion pipette for the determination of nitrous oxide.

Calculations. The volumes given in the tables are those at 0°C, 760 mm. and dry. The volume of nitric oxide not reduced is the volume of gas left after the treatment with the reducing solution minus the volume left after the treatment with mixed acid plus the volume of nitrous oxide dissolved in the acid (2.06 cc.). This volume subtracted from the volume of nitric oxide taken, i.e. the volume of nitric oxide as measured plus the volume of the tubing from the stopcock C to stopcock D, (0.4 cc.) gave the volume of nitric oxide reduced. The volume of nitrous oxide produced was the sum of the volume found by combustion and the volume dissolved in the mixed acid. In calculating the volume of nitric oxide equivalent to the weight of hydroxylamine or ammonia found, the weight of a liter of dry nitric oxide at 0°C, 760 mm. was taken as 1.340 g.[1]

Experimental. Using solutions of stannous chloride, the effects of the variation of the temperature, the acidity and the concentration of the re-reducing agent were determined. The results of these experiments are given in Tables I, II and III and Figs. 2, 3 and 4. Similar experiments were performed using solutions of titanous chloride. In addition, the effect of different times of contact was determined. See Tables IV, V, VI and VII and Figs. 2, 3 and 4.

TABLE I

The Reduction of Nitric Oxide with Stannous Chloride.

Variation of the Temperature
Volume of Solution — 50 cc.
Concentration, $SnCl_2$— 15.6 g./50 cc.
Time of Contact — 30 min.
Acidity — none

Temp., °C.	NO reduced cc., N.T.P.	Percent NO reduced to N_2O	N_2	NH_2OH
0	53.8	57.8	21.3	21.4
10	45.0	53.5	21.0	25.6
21	39.7	50.2	22.9	25.8
35	32.0	46.1	24.3	29.7
51	22.2	40.0	25.0	37.1
60	16.8	37.0	25.7	38.6
75	8.3	—	—	42.2

Note: the small volume of gas at 75° would not permit of an accurate analysis.

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[1] "International Critical Tables," 3, 3 (1928).

TABLE II

The Reduction of Nitric Oxide with Stannous Chloride
Variation of the Acidity

Temperature — 24.5° C.
Volume of Solution — 50 cc.
Concentration, $SnCl_2$ — 15.6 g./50 cc.
Time of Contact — 30 min.

cc. Conc. HCl per 50 cc.	NO reduced cc., N.T.P.	Percent NO reduced to		
		N_2O	N_2	NH_2OH
0	39.4	50.1	26.8	23.5
2.5	35.2	46.4	25.6	29.1
5.0	35.3	41.5	27.8	30.5
10.0	36.8	38.7	25.5	35.1
15.0	34.5	31.7	25.6	43.3
20.0	33.7	26.1	25.6	47.2
25.0	30.4	25.6	23.4	52.2

TABLE III

The Reduction of Nitric Oxide with Stannous Chloride
Variation of the Concentration of Stannous Chloride

Temperature — 22.5° C.
Volume of Solution — 50 cc.
Time of Contact — 30 min.
Acidity — none

Conc. $SnCl_2$ G./50 cc.	NO reduced cc., N.T.P.	Percent NO reduced to		
		N_2O	N_2	NH_2OH
5.2	42.8	61.0	25.9	14.2
15.6	39.4	50.1	26.8	23.5
26.1	35.6	45.5	24.7	28.9
36.2	32.2	40.7	24.6	34.7
52.1	27.2	35.3	23.3	41.5
78.2	25.6	29.9	22.5	47.0
15.6[1]	47.8	51.7	26.2	21.1

Platinized platinum present.

TABLE IV

The Reduction of Nitric Oxide with Titanous Chloride
Variation of the Temperature

Volume of Solution — 50 cc.
Time of Contact — 30 min.
Concentration, $TiCl_3$ — 2.5 g./50 cc.
Acidity — No Acid added

Temp., °C.	NO reduced, cc., N.T.P.	Percent NO reduced to		
		N_2O	N_2	NH_3
0	4.7	100		0
10	11.2	100		0
15	18.1	80.0	19.2	0
24	25.2	80.0	19.2	0
30	25.0	83.4	16.7	0
40	23.6	86.6	14.4	0
50	24.2	86.8	10.8	2.4
60	20.8	80.6	11.5	8.1

TABLE V

The Reduction of Nitric Oxide with Titanous Chloride
Variation of the Acidity

Temperature — 24.0° C.
Volume of Solution — 50 cc.
Time of Contact — 30 min.
Concentration, $TiCl_3$ — 2.5 g./50 cc.

cc. Conc. HCl per 50 cc.	NO reduced cc., N.T.P.	Percent NO reduced to		
		N_2O	N_2	NH_3
−4.5	46.0	74.7	12.1	13.2
−2.5	40.1	82.7	15.3	1.3
−1.0	36.1	85.6	14.0	0
0	31.0	85.6	16.1	0
+2.5	22.4	83.5	16.0	0
5.0	14.9	82.5	18.2	0

Note: In the first three experiments a solution of sodium hydroxide, whose strength was equivalent to that of concentrated hydrochloric acid, was used.

TABLE VI

The Reduction of Nitric Oxide with Titanous Chloride
Variation of the Concentration of Titanous Chloride

Temperature — 24.0° C.
Volume of Solution — 50 cc.
Time of Contact — 30 min.
Acidity — Increases with concentration, $TiCl_3$

Conc. $TiCl_3$ g./50 cc.	NO reduced cc., N.T.P.	Percent NO reduced to		
		N_2O	N_2	NH_3
0.5	29.4	80.2	19.3	0
1.0	29.3	82.5	17.4	0
2.5	25.2	80.0	19.2	0
4.0	24.6	80.8	18.4	0
6.0	22.1	79.5	16.0	2.6
8.0	23.2	78.8	13.4	6.8
10.0	22.5	76.5	6.1	17.6
10.0 + 2 cc. $FeCl_3$	48.4	61.2	21.7	16.1

TABLE VII

The Reduction of Nitric Oxide with Titanous Chloride
Variation of the Time of Contact

Temperature — 24.0° C.
Volume of Solution — 50 cc.
Concentration, $TiCl_3$ — 2 g./50 cc.
Acidity — No Acid added.

Time, Min.	NO reduced, cc., N.T.P.	Percent NO reduced to		
		N_2O	N_2	NH_3
30	26.3	82.5	17.4	0
60	43.8	82.8	16.6	0
120	64.9	82.0	19.1	0

Miscellaneous Experiments

Attempts were also made to reduce nitrous oxide in the apparatus shown in Fig. 1. Various concentrations of stannous chloride and titanous chloride were used and the time of contact was varied from one-half hour to four hours. No appreciable reduction could be detected. A solution of titanous chloride to which sodium hydroxide had been added (Cf. Table V) had no effect. The presence of carbon dioxide produced no reduction. The addition of stannous chloride or ferrous chloride, possible catalysts, to solutions of titanous chloride induced no reduction. The apparatus previously used by Nichols and Derbigny was rebuilt and experiments were made in it to see if the glass surface catalyzed the reduction of nitrous oxide. However under the conditions existing at this time it was impossible to obtain any indication of a reduction of the nitrous oxide with either stannous chloride or titanous chloride.

The effect of the presence of platinized platinum on the reduction of nitric oxide by stannous chloride was also determined, Table III, Fig. 4. A similar experiment was tried with titanous chloride but it was found that at low pressures, hydrogen was continuously evolved at the platinum surface. To increase the solubility of nitric oxide in titanous chloride, 2 cc. of dilute solution of ferrous chloride was added. The effect of the ferrous salt is shown in Table VI.

The experiments of Coblens and Bernstein[1] on the reduction of silver hyponitrite by stannous chloride and titanous chloride were repeated. When titanous chloride was used, a gas, presumably nitrous oxide, was rapidly evolved but no qualitative test for ammonia could be obtained. With stannous chloride, less gas was given off and a faint ammonia test was obtained after treatment with a solution of titanous chloride. That the evolution of nitrous oxide in the first experiment was due to the large amount of hydrochloric acid used to stabilize the solution of titanous chloride, was shown by an experiment in which the acid was almost neutralized with sodium hydroxide before the addition of the silver hyponitrite. In this experiment, the evolution of gas was much more feeble and a faint test for ammonia was obtained. These tests were not sufficiently positive to say that silver hyponitrite can be readily reduced.

Discussion

Joss[2] has shown that the mixture of nitric and nitrous acids that results from the solution of nitrogen peroxide in water is undoubtedly due to the decomposition of nitrosic acid, the reaction being

$$2\ NO_2 + H_2O = H_2N_2O_5 = HNO_3 + HNO_2$$

An analogous reaction occurs when nitric oxide dissolves in water. An aqueous solution of nitric oxide has an electrical conductivity that is much

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[1] J. Phys. Chem., 29, 750 (1925).

[2] J. Phys. Chem., 30, 1222 (1926).

higher than that of pure water, indicating that an acid solution is formed.[1] Salts of nitrohydroxylaminic acid, whose formula corresponds to two molecules of nitric oxide plus one molecule of water, have been prepared.[2] Sodium nitrohydroxylaminate decomposes into sodium nitrite, sodium hydroxide and nitrous oxide when boiled with water.[3] Aqueous solutions of nitric oxide have been observed to decompose, after standing several months, into nitrous acid and nitrous oxide.[4]

These reactions may be expressed

$$2\ NO + H_2O = H_2N_2O_3$$
$$H_2N_2O_3 = NOH + HNO_2$$
$$2\ NOH = H_2N_2O_2 = N_2O + H_2O$$

When reducing agents act upon aqueous solutions of nitric oxide they may act directly upon the nitrohydroxylaminic acid or upon the mixture of nitrous acid and nitroxyl. Since the latter view is not necessary to explain the reduction, it is simpler to consider that the nitrohydroxylaminic acid is reduced directly, although this may not be the case.

The rate at which nitric oxide is reduced will depend upon the rate of formation of the nitrohydroxylaminic acid and upon the velocity of the reducing reaction. Pressure, temperature, nature and concentration of reducing agent, and efficiency of mixing will affect the rate of solution as well as the total solubility of nitric oxide; and, consequently, the rate of formation and concentration of nitrohydroxylaminic acid. Temperature, acidity and concentration of the reducing agent will be factors in determining the speed of the reduction reaction. To eliminate pressure and mixing variables, these factors were kept as constant as possible during the previously described experiments.

When using solutions of stannous chloride of constant concentration as reducing agents, the quantity of nitric oxide reduced in one-half hour decreases almost linearly with rising temperature (Table I, Fig. 2), while with titanous chloride, a pronounced maximum is produced at about 25°C (Table IV, Fig. 2). Since an increase in temperature should accelerate the chemical reduction and thereby tend to increase the amount of nitric oxide reduced in a unit time, these results show that, at all temperatures above 0°C, the speed of the reaction between stannous chloride and nitrohydroxylaminic acid is greater than the rate of formation of the acid. But with titanous chloride, at temperatures below 25° C, the speed of the reduction is slower than that of the formation of nitrohydroxylaminic acid, while at higher temperatures, the decreasing solubility of nitric oxide causes the opposite to be true.

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[1] Joss: Op. cit., 1270, 1271.

[2] Thum: Monatsheft, 14, 294, (1893); Angeli and co-workers: Gazz., 26II, 17 (1896); 27II, 357 (1897);30I, 593 (1900); 31II, 15 (1901); 33II, 245 (1903).

[3] Angeli and Angelico: Gazz., 30I, 593 (1900).

[4] Russell and Lapraik: J. Chem. Soc., 32, 35 (1877); Cooke: Chem. News, 58, 155 (1888); Zimmermann: Monatsheft, 26, 277 (1893).

The quantity of nitric oxide reduced in one-half hour decreases when the acidity of the solutions of the reducing agents is increased. This diminution in rate of reduction is slight in the case of stannous chloride (Table II, Fig. 3) but, with titanous chloride, it is very marked (Table V, Fig. 3). It is known that the reducing power of stannous chloride becomes greater as the concentration of acid is increased, while that of titanous chloride becomes less.[1] The effect of the concentration of acid upon the rate of reduction may be attributed to two causes; first, the different reducing power of the reagent and, second, the lower concentration of nitrohydroxylaminic acid in the more acid solutions. When these two factors are opposing one another, as in the case of stannous chloride, they produce little effect, but when they are working in the same direction, as they do with titanous chloride, the resulting change is great.

With both stannous chloride and titanous chloride solutions, increasing the concentration of reducing agent decreases the amount of nitric oxide reduced in unit time (Tables III and VI, Fig. 4). It has already been shown that the reducing reaction is the more rapid one at room temperature and above. This means that anything tending to increase the rate of this reaction will have no effect unless it influences something other than the speed of the reducing reaction. The addition of reducing agent decreases the rate of solution of the nitric oxide, its total solubility or both and thus causes a decrease in the rate of reduction.

That the rate of solution of nitric oxide is the factor determining the rate of reduction is shown by the experiments in which platinized platinum was added to a solution of stannous chloride, and ferrous chloride to titanous chloride. The volume of nitric oxide reduced in one-half hour was increased in both cases (Tables III and VI).

The reducing power of both stannous chloride and titanous chloride is sufficiently great to reduce the oxides of nitrogen to ammonia.[2] The presence of compounds intermediate between the oxide and ammonia may be accounted for in two ways; first, by secondary reaction between the reduced product and the original, more oxidized compound and, second, by decomposition of intermediate products before further reduction takes place. The first assumption does not seem to be tenable in the case of these experiments as it is very doubtful that oxidation of the reduced products will occur in the presence of large quantities of reducing agent, especially when the concentration of the oxidizing agent is small. It is more probable that the second is the true explanation.

The intermediate products in the reduction of nitrohydroxylaminic acid are hyponitrous acid $H_2N_2O_2$, the hypothetical compound $H_4N_2O_2$ and hydroxylamine. The first two decompose giving nitrous oxide and nitrogen,

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[1] Nichols and Derbigny: J. Phys. Chem., 30, 504 (1926).

[2] Joss: J. Phys. Chem., 30, 1260 (1926).

respectively. The difficulty of reducing nitrogen is well known and it has been found practically impossible to reduce nitrous oxide under the conditions of the present experiments. Thus it is seen that if these two gases are once evolved, there can be no further action of the reducing agent upon them and they will appear in the final product. The proportion of nitrous oxide and nitrogen in the product, will depend upon the relation of the speed of the decomposition reactions to the speed of the reduction reactions but, unless the rates of decomposition are zero, both gases will be present.

Increasing the temperature will increase the velocity of both the decomposition and the reduction reactions, and, since these oppose each other, the net effect will be due to that reaction whose rate changes more rapidly. With stannous chloride solutions, the proportion of nitrous oxide decreases with rising temperature (Table I, Fig. 2). This shows that the rate of reduction increases more rapidly than the rate of decomposition. With titanous chloride solution the opposite is true, i.e., the rate of decomposition of hyponitrous acid increases more rapidly than the rate of reduction (Table IV, Fig. 2).

At higher temperatures stannous chloride solutions produce a greater proportion of nitrogen than they do at lower temperatures (Table I, Fig. 2). In this case the rate of decomposition of $H_4N_2O_2$ increases faster than the rate of reduction. The reverse takes place with titanous chloride solutions, i.e., the rate of reduction increasing more rapidly than the rate of decomposition (Table IV, Fig. 2).

The other experiments show the same effect. An increase in the concentration of acid increases the reducing power of solutions of stannous chloride and decreases that of titanous chloride. Tables II and V and Fig. 3 show that in the first case the proportion of nitrous oxide and nitrogen diminishes with increasing acidity, while in the other it increases. Greater concentrations of reducing agent will accelerate the rate of reduction and thus decrease the proportion of nitrous oxide and nitrogen in the product as shown by Tables III and VI, Fig. 4.

Since any hydroxylamine that is formed remains in solution as such it can be reduced further if the reducing agent is sufficiently powerful. If the reduction of hydroxylamine to ammonia is a rapid reaction, no hydroxylamine will appear in the final product. This is the case when titanous chloride is the reducing agent. But, when stannous chloride solutions are used, the rate of reduction of hydroxylamine to ammonia is very low and, unless the solutions are allowed to stand for several hours, no ammonia can be found.

From the above discussion, it is seen that the composition of the product obtained by the reduction of nitric oxide with reducing agents strong enough to carry the reduction to ammonia depends almost entirely upon the relative rates of several reactions. Any catalytic effect of the reagent or of its oxidation product upon one or more stages of the reduction is probably the main factor in determining the chief components of the final product of the reduction.

Summary

1. Nitric oxide dissolves in water to form nitrohydroxylaminic acid, $H_2N_2O_3$, or a compound of the same constitution.

2. At temperatures above 0°C the rate of reduction of nitric oxide by stannous chloride depends wholly upon the rate of formation of nitrohydroxylaminic acid.

3. At temperatures below 25°C the rate of reduction of nitric oxide by titanous chloride depends upon the speed of the reduction reaction, at temperatures above 25°, the formation of nitrohydroxylaminic acid is the limiting factor.

4. The reduction of nitrohydroxylaminic acid proceeds through various intermediate stages which may be represented

$$H_2N_2O_3 \rightarrow H_2N_2O_2 \rightarrow H_4N_2O_2 \rightarrow H_2NOH \rightarrow NH_3$$

5. Nitrous oxide and nitrogen are the result of the decomposition of hyponitrous acid and $H_4N_2O_2$, respectively, and, since these decompositions have sensible velocities, they will always be present in the products. The relative proportion of these gases in the final product depends upon the relation of the speed of the decomposition reaction to the speed of the reducing reaction.

6. Hydroxylamine is the apparent end-product when stannous chloride is the reducing agent because of the extreme slowness of the rate of its reduction to ammonia by this reagent.

7. Any catalytic effect by the reagent or oxidation product of the reagent upon one or more stages of the reduction will have a marked influence upon the composition of the product obtained by the reduction of nitric oxide.

REAGENT CONCENTRATION IN THE WALDEN INVERSION*

BY WILDER D. BANCROFT AND HERBERT L. DAVIS

In the thirty-five years that have passed since Walden discovered what Fischer later called, "the most surprising observation in the field of optically active substances since the fundamental investigations of Pasteur" and to which he gave the name "the Walden Inversion," countless perplexed chemists have made repeated attacks on the problem presented, but the actual increase in our knowledge of the essential conditions which determine whether or not a given reaction will be accompanied by an inversion is very slight. Walden[1] himself, concluded a recent discussion of the problem with these words:

"Finally, chemical theory and scientific speculation in general were stimulated to a remarkable degree by this discovery. An explanation, a theoretical basis, was necessary for this new group of facts which ran contrary to all current theoretical ideas.

"Actually, the reality has surpassed all expectations. Up to the present time no less than twenty-five theories have been advanced to explain this phenomenon. The discoverer of this inversion has had the unusual honor of seeing the most influential men gathered around his 'brain child.' They have bestowed gifts upon this child, and many of them have proposed chemical or physical theories to explain the nature of this phenomenon. Although in the meantime this child has grown up, and has reached the age of thirty years, chemists who are studying the configuration of molecules still regard it as an *enfant terrible*. Although many suggestions have been advanced to explain the phenomena grouped under the 'Walden Inversion,' a completely satisfactory solution has not yet been attained nor has it been found possible to predict the course of an inversion."

The present paper will show that there are certain conditions which have a determining effect on the course of such reactions and that in the conversion of halosuccinic acids to malic acid a very important condition is the acidity or the concentration of the reagent.

In the years preceding 1896 the foundations of organic chemistry had been laid on the fundamental assumption that reactions of replacement go directly, the replacing group occupying the same relative position in the molecule as had been occupied by the displaced radical. In 1896 Walden published the first results which showed that this is by no means always the case and that sometimes displacing groups take other positions in the molecule than that of the displaced group. Proof of this had to rest on the optical rotatory power of the molecules concerned and can today be demonstrated only for those

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[1] Walden: "Salts, Acids, and Bases: Electrolytes: Stereochemistry," 384 (1929).

molecules which rotate the plane of polarized light. None of the other common properties lend themselves to distinguishing between optical enantiomorphs although the same type of reactions must occur also in optically inactive molecules. It makes no difference whether the entering chlorine atom definitely takes the place of the hydrogen atom it displaced in forming methyl chloride, for the remaining hydrogens are all alike and the product molecules have identical properties. But if the three attached groups are all different from each other and from the entering group the result will be the formation of an optically active carbon atom and if in one reaction the entering group replaces a group directly while in another reaction it enters at a different position, the result will in both cases be optically active carbon atoms and they will be mirror images of each other, turning the plane of polarized light in opposite directions, and hence called optical antipodes. This was somewhat equivalent to adding a Bohr-like dynamic concept to the previously accepted and very useful static tetrahedron picture of the carbon atom, and produced similar disquietude.

Some of the history of the problem will aid in its comprehension. The optical rotatory power of certain substances was discovered by Malus in 1808 and studied extensively by Biot. About 1850 Pasteur carried out his epoch-making investigations which related rotation and crystal form and established that the oppositely rotatory types of certain salts of tartaric acid form crystals which are mirror images of each other. In 1874 van't Hoff and Le Bel, studying the work of Pasteur, hit independently upon the idea of the asymmetric carbon which still remains the best theoretical basis for the study of optical activity. No one yet has been able to explain why a carbon atom which is attached to four different groups or atoms can rotate the plane of polarized light, but it is a fact of nature.

The attempt to measure the effect and to predict it was made by Guye in 1890. He assumed that the relative masses of the attached atoms or groups is a measure of the rotatory power of the molecule and was able to apply his criterion to some optically active compounds. It was while Walden was attempting to test the validity of van't Hoff's theory and that of Guye that Walden discovered the Walden Inversion.

The first idea of Walden was to discover if a mere difference in the four groups attached to the carbon atom was sufficient to impart optical activity. Working at low temperatures he was able to convert l-malic acid, by the use of phosphorus pentachloride, to chlorosuccinic acid which proved to be strongly dextrorotatory,[1] this being the first preparation of this acid in an active form.

Two years later he returned to the same problem, "to determine by repetition and variation of the previously reported negative reactions, whether inactivation on displacement of hydroxyl groups by chlorine or bromine is a consequence of the specific properties of these halogens or whether the conditions of the previous researches made racemization inevitable and that there-

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[1] Walden: Ber., 26, 210 (1893).

fore the observed exceptions are only apparent." Walden[1] used PCl_5 and PBr_5 instead of HCl and HBr and reported the preparation and properties of several derivatives of chlorosuccinic and other active acids, treating not only malic but also tartaric and lactic acids to form the halogen derivatives and retaining optical activity in all. He therefore confirmed the conclusion that a difference in the four groups bound to the carbon atom is the only necessary condition for optical activity and that the specific nature of these groups determines only the magnitude and direction of the rotation. Later in the same year he reported the formation of dextro and levorotatory bromosuccinic[2] acids from the same levorotatory asparagine.

The next paper[3] in the series is really the most important of all for in it was reported the first optical cycle. "We have then the following cyclical process: starting with l-malic acid we prepared (by PCl_5) a chlorosuccinic acid which is dextrorotatory; in this dextro-acid we replace chlorine by hydroxyl and obtain a malic acid which is just as dextrorotatory as and which represents the optical antipode to our starting-out material. If we treat this dextro-malic acid again with PCl_5 there results a levorotatory chlorosuccinic acid which is the optical antipode to the first mentioned chlorosuccinic acid. On displacing the halogen by hydroxyl again this acid is converted to levorotatory malic acid the material first used." Thus Walden changed an optically active substance into its optical antipode without racemizing and resolving.

This work was continued with the conversion of l-bromo- or l-chlorosuccinic acids into a dextrorotatory amino succinic acid which in turn produced d-malic acid.[4] Ammonia gave a change in the direction of rotation but silver oxide in the same reaction gave an opposite result. Then as a very useful aid in the following of these reactions which involve malic acid the use of uranyl nitrate was described.[5] Pure malic acid in aqueous solution gives a specific rotation, $(a)_D = -0.77°$, but when the aqueous or alcoholic solution of malic acid contained for every mol of malic acid 4 mols of KOH and one to four mols of uranyl nitrate, the rotation became $(a)_D = -475°$. Similar changes were wrought on some other active substances but d-chlorosuccinic acid remained practically unchanged and l-bromosuccinic acid decreased its rotation slightly on addition of uranyl nitrate. This type of activation seems restricted to alpha hydroxy acids and has been shown to be associated with a tautomeric equilibrium in such compounds.[6] Walden practically always used the solutions as above or with ammonia in place of KOH, and Holmberg has followed him in this.

The next paper[7] in the series reported the effect of potassium hydroxide on the halosuccinic acids. It was shown that KOH or ammonia on a given

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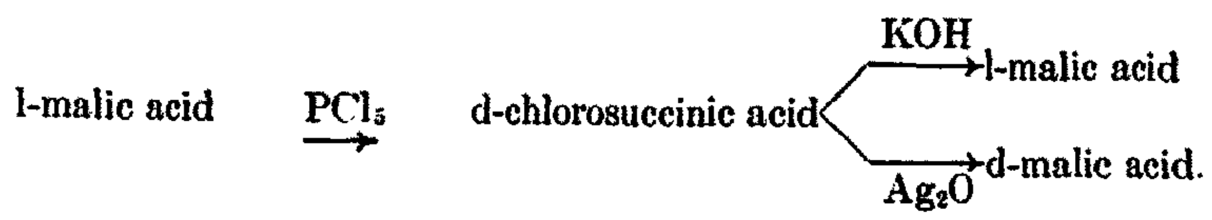
[1] Walden: Ber., 28, 1287 (1895).
[2] Walden: Ber., 28, 2766 (1895).
[3] Walden: Ber., 29, 133 (1896).
[4] Walden and Lutz: Ber., 30, 2795 (1897).
[5] Walden: Ber., 30, 2889 (1897).
[6] Bancroft and Davis: J. Phys. Chem., 34, 897 (1930).
[7] Walden: Ber., 30, 3146 (1897).

halogen-substituted succinic acid gave malic acid of the opposite rotatory power while silver oxide in the same reaction produced a malic acid of the same direction of rotation as the original chlorosuccinic acid.

Then Walden[1] prepared a summary of the work and included new experiments designed to show the effect of various hydroxides on the hydrolysis of the halosuccinic acids, and attempting to discover which type of reaction represented normal and which abnormal replacement. These papers include the data for the reactions in the presence of seventeen oxides and hydroxides. Five of the systems were homogeneous while the rest contained the suspended, difficultly soluble, base. The whole comparison has several inconsistencies in it but has long served to baffle chemists. All of the experiments were started with levorotatory chloro- or bromosuccinic acid. The hydroxides can be arranged in a series ranging from silver oxide which gave practically only l-malic acid to ammonium hydroxide which gave equally pure d-malic acid as indicated by the specific rotation in presence of uranyl nitrate. In order these compounds are: Ag_2O, H_2O, TlOH, HgO, Hg_2O, PdO all gave levorotatory mixtures of decreasing rotatory power, Tl_2O_3 gave an inactive malic acid, and the following gave dextrorotatory mixtures of increasing rotatory power: LiOH, $Sn(OH)_2$, NaOH, $Pb(OH)_2$, $Ba(OH)_2$, $Cd(OH)_2$, CuO, KOH, RbOH, NH_4OH. It should be emphasized that these results are not truly comparable; for the conditions, concentrations and methods of handling were scarcely alike for any two substances. These considerations are mentioned in no criticism of this pioneer work of Walden who admits that he had difficulty getting any reproducible results at all, but possibly to explain why this table does not appear to fall in line with any other properties of the substances concerned.

We are therefore in a position to formulate simply the essential problem of the Walden inversion in terms of the compounds studied by Walden who showed these reactions to take place:



Evidently in passing from l-malic to d-malic acid we have changed the relative position of the hydroxyl group and thus changed the configuration of the optically active molecule. In which of these two sets of reactions did inversion take place? If PCl_5 substituted the chlorine atom in a position other than that originally occupied by the hydroxyl group then this is inversion and the action of the silver oxide is normal, while that of the potassium hydroxide is abnormal or accompanied by inversion. But if the PCl_5 reaction is normal then that of the potassium hydroxide is also, while the silver oxide is abnormal. The crux of the Walden Inversion problem is the question: do malic and chlorosuccinic acids having the same configuration also possess the

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[1] Walden: Ber., 32, 1833, 1855 (1899).

same sign of rotation? In thirty-five years we have not found the answer to that question that could be accepted, as witness the statement of Holmberg[1] recently. After a critical survey of recent work on d- and l-isomers of lactic, malic, succinic acids, etc., and more than thirty years of work on them himself, he concludes that there is no general method available for ascertaining the configuration of mirror image isomers. Those offered are objectively unsatisfactory and allow subjective evaluation of evidence leading to conflicting conclusions. But real progress can be made in this field only by postulating one thing or the other and discovering where the postulate will lead. For reasons which will be elaborated in a forthcoming paper it appears to us reasonable to assume that malic acid and chlorosuccinic acid having the same configuration will also show the same sign of rotation. This is not a general rule and the criterion must be worked out for each set of compounds. It so happens that the bromosuccinic and iodosuccinic acids of the same configuration as malic acid will have the same sign of rotation. This will be reverted to, but first its seems advisable to survey some of the more recent work on the Walden Inversion, especially that of Holmberg.

In 1912 Holmberg[2] started what has probably been the soundest work done on the Walden Inversion. He attacked the problem by the kinetic methods of physical chemistry and one of his early experiments made a study of the hydrolysis of chlorosuccinic acid by neutralizing the acid and following its rotation and the amount of alkali needed to keep it alkaline to phenolphthalein, and the amount of chlorine ions split off (titration with silver nitrate). The rotation of his solution started at −4.17° and at the end of 102 hours was −1.08°, having passed through a minimum at −0.42°. The base used rose very slowly, while the silver titration rose quite rapidly, in a manner rather similar to the rotation. The curves so obtained were interpreted as follows: "The l-bromo anion decomposes quickly into the bromine and lactone acid anions, the latter being dextrorotatory. In neutral solutions the lactone is hydrolyzed only slowly, but as malic acid is formed, the H^+ catalyzes the process but retards the lactone formation, and when enough of the d-rotatory lactone has been converted into the feebly rotatory malic acid, the l-rotation begins to increase owing to the presence of undecomposed l-bromosuccinic acid." The Walden Inversion may therefore be represented thus:

l-bromo acid → d-malic acid lactone → d-malic acid.

The confirmation of this conclusion has been the purpose and the result of much of Holmberg's subsequent work in this field and has brought to light some very interesting data.

The following year Holmberg[3] published more complete accounts of similar experiments extending to l-chloro-, l-bromo-, and l-iodo-succinic acids. He showed that if l-bromosuccinic acid be neutralized and set aside, the

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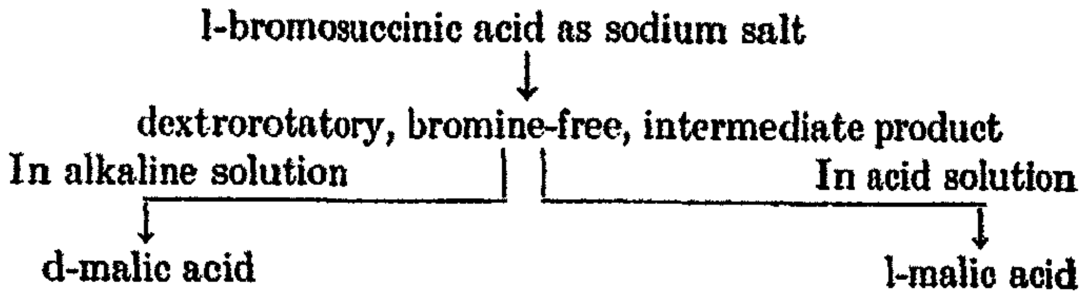
[1] Holmberg: Svensk. Kem. Tid., 41, 60 (1929); Chem. Abs., 23, 3441 (1929).

[2] Holmberg: Ber., 45, 1713 (1912).

[3] Holmberg: J. prakt. Chem., 87, 456 (1913).

solutions becoming acid by reason of the hydrolysis process, the product was mainly (74%) l-malic acid. Then by adding sodium hydroxide so that the solution was alkaline most of the time he showed that "the malic acid lactone formed from the sodium salt of l-bromosuccinic acid forms principally d-malic acid on alkaline hydrolysis". This is represented by:



Further experiments demonstrated certain properties of this lactone; it is stable in neutral solution; but in acids and yet more rapidly in alkaline solution it is converted into malic acid; it is chemically active; its conversions are accompanied by little racemization. Holmberg[1] believed that no change in configuration takes place and says: "Since from the change of rotation of a neutral solution of sodium bromosuccinate it must be concluded that the resulting malic acid lactone is dextrorotatory, at least in aqueous solution, this acid will be designated as the d-acid, and therefore the l-bromosuccinic acid and the d-malic acid lactone must be of the same configuration." Actually there is nothing to show that this is true or that the lactone is really formed by inversion in the first step.

In 1927 Holmberg[2] returned to this problem in a series of papers. Some experiments on the alkaline decomposition of chlorosuccinic acid showed that the velocity constant of the bimolecular reaction for the hydrolysis to malic acid is dependent on the kind and concentration of the metallic ions present. The second paper is entitled, "The Hydrolysis of Monohalogen Succinic Acids," and represents one of the best pieces of work done on the Walden Inversion. In his review of his earlier work he says: "Since the influence of ammonia on the dextro-malic acid lactone causes the formation of dextro-β-amido malic acid, we recognize the d(−) configuration for that acid, and since the (alkaline) saponification of this form (to be indicated as d(+) malic acid lactone), leads to d(+) malic acid we conclude that the influence of hydroxyl ions on the malic acid lactone is without inversion. For similar reasons we may conclude that the addition of other ions will likewise proceed without inversion, and since finally, the halogen- and sulphur-substituted succinic acids from d(+) malic acid are levorotatory, one must indicate these acids as the d(−) form." Again this appears to be merely an assumption and the opposite assumption would explain the facts and be about as well justified.

The experiments of this paper, however, are quite interesting. A glance at the list of reagents used by Walden would suggest the possibility that the character of the product resulting from the hydrolysis of chlorosuccinic acid

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[1] Holmberg: J. prakt. Chem., 88, 553 (1913).

[2] Holmberg: Ber., 60, 2194, 2198 (1927).

might be influenced by the acidity of the medium. In general those oxides which are the weakest as bases gave a preponderance of the l-malic acid, while the strong bases gave d-malic acid. For such a substance as sodium hydroxide which should give a large quantity of d-malic the lower yield is to be attributed to the too vigorous action of the alkali leading to more racemization and to the formation of fumaric acid which had prevented so much of the earlier work from bearing fruit. Also most of Walden's experiments involved variable amounts of heating and these compounds are easily racemized by heating, especially the halosuccinic acids. Holmberg also had this idea about the acidity of the medium and a group of experiments show that starting with levorotatory chlorosuccinic acid, hydrolysis resulted in an excess of the d-malic acid in alkaline solutions and in an excess of l-malic acid in acid solutions. The relative proportions of these forms is roughly proportional to the acidity or basicity of the solutions. Indicators were not used but additions of acid or of base kept the solutions approximately in the required condition.

We have confirmed these findings of Holmberg in regard to the course of this hydrolysis. A first attempt to prepare chlorosuccinic acid by the use of malic acid and phosphorus pentachloride[1] met with limited success, the same difficulties being encountered as were met by Walden. The yield is low, much of the product being fumaric acid. However, some d-chlorosuccinic was thus prepared and hydrolyzed. The principal amount of the halosuccinic acids used was prepared by the methods of Holmberg (1927).

Actually Walden had used some asparagine and aspartic acid as sources of chlorosuccinic acid but Holmberg perfected the method and made quantities. The Holmberg method consists in treating aspartic acid in the presence of NaCl and HCl with sodium nitrite. The reaction proceeds nicely, requires no heating at any time and apparently always works. Holmberg reported 14-15 grams of chlorosuccinic acid from 15 grams of aspartic acid. Three separate preparations have borne this out both as to quantity and quality of yield. The acid prepared has properties that check with those reported by Holmberg.

Then came the problem of hydrolyzing the acid under conditions of approximately constant pH and for this it was decided to use suitable buffer solutions which were checked by means of the hydrogen electrode. Since the reaction used up hydroxyl ions, fresh alkali must be added to keep the pH up to the required value. The chief difficulty in the experiment was to get reliable readings from the platinum-hydrogen electrode in the alkaline solutions, so much so that good control proved impossible under the conditions. We shall therefore present only the qualitative results. Possibly the repetition of such an experiment with suitable indicators will prove of interest later.

As buffer solutions, the glycocoll-sodium hydroxide mixtures were found to be the only common ones covering the range desired, namely from pH 9

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[1] Walden: Ber., 29, 133 (1996).

to pH 13. Buffer solutions were made up for pH 9, 10, 12, and 13, the solution for pH 11 being omitted because the titration curve at that point is steeper and the solution would be more sensitive.

The plan for the runs was to take four grams of the chlorosuccinic acid neutralized by sodium hydroxide and diluted to 50 cc. To this 50 cc of the appropriate buffer solution was added and the pH determined, more alkali being added as necessary, the attempt being made to keep each solution within 0.3 units of the indicated pH value.

The progress of the inversion can be followed by the change in the polarimetric readings since it has been shown that the presence of the glycocoll and excess base has no appreciable effect on the rotation of the two acids concerned. These solutions will thus contain sodium chlorosuccinate and glycocoll and will develop sodium malate. Solutions A, B, C, and D contain chlorosuccinic acid or its sodium salt while solutions M, N, O, and P contain malic acid or its sodium salt. In solution A one gram of chlorosuccinic acid was dissolved in 25 cc of solution; in solution B one gram of this acid was neutralized by NaOH and diluted to 25 cc; in solution C one gram of the acid was neutralized and then diluted to 25 cc with buffer solution pH 9; while solution D contains one gram of the acid neutralized and diluted with buffer solution pH 13. Solutions M, N, O, and P were made up in the same way using 0.879 g of malic acid (equivalent to one gram of chlorosuccinic acid) in each 25 cc of solution. The observed rotations of these solutions were:

A	B	C	D
−0.84°	−1.11°	−1.11°	−1.09°
M	N	O	P
−0.05°	−0.35°	−0.35°	−0.35°

These results show that although the sodium salts of both of these acids are more strongly rotatory than the acids themselves, the presence of the glycocoll has no effect. The concentrations here taken represent the original and final concentrations of the ions if there were no dilution during the run. This dilution will affect the rotatory power of malic acid but will be comparable since the same amount of alkali will be required in each case.

In agreement with the findings of Holmberg the originally levorotatory chlorosuccinic acid in all these alkaline solutions was converted to dextrorotatory malic acid. The levorotation of the solutions decreased to zero and then became increasingly a positive rotation which in no case reached the value of +0.35°, the value for pure d-malic acid. The speed of this conversion is proportional to the hydroxyl ion concentration, the most alkaline solution becoming inactive optically at about 100 hours, while the solution in the pH 9 buffer required 200 hours at room temperature to reach zero optical activity. After that point the solutions became increasingly dextrorotatory appearing asymptotically to approach a limiting value which varied with the pH of the solution and indicated that the higher the pH of the solution the more did d-malic acid predominate in the product of hydrolysis. This experiment then completely confirms the findings of Holmberg and throws a new light on the

Walden Inversion. Apparently in those solutions in which the concentration of hydroxyl ions is high this ion is forced into the molecule of chlorosuccinic acid somewhat disruptively and in such a way that direct replacement is impossible and a Walden Inversion results. In acid solutions the hydrolysis results in the formation of l-malic acid as the final product.

As a method of preparing d-malic acid this procedure may be modified and gives very good results. The solution of chlorosuccinic acid is neutralized and heated on the water bath, fresh alkali being added in small portions just sufficient to keep the solution alkaline to phenolphthalein. In about one and one half hours the reaction is complete. The chloride may be precipitated by silver nitrate and the malic acid subsequently by precipitation as the lead salt and treatment of the suspension with hydrogen sulphide. Study of the d-malic acid thus prepared showed it to have the proper melting point and to possess exactly the same rotatory power as a sample of l-malic from Eastman.

There are other examples of the determining power of the hydroxyl ion concentration on the product of such an hydrolysis. Levene, who has probably done more work on this problem than any other American, reports[1] the hydrolysis of a dextrorotatory propylene oxide. He finds that a comparatively high hydrogen ion concentration of the hydrolysis medium leads to a dextrorotatory glycol while a high hydroxyl ion concentration leads to a levorotatory glycol.

Hydrolysis in Presence of Silver Oxide

In addition to acidity Holmberg showed also that the amount of reagent present controlled the product resulting from hydrolysis of the halosuccinic acids. In the early work Walden had been much mystified that the action of silver oxide and of potassium hydroxide on a chlorosuccinic acid produced malic acids which were alike chemically but which were opposite stereochemically. In other words the formation of one acid involved an inversion and some of the theories proposed to account for the Walden Inversion have started from this point, calling attention to the greater tendency for the silver to abstract the chlorine more forcibly (and with the possibility of inversion) from the chlorosuccinic acid. In the treatment of chlorosuccinic acid it must be borne in mind that three molecules of such a base as sodium hydroxide will be required per molecule of free acid used, two of these forming the salt and the third furnishing the hydroxyl group for the molecule.

In 1913 Holmberg said: "Of my experiments I will now describe a few decompositions with silver oxide because they show that in the case of l-bromosuccinic acid there exists no essential difference in regard to the activity of the malic acid formed between this base and sodium hydroxide." The experiment indicated that starting with just enough silver oxide to form the silver bromosuccinate and letting the solution stand for thirty days (solution becoming acid), the malic acid obtained was 64% l-malic acid: while if 60% more silver oxide were used (a solution tending to have a more alkaline reaction) the product contained 65% d-malic acid.

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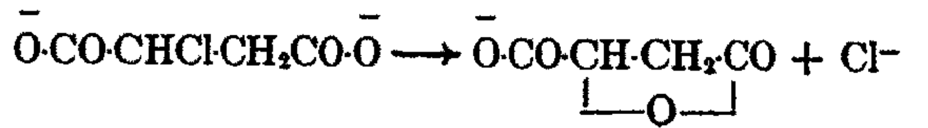
[1] Levene and Walti: J. Biol. Chem., 73, 263 (1927).

In the 1927 papers Holmberg returned to this feature of the problem and attempted to explain some of Walden's results with the heavy metals, where the solution could not have been strongly alkaline but in which dextrorotatory malic acid was obtained. It becomes necessary then to assume some catalytic activity for the metal ion complexes, especially since copper and lead are notorious for the formation of these complexes with oxygen acids. The experiments show that cupric ions favor the formation of d-malic acid so effectively that this influence is evident even in solutions which are undoubtedly acid. Beryllium and aluminum ions act similarly while magnesium and calcium have little effect. Identical solutions were prepared of the sodium salt of the malic acid lactone; left standing alone it produced l-malic acid (solution becoming acid), with addition of sodium hydroxide or of copper sulphate there formed some dextrorotatory malic acid, and in presence of cadmium sulphate an inactive acid was the product. Of the effect of silver oxide Holmberg[1] says: "Since the researches of Walden the silver ion has played a special role in almost all investigations of steric behavior during the hydrolysis of halogen-substituted acids. In my earlier experiments with halosuccinic acids and silver oxide I have found no other influence of the silver ions than a vigorous acceleration of the lactone formation. From a somewhat different point of view I have adopted the views of Euler and of Biilmann concerning the cause of this acceleration. According to their view there is first formed an organic cation with positively charged carbon. The salt of a halogen-succinic acid gives an intermediate ion, $\overset{-}{O}\cdot CO\cdot \overset{+}{C}H\cdot CH_2\cdot CO\cdot \overset{-}{O}$, which might then momentarily change into the univalent anion of the lactone malic acid, while the corresponding cation in the case of a free halogen-succinic acid must show the composition, $HO\cdot CO\cdot \overset{+}{C}H\cdot CH_2\cdot COOH$. Of such an ion one must expect that it would change so slowly into lactone malic acid (and hydrogen ion) that it would also in appreciable amounts be converted directly to malic acid and hydrogen ion. This conversion should occur with inversion and in agreement with this the free levorotatory halogen-succinic acids in the presence of silver nitrate give strongly levorotatory malic acid, while their acid or neutral salts under the same conditions behave not markedly different than in the absence of silver ions." It may be borne in mind that Holmberg's earlier mechanism and still alternative picture for the hydrolysis of the ion is:



$$\overset{-}{O}\cdot CO\cdot CHCl\cdot CH_2CO\cdot \overset{-}{O} \longrightarrow \overset{-}{O}\cdot CO\cdot \underbrace{CH\cdot CH_2\cdot CO}_{O} + Cl^-$$

anion of l-chlorosuccinic acid   anion of dextrorotatory malic acid lactone.

In order to confirm these findings of Holmberg and to extend them we have carried out some experiments hydrolyzing l-bromosuccinic acid in the presence of varying amounts of silver oxide. The acid was prepared from

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[1] Holmberg: Ber., 60, 2203 (1927).

aspartic acid according to the method of Holmberg[1], 0.02 mol being taken for each experiment, and 2, 2.8, 3.2, and 3.6 equivalents of silver oxide respectively being added to the acid. The calculated amount of silver nitrate was treated with alkali, the precipitated oxide washed and added to the acid in 100 cc of suspension. Bottles containing these suspensions were fixed on a rotating cage in a thermostat bath at 40° for nine weeks.

At the end of that time the suspensions were treated with 1.4N HCl until no further precipitation of silver chloride took place. The final solutions from the hydrolysis could contain only undecomposed bromosuccinic acid, malic acid, the silver salts of these acids and excess silver oxide, consequently the acid addition left in solution only malic acid and possibly some undecomposed bromosuccinic acid. The silver chloride was filtered off and the filtrates concentrated under vacuum to 25 cc. Two-cc samples of these solutions were titrated with $Ba(OH)_2$ solution and the rotations of the malic acid determined in the presence of one mol of uranyl nitrate and four mols of ammonium hydroxide per mol of malic acid. Practically no undecomposed bromosuccinic acid was left, as was shown by the fact that the final solutions did not increase in acidity on standing several days (hydrolysis of remaining bromosuccinic acid would have been shown by increased acidity of the solution), and by the fact that further addition of silver nitrate later caused no formation of any silver bromide from bromide ion that might have been split off. In the presence of uranyl nitrate Walden had reported as high as −475° as the specific rotation of his malic acid, Holmberg gave and used −436° as his value; while the malic acid furnished by Eastman showed −418° as its specific rotation and this value has been used in the present run. The results of the silver oxide hydrolysis were:

Equivalents of silver oxide per mol of l-bromosuccinic acid	Specific rotation of malic acid product	Product
2	−148.8°	67.8% l-malic
2.8	+ 22.0	52.6% d-malic
3.0	+ 42.0	55.0% d-malic
3.2	+ 55.4	56.6% d-malic

These results show that the malic acid produced is dependent on the amount of silver oxide present and that the production of equivalent amounts of d- and l-malic acids would take place in the presence of about 2.7 equivalents of silver oxide per mol of bromo-succinic acid instead of the three equivalents called for by the stoichiometric proportions. The fact that such a change should follow is the more remarkable when one considers that these systems are all heterogeneous, silver chloride being formed from the suspended silver oxide. In the bath which was kept dark, the first sample gave a white precipitate at the end, while in the last vessel the solid was deep black with the excess silver oxide. In this case as in the alkali run the determining

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[1] Holmberg: Ber., 60, 2194 (1927).

factor appears to be the chemical potential of the hydroxyl ion which is sustained at a higher level by the excess silver oxide in equilibrium with dissolved silver hydroxide. There may be a secondary influence due to the silver ions but certainly the dividing line between the production of d- or of l-malic acid does not come at pH 7, for all these solutions at the end were acid to litmus, even though three of them produced d-malic acid whose production is most favored in definitely alkaline solutions. It appears that that portion of the hydrolysis which takes place at the surface of the suspended silver oxide produced d-malic acid because of the higher pH there, while that hydrolysis which went on in the solution led to a l-malic acid and thus that a large factor in the experiments of Walden on the insoluble bases is the fineness of division and the character (activity) of the surface of the suspended oxide. It follows from this that we may not expect to obtain from such a suspension a much higher yield than 70 or 80% d-malic acid under the most favorable conditions in the presence of silver oxide, while a reaction in homogeneous solution of the proper alkalinity does lead to nearly complete conversion to d-malic acid.

Walden has not been oblivious to this contention of Holmberg's to the effect that in the hydrolysis of the chlorosuccinic acids a determining factor was the hydrogen ion concentration of the hydrolysis medium, but in 1919 subjected[1] it to scrutiny and concluded that it had no validity for other series of compounds for which he found data in the literature. In view of what we now know of these phenomena this discarding of the work of Holmberg is not justifiable and appears to be based on two principal errors. In the first place there is no thought that in any hydrolysis of a halogen acid to produce an optically active hydroxy acid, equal amounts of the two forms will be produced at a pH 7. Rather the idea is that there is some pH, which we can not now predict, below which one form of the hydroxy acid and above which the other form of the hydroxy acid will predominate in the product. The pH at which equal numbers of the two types of molecules are produced appears to be a specific property of the substances concerned and to be affected greatly by the conditions, especially the temperature. In general the higher the temperature employed the wider the band of pH range which produces inactive products and apparently even at low temperatures the activity does not increase suddenly on either side of this band.

A second objection to Walden's criticism of the Holmberg idea is that in almost all the critical cases cited by Walden the data do not mean what he thinks they mean. To be specific we will cite the first of the six reaction series noted by Walden, that from the work of McKenzie and Humphries[2] on the beta-hydroxy-beta-phenylpropionic acid. This hydroxy acid in alcohol showed a specific rotation of −18.9° for the pure acid and was obtained in each case from a dextro-bromo compound. In the first case the acid stood in water only for five days and the final hydroxy product showed (a)

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[1] Walden: "Optische Umkehrerscheinungen," 156 (1919).

[2] McKenzie and Humphries: J. Chem. Soc., 97, 125 (1910).

= −7.7°. There is no doubt but that this solution was acid not only with the acid itself but also by virtue of the hydroxyl ions going in to form the hydroxy acid. The second reaction involved 0.0030 mols of the bromo acid and 0.0037 mols of sodium carbonate. The carbonate in this case should be sufficient to neutralize the acid, provide hydroxyl ions, and have left 0.0007 mols for making the system alkaline. The hydroxy acid produced showed −5.5°. In the third reaction 0.003 mols of the bromo acid reacted with 0.003 mols of Ag_2O. This would be just sufficient to form the silver salt and furnish the necessary hydroxyl ions and there would be no reserve silver oxide to keep the solution on the alkaline side. The hydroxy acid resulting showed (a) = −13.7°. In these three reactions we have then; 2.-mildly alkaline (−5.5°), 3.-weakly acid (not alkaline as Walden states) (−13.7°), 1.-decidedly acid (−7.7°). In this case it appears that the acidity of the free acid alone is sufficient to cause some racemization and that a solution which is definitely alkaline would produce dextrorotatory beta-hydroxy-beta-phenylpropionic acid from levorotatory beta-bromo-beta-phenylpropionic acid. It should be borne in mind that strongly acid or alkaline solutions effect a racemization in these reactions and that the inevitable heating used in completing the reactions or separating the products will also tend to a lowered activity of the product which will be variable with the treatment.

This is a typical set of reactions which include those of alpha-bromo-beta-phenylpropionic acid, ($C_6H_5=CH_2CHClCOOH$),[1] alpha-chloro-alpha-phenylpropionic acid  $(\genfrac{}{}{0pt}{}{C_6H_5}{CH_3}{>}CCl{\cdot}COOH)$,[2] phenylchloroacetic acid into mandelic acid ($C_6H_5CH(OH)COOH$),[3] bromopropionic acid into lactic acid ($CH_3CH(OH)COOH$),[4] and bromoisovalerianic acid.[5]

There are therefore in these cases cited by Walden one or two other exceptions to the general rules but for the most part the reactions which appear to Walden to be exceptions are not really so. It should be noted in passing that, in so far as one may judge from such incomplete and non-comparable data, those halogen acids containing the phenyl group appear to react oppositely to the acids without the phenyl group, for alkaline hydrolysis in the former group is attended by no change of sign or of configuration, while both are present for instance in the malic acid or the lactic acid series. It may later appear that the phenyl-containing compounds are much less sensitive to changes in the hydrogen ion concentration than are those compounds which lack phenyl groups. Possibly this may be connected with the unsaturated character of the phenyl group but at present we have no complete evidence for this.

In the final analysis the hydrolysis of the halogen succinic acids produces molecules of malic acid each of which is optically active and all of which are

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[1] McKenzie and Wren: J. Chem. Soc., 97, 1358 (1910).

[2] McKenzie and Clough: J. Chem. Soc., 97, 1022 (1910).

[3] McKenzie and Clough: J. Chem. Soc., 95, 786 (1909).

[4] Fischer: Ber., 40, 503 (1907).

[5] Fischer and Scheibler: Ber., 41, 2894 (1908).

equally capable of turning the plane of polarized light to exactly the same degree; there are no optically inactive molecules of malic acid. The rotatory power of a sample of malic acid will therefore be determined by the proportions of each form present in the mixture, since any preparation will involve the formation simultaneously of both types of molecules. Thus it is questionable if anyone ever had in hand a pure specimen of either form unmixed with the other, and the best we can do is to take the highest rotatory power observable as that of the pure form. The ratio between the forms of malic acid produced, assuming temperature and other conditions constant and so chosen as to cause a minimum of racemization, will depend upon three principal factors; the original material used, such as the halogen succinic acid, the added hydrolyzing agent, and the medium in which the reaction is carried out. These are all capable of variation and in this paper particular attention has been focussed on the hydrolyzing agent, actually the water serving both as medium and as hydrolyzing agent—possibly with a catalytic factor added.

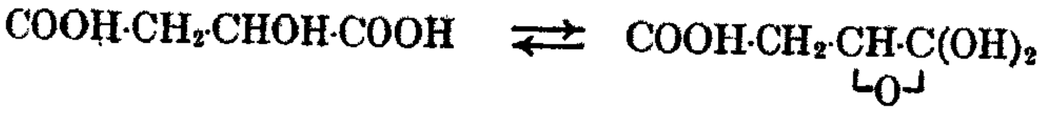
A mechanism of the hydrolysis of the chlorosuccinic acid to malic acid will be found to be somewhat different from that suggested by Holmberg (1927). Accepting a malic acid lactone as the probable intermediate, since the evidence of Holmberg seems clear on that point, the differences in the course of hydrolysis must occur in the hydrolysis of that lactone. The first step will be the formation of the lactone.

$$\bar{\mathrm{O}}\cdot\mathrm{CO}\cdot\mathrm{CHCl}\cdot\mathrm{CH_2}\cdot\mathrm{CO}\cdot\bar{\mathrm{O}} \longrightarrow \bar{\mathrm{O}}\cdot\mathrm{CO}\cdot\underbrace{\mathrm{CH}\cdot\mathrm{CH_2}\cdot\mathrm{CO}\cdot\mathrm{O}} + \bar{\mathrm{Cl}}$$

levorotatory anion of chlorosuccinic acid

dextrorotatory anion of the lactone of malic acid

There is nothing in Holmberg's work to establish whether the lactone in question is an alpha or a beta lactone. However, we[1] have previously shown that the fact that l-malic acid is dextrorotatory in concentrated aqueous solution, and under certain other conditions, is due to the fact that it consists of a mixture of tautomeric forms of the formulas:



$$\mathrm{COOH}\cdot\mathrm{CH_2}\cdot\mathrm{CHOH}\cdot\mathrm{COOH} \rightleftarrows \mathrm{COOH}\cdot\mathrm{CH_2}\cdot\underbrace{\mathrm{CH}\cdot\mathrm{C}}_{\mathrm{O}}(\mathrm{OH})_2$$

normal levorotatory form

ethylene oxide dextrorotatory form

The existence and dextrorotation of this ethylene oxide form was shown by a study of the properties, especially the optically rotatory power, of several related compounds and of the malic acid itself. It is well known that the formation of the lactide from lactic acid, while not commonly believed to be a lactone in the same sense, does involve a change from a chain to an oxygen-containing ring structure and does show the lactide to possess an opposite and remarkable enhanced rotation when compared with the original lactic acid. A similar lactone has been described by Levene and Haller.[2] They reported that a levorotatory gamma-valerolactone ([a] = −27°) was converted by

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[1] Bancroft and Davis: J. Phys. Chem., 34, 897 (1930).

[2] Levene and Haller: J. Biol. Chem., 69, 165 (1926).

treatment with alkali into the dextrorotatory salt ([a] = +2.7°) and that this salt on addition of sulphuric acid gave the free gamma hydroxyvaleric acid ([a] = +14°). This indicates that the formation of such a lactone as is here postulated would be accomplished without change of configuration and that the lactone would have the opposite sign of rotation to that of the original acid.

Some light might be thrown on the question as to the type of lactone formed from the chlorosuccinic acid by a comparison of similar reactions in the case of alpha and beta-hydroxybutyric acids. Only one type of lactone could be formed in each of these substances while either type could be formed from malic acid. The data are not very extensive, but Fischer and Scheibler[1] did hydrolyze a dextrorotatory beta-chlorobutyric acid at room temperature to obtain a levorotatory beta-hydroxybutyric acid. This is opposite to the effect of silver oxide in the usual tables of the Walden inversion; but further study shows that this hydrolysis was effected by four equivalents of silver oxide per mol of neutralized acid. This excess of silver oxide is larger than any excess reported in this paper and must therefore give the same effects as would have been obtained in an alkaline solution. Therefore the beta-chlorobutyric acid hydrolyzed exactly as the chlorosuccinic acid would under the same conditions. On the other hand the same authors also hydrolyzed some of the same acid in water only (therefore in acid solution) and obtained again a levorotatory beta-hydroxybutyric acid. This experiment was carried out at the boiling point under poor control and resulted in extensive racemization. On their face these two experiments appear to show that in a case in which only beta-lactone could form the course of the hydrolysis is less affected by the acidity of the medium than is the hydrolysis of the chlorosuccinic acid. This would establish the probability that the hydrolysis of the latter acid which is so sensitive to changes in acidity goes through the intermediate formation of an alpha-lactone and not the beta-lactone given by Holmberg. Lacking any comparable data on the alpha-chlorobutyric acid, we are unable to draw any conclusions. Again is emphasized the necessity of carrying out these reactions under very definite conditions, especially with regard to the relative amounts of substances employed.

These considerations indicate that we should accept a lactone as the intermediate step in the hydrolysis, that the rotation of the lactone is in the opposite direction to that of the free chlorosuccinic acid, and that the weight of evidence inclines toward the view that the lactone in question is an alpha lactone of the type we have previously discussed in connection with malic acid. We assume for such an alpha lactone, as Holmberg did for the beta lactone, that no change in configuration takes place in the formation of the lactone from the chlorosuccinic acid.

The way in which the lactone ring breaks down determines whether or not inversion takes place. Disregarding the optical activity for the moment, it is evident that there are two ways in which the lactone ring can break:

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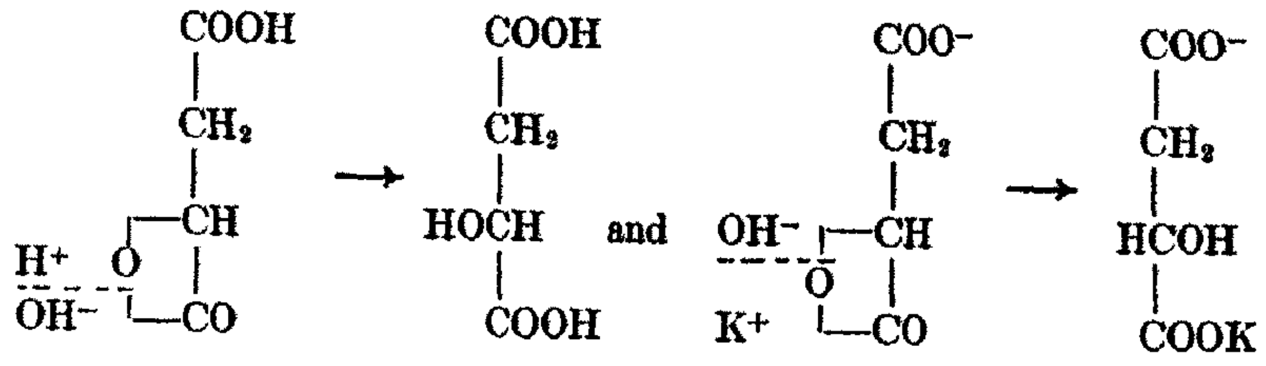
[1] Fischer and Scheibler: Ber., 42, 1227 (1909).



Coming back to the question of optical activity, it is equally evident that the two different ways of reacting would be expected to give two different optically active substances. In the acid reaction as postulated there is no break of the bond between the asymmetric carbon atom and the oxygen. Consequently there can be no inversion and consequently the levorotatory malic acid (the product in acid solutions) has the same configuration as the levorotatory chlorosuccinic acid. Hydrolysis in alkaline solutions produces the oppositely rotatory malic acid showing that the hydroxyl group goes in at some other bond position than the original lactone oxygen bond. Hydrolysis in alkaline solution must produce the salt and is accompanied by inversion.

Conclusions

1. Thirty-five years of study have brought no satisfactory solution of the baffling problems of the Walden Inversion. One important reason for this is the lack of data which are really comparable.

2. Among the first and most widely used substances for the study of the inversion are malic acid and its derivatives. In this series, hydrolysis reactions are governed by the acidities of the solutions and by the varying amounts of suspended hydrolyzing agents.

3. It has been shown that in the conversion of levorotatory chlorosuccinic acid into malic acid, the speed of the reaction is proportional to the hydroxyl ion concentration, and the final products are mixtures of d- and l-malic acids, alkaline solutions favoring the preponderance of the d-malic acid to an extent which, within limits, is proportional to their alkalinity.

4. This is in agreement with the extensive work of Holmberg who postulates an intermediate dextrorotatory malic acid lactone from which acids and alkalies produce oppositely rotatory forms of malic acid.

5. A similar phenomenon has been observed when l-bromosuccinic acid is hydrolyzed in the presence of varying quantities of silver oxide. In the presence of less than 2.7 equivalents of the oxide per mol of acid, the product contains an excess of l-malic acid while more silver oxide causes the product to contain more than 50% d-malic acid.

6. This also confirms the findings of Holmberg and these phenomena throw some light on the failure of the data of the Walden Inversion to agree with some of the other properties of the insoluble oxides, for instance, and on the method which should govern future research in this field.

7. It is pointed out that little more actual progress can be made on this problem until a definite correlation between the rotations and the configurations be established for such simple substances as the halogen succinic acids and malic acid. It is necessary to know when a Walden Inversion takes place in order to study it intelligently.

8. The mechanism is outlined by which the acid hydrolysis of the lactone produces a malic acid of the same rotation and configuration as the original chlorosuccinic acid while the alkaline hydrolysis results in a Walden Inversion, with the oppositely rotatory malic acid. This is opposite to the conclusions of Holmberg and of Levene but in agreement with those of Freudenberg.

Cornell University.

PRINCIPLES DETERMINING THE ARRANGEMENT OF ATOMS AND IONS IN CRYSTALS*

BY M. L. HUGGINS

So many types of crystal structure have been worked out and so much is known concerning the structures of the atoms of which they are composed that it is now possible to determine to a large extent what are the principles determining the arrangement assumed. Such principles are useful in arriving at the structures of other substances. They are also of aid in studies of interatomic forces, and so of molecular structures.

Although some of the ideas to be expressed in this paper originated with the author, many are due to Lewis,[1] the Braggs,[2,3] Goldschmidt,[4] Cuy,[5] Pauling[6] and others.

The first principle to be mentioned is that the influence of an atom on other atoms decreases very rapidly with distance, so that the effect on all but those atoms immediately adjacent to the given atom is almost negligible. Second, atoms of the same kind crystallizing in the same environment, tend to be surrounded similarly. As a result of this, all like atoms or ions are almost invariably surrounded in a similar fashion throughout a given crystal, except of course in such cases as crystals of organic molecules where the surroundings of the atoms were in part determined long before the crystallization.

Combining these two principles, one concludes that the arrangement in a crystal should repeat itself at rather short intervals—that the unit cell should contain relatively few atoms or ions or molecules—and this is known to be the case.

The third principle is that of neutrality. Neglecting the surfaces, which might possess slight excesses of electrical charges, the whole crystal (and hence the unit cell) must be electrically neutral. If a crystal is built up of ions, this determines for simple salts or limits for complex salts the relative numbers of the different kinds of ions, and so the chemical formula.

Another closely related principle may be stated as follows: Negatively charged ions tend to be surrounded by positively charged ions, and vice-versa. No exceptions to this rule are knowm. Both this and the preceding rule are of course derivable from potential theory or from a consideration of the fact that during crystallization an ion would always be drawn toward an ion or group of ions of opposite sign.

One can generalize still further from potential theory and conclude that if a crystal contains anions of more than one kind, those having the greatest negative charge would tend to be in the positions of greatest positive potential,

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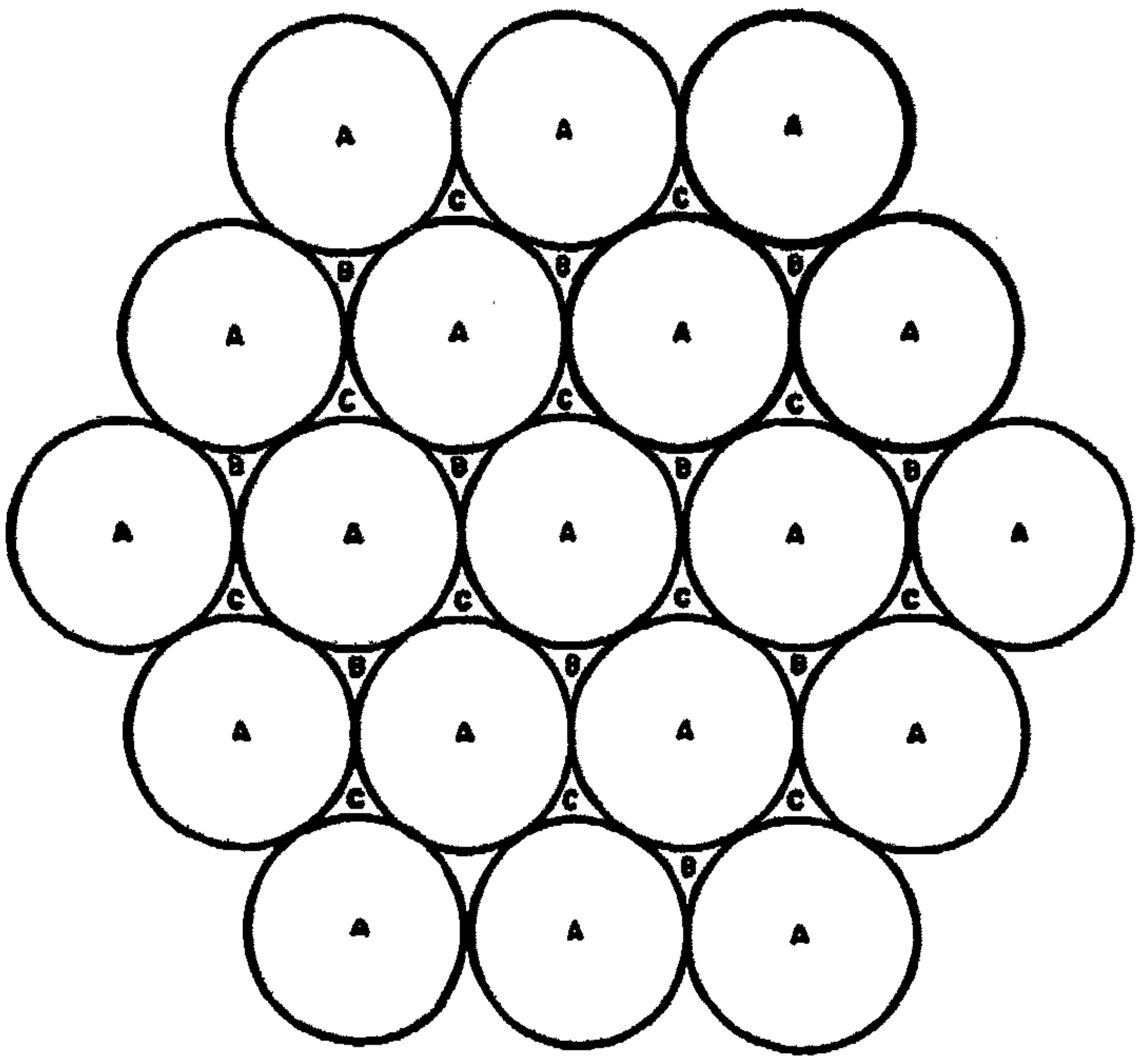

Fig. 1

A layer of spheres in a "close-packed" assemblage. The sphere centers in the next layer are over points marked "B." In the "hexagonal close-packed arrangement" the spheres in the third layer are directly over those in the first, giving the sequence ABABAB.... In the "cubic close-packed arrangement" the sequence is ABCABCABC....

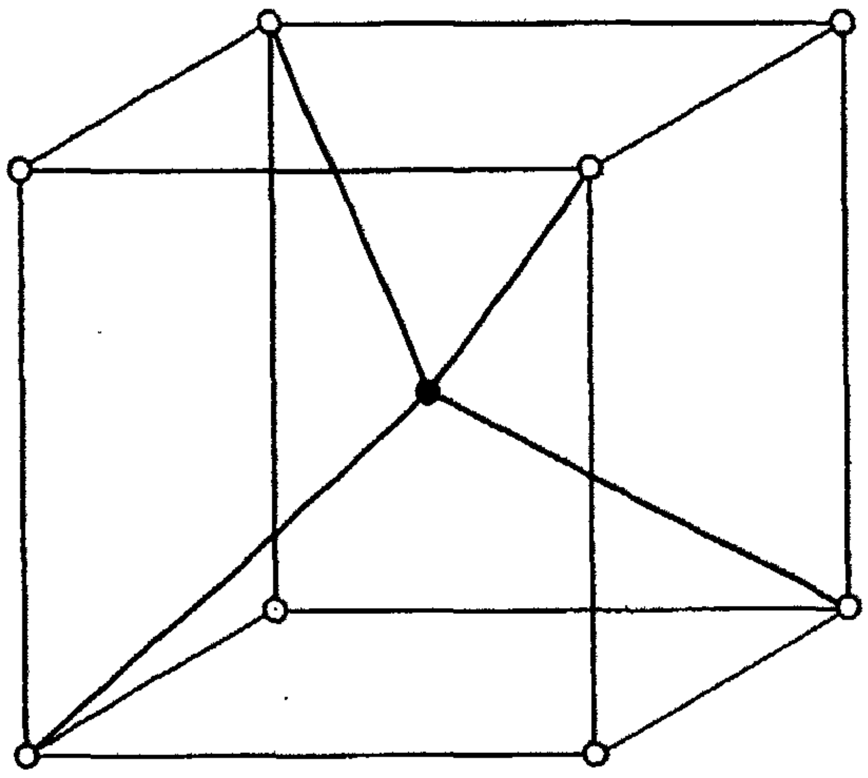

Fig. 2
The unit cube of the CsCl structure.

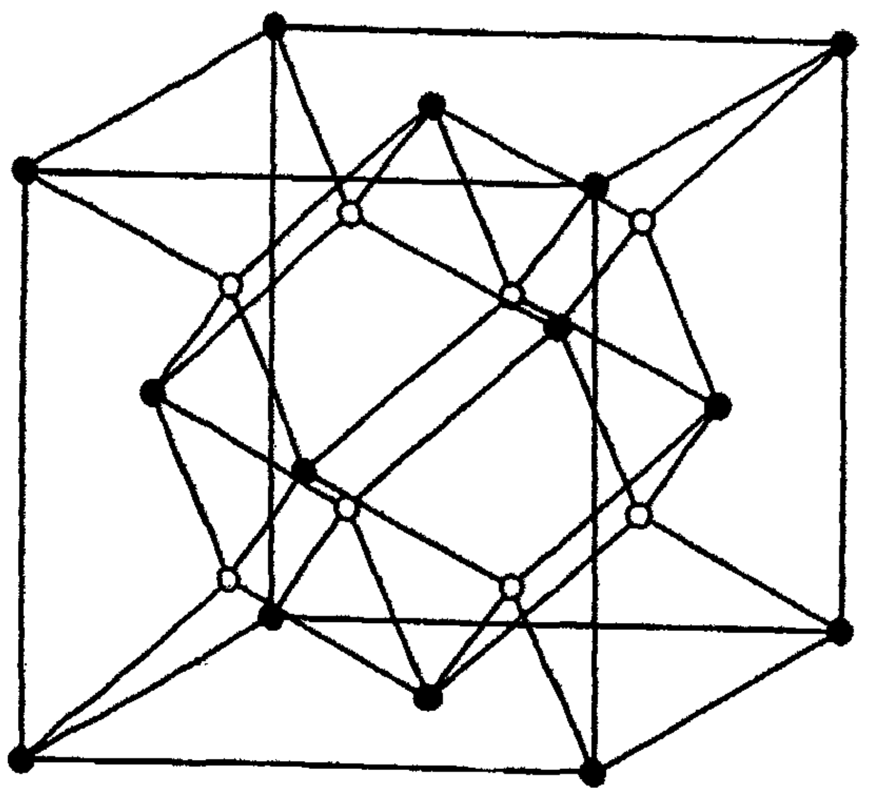

FIG. 3
The unit cube of the CaF_2 structure.

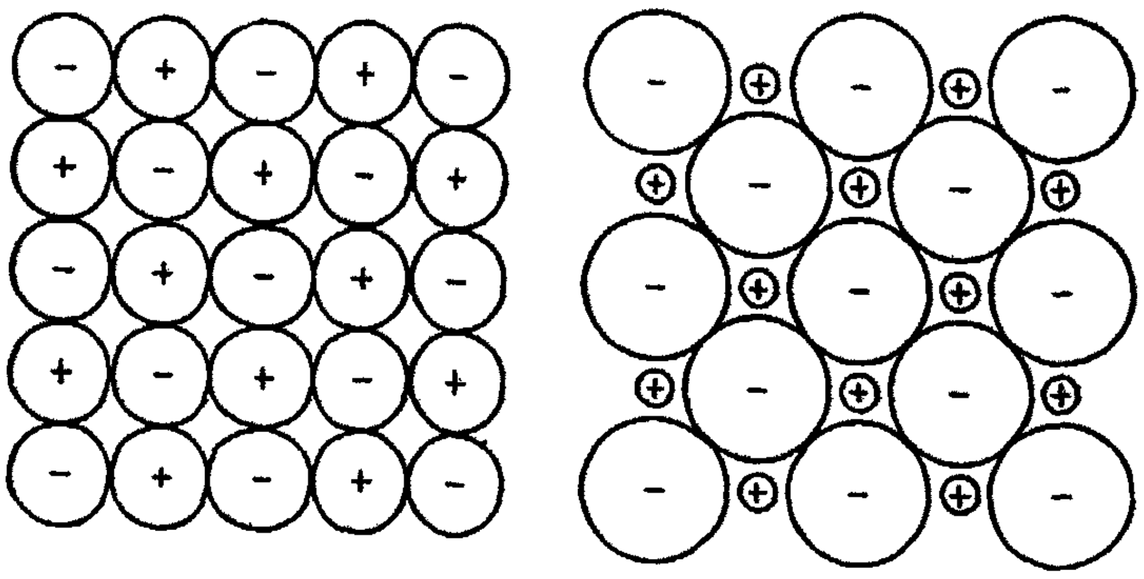

FIG. 4
Illustrating by a two-dimensional analogy, the principle of relative ionic size. This arrangement of ionic centers would be stable for ions of approximately the same size (as shown on the left) but unstable for ions differing greatly in size (as on the right).

those having a smaller charge would tend to be in a position of less positive potential (although still surrounded by positive ions.) This is equivalent to Pauling's "electrostatic valence principle".[6] That something else is involved than potential theory, as applied to point charges, is evident from the fact that the corresponding relationship for cations does not hold.

The next principle to be mentioned is that of "close-packing".[1] It can readily be shown that the most stable arrangements for atoms with spherical force-fields are the same as the arrangements one would get by packing spheres of equal size as closely together as possible,—arrangements in which each atom or sphere is surrounded at equal distances by twelve others (Fig. 1).

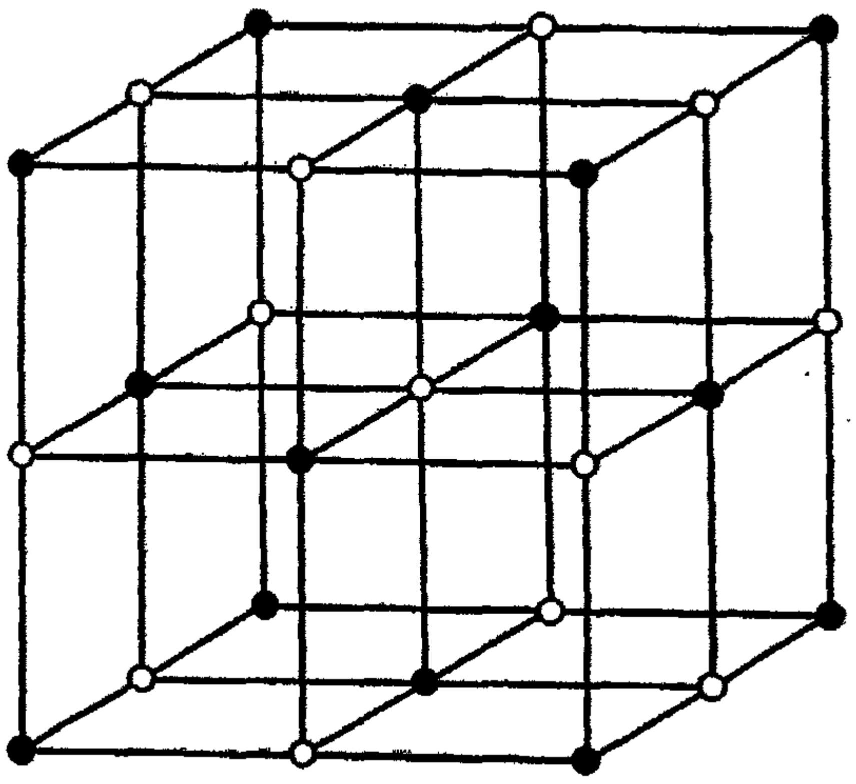

Fig. 5

The unit cube of the NaCl structure. The arrangement of like atoms is the "face-centered cubic" or "cubic close-packed" arrangement. Each atom is surrounded symmetrically by six of the other kind.

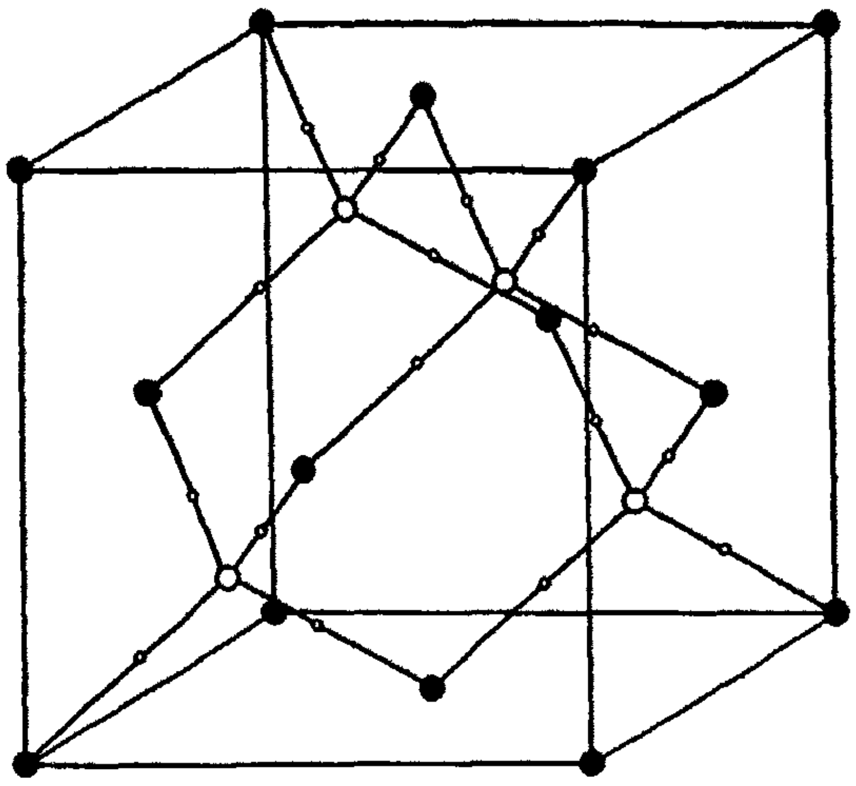

Fig. 6

The unit cube of the ZnS structure. The distribution of the valence electron pairs is indicated by the small circles. Each atom is surrounded symmetrically by four of the other kind. The arrangement of like atoms, considered by themselves, is the same as in the NaCl structure.

The most symmetrical of these arrangements—that of "cubic close-packing" is the one found for solid argon.

The close-packing principle is important also for crystals composed of ions. If the ions are of approximately equal size the closest packing consistent with the rule that each ion is to be surrounded by ions of opposite charge, will be that in which each is surrounded by as many as possible ions of the other kind. If the compound is of the type AB, with equal numbers of A and B ions, this number is eight and the structure is that known as the cesium chloride structure (Fig. 2). In an AB_2 compound there can at most be eight B ions around each A ion and four A ions around each B ion—as in the calcium fluoride structure (Fig. 3).

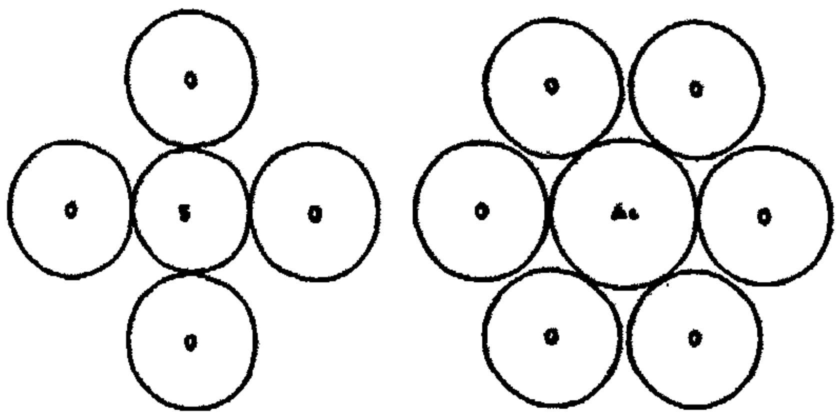

Fig. 7

Illustrating in two dimensions the distribution of oxygen atoms around Si and Al in silicates.

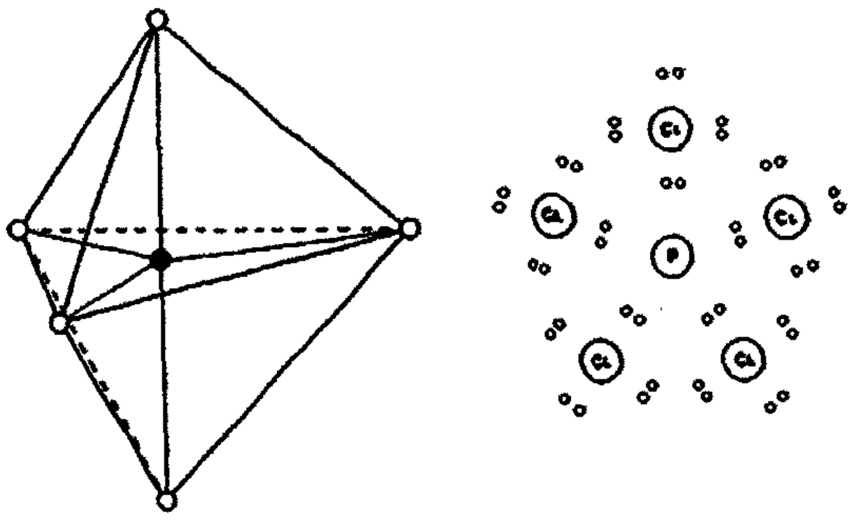

Fig. 8

The probable distribution in space of the atoms in PCl_5, with the corresponding electron formula.

If the ions are of quite different size[4,5,6] arrangements such as these would place like ions too close together as compared with the distances between unlike ions. Closer packing and greater stability is obtained then if the like ions, considered by themselves, form a close-packed lattice. One can roughly approximate the facts by considering the ions as spheres, and assuming that any structure with the spheres of like ions in contact is unstable (Fig. 4). The cesium chloride structure then becomes less stable than the sodium chloride structure (Fig. 5) and that in turn less stable than the zinc sulfide

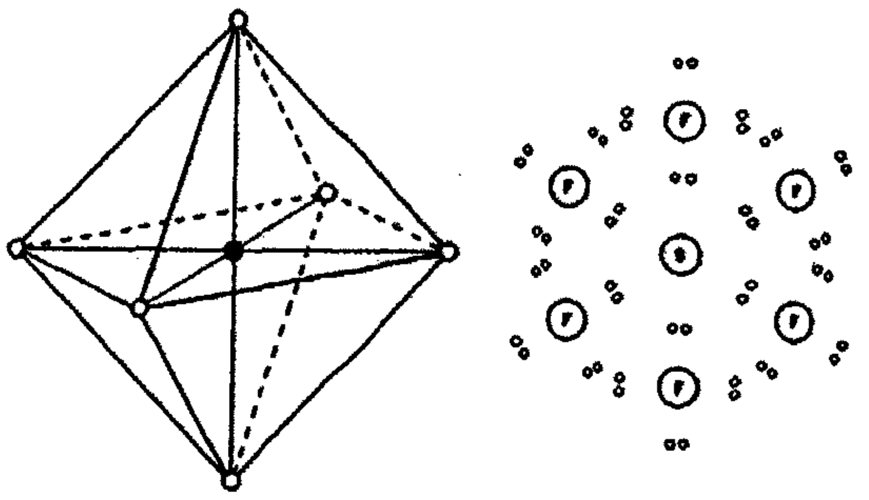

FIG. 9
The probable arrangement of atoms in SF$_6$, with the corresponding electron formula. (This arrangement is the same as that found for SiF$_6^{=}$ in crystals.)

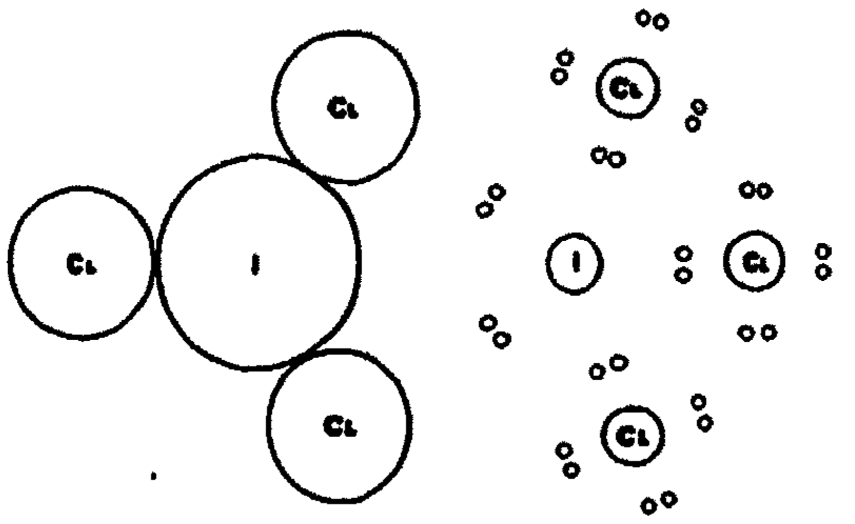

FIG. 10
Probable atomic distribution in ICl$_4$, with the corresponding electron formula.

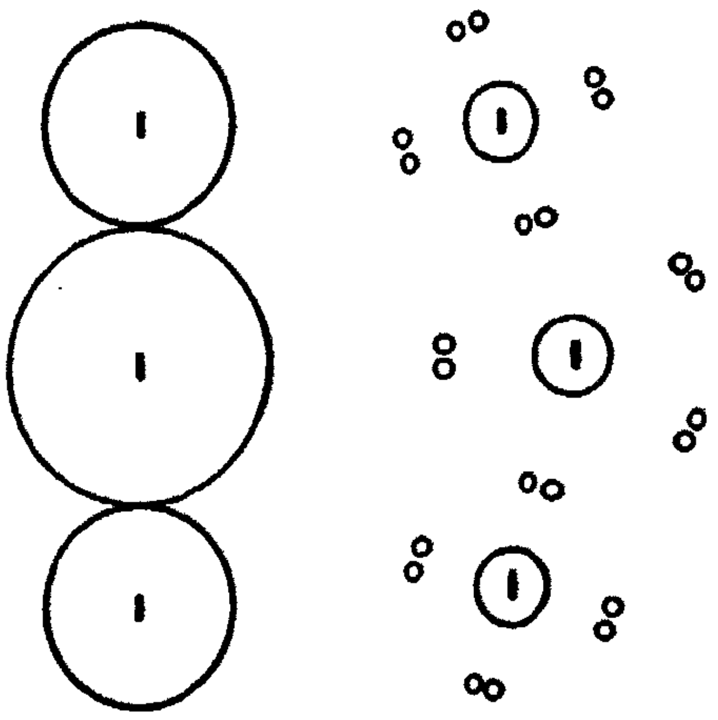

FIG. 11
The arrangement of the atoms in the I$_3^-$ and ICl$_2^-$ ions, with the corresponding electron formula.

structure (Fig. 6) as the ratio of the two radii departs further from one. In both the sodium chloride and the zinc sulfide distributions each ion is equidistant from twelve others of the same sign while in the cesium chloride structure each is equidistant from only eight other like ions.

Similar considerations often determine the number of atoms or ions of opposite sign around a given atom or ion in more complex structures. If the central atom is relatively large compared with the outer atoms, the co-ordination number will be large (say 6 or 8) unless other factors interfere, while if the central atom is relatively small the coordination number must be small, usually four. Thus silicon in silicates seems to be surrounded invariably by four oxygen atoms, while aluminum, somewhat larger, always has six oxygen atoms around it[3] (Fig. 7). The substitution of fluorine for oxygen, however, increases the coordination number of silicon to six, due partly to the smaller size of the fluorine and partly to the decreased repulsion between the negative atoms.

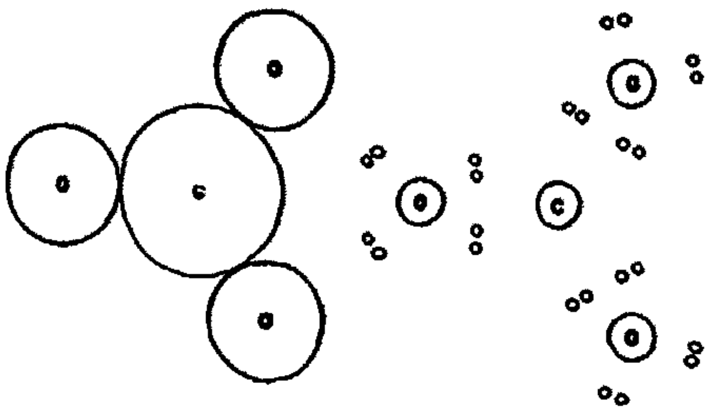

FIG. 12

The arrangement of the atoms in the carbonate and nitrate ions in crystals, with the corresponding electron formula.

Another factor in this and some other cases is the mutual repulsion between the electron pairs of the valence shell of the central atom. If this valence shell has a relatively small radius, as is usually the case for electronegative atoms, only four pairs can surround the kernel without making them too close to each other. However, with more electropositive atoms the valence shells are relatively large and six or more valence pairs can be accommodated. The determining factor then seems to be the repulsion between the surrounding atoms rather than between the electron pairs. Examples of electronegative atoms probably having 5 or 6 pair valence shells are found in phosphorous pentachloride (Fig. 8), sulfur hexafluoride (Fig. 9), iodine trichloride (Fig 10), the tri-iodide and dichloroiodide ions (Fig. 11) and the carbonate and nitrate ions (Fig. 12).

Atoms of electronegative atoms frequently complete their valence shells by sharing electron pairs with other electronegative atoms.[1] From the chemical formula and the number of valence electrons each atom furnishes one can readily calculate the number of shared pairs necessary to give each negative atom its complete shell. Thus in iodine crystals, with seven valence electrons per atom, each atom shares one pair; in selenium and tellurium and probably also sulfur, each atom shares two pairs; in phosphorous, arsenic, antimony and bismuth each atom shares three pairs; and in carbon and silicon each atom shares four (Fig. 13). In the last case the angles between the bonds are those between the lines joining the center of a regular tetrahedron with its corners. If only two or three of the four pairs around an atomic kernel serve as bonds, this angle tends to be somewhat larger, due to the repulsion between the bonded atoms.

As another example may be mentioned "arsenic trioxide", so-called. Each arsenic atom furnishes five valence electrons and each oxygen six. To complete the valence shells each arsenic shares three pairs with oxygens and each oxygen two pairs with arsenic atoms. This determines the empirical formula As_2O_3. The angles between bonds in a molecule of this complexity however would be far from those of a regular tetrahedron and like atoms would be drawn too close together for great stability, so a molecule of the formula As_4O_6, having the structure shown in Fig. 14 is formed.[7] For this molecule the objections mentioned do not hold.

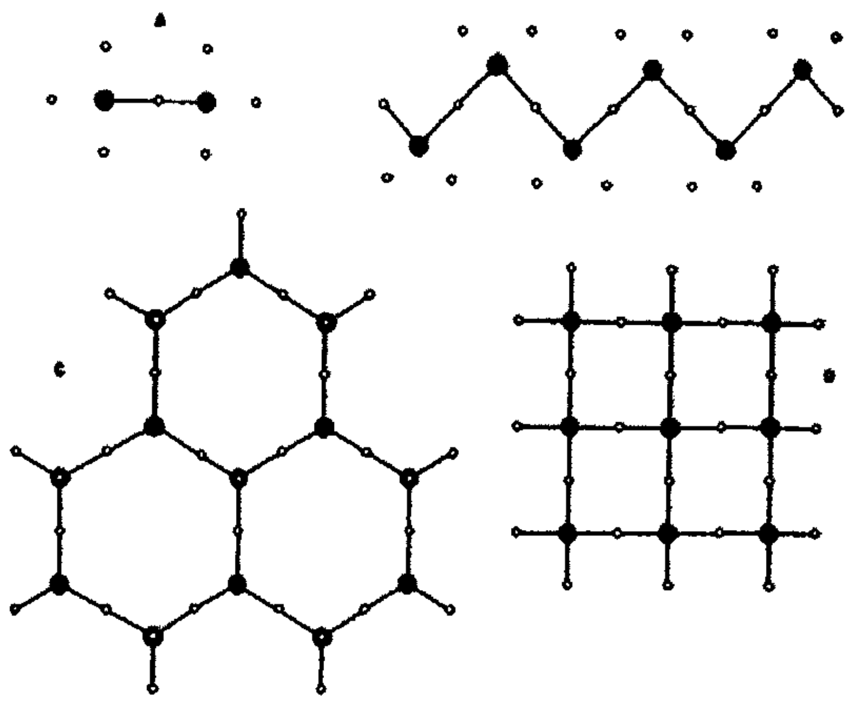

FIG. 13
Illustrating the formation of (A) diatomic molecules as in I_2, (B) string molecules as in Se, (C) layer molecules as in As, and (D) whole crystal molecules as in the diamond, as the result of the tendency of electronegative atoms to complete their valence shells.

The principles thus far mentioned do not in every case determine the orientation of the valence shells of the electronegative atoms or ions with respect to the surrounding electropositive atoms or ions. In some cases the valence electron pairs must be on or near the centerlines joining these atoms, and it would seem reasonable to assume that this would be the case wherever it is structurally possible. In a crystal of the zinc sulfide type for instance, we should expect the sulfur valence tetrahedra to be pointed toward the zinc kernels, giving a tetrahedron also around the latter (Fig. 6). In ferrous disulfide or pyrite, FeS_2, one of the four valence pairs around each sulfur kernel is shared with another sulfur; the others we should expect to be pointing

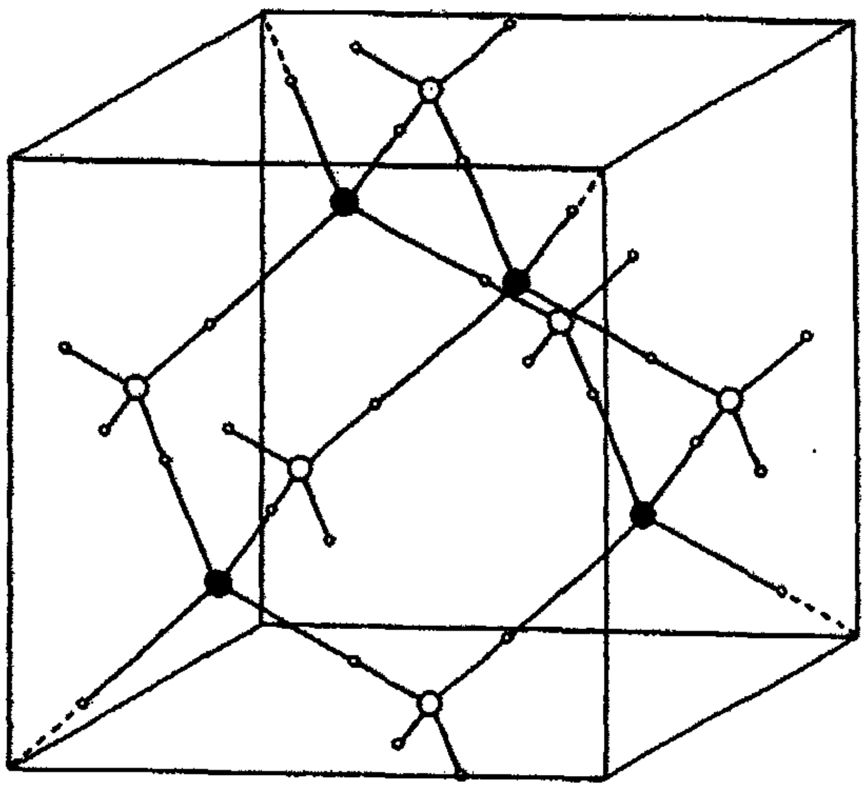

FIG. 14

The arrangement of atoms and of valence electron pairs (small circles) in a molecule of As_4O_6, as found in crystals of "arsenic trioxide." Large dots denote As, large circles O atoms.

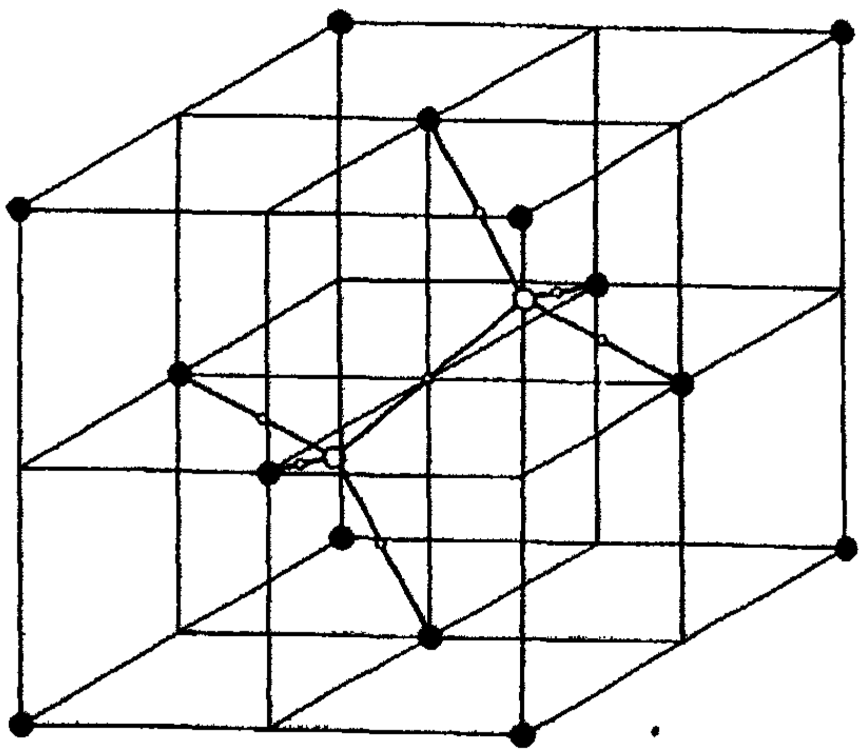

FIG. 15

Showing the arrangement of pairs of valence electrons (small circles) and iron kernels (large dots) around the sulfur kernels (large circles) in a crystal of FeS_2, pyrite. The structure is like that of NaCl (Fig. 5) with Na and Cl replaced by Fe and S_2 groups, respectively.

toward the three neighboring doubly charged iron kernels (Fig. 5) giving an octahedron of six pairs around each of the latter.

One more example will be given. Mercuric iodide consists[8] of layers in which each mercury is tetrahedrally surrounded by four iodines, while each iodine has two mercury atoms adjacent roughly at two corners of a tetrahedron. Orientation of the valence tetrahedra around the iodine kernels toward the mercury atoms gives a similar but larger tetrahedron around each mercury kernel (Fig. 16).

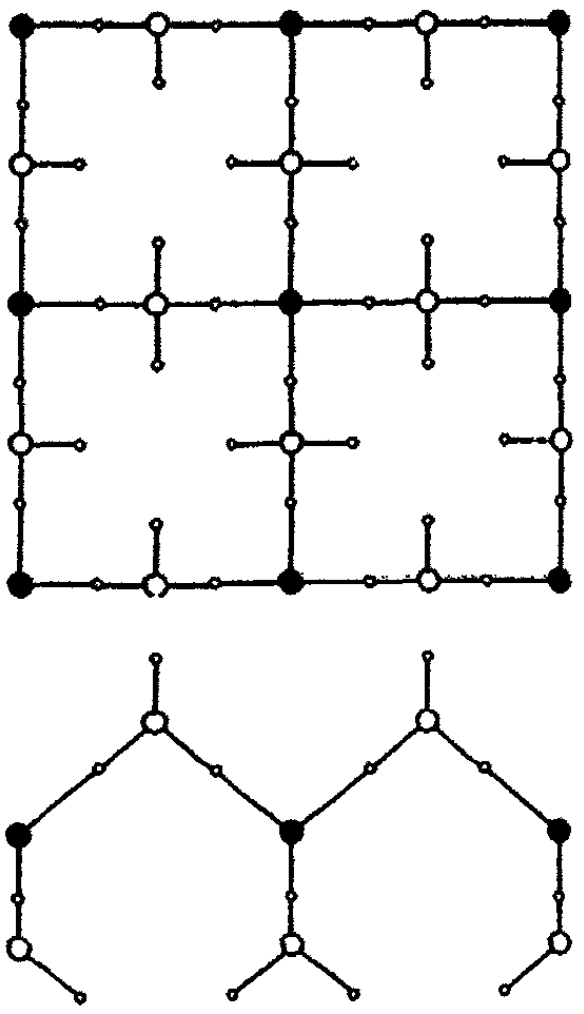

Fig. 16

Showing, in plan and elevation, the arrangement of atomic kernels and valence electron pairs in a layer of the HgI_2 structure. Large dots denote Hg, large circles I atomic centers.

Structures such as this cannot be attributed solely to the attractions between spherical ions. There is apparently also a definite attraction between the kernels of the metal atoms and the valence pairs, resulting usually in tetrahedral or octahedral or cubic valence shells around these metal kernels, depending on the size relationships and structural limitations.

These structural limitations are largely a matter of pure geometry. It frequently happens that all of the tendencies I have mentioned cannot be completely satisfied. Either one of the weaker tendencies remains unsatisfied, as in sodium chloride, where it is impossible for the chlorine valence pairs to be on the atomic centerlines—there being six centerlines and only four pairs—or a compromise is reached, as in corundum, Al_2O_3. Each aluminum wants to be surrounded by six oxygens at corners of a regular octahedron, and each oxygen wants to have four aluminum atoms around it at corners of a regular tetrahedron, but both of these tendencies cannot be satisfied. So actually each aluminum is surrounded by oxygens at corners of a very much distorted octahedron and each oxygen by aluminums at corners of a very much distorted tetrahedron.

Another principle of which considerable use has been made is that of the approximate constancy of size of an atom in similar structures. What is meant by "size" depends on one's definition or method of calculation, but in spite of differences of opinion in this regard, the idea has proved a most useful one. One can also generalize regarding the relative sizes of different atoms—the effect of increasing the kernel charge or the number of shells in the kernel, etc.—and the differences in size of the same kind of atom in different structures but time will not permit of more discussion of this now.

In presenting these principles no attempt has been made at completeness, nor have they been given in what will probably be their simplest or most useful forms. However if this paper will help to promote a better understanding of the reasons for the various types of crystal structures observed, my object will have been fulfilled. The better these reasons are understood the easier it will be to work out new arrangements and the better we will understand atomic structures, molecular structures and the explanation of properties in terms of these structures.

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CHEMICAL ACTION IN THE GLOW DISCHARGE

VI. The Oxidation of Carbon Monoxide

BY A. KEITH BREWER AND PAUL D. KUECK*

The oxidation of carbon monoxide in the glow discharge is of particular interest from two angles. First, it shows the physical state in which the molecules must be placed to become chemically active. Second, it enables the reaction to be studied in steps from the simple non-propagating oxidation, through various lengths of reaction chains, until ignition point is reached.

The cathodic combustion of carbon monoxide has been studied by Finch and Hodge.[1] The investigators conclude the combustion to be determined by ions of both constituent molecules, and that metal atoms sputtered from the cathode are of vital importance in aiding the reaction by overcoming the electrostatic repulsion between the ions.

Recently Finch and Thompson[2] failed to find bands due to ionized carbon monoxide in the cathode zone of an electric discharge in a $2CO/O_2$ mixture. From this they conclude, in contradiction to their previous contentions, that the ionization of carbon monoxide is unnecessary in this reaction. At the same time they state that the failure to find bands due to ionized oxygen is no indication of the absence of these ions.

Lind and Bardwell,[3] studying this reaction in the presence of radon, found that carbon monoxide, when sufficient oxygen was present for combustion, was completely oxidized to carbon dioxide. The maximum ratio of molecules formed to ions reacting was obtained with the combining mixture; from this it was concluded that CO^+ and O_2^+ ions are equally effective. Average values of $M_{(CO+O_2)}/N_{(CO+O_2)} = 6$, or $M_{CO_2}/N_{(CO+O_2)} = 4$, were obtained.

Hunt and Schumb,[4] investigating the carbon monoxide oxygen equilibrium found in general that the rate of oxidation was increased by excess carbon monoxide and retarded by excess oxygen.

The ignition of carbon monoxide oxygen mixtures in the condensed electric discharge has been studied by several investigators[5,6,7] with the apparent agreement that propagation takes place when the ion density in the discharge reaches a definite value depending on the conditions involved.

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* Fertilizer and Fixed Nitrogen Investigations, Bureau of Chemistry and Soils, Washington, D. C.

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Apparatus

The apparatus and general method of procedure employed were described[8] in earlier article appearing in this series.[8,9]

The carbon monoxide used was prepared by the action of formic acid on phosphoric acid. The other gases were purified as described in previous communications.

Results

The oxidation of carbon monoxide follows much more closely the oxidation of hydrogen[9] than it does the oxidation of nitrogen.[10] This is due to the fact that at pressures higher than about one centimeter propogation or chain reactions occur with both hydrogen and carbon monoxide.

An electric discharge in a $2CO/O_2$ mixture at liquid air temperatures gives carbon dioxide as the reaction product, while in the presence of excess carbon monoxide or of neutral gases, carbon suboxide is deposited on the walls of the tube along with carbon dioxide. Carbon monoxide alone dissociates into carbon dioxide and carbon suboxide; the rate is from a quarter to a half that for the oxidation.

Reaction in the Negative Glow. A typical curve for the rate of carbon dioxide synthesis from a $2CO/O_2$ mixture in the negative glow is illustrated in Fig. 1, curve 1. Curves of this type have been taken with discharge tube No. I, at pressures as high as 30 mm, without any further increase in rate than that occurring at 15 mm., and with no tendency towards ignition. Indeed it has never been possible to produce ignition of a $2CO/O_2$ or $2H_2/O_2$ mixture in the negative glow; propagation appears to start only in the positive column.

At pressures below about 9 mm., the rate accelerates in a manner very different from that observed for the previous reactions of this series. It will be noted that the voltage as given by curve IV increases simultaneously with the increase in rate. The rise in voltage at these pressures appears to be due to a change in the normal cathode fall of potential occasioned by the deposition of carbon dioxide and possibly the suboxide on the cathode. Since the rate of ion production is very nearly proportional to the normal cathode fall, the observed increase in synthesis is to be expected.

The effect of current on the rate of synthesis was investigated over the range from 10 ma to 50 ma. The rate was found proportional to the current in tubes I and II over the entire current and pressure range for the negative glow.

The results obtained by varying the ratio of carbon monoxide to oxygen are illustrated in Fig. 2. Curve 2 was taken at 3.5 mm. in tube No. II, equipped with aluminum electrodes, while curve 1 was taken at 10 mm. with iron electrodes in tube No. 1.

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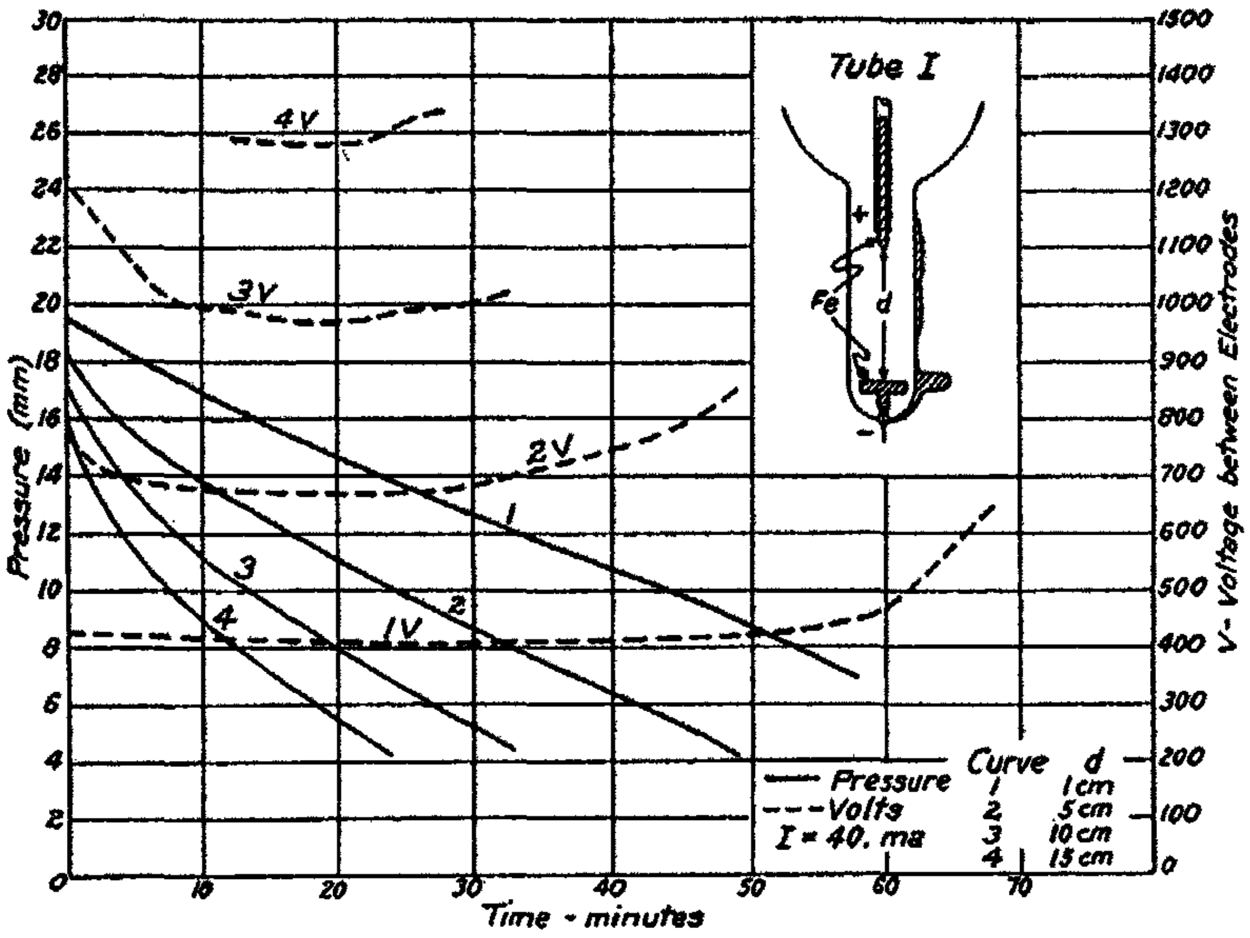
Tube I
Fe
d
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4V
3V
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1
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Pressure (mm)
V- Voltage between Electrodes
Time - minutes
— Pressure
--- Volts
I = 40. ma
Curve d
1 1cm
2 5cm
3 10cm
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0 2 4 6 8 10 12 14 16 18 20 22 24 26 28 30
0 100 200 300 400 500 600 700 800 900 1000 1100 1200 1300 1400 1500
10 20 30 40 50 60 70

FIG. 1

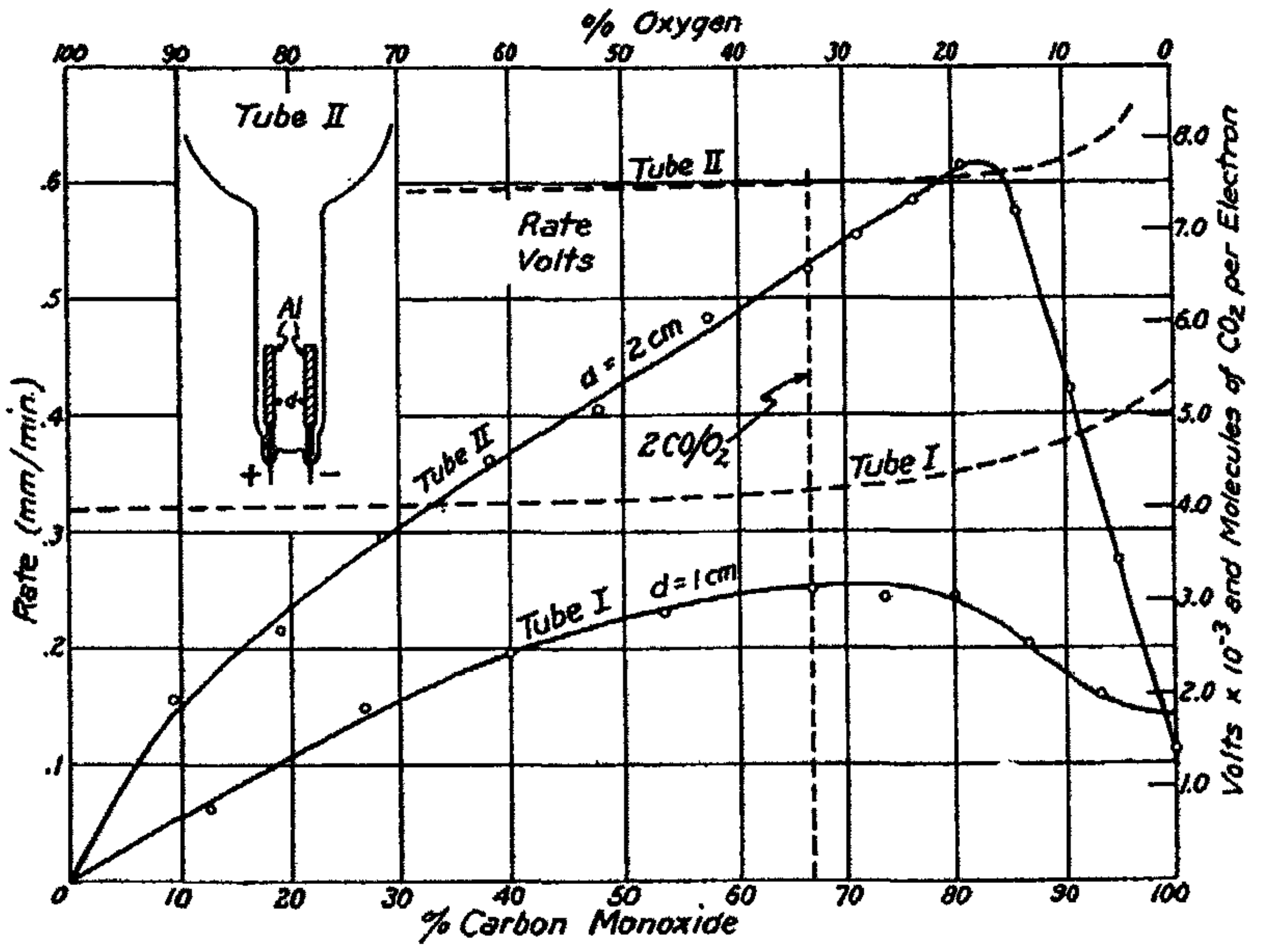
% Oxygen
100 90 80 70 60 50 40 30 20 10 0
Tube II
Al
d
+
-
Tube II
Rate
Volts
d = 2cm
Tube II
2CO/O₂
Tube I
Tube I
d = 1cm
Rate (mm/min.)
.1 .2 .3 .4 .5 .6
Volts × 10⁻³ and Molecules of CO₂ per Electron
1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0
% Carbon Monoxide
0 10 20 30 40 50 60 70 80 90 100

FIG. 2

The difference in rate for curves 1 and 2 is due primarily to a difference in the voltage characteristics of the two tubes rather than to the difference in pressure. The cathode drop in potential was about twice as great for tube II as for tube I.

The effects of excess carbon monoxide and oxygen are shown further in Fig. 3; the results with helium and argon are also given. These data were taken under the same conditions as was curve 2 of Fig. 2.

It will be noted from Figs. 2 and 3 that excess carbon monoxide has an accelerating effect on the rate in all mixtures in which it constitutes less than 80% of the entire volume. Over this composition range oxygen retards the rate almost in proportion to the amount present.

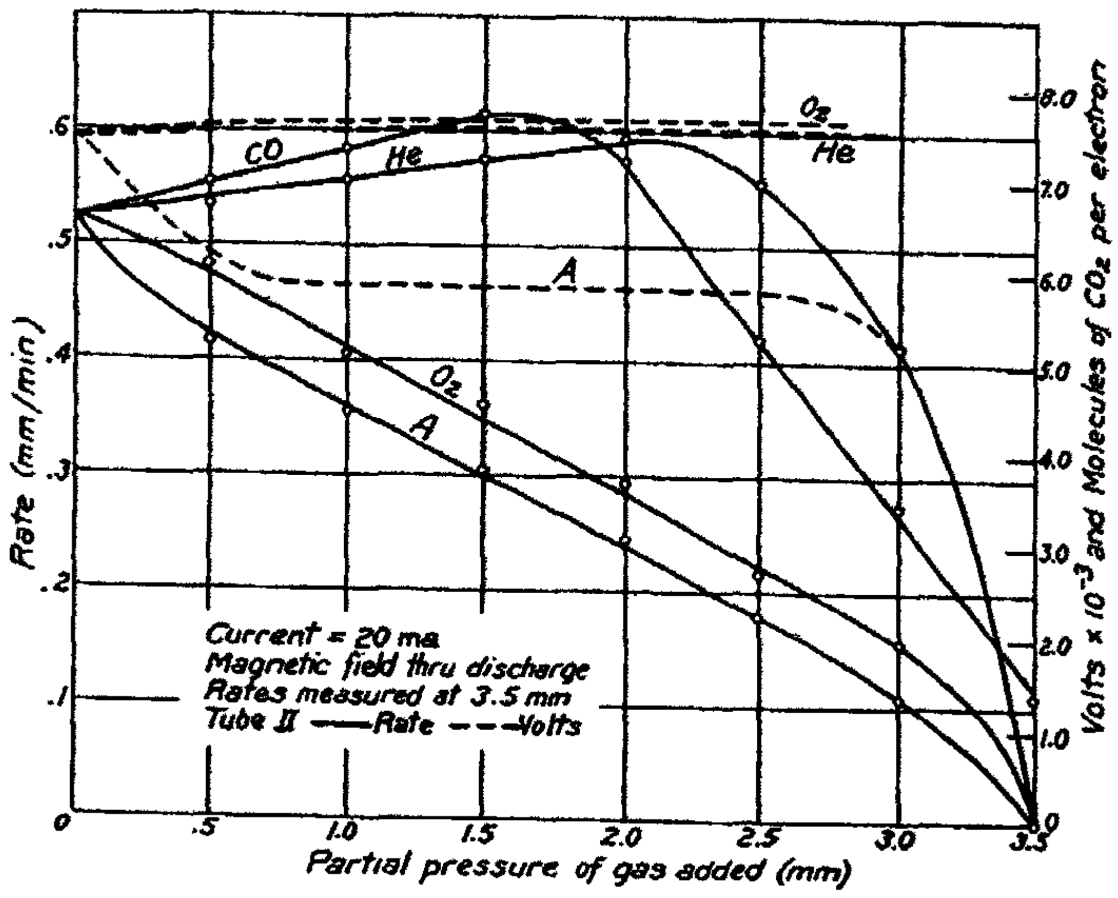

Fig. 3

The fact that excess carbon monoxide shows a more pronounced accelerating effect in curve 2 than in curve 1 of Fig. 2 is due primarily to the proximity of the electrodes to the walls. The cathode in tube II was 1 cm. from the walls, while in tube I it was but 5 mm.; the composition for maximum rate approaches a $2CO/O_2$ mixture as the distance between the cathode and the walls increases.

Reaction in the Positive Column. The reactivity in the positive column for various lengths of electrode separation is given in Fig. 1. Curve 1 gives the rate of synthesis in the negative glow alone. The difference in the slopes of the curves represents the reactivity in the positive column for the length and pressures given.

The rates for different pressures and electrode separations are tabulated in Table I.

A comparison of the values at 8 mm. and 16 mm. shows that the rate increases rapidly with increasing pressure, the longer the positive column the more pronounced the effect. The difficulty involved in starting the discharge made it impossible to determine the rate at pressures just under the ignition point. However, curve 4 of Fig. 1 is started not far below this pressure. Propogation apparently takes place when the rate curve approaches an asymptote parallel to the voltage axis.

TABLE I

Curve	d	6 mm	8 mm	10 mm	12 mm	14 mm	16 mm
1	1.0	.260	.210	.200	.200	.202	.230
2	5.0	.230	.230	.240	.270	.300	.430
3	10.0	.270	.275	.325	.460	.590	.860
4	15.0	.320	.330	.490	.665	.940	1.360

The effect of the current on the rate of synthesis is shown in Fig. 4.

It will be seen that the rate is proportional to the current below 10 mm. pressure, while at higher pressures it becomes slightly less than proportional. These data were taken with tube I, using a 10 cm. electrode separation.

A determination of the effect of excess gases involved considerable difficulty. In the presence of excess carbon monoxide dissociation as well as oxidation occurred, while in the presence of excess oxygen, ozone was formed, along with the carbon dioxide. Additions of inert gases such as nitrogen impeded the oxidation and resulted in the deposition of large quantities of carbon suboxide on the walls. The complicating reactions made it impossible to determine the rate of oxidation under these conditions. The maximum rate, however, was obtained not far from the combining mixture; possibly oxygen accelerated the rate at the higher pressures.

Nature of the Reactants. The characteristics of the time-pressure curves and the proportionality between current and rate are direct indications that the observed reactivity is due to positive ions. The nature of the deposit in the negative glow offers still further evidence of this fact. The carbon dioxide deposit is illustrated in Fig. 1, and is very similar to that obtained in the water reaction. The sharply-defined band of carbon dioxide in the negative glow can not possibly be produced by a diffusion of electrically neutral molecules to the walls; it shows definitely that the molecules synthesized within the glow reach the negatively charged walls as positive ions. The light diffused deposit surrounding the cathode probably comes from the CO_2^+ ions which are neutralized on the cathode or in the gas phase.

A further test of the hypothesis that the chemical action in the negative glow results from positive ions or positive ion clusters neutralized on the walls, was made by placing a positive potential on a tungsten electrode sealed in the side of the tube in the path of the banded deposit. In case no potential was applied to the side electrode the band was quite uniformly distributed around the tube. When a positive potential was applied, only a very light diffused deposit appeared near the electrode, while the deposit on the opposite side was markedly increased. Potentials from 45 to 180 volts were used. The presence of the positive field could have no effect on the deposition of neutral molecules; the very light deposit in the presence of the field, therefore, was probably due to those molecules which had been neutralized on the cathode and in the gas phase. It should be mentioned that these results are doubly effective since the field tends to deflect the electrons towards the side electrode, thus causing an increase in the concentration of positive ions in the adjacent position of the discharge.

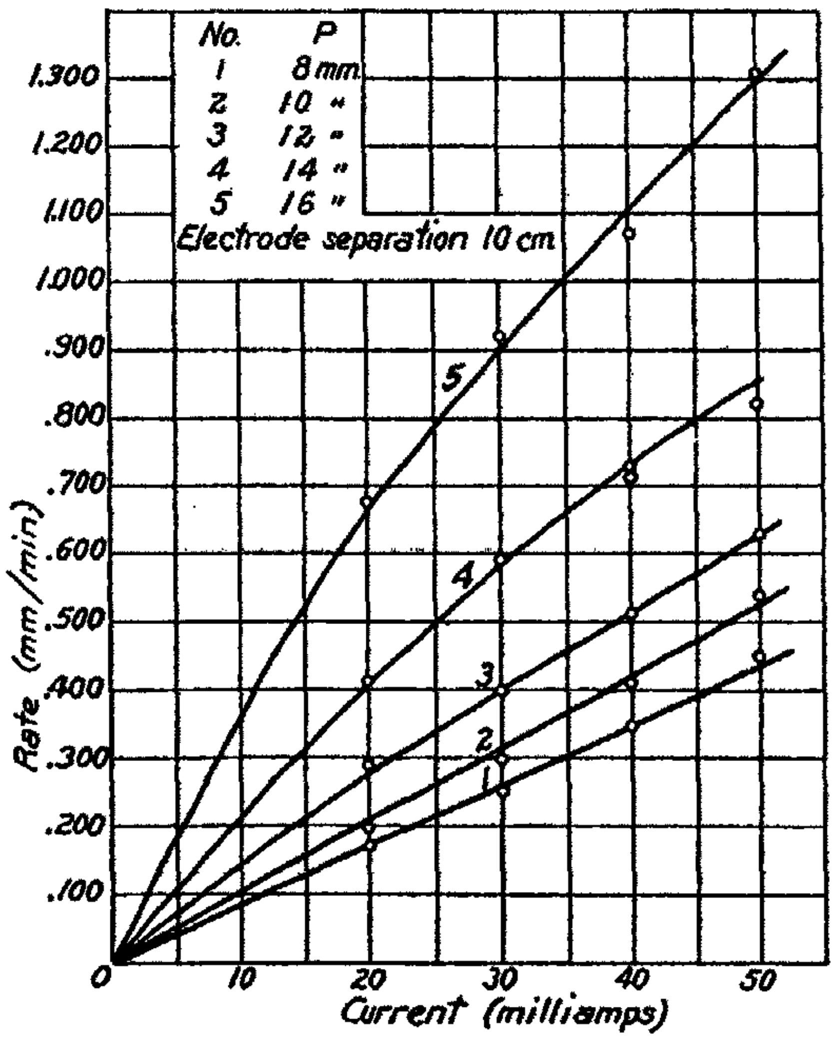

FIG. 4

A similar test was carried out for the positive column by imposing a difference of potential of 180 volts between two electrodes sealed in opposite sides of the tube about two centimeters below the anode. The potential gradient, therefore, was much greater between the auxiliary electrodes than in the path of the discharge. The result differed markedly from that obtained in the negative glow; very little difference could be observed in the thickness of the deposit at the two electrodes, irrespective of the potential applied. Since a test of this type will show only a pronounced difference in the amount of material deposited, all that can be said is that the majority of the molecules synthesized in the positive column strike the walls in the electrically neutral condition. It is possible that the deposit was slightly less at the positive electrode, hence a small fraction of the molecules may have reached the walls as ions or ion clusters.

A Spectrographic Analysis. An examination of the radiation emitted in the negative glow showed, in addition to the bands due to the neutral carbon monoxide molecule, those due to the ionized molecule. With a 60 minute exposure the more intense bands of the first negative group were observed. The approximate wavelengths of the band heads are 2190, 2300, 2325, 2419, 2446, and 2474 Å. These bands were obtained with about the same intensity at pressures from .5 mm. to 10 mm. of mercury.

It should be stated that while these bands show the presence of the excited CO^+ ion, no question exists about the presence of either CO^+ or O_2^+ ions in a $2CO/O_2$ mixture, since the high speed electrons found in the cathode zone will necessarily ionize both gases, the distribution of ions between the two gases being determined by their relative stopping powers and partial pressures.

Computation of Yield

The energy expenditure can best be expressed in terms of the potential through which one electron must drop to bring about the formation of one molecule. In the particular apparatus used the number of molecules of carbon dioxide formed per electron is given by $M = 256\ R/I$, where R is the rate of pressure decrease in mm. per minute, I the current in milliamps, and 256 a constant for the 4.3 liter system assumed to be at room temperature.

The yield expressed in terms of electron volts in the negative glow for tube I is given in Table II.

TABLE II

P	I	E	M	V_n
8	40	430	1.34	322
12	40	410	1.28	322
16	40	415	1.47	303
20	40	430	1.53	280

P = pressure in mm.; E = potential drop in negative glow; M = molecules formed per electron of current; V_n = energy in electron volts per molecule.

A maximum value of $V_n = 115$ was obtained with tube II, using a small aluminum cathode 1 cm. from the wall and with a 2 cm. electrode separation. In comparison, the values of V_n for ammonia and for nitrogen dioxide fell between 400 and 450 electron volts. Water, on the other hand, gave a maximum efficiency of $V_n = 41$.

The energy expended per molecule synthesized in the positive column is given in Table III.

TABLE III

P	I	E	M	V_pI	V_pII
6	40	250	.026	975	940
8	40	280	.029	965	915
12	40	330	.122	270	265
16	40	375	.275	137	133

E is the difference in the potential drop through tubes of 5 cm. and 10 cm. electrode separation, while M is the difference in the number of molecules synthesized; V_pI is the yield computed from the above data; V_pII, is the yield computed from similar data taken between 10 cm. and 15 cm. electrode separations.

It will be noted that below 10 mm. pressure the energy expended per molecule is high and very nearly constant. Above this pressure the efficiency of the process increases rapidly.

Discussion of Results

Comparison with Previous Reactions. The results presented above are markedly similar to those stated previously for the oxidation of hydrogen,[9] but exhibit several points of contrast to those obtained in the synthesis of ammonia and nitrogen dioxide. The data show unmistakably that the present reaction, like the others of this series, is purely ionic in character; while it is possible that atoms and excited molecules are chemically active, their reactivity is too slow to be detected in the presence of the fast ionic reaction.

In the negative glow, line 1 of Fig. 1 is very similar to line 1 of Fig. 1 for the water reaction, with the exception that the slight increase in rate occurring above 7 mm. pressure for water now occurs at 15 mm. A further difference is to be seen in the increase in rate below 7.5 mm. This increase, as has been pointed out, results from an increase in the normal cathode fall of potential and does not represent an enhanced reactivity at these pressures. In contrast to the increased rate observed above, 7 mm. and 15 mm. for H_2O and CO_2, respectively, it should be mentioned that recent experiments have shown the rate of synthesis of NH_3 to be constant from 40 mm. to about 0.2 mm. The reactivity in the positive column is very similar to that observed for H_2O, as can be seen by comparing curves 2, 3, and 4 of Fig. 1 in this paper with curves 3 and 4 of Fig. 1 of the preceding paper.[9] Both reactions show a rate that is independent of the pressure up to some particular pressure above which the rate increases rapidly to the ignition point. This is again in direct contrast to the ammonia reaction where no such enhancement was observed, the phenomenon being found only in cases where ignition is possible.

The Nature of the Reaction. The results which have been presented show very clearly that the molecules synthesized in the negative glow reach the walls carrying a positive charge. This means either that the molecules are built around positive ions as reaction centers, or that, if the molecules are formed from neutral reactants (for instance, $O + CO = CO_2$) all the molecules become ionized before reaching the walls. The evidence, as has been stated before, supports the former contention, namely, that positive ions are the reaction centers. The low current density combined with the rapid wall neutralization, as shown by the narrow banded deposit, indicates that the probability of a neutral carbon dioxide molecule being ionized in the discharge is small; complete ionization, therefore, is highly improbable.

The fact that most of the molecules synthesized in the positive column reach the walls in the neutral form necessitates either an entirely different mechanism for this region of the discharge, or the conditions must be such that a gas phase neutralization of the ions is possible. It seems improbable that the mechanism of reaction should be different, since below 10 mm. pressure the characteristics of the reactions are identical to those of the negative glow, i.e., the rate is independent of the pressure and proportional to the current, and the effect of excess gases is the same in the two regions of the discharge. On the other hand at the pressures where the reactivity in the positive column was studied (4 mm. to 30 mm.) a rapid gas phase neutralization of the ions—is expected from the O_2^- ions present under these conditions.

The Presence of a Chain Reaction. A comparison of line 1 of Fig. 1 for the negative glow with lines 2, 3, and 4 for the positive columns shows that at pressures below about 8.0 mm. a simple ionic reaction exists in both cases. The energy expended in electron volts per molecule changes but little at any point in the negative glow and is also very nearly constant at the lower pressures in the positive column. At pressures above 8 to 10 mm., however, the energy expended in the positive column drops rapidly with increasing pressure until ignition takes place. This is clearly the transition of the simple ionic reaction into the chain reaction found in ignition. A similar condition exists for the oxidation of hydrogen where chains can be detected at pressures as low as 5.0 mm.

The most reasonable interpretation for these observations is that given in the previous communication[9] for the oxidation of hydrogen. Chains are detectable only where the deposits show the CO_2 to reach the walls in the neutral and not the charged form, the activity of the ions ceasing upon striking the walls. The head of the reaction chain, therefore, is either an ion, some product of the ionic neutralization, or some new active state produced at the higher pressures. The latter possibility seems small since the chain is clearly an outgrowth of the simple ionic reaction and since it is not observable in the negative glow. It is more difficult to distinguish between the first two possibilities, although the evidence appears to favor the former hypothesis since chains were not observed by Lind using α rays, and since it is doubtful if any active state such as atomic oxygen could be produced by neutralization, that is not produced throughout the discharge by electron impact.

Relative Reactivity of the Ions. A high-speed electron on entering the negative glow from the Crookes' dark space, produces both CO^+ and O_2^+ ions. It becomes of interest, therefore, to contrast the reactivity of these two ions. In referring to Fig. 2, it may be seen that oxygen retards the rate almost in proportion to the amount present, while carbon monoxide accelerates the rate in all mixtures containing more than 15% oxygen. This fact may also be seen in Fig. 3, where the addition of excess oxygen has practically the same retarding action on the rate as does added argon. The normal cathode fall of potential being slightly lower in argon than in oxygen causes the observed difference in the effects of these two gases.

The conclusion to be drawn from the above results is that the reaction is initiated by the CO^+ ions, and that O_2^+ ions are comparatively inert. In the water reaction it will be recalled that the reactivity was attributed primarily to H_2^+ ions and that O_2^+ ions appeared inert at pressures below 7mm. The same interpretation holds in the negative glow for the present reaction. CO^+ ions exhibit reactivity over the entire pressure range, while O_2^+ ions appear inactive below 15 mm. pressure in the negative glow.

It is now possible to estimate the minimum number of collisions that an O_2^+ or a CO^+ ion must make in a $2CO/O_2$ mixture for the reaction to take place, from the breaks in the time-pressure curves and from the distance between the cathode and the walls. This value for CO^+ is of the order of 40 collisions in contrast to 20 for H_2^+ ions. Similarly, assuming the reactivity of O_2^+ ions to begin at 15 mm. about 2200 such collisions will be required for reaction, as compared to 1000 collisions for O_2^+ ions in a $2H_2/O_2$ mixture.

The M/N Ratio. The M/N ratio, i.e., the number of molecules synthesized per ion, may be determined from the value of M as given by the rate, and from N, the computed number of ions formed per electron of current. M may be measured accurately, but N involves considerable speculation. In evaluating N the negative glow and the positive column will be discussed separately.

Heretofore in considering the rate of positive ion formation in the negative glow the positive ion current has been neglected. Recent experiments have shown the positive ion current reaching the cathode contstitutes but a small per cent of the total current at pressures above 1 mm., hence the above assumption seems approximately correct. It has been assumed, further, that the energy of an electron entering the negative glow from the Crookes' dark space is very nearly that of the normal cathode fall of potential. The number of ions formed per electron has been computed from the extrapolated results of Langmuir and Jones[11] on the ionizing efficiency of various speed electrons. Recent tests with a large number of cathode materials have shown that the rate is roughly proportional to the normal cathode fall; this is in line with the above method of computing N. It should be mentioned in this connection that the rate is unaffected by changes in voltage occasioned solely by changes in pressure; this fact has also been observed by Linder[12] studying organic reactions under somewhat similar conditions. On the other hand, changes in voltage which result from changes in the electrode material or from a deposit forming on the cathode produce very nearly proportional changes in the rate.

It is not possible to obtain more than the order of magnitude for the value of N in the present case, since the ionizing efficiency of an electron in oxygen and carbon monoxide is not known. α ray studies show these gases to be similar to nitrogen, hence the total number of ions per electron will be considered the same as for nitrogen. Since the stopping powers of the two gases are very nearly identical, the distribution of ions between the gases is proportional to their relative concentration.

In Fig. 2, line 2, it will be seen that 6.7 molecules of carbon dioxide are formed per electron of current, while the potential drop is 750 volts. A 750

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[11] Langmuir and Jones: Phys. Rev., (2) **31**, 357 (1928).

[12] Linder: Phys. Rev., (2) **36**, 1375 (1930).

volt electron produces about 5.5 positive ions, or 3.6 CO^+ ions for the combining mixture. This value, in the absence of accurate data, is necessarily an approximation, but is probably correct to within a factor of two. From these considerations the number of molecules formed per ion is $M/N = 6.7/3.6 = 1.85$. This is very close to $M/N = 2$. This value, therefore, can be considered as representing the order of magnitude of the ratio of molecules formed to ions reacting. Lind, using α rays, gives $M/N = 4$, but it does not seem probable that such a high efficiency exists under the present conditions.

A Possible Mechanism. The data presented above yield a fairly accurate picture of the processes involved in the reaction mechanism. The fact that the carbon dioxide synthesized in the negative glow reaches the walls carrying a positive charge is definite evidence in favor of the ion cluster theory.

The conditions imposed by the character of the reaction in the negative glow are satisfied by the following equation:

$$CO^+ + CO + O_2 = (C_2O_4)^+ \text{ (wall)}$$

also for high pressures,

$$O_2^+ + 2CO = (C_2O_4)^+ \text{ (wall)}$$

Gas phase neutralization is possible in both the negative glow and the positive column, according to the equation

$$CO^+ + CO + O_2 = (C_2O_4)^+ \quad \text{(ion cluster)}$$
$$(C_2O_4)^+ + O_2^- = 2CO_2 + O_2$$

The simple cluster reaction just presented readily develops into the ionic chain mechanism postulated for the positive column, if neutral carbon dioxide splits out of the ion cluster, leaving the ion free to act as a further clustering center. The fact that oxidation is greatly retarded and decomposition increased in the positive column when nitrogen is present is an argument in favor of the ion cluster chain; the addition of neutral molecules to the cluster appears to break the reaction chain.

The writers wish to express their thanks to Dr. C. H. Kunsman for the interest he has taken in these researches, and to Mr. J. W. Westhaver, for his contributions to this paper.

Summary

The rate of oxidation of carbon monoxide in the negative glow is very nearly independent of the pressure over a wide range. It is proportional to the current, and is accelerated by excess carbon monoxide and retarded by excess oxygen almost in proportion to the amount added.

In the positive column the rate is proportional to the current and independent of the pressure below 10 mm. At higher pressures it increases rapidly to the ignition point. Ignition, apparently, starts only in this region of the discharge.

The carbon dioxide synthesized in the negative glow reaches the walls as positive ions. In the positive column, on the other hand, it is deposited largely as neutral molecules.

The bands of the first negative group for carbon monoxide appear with about equal intensity over a wide pressure range.

The data are interpreted as indicating a simple ion cluster mechanism for the negative glow, and an ion chain mechanism for the positive column. CO^+ ions appear much more effective than O_2^+ ions in initiating the reaction; a comparison of the reactivities of the two ions is given.

An estimation of the rate of production of positive ions in the negative glow yields a ratio of $M/N = 2$, for the number of molecules synthesized to positive ions formed.

CHEMICAL ACTION IN THE GLOW DISCHARGE

VII. The Dissociation and Oxidation of Methane

BY A. KEITH BREWER AND PAUL D. KUECK[*]

In the previous papers of this series it has been shown that the chemical action in the glow discharge is initiated primarily, if not entirely, by positive ions; an Electrochemical Equivalence Law[1] comparable to Faraday's Laws for Electrolytes has been proposed for the relationship existing between the current flowing and the amount of material reacting.

The present paper, which concerns the dissociation and oxidation of methane, is of interest from several angles: it furnishes another test for the Equivalence Law mentioned above; in connection with the results obtained in the oxidation of hydrogen it offers a comparison of the reactivities of free and combined hydrogen; the complexity of the reaction products obtained from the dissociation of methane throw considerable light on the steps involved in the reaction process; and lastly it is an addition to the large amount of work already done on the dissociation and oxidation of methane by α rays and in the corona discharge.

The effect of α radiation on methane has been studied in detail by Lind and Bardwell.[2] The results show that the reaction takes place at room temperature without an appreciable change in pressure, methane being converted in almost equal proportions into ethane and an unsaturated oil having the empirical formula C_nH_{2n}; other saturated hydrocarbons are formed in amounts decreasing with the complexity of the molecule.

Lind and Glockler[3] have recently shown that methane undergoes similar changes when acted on by α rays and by the semi-corona discharge. In both cases hydrogen is liberated and saturated hydrocarbons formed in amounts decreasing with the length of the carbon chain. A liquid phase having the general formula C_nH_{2n} also appears.

The condensation of several normal hydrocarbons heavier than pentane has been found by Linder[4] to obey the Electrochemical Equivalence Law mentioned above.

The oxidation of methane by α radiation has been shown by Lind and Bardwell[5] to proceed completely to carbon dioxide and water. The observed value for the ratio of molecules synthesized to ions formed is $M/N = 4.4$.

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[*] Fertilizer and Fixed Nitrogen Investigations, Bureau of Chemistry and Soils, Washington, D. C.

[1] Brewer and Westhaver: J. Phys. Chem., 33, 883 (1929).

[2] Lind and Bardwell: J. Am. Chem. Soc., 48, 2335 (1926).

[3] Lind and Glockler: J. Am. Chem. Soc., 52, 4450 (1930).

[4] Linder: Phys. Rev., (2) 36, 1375 (1930).

[5] Lind and Bardwell: Science, 62, 422 (1925).

Apparatus

The apparatus and method of procedure are the same as were employed in the oxidation of hydrogen[6] and of carbon monoxide.[7]

Commercial methane, about 96% pure, was further purified by fractional distillation at liquid air temperatures. The other gases used were purified as described in the previous communications.

Results

The Dissociation of Methane. Methane underwent a dissociation and subsequent condensation in the negative glow at liquid air temperatures without a detectable change in pressure. The removal of the liquid air, after the discharge had been in operation for some time, showed an increase in pressure in the enclosed system approaching 50%. The original pressure was again obtained when the tube was brought to liquid air temperatures.

An analysis of the spectrum of the residual gas showed it to be hydrogen. A detailed study of the condensate was made after the residual gas had been pumped off. When the system was well evacuated, the liquid air level was lowered and the rate of evaporation of the condensed product was measured by observing the increase in pressure with time. The points all fell on a smooth curve, indicating the presence of only a single component.

An idea of the vapor pressure of the condensate was obtained by cooling the tube with dry ice dissolved in alcohol. No decrease in pressure except that due to temperature was observed when the system was cooled to −80°C, while a total clean-up took place at −180°C. The vapor pressure, therefore, was above 4 cm. at −80°C.

It is now possible to identify the condensate from the vapor pressures and from the pressure change. The only hydrocarbons possessing the necessary vapor pressures are ethylene and ethane, possibly propylene and propane. The fact that dissociation takes place at liquid air temperatures without a change in pressure necessitates that for every molecule of methane condensed a molecule of hydrogen is freed. This limits the reaction product to either ethylene or propylene. The pressure increase observed upon evaporation of the condensate shows it to be ethylene. A further confirmation was made by passing bromine into a tube containing a sample of the condensate; the bromine was decolorized almost instantly, showing the hydrocarbon to be unsaturated.

The conclusion to be drawn from the above observations is that methane in the glow discharge operating at liquid air temperature is converted quantitatively into ethylene and hydrogen. This is in distinct contrast to the α ray reaction at room temperature where the products are ethane and several higher saturated hydrocarbons, as well as a liquid unsaturated condensate.

The number of molecules formed per electron of current was determined by running a discharge of 20 m.a., for three minutes and then pumping off the

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[6] Brewer and Westhaver: J. Phys. Chem., 34, 2343 (1930).

[7] Brewer and Kueck: J. Phys. Chem., 35, 1281 (1931).

hydrogen and undecomposed methane. When the liquid air was removed the pressure in the 4.3 liter static system at room temperature was 0.465 mm. This is equivalent to 3.1 molecules of ethylene synthesized per electron.

The electric discharge in methane at room temperatures differed materially from the cooled discharge in that a large amount of grayish yellow deposit formed on the walls. This material proved inert to the ordinary solvents and was probably the same substance observed by Lind and Glockler in the semi-corona discharge.

The Oxidation of Methane in the Negative Glow. A $CH_4/2O_2$ mixture is converted entirely to water and carbon dioxide in the negative glow. The characteristics of the reaction are similar to those previously studied in this series in that the rate is independent of the pressure and is directly proportional to the current. It, therefore, obeys the Electrochemical Equivalence Law for the glow discharge, namely:

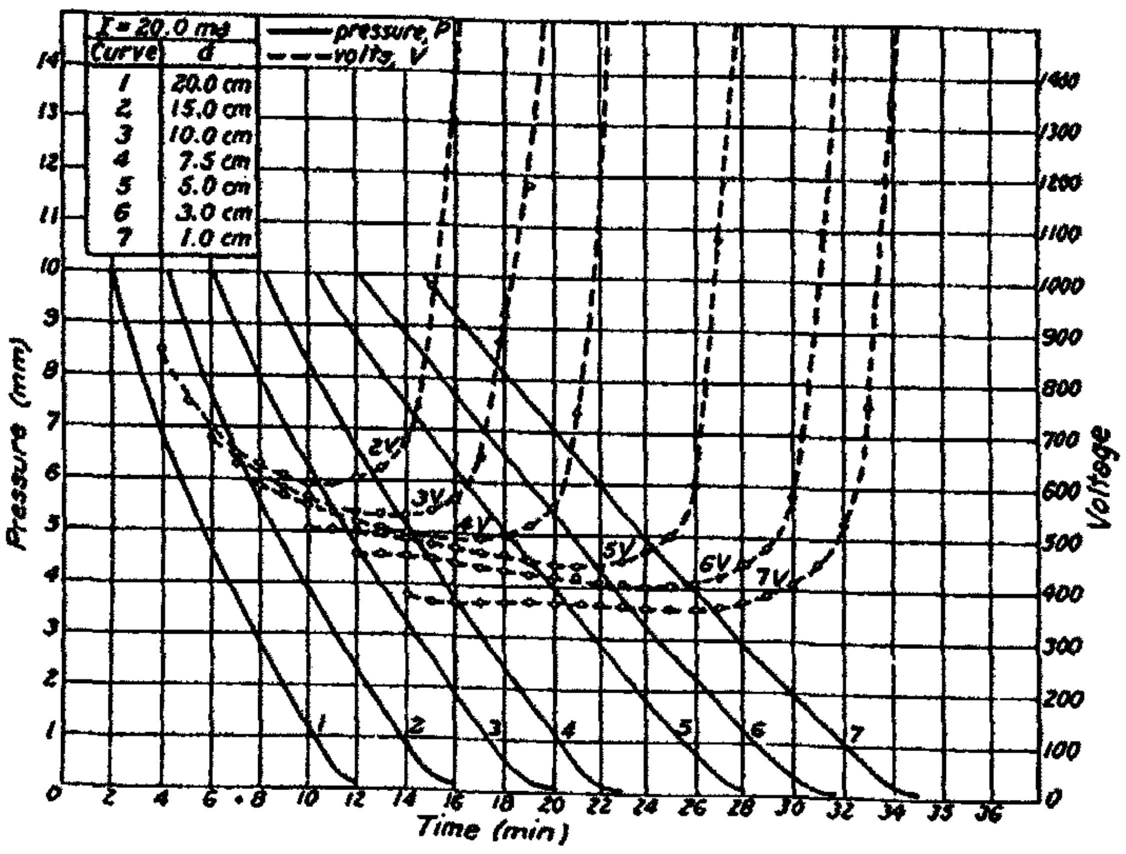

FIG. 1

$$dP/dt = \alpha I$$

where P is the equivalent pressure of the reaction product, α a constant for the reaction, and I, the current.

Line 7 of Fig. 1 is characteristic of the results obtained with a $CH_4/2O_2$ mixture. The discharge tube was of the type illustrated in Fig. 4, the separation of the iron electrodes being 1 cm.

The time-pressure curves starting at any pressure below 10 mm. were very nearly straight lines down to 0.1 mm., where the reaction ceased abruptly. Runs starting above 10 mm. showed a variation in rate with pressure, although the effect was negligible below 25 mm. The formation of ozone along with the regular reaction gave an enhanced rate at the higher pressures, while the decrease in rate at the lower pressures resulted from insufficient oxygen. It is significant to note that while a $2H_2/O_2$ mixture cooled in liquid air yielded about 20% hydrogen peroxide at all pressures, the $CH_4/2O_2$ mixture gave a clean-up to 0.1 mm. for all runs starting under 15 mm. pressure; water and carbon dioxide, therefore, are the only oxidation products formed.

The effect of varying the ratio of methane to oxygen is shown in Fig. 2.

It will be noted that the maximum rate occurs for a 1:1 and not for a combining mixture. The rate curve resembles more nearly the curve for the oxygen-nitrogen mixture, than it does the corresponding curves for water and carbon dioxide, in spite of the fact that these two substances are the sole reaction products. This indicates that the combining ratio of the reacting molecules, as well as their chemical nature, determines the rate.

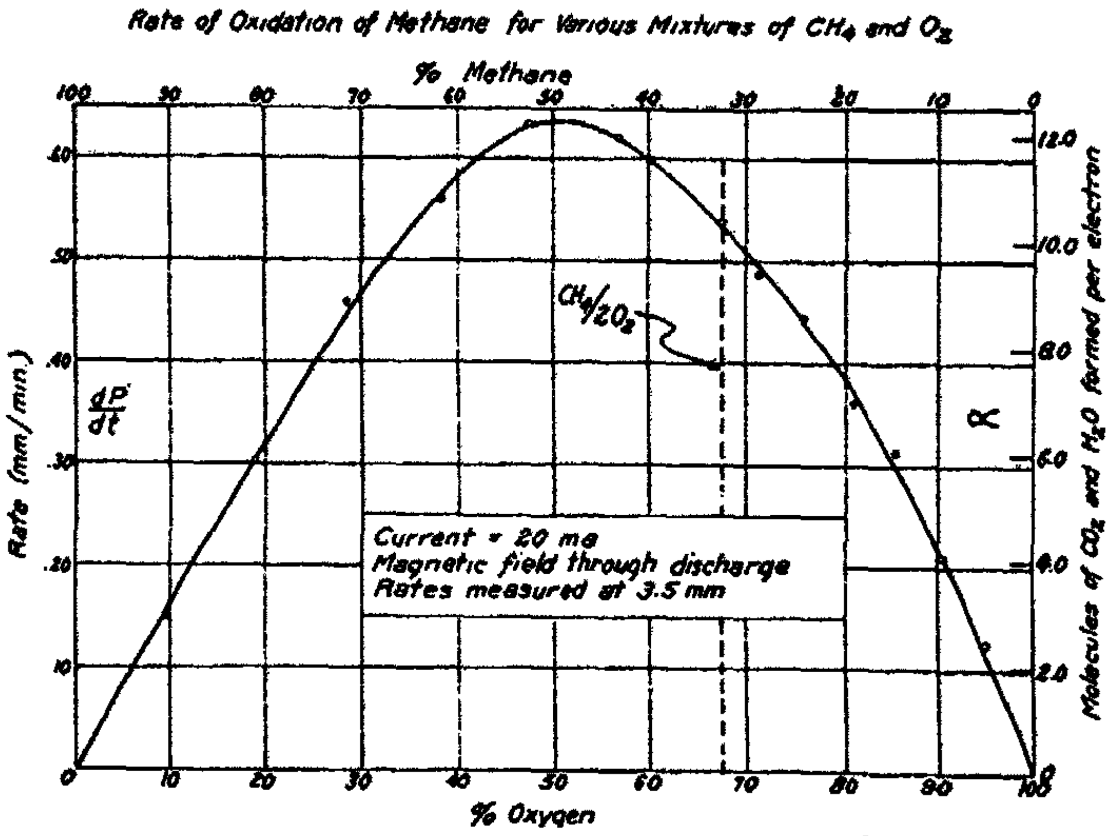

Fig. 2

The effect on the rate caused by the addition of various gases to the $CH_4/2O_2$ mixture is shown in Fig. 3. The data presented in Figs. 2 and 3 were taken with a tube of the type shown in the inset, aluminum electrodes being used.

These curves are in general quite similar to those obtained for the previous reactions. It is of interest to note that in all the oxidation reactions studied

Table I

P	dR	dV	dM/e	V_p
10	.68	230	13.10	17.7
8	.35	210	6.72	32.0
6	.26	130	5.00	38.5
4	.09	75	1.74	43.0

the additions of oxygen and argon produce similar effects, both decreasing the rate almost in proportion to the amount added. The accelerating effect of excess methane is illustrated in Figs. 1 and 2. The curves for added helium and argon are markedly different, in that helium has an accelerating effect even when presented in relatively large amounts; the rate for 75% helium is the same as for the combining mixture. The fact that the maximum is the same for excess helium as for excess methane suggests the possibility that helium transfers its activity to the methane.

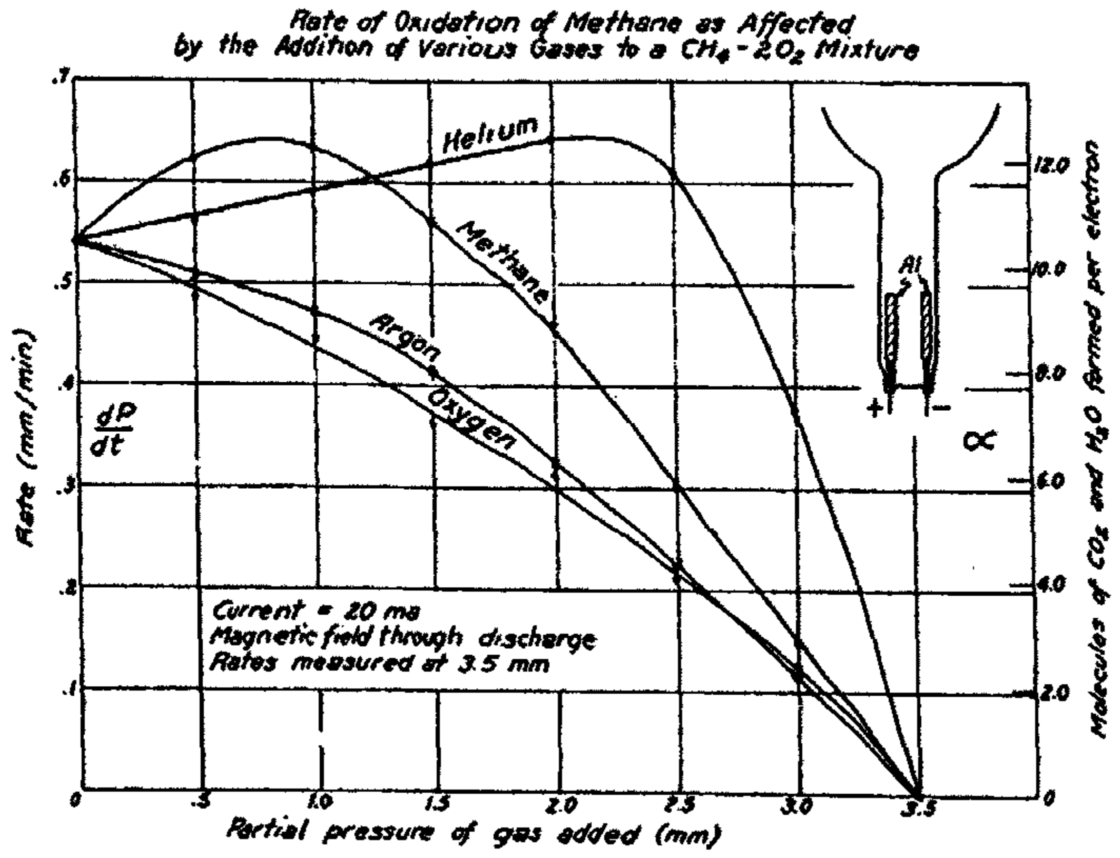

FIG. 3

Oxidation in the Positive Column. The effect of the electrode separation on the rate of synthesis in a $CH_4/2O_2$ mixture is shown in Fig. 1. All curves show a clean-up to 0.1 mm., indicating that carbon dioxide and water are the only reaction products formed.

The effect of the positive column can be seen from the character of the curves. Beginning with curve 5 for 5 cm. electrode separation, the progressive acceleration in rate at the higher pressures is indicative of a positive column. The rate of synthesis in the positive column is independent of the pressure below about 5.5 mm., as shown by curves 1, 2, and 3, while above this point the rate increases with increasing pressure. A similar effect was observed for the oxidation of hydrogen and of carbon monoxide; the synthesis of ammonia, on the other hand, showed no acceleration in the positive column at the higher pressures.

The effect of pressure on the efficiency in the positive column is shown in Table I.

P is the pressure; dR is the difference in rate for 20 cm. and 15 cm. electrode separation; dV is the difference in the corresponding voltages; dM/e is the difference in the number of molecules synthesized per electron of current; V_p is the electron volts necessary for the synthesis of one molecule.

Table I shows very clearly that energy expended per molecule synthesized decreases rapidly with increasing pressure.

The rates and voltages at 4 mm. pressure for various electrode separations are tabulated in Table II.

TABLE II

Curve	d	I	R	$V_{(min)}$
1	1.0 cm.	20 m.a.	.500	360
2	3.0	"	.515	405
3	5.0	"	.550	445
4	7.5	"	.660	492
5	10.0	"	.715	535
6	15.0	"	.800	595
7	20.0	"	.890	670

d is the electrode separation, I the current, R the rate in mm/min., and V the potential drop between the electrodes.

The reactivity in various portions of the discharge is illustrated in Fig. 4. The electrode separation is plotted against the number of molecules synthesized per electron of current in the outer circuit. All values given are for the number of molecules formed per centimeter of tube length; i.e., with an electrode separation of 1 cm., a yield of 9.6 molecules per electron was obtained, et cetera.

It will be seen that the synthesis takes place primarily in the negative glow. The dark spaces are relatively inert, while the reactivity in the positive column is small and very nearly uniform.

Discussion of Results

The Decomposition of Methane. The decomposition of methane in the negative glow takes place according to the equation

$$2CH_4 \xrightarrow{e} C_2H_4 + 2H_2$$

The formation of ethylene as the only hydrocarbon is significant in that it shows the reaction process to be a very simple one. Lind and Glockler[3] observed the formation of most of the light saturated hydrocarbons, as well as unsaturated oils, in the uncooled electric discharge wherein the reaction products were not removed as fast as formed. As a result of finding only ethylene in the present experiment, it must be concluded that the complex molecules obtained in the hot discharge are due entirely to secondary reactions about ethylene.

The character of the results is such that there can be no doubt that this reaction, like those studied before, is initiated entirely by the positive ions formed in the discharge. An idea as to the simplicity of the ionic processes involved can be obtained from the ratio of molecules of ethylene synthesized (M) to CH_4^+ ions formed (N).

The value of N can be computed from the ionizing efficiency of an electron possessing an energy equal to the observed normal cathode fall of potential. Unfortunately the ionizing efficiency in methane is not known, although the work of Hughes and Klein[8] shows this gas to be very similar to nitrogen and hydrogen. Assuming the value to be the same as that of hydrogen, a 350 volt electron should produce about 3.5 positive ions. At the same time 3.1 molecules of ethylene are formed. This gives a ratio of $M/N = 3.1/3.5 \doteq 1$. It seems reasonable that the observed ratio should be less than one, since neither the positive ion current nor the possibility of H_2^+ ions are taken into account.

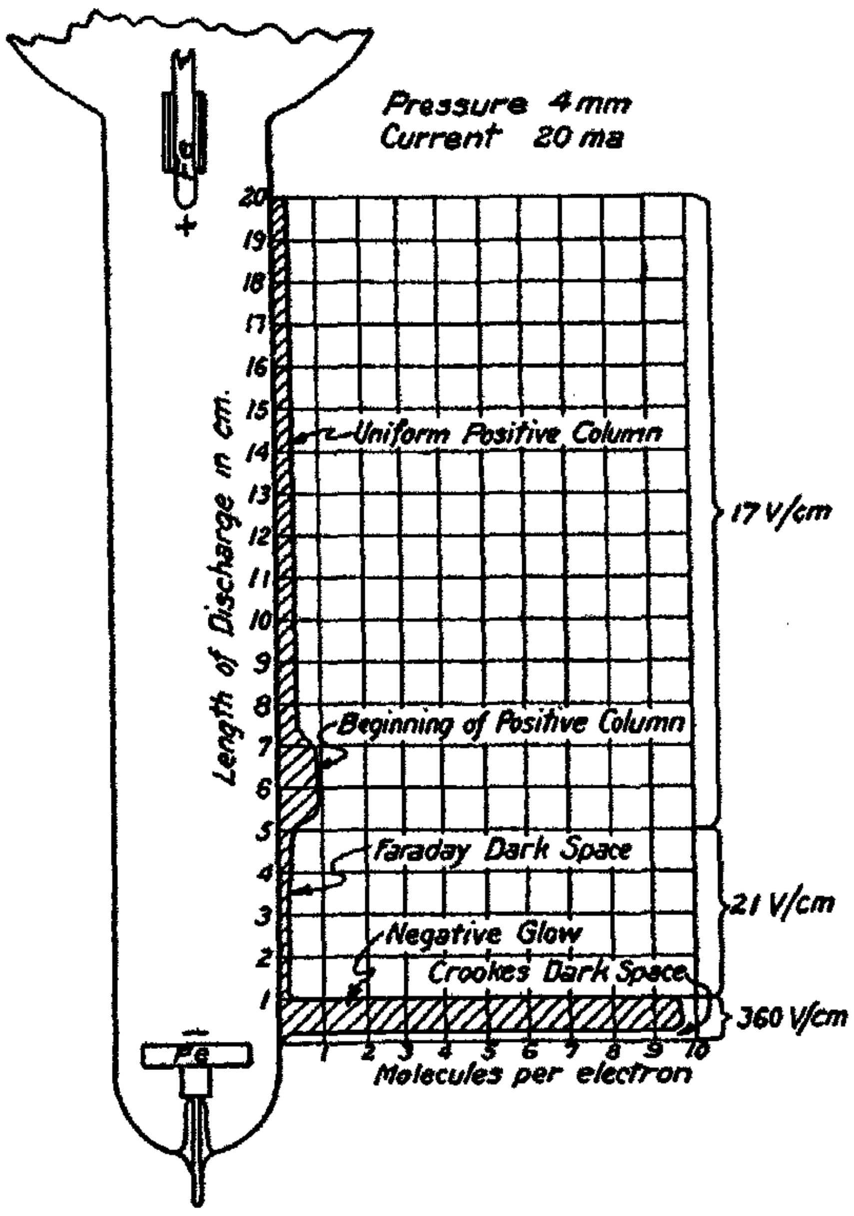

Fig. 4

The reaction process may be expressed by the following equation.

$$(CH_4)^+ + CH_4 \longrightarrow (C_2H_4)^+ + 2H_2$$

In the absence of rapid wall neutralization and especially at high pressures,

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[8] Hughes and Klein: Phys. Rev., (2) 23, 450 (1924).

it is to be expected that $(C_2H_4)^+$ might react with hydrogen to form $(C_2H_6)^+$ or with ethylene to form the condensation products observed by Lind and Glockler.

The Oxidation of Methane. The oxidation of methane presents no marked contrast to the reactions discussed in the preceding papers. The results, therefore, necessitate the same general interpretation.

The rate of reaction, as shown in Fig. 3, is accelerated by excess methane and is retarded by excess oxygen almost in proportion to the amount present. The inference to be drawn is that the reaction takes place primarily around the CH_4^+ ions and that O_2^+ ions are relatively inert. *The fact that the activity is due to CH_4^+ ions is of particular interest since in every case so far studied the ions of the reacting gas having the higher ionization potential show the greater activity.* The ionization potential of methane, as given by Glockler, lies between 14.4 and 15.2 volts, while that of oxygen is 14.1 volts.

The failure to detect hydrogen peroxide in the reaction product at pressures below 10 mm. at least, indicates that the oxidation is not preceded by a dissociation into ethylene and hydrogen, the oxygen then reacting with these two products separately, since the reaction of hydrogen and oxygen alone at liquid air temperatures results in the formation of at least 20% peroxide. It is evident, therefore, that the oxidation takes place directly in the ion cluster without the necessity of dissociation. Since the experiment on the dissociation of methane showed that two molecules of hydrogen readily split out of a $(2CH_4)^+$ cluster it seems possible that water might be expected to split off from a $(2CH_4O_2)^+$ cluster before it becames neutralized on the walls.

The Activity of the Ions. The readiness with which the reaction takes place around a CH^+_4 ion may be seen from the minimum pressure to which the reaction can be carried. Line 1 of Fig. 1 shows that the rate of reaction, while independent of pressure over a wide range, abruptly drops to zero at 0.1 mm. Assuming an ion must travel 1 cm. before reaching the walls, and using kinetic theory values for the collision frequency, the minimum number of collisions a CH_4^+ ion must make for the reaction to take place comes out to be about 15. This value is a very rough approximation, however, since the temperature of the gas near the cathode may be several hundred degrees centigrade, while near the walls it approaches that of liquid air. Again, if the cluster mechanism is correct and an ion grows in size with successive collisions, the collision frequency will not remain constant but will increase with the complexity of the cluster. The value of 15, therefore, gives only the order of magnitude for the minimum number of necessary collisions. A similar estimation in previous reactions was $H_2^+ = 20$, and $CO^+ = 40$.

The M/N Ratio in the Negative Glow. The number of O_2^+ and CH_4^+ ions formed per electron with an energy equal to the normal cathode fall of potential is very close to 4, as deduced from the extrapolated values of Langmuir and Jones.[9] Since the stopping power of methane does not differ materially from that of oxygen, the ions will be divided according to the ratio of the gases

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[9] Langmuir and Jones: Phys. Rev., (2) **31**, 357 (1928).

present. Thus, about 1.4 CH_4^+ ions will be formed per electron. In Fig. 3 it will be seen that 10 molecules of water and carbon dioxide are synthesized for each electron of current. The number of molecules synthesized per ion is, therefore, $M/N = 10/1.4 = 7.1$. Lind, using α rays, obtained a value of $M/N = 4.5$.

The ratio just obtained seems excessively high, in spite of the fact that the rate is fast and the voltage low. Of course, the value of N may easily be in error by a factor of 2, since the ionizing efficiency of an electron is not known accurately in either methane or oxygen; α rays, however, show both gases to be similar to nitrogen. Again, the assumption that O^+_2 ions are completely ineffective may be in error, since a comparison of the methane curve in Fig. 3 with similar curves for hydrogen, carbon monoxide, and nitrogen, with oxygen, shows that excess methane accelerates the reaction only over about half the pressure range observed for the other gases. Thus, there is a possibility that O_2^+ ions are more effective in this case than in the previous reactions.

The M/N Ratio in the Positive Column. An estimation of the number of ions formed in the positive column entails a large amount of uncertainty, since the amount of energy expended in ionization as well as the distribution of ions between the reactants are both unknown. The electrons in this region of the discharge are generally conceded to possess a Maxwellian distribution of velocity, the average energy being far below that necessary for ionization; much of the energy, therefore, is spent in processes other than ionization. Again, since the energy of the electron seldom, if ever, exceeds that necessary for ionization the distribution of the ions between the gases present will be a function of the ionization potential as well as the stopping power and the partial pressure. For instance, in a $CH_4/2O_2$ mixture a 14.1 volt electron can form O_2^+ ions by direct impact, but CH_4^+ ions can only result from secondary processes when the electron energy is below 15.0 ± .2 volts. The number of CH_4^+ ions formed, therefore, is less than would be expected from the ratio of the two gases present.

In the light of the above consideration, the best that can be done is to see if a reasonable value can be obtained for the ratio of M/N. Assuming that the total expenditure of energy is divided equally between ionizing and non-ionizing processes a ratio of $M/N \doteq 6$ is obtained if the ionizing efficiency for oxygen is three or more times greater than for methane. It seems reasonable that this difference in efficiency should exist for the slow speed electrons found in the positive column. At pressures above 5.5 mm. where ionic chain reactions are in evidence the M/N ratio rises rapidly with increasing pressure.

The Mechanism. It was pointed out in the preceding papers [6,7] that the ratio of M/N may be a statistical rather than a fixed quantity. Nevertheless, it is interesting to note that in every case so far studied the observed value is either expressed by the simplest equation that can be written for the combining gases, or in the case for water, by the simplest equation multiplied by two. The combination of CH_4^+ with two molecules of oxygen is the simplest combining ratio for the present reaction; the value of $M/N = 3$ thus obtained is obviously too low. From the results of the decomposition experiments it seems probable that the reaction might be expressed by the following equations:

$$(1)\quad (2CH_4)^+ + O_2 = (C_2H_4)^+ + 2H_2O$$
$$(2)\quad (C_2H_4)^+ + 2O_2 = (2CO_2.2H_2O)^+ \text{ (wall)}$$

This gives a ratio of $M/N = 6$, which is of the order of magnitude of that observed, and is certainly not far from correct.

The equations just presented possess the further advantage of accounting for the character of the deposit on the walls of the tube. It will be recalled that in the case of the oxidation of hydrogen and carbon monoxide, the reaction products were frozen out in sharply defined bands near the cathode, thus indicating a wall neutralization of the ion clusters. In the present case, the banded deposit was still in evidence, showing that wall neutralization was an important factor, but at the same time a deposit was observed well up along the walls of the tube, showing that an appreciable number of neutral molecules were formed in the gas phase. The equations given above permit the formation of two neutral water molecules in the gas phase for every two water and two carbon dioxide molecules neutralized on the walls.

The writers wish to thank Mr. J. W. Westhaver for his assistance in procuring part of the data presented in this paper.

Summary

Methane is converted quantitatively into ethylene and hydrogen in the glow discharge at liquid air temperatures. Approximately one molecule of ethylene is formed per CH_4^+ ion.

The reaction in a $CH_4/2O_2$ mixture goes entirely to carbon dioxide and water. In contrast to a $2H_2/O_2$ mixture no hydrogen peroxide is formed.

The rate of oxidation is accelerated by excess methane; oxygen retards the rate even more than does argon. From this it is concluded that the reaction is initiated primarily by CH_4^+ ions.

The reactivity is most pronounced in the negative glow, is negligible in the dark spaces, and is fairly constant throughout the positive column. The observed ratio of molecules formed to CH_4^+ ions is about seven; probably $M/N \doteq 6$ is nearer the correct value.

The efficiency of the positive column in terms of electron volts per molecule increases rapidly with the pressure above 5.5 mm., indicating the presence of ionic chain reactions.

THE EFFECT OF PREHEATING ON THE DISPERSITY OF CALCIUM CASEINATE IN SKIM MILK*

BY J. B. NICHOLS,[1] E. D. BAILEY,[1] G. E. HOLM,[2] G. R. GREENBANK,[2] AND E. F. DEYSHER[2]

Casein is suspended in milk in the form of highly dispersed calcium caseinate which may be separated from the serum by means of a clay or collodion ultrafilter or by high-speed centrifuging.[3]

Attempts to estimate the degree of dispersion of calcium caseinate have been made by Svedberg, Wiegner, and Bechhold.[4] Svedberg and Fåhraeus, from preliminary ultracentrifugal studies made in 1924, concluded that the particles were of the order of magnitude of 10 to 70 mμ radius ($m\mu = 10^{-7}$cm).

Wiegner considers that the major proportion of the particles are amicrons and that the probable range in size is from 5 mμ to 100 mμ in diameter. He found the number of particles to be constant even when the milks had been heated or slight amounts of acid had been added. Bechhold considers, from ultrafiltration data on a series of proteins and inorganic colloids, that the calcium caseinate particles in milk are probably greater than 40 mμ in diameter.

The dispersity of calcium caseinate is of considerable practical as well as theoretical interest. One of the chief problems of the evaporated-milk industry, as well as of other branches of the dairy industry, is the development of proper stability to heat. Little is known concerning the mechanism involved in coagulation, though the industrial methods used for its prevention are well established. In the manufacture of evaporated milk, the milk is first heated to 95°C. for a short time prior to its concentration. This practice insures a greater stability of the finished product in the sterilization process. If temperatures of approximately 70°C. are used, the tendency seems to be to decrease the stability.[5]

These heat treatments also seem to affect certain physical properties of the dispersion. For example, heating milk to 70° lowers the viscosity of the milk, whereas heating to higher temperatures increases the viscosity. These changes in viscosity are accompanied by changes in density (unpublished data). Though stabilization is affected largely by the electrolytes present

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[1] Experimental Station, E. I. du Pont de Nemours & Company.

[2] Bureau of Dairy Industry, U. S. Department of Agriculture.

[3] Friedenthal: Ber., 44, 904 (1911); Van Slyke and Bosworth: New York (Geneva) Agr. Exp. Sta. Tech. Bull. 39.

[4] Svedberg: Kolloid-Z., 51, 10 (1930); Wiegner: Z. Nahr. Genussm., 27, 425 (1914); Bechhold: Z. physik. Chem., 60, 257 (1907).

[5] Deysher, Webb, and Holm: J. Dairy Sci., 12, 80 (1929).

in the serum, it is possible that the process may depend in part upon changes in particle size. Ultracentrifuge studies were therefore undertaken to determine the distribution curve of untreated calcium caseinate and to ascertain whether heating affects the distribution of particles in skim milk.

Experimental

Preparation of Samples:

Fresh skim milk was warmed to approximately 40°C. and passed through a De Laval clarifier three times in order to remove as completely as possible the finely divided fat, leucocytes, and other material of relatively large particle size. One sample was heated on a water bath at 65°C. and another at 95° for ten minutes in flasks equipped with reflux condensers. These samples, as well as a control sample, were then packed in ice until used in the following experiments. Since the amount of calcium united with casein is a function of the electrolyte content of the serum, serum from the original milk was used as a diluent to maintain the original equilibria throughout the experiments. This serum was obtained by means of a collodion ultra-filter and was kept in ice until used. When a sample was allowed to stand at room temperature for some time a flocculent precipitate formed which presumably was a calcium phosphate.

FIG. 1.
Sedimentation of unheated skim milk (Pictures taken at 10-minute intervals)

Ultracentrifugal Determinations:

In the ultracentrifugal determination of the particle-size distribution of a polydisperse material, the following modified form of Stokes' law is used to determine the radius of a particle[1]:

$$r = \sqrt{\frac{9\eta \ln((x+a)/a)}{2(\rho_p - \rho_l)\,\omega^2 t}}$$

where r is the radius of the particle in centimeters, η the viscosity of the medium, ρ_p the density of the particle, ρ_l the density of the medium, $\omega\left(=2\pi\frac{N}{60}\right)$ the angular velocity, N the centrifuge speed in r.p.m., t the time of centrifuging in seconds, x the distance in centimeters along the cell from the meniscus, and a the distance of the meniscus from the center of rotation. The other data needed in addition to that obtained from the ultracentrifuge for the determination of the distribution curve are the viscosities of the solutions, the density of the calcium caseinate particles, and the density of the serum in which the particles are dispersed. Table I gives these data.

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[1] For the theory underlying the determination of distribution curves by means of the ultracentrifuge, see Svedberg and Rinde: J. Am. Chem. Soc., 46, 2681-2685 (1924); Rinde: "The Distribution of the Sizes of Particles in Gold Sols," Diss. Upsala, 1928; and Svedberg: "Colloid Chemistry," Second Edition, pp. 171 et seq. (1928).

The apparent density of the calcium caseinate was taken as the reciprocal of the partial specific volume. In order to calculate the partial specific volume from the pycnometric data, the concentration of the suspended solids, composed mainly of calcium caseinate, must be determined accurately.

Skim milks are quite constant in the amount of lactalbumin and lactoglobulin they contain, this value being approximately 0.55%.[1] The serum used contained 0.40% of protein, hence a portion of the soluble proteins was retained by the filter. Had no lactalbumin or globulin been retained by the filter the protein content of the serum would have been approximately 0.55% and the resulting solids content approximately 6.37%. Thus 3.03% (=9.40 − 6.37) of the solids of skim milk represents the content of suspended solids, mainly calcium caseinate. In addition to calcium caseinate the fraction undoubtedly contains a small amount of highly dispersed fat, some leucocytes, and perhaps some colloidal phosphates.

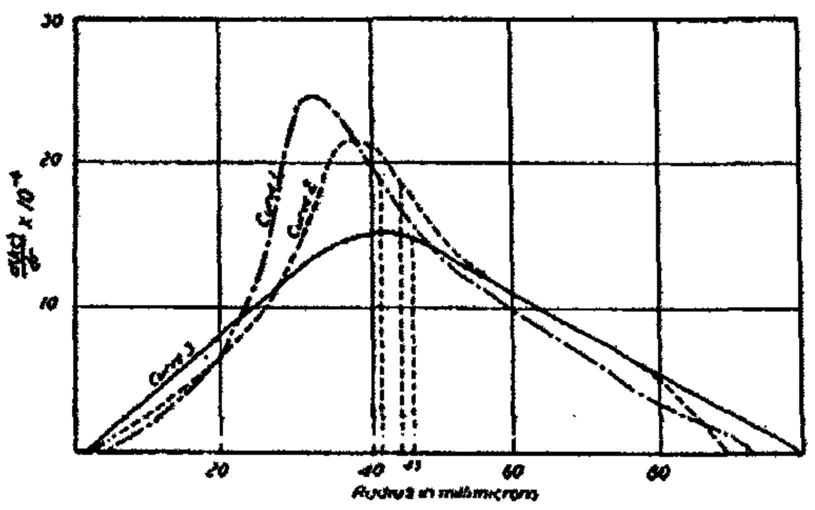

FIG. 2.

"Weight optical" distribution curves of calcium caseinate from milk

(1) Heated to 95°C.
(2) Heated to 65°C.
(3) Unheated

Curve areas { Curve 1-87%
Curve 2-85%
Curve 3-81%

1 sq. = 20%

TABLE I

	Skim Milk	Serum
Solids*	9.40%	6.22%
Proteins	3.39%	0.40%
Density at 30°C.	1.0317	1.022

Apparent density of calcium caseinate = 1.504
Viscosity of serum at 30°C. = 0.0116
Viscosity of 4:1 serum-skim milk at 30°C. = 0.0120

* Solids content determined at 100°C and 25-27 in. vacuum.

From other data on these samples the weight of the calcium caseinate has been calculated as 2.94%. From these considerations and for the purpose at hand 3.03% has been chosen as the total amount of the suspended

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[1] Rogers: "Fundamentals of Dairy Science," p. 43 (1928).

phase. The value found for V, the partial specific volume, was 0.665, or 1.504 for the apparent density of the calcium caseinate.

The three samples of skim milk ((1) control, (2) sample heated to 65°C. for ten minutes, and (3) sample heated to 95° for ten minutes), which contained approximately 3% of solids, were diluted to one-fifth the original concentration with the milk serum prepared by ultrafiltration and centrifuged at a speed of 4,000 r.p.m. Eastman Process Plates were used to record the effect of centrifuging. Since the illumination came from a Pointolite lamp, the effective radiation was the blue region of the spectrum. Exposures ten and fifteen seconds in length were made every ten minutes, each exposure yielding data on which a complete distribution could be calculated. Figure 1 represents a series of photographic exposures taken of the sedimenting calcium caseinate in the control sample. The exposure at the left represents the sedimentation which has occurred in the first ten minutes, and the succeeding exposures represent the condition at ten-minute intervals up to sixty minutes from the start. The weight-optical distribution curves obtained for the three samples are shown in Fig. 2. The three distribution curves are similar enough to be considered almost identical within the limit of experimental error, although there is an indication of a slight shift in the mean radius to a smaller particle size as the temperature of forewarming is raised —from a mean size of 45mμ for the control sample to a mean size of 41 mμ for the sample heated to 95°C. This slight shift could hardly account for the rather large differences in stability observed for the samples when subjected to the coagulation test subsequent to forewarming.

Discussion

The results indicate that the calcium caseinate particles in milk range in size from about 100 mμ radius (200 mμ diameter) down to molecular sizes, which, according to recent work of Svedberg, Carpenter, and Carpenter[1] are of the order of 4 mμ radius for casein. The mean radius is 40 to 50 mμ (80 to 90 mμ diameter). However, an appreciable portion (ca. 15% on the basis of its light absorption) of the suspended material had left the field of observation between the time of the original exposure of the photographic plate and the second exposure ten minutes later. This fraction undoubtedly consists of small amounts of fat, leucocytes, some colloidal calcium phosphate and perhaps some large aggregates of calcium caseinate.

In a polydisperse system having the range of sizes of the calcium caseinate system under consideration, the light absorption of particles increases rapidly with increasing radius in accordance with the Rayleigh scattering of small particles; therefore, the curves presented in Fig. 2 do not represent the true relation of weight of material to radius but the so-called weight-optical relation, the term "weight-optical "referring to an apparent concentration which is the product of the absorption constant k of the given radius by the concentration c of material of that radius. If the distribution curves had been

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[1] Svedberg, Carpenter, and Carpenter: J. Am. Chem. Soc., 52, 241, 701 (1930).

markedly different this variation of light absorption with particle size would have rendered difficult the comparison of the different samples. However, since the curves are so nearly identical in spite of the large variation of light absorption with particle size, we may safely conclude that the particle-size distribution of calcium caseinate is very little affected by forewarming up to 95°C. for a short time.

Prolonged heating of milk results in flocculation; thus it would be entirely reasonable to suppose that the particles would increase progressively in size with the time and temperature of heating.[1] Although this may occur in the later stages, the results presented indicate that particle-size changes are not of primary importance in the phenomenon of the stabilization of a milk to heat by forewarming, that is, unless the *ad hoc* assumption is made that the small shifts in the distribution curve to smaller particle sizes are capable of producing the large changes in stability observed. Hydrolytic changes may be responsible for the stabilization.

Summary

1. The weight-optical particle-size distribution curves have been determined for samples of the calcium caseinate of skim milk subjected to different temperatures of preheating.

2. The majority of the material is less than 200 mμ in diameter with a mean size of about 90 mμ.

3. A small amount of coarser material, probably colloidal calcium phosphate and large aggregates of calcium caseinate, is also present.

4. Preheating up to 95°C. has little effect on the distribution curve of particle size.

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[1] Svedberg, Carpenter, and Carpenter: loc. cit. p. 708, have observed an increase in size of the casein molecule at 40°C; if such a low-temperature change occurs in the calcium caseinate suspension in skim milk, the control sample would undergo the same change as the heated samples because the milk was warmed to 40°C. previous to skimming.

THE ADSORPTION OF WATER FROM ETHYL ALCOHOL-WATER MIXTURES BY SILICA GEL*

BY HENRY MAUZEE DAVIS AND LLOYD E. SWEARINGEN

Introduction

The problem of producing ethyl alcohol of more than 94 to 95% purity from mixtures of the alcohol and water has been the object of many investigations. The problem reduces almost entirely to one of devising a method for breaking up or changing the composition of the azeotrope formed by these two substances.

Both chemical and physical methods have been used to accomplish this result. Of the chemical procedures for removing water from alcohol-water mixtures, distillation from quick lime or sodium are the most common. The nearness of the constant boiling temperature of the azeotrope to the boiling point of pure alcohol makes ordinary fractional distillation impractical. Young and Fortey,[1] by adding benzene to the alcohol-water azeotrope converted it into a lower boiling point ternary system. Alcohol of high purity is recoverable from this ternary system on distillation. Wade and Merriman,[2] making use of the fact that the composition of the azeotrope is influenced by pressure, have succeeded in producing alcohol of high purity by fractional distillation under reduced pressure. Thus, starting with an alcohol-water mixture containing 5.14% water, after ten fractionations under pressures of 57-59 mm. mercury, only 0.95% water remained. Grimm and Wolff,[3] and Grimm, Raudenbusch and Wolff[4] have successfully broken up azeotropic mixtures of ethyl alcohol and carbon tetrachloride by adsorption processes, using silica gel as the adsorbent.

Since it has been demonstrated that the composition of an azeotropic mixture can be changed by the preferential adsorption of one component of the mixture, this procedure should yield results with the alcohol-water system. Since silica gel is know to have a high adsorptive capacity for water, it should be a good medium for the removal of water from the alcohol-water mixtures.

The adsorption of fluids by silica gel is generally conceded to be a process of capillary condensation.[5] Within the minute capillaries of this adsorbent, the surface of any condensed liquid must have a radius of curvature about equal to that of the capillary in which it stands. The vapor pressure of a liquid in a capillary tube is lower than the vapor pressure of the liquid over

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* Contribution from the Chemical Laboratory, University of Oklahoma.

[1] J. Chem. Soc., 81, 717, 739 (1902).

[2] J. Chem. Soc., 99, 997 (1911).

[3] Z. angew. Chem., 41, 98 (1928).

[4] Z. angew. Chem., 41, 104 (1928).

[5] Patrick and Eberman: J. Phys. Chem., 29, 220 (1925).

the plane surface. The Kelvin equation, $\ln \frac{P}{P_0} = -\frac{2\sigma v}{RTr}$ affords a means of predicting the magnitude of the vapor pressure lowering in small capillaries. P_0 and P are the vapor pressures over the plane and concave surfaces respectively, at temperature T, R is the gas constant, σ the surface tension, r the radius of the capillary and v the molar volume of the liquid. Shereshefsky[1] has shown that the vapor pressure lowering for water in small capillaries is much greater than can be accounted for by the Kelvin equation. His results indicate that this lowering of the vapor pressure is due to the increase in surface tension of the water.

The Kelvin equation predicts that the greater the surface tension of the liquid, the greater will be the reduction in vapor pressure. That is, P/P_0 is proportional to $e^{-\sigma}$. The surface tension of water will vary from three to four times greater than that of ethyl alcohol between 0°C. and the boiling point of alcohol. The molar volumes of water and alcohol, near the boiling point of alcohol will be roughly in the ratio of 18 to 63. The radius of the capillaries being the same for both water and alcohol, then the lowering of the vapor pressures for each of these liquids should be proportional to their respective ($\sigma v/T$) values. It is seen that the ($\sigma v/T$) value for water is slightly greater than the ($\sigma v/T$) for alcohol. Consequently the vapor pressure lowering for water in the capillaries of silica gel should be greater than the vapor pressure lowering for alcohol. It follows that the component suffering the greatest vapor pressure lowering will be more readily condensed.

The preferential adsorption of water from an alcohol-water mixture, which this treatment predicts, is somewhat meager. It is further complicated by the fact that the heats of wetting of silica gel by alcohol and water are slightly different. Grimm, Raudenbusch and Wolff[2] report the heats of wetting of silica gel by alcohol and water to be 23.7 and 20.95 calories per gram, respectively. However, it was believed that if the proper conditions could be discovered, the passage of vapor from the alcohol-water mixture over silica gel should result in the adsorption and removal of at least a part of the water vapor from the mixture. Subsequent condensation of the vapor phase remaining should yield an alcohol-water mixture enriched in alcohol.

Experimental

The general plan for attacking the problem may be stated in the following manner. The vapors from the boiling alcohol-water mixture were passed through a column of silica gel, maintained at some suitable temperature above the boiling point of alcohol and below the boiling point of water. The surviving vapors were then condensed and collected in 10 c.c. portions. The composition of each of these portions was determined by specific gravity methods. Fifty cubic centimeters of the alcohol-water mixture were used in each experiment. Fifty-six grams of silica gel, prepared by Patrick's method,

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[1] J. Am. Chem. Soc., 50, 2966 (1928).

[2] Loc. cit.

were used in each experiment, except as otherwise noted. The silica gel was packed loosely in a straight piece of glass tubing, 45 cm. long and 2 cm. in diameter. The gel column was kept at the desired temperature by means of a water bath. The gel was activated by heating to 130°C. under a pressure of from 25-28 mm. of mercury.

The Effect of Temperature on the Adsorption Process.

The effect of temperature on the adsorption process is complicated somewhat by the fact that considerable quantities of heat are evolved during the adsorption process. The data in Table I show that the temperature of the adsorbent may vary from 2° to 15°C. above the temperature of the constant temperature bath. These experiments were carried out with a thermometer imbedded in the gel column, about midway of the column. The temperature of the gel column and that of the constant temperature bath were compared several times during the distillation of an alcohol-water sample. These experiments were made on an alcohol-water mixture containing 7.4% water. A typical set of data are given in Table. I

Table I

The Variation in the Temperature of the Adsorbent due to Heat of Wetting.

Time of Reading	Temperature of Bath	Temperature of Adsorbent	Remarks
3:55 P.M.	82°C.	82°C.	Vapors enter gel column.
——	81.8°	96°	Vapors emerge from gel column.
3:58	82.0°	97°	
4:01	81.7°	90°	
4:06	82.0°	85°	
4:09	82.0°	84.5°	
.	.	.	
.	.	.	
.	.	.	Temperature of adsorbent never below 84°C.
4:18	82.0°	84.0°	

Table II and Fig. 1 give the results of experiments carried out for the purpose of determining the optimum temperature for water removal from a given alcohol-water mixture. The samples used in these experiments contained 7.4% water, weight percent. All conditions except temperature were maintained uniform throughout these experiments.

From Table I it is seen that the heat of wetting is sufficient to keep the gel at least 2°C. above the temperature of the bath as long as vapors are passing through. In experiments number 8 to 12, Table II, the bath temperature was kept below the boiling temperature of the mixture, with the expectation that the heat of wetting would keep both components largely in the vapor phase. However, due to the fact that the walls of the tube containing the gel remained at the temperature of the bath, a considerable amount of purely thermal condensation occurred. This condensate was trapped in

TABLE II

The Effect of Temperature of the Adsorbent on Water Removal

Experiment Number	Bath Temperature	Best Fraction	Maximum Percent Water lost	Percent of Total Sample retained by Gel.
1.	91.5°C.	2	0.76	16
2.	86.5	1	1.12	16.2
3.	84.6	2	1.14	22.8
4.	83.5	2	1.44	24.8
5.	82.0	1	1.76	....
6.	80.0	1	2.39	25.8
7.	78.0	1	2.71	24.0
8.	77.2	1	2.20	34.4
9.	76.5	1	2.17	41.0
10.	75.4	1	2.31	48.8
11.	74.5	1	2.62	54.0
12.	72.0	1	2.62	66.0

the gel column. Data given in Table II show how important purely thermal condensation becomes at temperatures below 78°C. Table II makes the meaning of Fig. 1 rather apparent. At temperatures well below the boiling point of the mixture, (Ex. No. 11 and 12) the percent of water lost (in the liquid phase) is approximately constant. As we approach the boiling point of the mixture, (Ex. No. 10, 9 and 8) while we have increasingly larger quantities of vapor phase present, the liquid present apparently effectively prevents it from being adsorbed to any appreciable extent. Once the boiling point of the mixture is passed, the amount of water adsorbed increases rapidly to a maximum, just above the boiling point of pure alcohol. When considerable quantities of both liquid and vapor phases are in contact with the gel, the amount of water removed is smaller than for either of the phases present in large excess. The amount of water removed again falls off as the boiling point of water is approached. The results indicate that the removal of water from the alcohol mixtures is more pronounced in the vapor than in the liquid phase. The optimum bath temperature for water removal is 78°C.

The Effect of Water Content of Mixtures on the Amount of Water adsorbed from Alcohol-Water Mixtures.

Data for other alcohol-water mixtures, including the true azeotrope are given in Table III and Fig. 2. These data were obtained in experiments similar to those used for the data in Table II, except that all conditions except composition were maintained constant. The composition of the true azeotrope for the particular pressure desired (737.4 mm.) was obtained by interpolation of the data of Wade and Merriman. It contained 95.62% alcohol and boiled with utter constancy at 77.26°C. The gel column was maintained at 78° to 78.2°C.

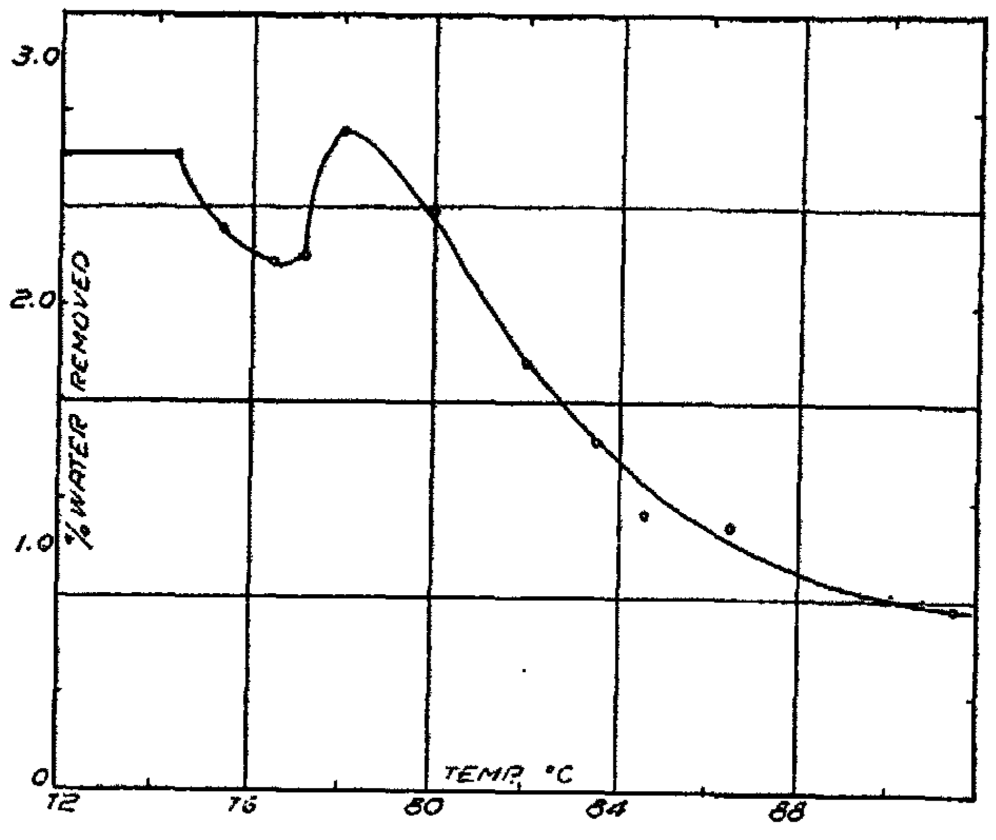
3.0
2.0
1.0
0
% WATER REMOVED
TEMP. °C
72
76
80
84
88

Fig 1

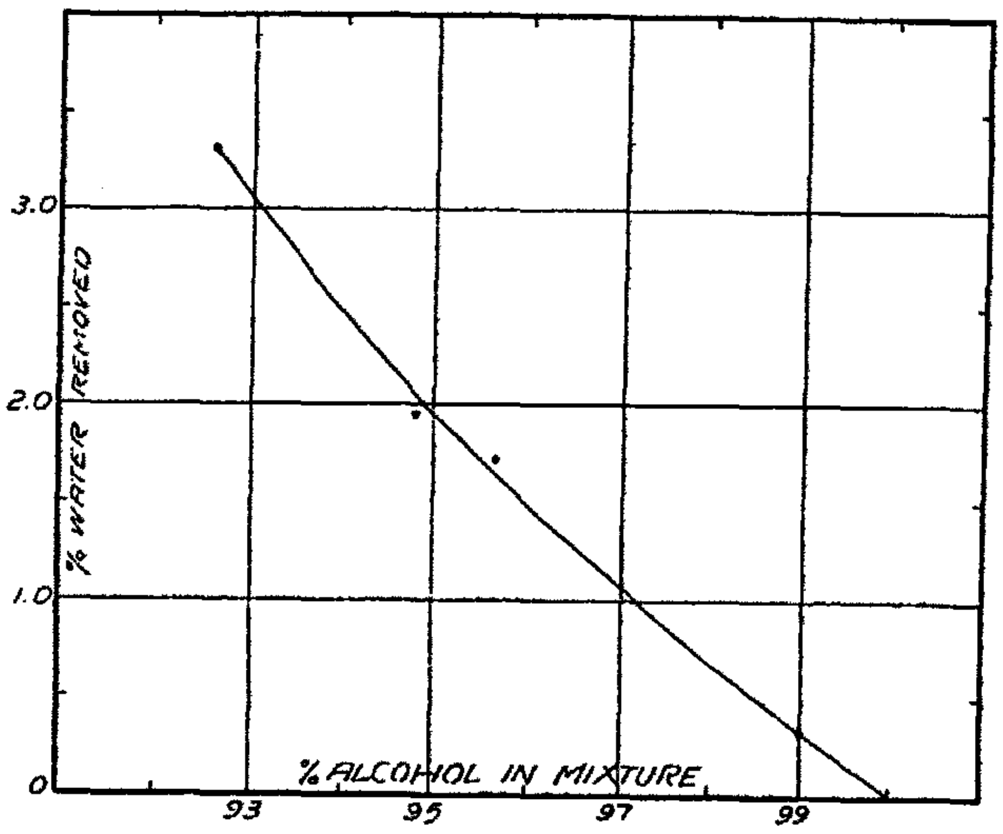
3.0
2.0
1.0
0
% WATER REMOVED
% ALCOHOL IN MIXTURE
93
95
97
99

Fig. 2

TABLE III

The Relation of Water Content of Mixture to Water adsorbed.

Weight Percent Alcohol in Mixture	Percent Water Lost
92.6	3.31
94.8	1.95
95.62+	1.72
99.0	0.33

+ True Azeotrope.

Change in Composition of Condensate during Progress of Distillation.

The results given in Table IV show how the composition of the condensate changed during the progress of a single distillation. Fifty cubic centimeters of the true azeotrope were distilled over 155 grams of gel, the gel temperature being maintained at 78°C. The successive 10 c.c. portions collected showed the following compositions.

TABLE IV

The Relation of Alcohol Content to Fraction collected.

Fraction Number	Alcohol Content	Water Removed
1.	99.11%	3.49%
2.	97.82%	2.20%
3.	96.89%	1.27%
4.	96.25%	0.63%

Effect of Variation in Quantity of Gel.

Experiments similar to those recorded in Table II were carried out with 155 grams of gel, all other factors being maintianed the same. The maximum amount of water lost with this larger quantity of gel was 3.44% as compared with 1.72%. The azeotropic mixture, with 95.62% alcohol was used in these experiments. With 2.76 times more gel present, the water removed is exactly twice as great.

Summary

1. Water may be preferentially adsorbed from alcohol-water mixtures by silica gel.

2. Adsorption of water from the mixtures is greater when adsorption takes place from the vapor than from the liquid phase.

3. The optimum temperature for the preferential adsorption of water vapor from the mixtures has been found to be 78°C.

4. The fraction of the total water present which is removed by adsorption decreases as the total water content of the mixture decreases.

5. The true azeotrope was studied and one fraction of the condensate (about 20% of the quantity started with) recovered showed an alcohol content better than 99%.

6. The adsorption of water increases with an increase in quantity of adsorbent, but not as a direct proportion.

THE SYSTEM NORMAL BUTYL ALCOHOL-METHYL ALCOHOL-WATER

BY A. J. MUELLER, L. I. PUGSLEY AND J. B. FERGUSON

Methyl alcohol is completely miscible in water and in n. butyl alcohol but water and n. butyl alcohol are themselves only partially miscible at ordinary temperatures. The ternary system composed of these liquids does not appear to have been previously investigated. Our results[1] include the values for the binodal curves, the tie lines and the plait points at a series of temperatures ranging from 0°C. to 105°C.

Normal Butyl Alcohol. A carefully prepared product obtained from the British Acetone Company in 1917. After treating with lime in the cold and distillation, it yielded an alcohol with $D_4^{20} = 0.8095$ and boiling point 117.6°C. This density agrees with that given by Reilly and Ralph[2] for the pure alcohol and therefore we assumed the impurity to be water. Pugsley's stock sample was estimated[3] to be 97.25 weight percent alcohol and this he checked by a density determination using a synthetic solution prepared from his dried alcohol and distilled water. Mueller's stock sample was estimated to contain 97.5 weight percent alcohol and on drying he obtained a product with density $D_4^{20} = 0.8097$.

Methyl Alcohol. Eastman Kodak Research Laboratory and Kahlbaum, acetone free. Pugsley's sample gave $D_4^{20} = 0.7938$ and Mueller's gave $D_4^{20} = 0.7923$. Upon the assumption that the impurity was water, the former sample was estimated[4] to contain 99.35 weight percent alcohol and the latter 99.8 percent.

We considered that the water content of the experimental charges would be more accurately known by making an allowance for the water present in the stock alcohols than by working with the absolutely dry alcohols which would so readily absorb moisture from the air. Distilled water was used.

Apparatus and Procedure

For the measurements at 0°C. a glass thermostat containing ice and water was employed. For higher temperatures the bath contained either water or a strong solution of glycerol. The temperature could be regulated to 0.1°C. and the thermometer read to 0.05°C.

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[1] Results at 0°C. by Mr. Pugsley (1927-28), those at other temperatures by Mr. Mueller (1928-29-30).

[2] Reilly and Ralph: Sci. Proc. Roy. Dublin Soc., 15, 597 (1919).

[3] Young: "Distillation Principles and Processes," 262 (1922).

[4] International Critical Tables, 3, 116 (1928).

The binodal curves were determined by three methods. At 0°C. Pugsley added a suitable component to a known homogeneous solution of the other components and found, by weighing, the amount of this component necessary to give rise to heterogeneity. At 15°C., 30°C., 45°C. and 60°C. Mueller determined in a similar manner the amount of the consolute (methyl alcohol) required to change a heterogeneous system into a homogeneous one. At higher temperatures, the evaporation losses rendered unsuitable this procedure and a method similar to that of Drouilon[5] was employed. Samples containing equal percentages of methyl alcohol, but different percentages of butyl alcohol and water, were placed in tubes of soda-glass and the tubes sealed, care being taken to leave an air bubble large enough to ensure the presence of a gas phase at all temperatures and to provide adequate stirring. A tube was placed in the thermostat in an inclined position and slowly rotated (46 times per minute) while the bath was either heated or cooled. The critical solution temperature for each sample was thus obtained. Such temperatures were plotted against the n. butyl alcohol-water, content of the samples. A number of such graphs were thus obtained, each graph relating to systems of constant methyl alcohol content. From these graphs, the points on the binodal curves could be obtained.

In the experiments at 15°C.-60°C., a sample was held in a calibrated Pyrex glass tube and the volume of the final homogeneous solution was obtained from cathetometer readings. The densities of these solutions were calculated from the volumes and weights. The volumes of the two phases present in the sample selected for the determination of a tie line were found in a similar manner and the tie lines were then obtained by the graphical method of Miller and McPherson.[6] The tie lines at 0°C. were more directly determined since the two phases were separated, weighed and the weights checked against the original total weight. This rendered unnecessary the approximations involving the densities but the whole procedure was more tedious than the former method.

At 75°C. and 90°C. density determinations were not made and a modification of the latter method was employed. Owing to the high temperatures, certain precautions were necessary since appreciable losses would occur if the sample were exposed to the air even for a short time. A capillary tube was sealed to the bottom of the sample tube and bent so that its upper end was well above the bath liquid. To this end was sealed a stopcock. At 75°C. the phases were separated by forcing the lower layer out through the capillary using compressed air; at 90°C., the vapour pressure alone was sufficient for this purpose, and in this case the upper end of the sample tube was sealed off after filling. The weight of the phase removed was obtained by difference from the weights of the original charge and of the residual layer since the evaporation of the lower layer during its removal rendered the directly determined weight of this phase of dubious value.

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[5] Drouilon: J. Chim. phys., 22, 149 (1925).

[6] Miller and McPherson: J. Phys. Chem., 12, 709 (1908).

The plait points at 0°C.-75°C. were obtained graphically by drawing a smooth curve through the bisectors of the tie lines to meet the binodal curves. Solutions with compositions corresponding to the location of these points of contact were then made up. To each solution of five cubic centimeters was added two drops of water and the ratio of the volumes of the phases which formed was noted. Three drops of butyl alcohol and sufficient methyl alcohol (usually three drops) to bring the system to such a state that one more drop would cause homogeneity, were added and the ratio of the volumes of the phases which separated was again noted. In the first case, the volume of the aqueous phase was the greater and in the second case the volume of the alcoholic phase was the greater, the excess in each case not exceeding 0.2 cc. The positions of these plait points were checked and established in this manner.

The plait points at 90° and 105°C. were obtained by interpolation from the smooth curve on a ternary diagram connecting our experimental points with the point representing the consolute composition in the binary system.

Sources of Error

Measurements at 0°C. to 60°C. The temperature of the thermostat was held to within 0.1°C. and the actual temperatures were accurate within these limits.

The sample tube was kept stoppered as much as possible during a determination. The time, exclusive of time taken for weighings, required to establish a point on the binodal curve seldom exceeded an hour. A test with methyl alcohol, the most volatile component, indicated that the loss by evaporation at 50°C. in one hour was 0.0135 g. A loss of this amount would correspond to an error of 0.17 weight percent in the total composition.

Upon the assumption that the solution-air surface was elliptical, a volume reading of 3 cc. was in error not more than 0.3 weight percent.

The detection of homogeneity or heterogeneity was not difficult but the composition of the saturated solution could only be determined to one drop of the liquid which was added. Care was taken to use as small drops as possible and the error was not greater than 0.11 weight percent of the composition of the system.

The liquid-liquid interface was plainly visible, and the cathetometer reading readily obtained.

Measurements above 60°C. Owing to the uncertainty in the stem correction of our mercury thermometer, the accuracy of the temperature measurements was 0.2°C. at 100°C. and 0.3°C. at 120°C.

The temperature difference between the thermometer bulb and the liquid in the sample tube was probably not in excess of 0.1°C. except at the highest temperatures. The change from heterogeneity to homogeneity and vice versa could be determined for points on the flat parts of the temperature-composition curves within a range of 0.2°C. but toward the ends of these curves only to within 0.8°C. An error of not more than 0.5 percent in the butyl alcohol or water content (B + W = 100) might be caused through this source.

In any one series of experiments, the methyl alcohol was maintained as nearly constant as possible. The actual deviations from constancy are indicated in the table of results. This degree of constancy was deemed sufficient in view of the other sources of error but to attain even this degree, with the small samples (4-6 g.) used, it was necessary to discard one in every four samples prepared (approx.) at a time when we were experienced in the art.

Jones[7] reports a difference between results obtained using soda glass and Pyrex glass when studying the system water-n. butyl alcohol. Since our experiments were made with containers of soda glass, we repeated this comparison and observed with fresh soda glass a consolute temperature 0.4°C. higher than that observed with Pyrex glass. Jones' observation was thus confirmed. If the results with Pyrex glass are the more accurate, then our results are subject to this error, the magnitude of which would vary from experiment to experiment, especially with experiments at different temperatures and which would probably have a maximum value of 0.4°C. Since most of our experiments were made at temperatures much lower than the consolute temperature in the binary system, we did not consider that the possible magnitude of this error warranted a repetition of the many measurements which we had previously obtained.

Weighings were made to 0.0001 g. using carefully standardized weights but owing to the nature of our results, the weights recorded in this paper have usually been rounded off to three significant figures.

Experimental Results and Discussion

In the tables the following abbreviations are used: n. butyl alcohol, B; methyl alcohol, M; water, W. The results have been calculated on the basis B + W = 100, since the infinite diagram enables one to select a scale suitable for the indication of the methyl alcohol content.

Tables I to V, inclusive, give our results at 0°C., 15°C., 30°C., 45°C., and 60°C. In Table VI are tabulated the critical temperatures observed with the various series of samples, each series at constant methyl alcohol content. The results on the binodal curves at 75°C., 90°C., and 105°C. are given in Table VII, and those on the tie lines at 75°C. and 90°C. in Table VIII. The composition of the plait points at various temperatures are given in Table IX. The temperatures of a series of points on the saturation surface (solid model) corresponding to systems of constant butyl alcohol and water contents but variable methyl alcohol content are given in Table X.

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[7] Jones: J. Chem. Soc., 1929, 799.

TABLE I

Binodal Curve, Tie Lines and Plait Point at 0°C.

Binodal Curve

Composition in grams		
M.	W.	B.
—	90.45	9.55*
2.89	90.21	9.79
4.68	90.07	9.93
9.68	89.26	10.74
13.03	86.72	13.28
16.73	83.63	16.37
19.03	76.70	23.30
18.52	66.55	33.45
16.87	56.76	43.24
15.70	46.77	53.23
14.34	44.52	55.48
12.38	37.20	62.80
9.80	32.33	67.67
6.47	25.86	74.14
3.518	22.91	77.09
—	19.62	80.38*

* H. & M. extrapolated.

Tie Lines

	Comp. of system			Phase weight ratio
	M.	W.	B.	
(a)	5.81	62.46	37.54	0.697
(b)	10.69	60.68	39.32	0.870
(c)	14.30	63.18	36.82	0.840
(d)	16.72	64.60	35.40	0.702
(e)	17.62	63.31	36.69	0.941

	Comp. upper phase			Comp. lower phase		
	M.	W.	B.	M.	W.	B.
(a)	4.20	23.30	76.70	7.00	90.00	10.00
(b)	8.75	30.10	79.90	12.50	87.50	12.50
(c)	12.25	36.90	63.10	15.50	84.80	15.20
(d)	14.50	44.25	57.20	18.90	79.50	20.50
(e)	16.50	51.50	48.50	19.40	74.50	26.50

Plait Point 18.50 M. 63.10 W. 36.90 B.

TABLE II

Binodal Curve, Tie Lines, Plait Point and Density Determinations at 15°C.

Binodal Curve

Comp. in grams M.	Comp. in grams W.	Comp. in grams B.	Density	Comp. in grams M.	Comp. in grams W.	Comp. in grams B.	Density
				16.0	66.1	33.9	0.926
—	91.7	8.30*	0.988	15.7	61.1	38.9	0.922
6.29	91.4	8.56	0.981	15.1	54.5	45.5	0.913
12.2	89.3	10.7	0.981	14.6	48.7	51.3	0.899
14.4	86.8	13.2	0.970	13.3	42.8	57.2	0.890
15.7	83.9	16.1	0.960	11.1	36.2	63.8	0.881
16.2	80.5	19.5	0.954	7.63	29.0	71.0	0.870
16.7	76.0	24.0	0.945	2.55	21.9	78.1	0.861
16.3	71.3	28.7	0.934	—	19.9	80.2*	0.853

* (H. & M. interpolated).

Tie Lines

	Comp of system M.	Comp of system W.	Comp of system B.	Phase volume ratio	Phase weight ratio
(a)	3.64	61.1	38.9	1.13	1.29
(b)	6.55	61.1	38.9	1.11	1.25
(c)	8.90	61.1	38.9	1.05	1.18
(d)	11.4	61.1	38.9	0.965	1.07
(e)	14.1	61.1	38.9	0.830	0.900
(f)	15.3	64.2	35.8	0.975	1.06

	Comp. upper phase M.	Comp. upper phase W.	Comp. upper phase B.	Comp. lower phase M.	Comp. lower phase W.	Comp. lower phase B.
(a)	2.3	21.7	78.3	4.8	91.6	8.4
(b)	4.3	24.0	76.0	8.4	90.7	9.3
(c)	6.7	27.5	72.5	10.7	89.7	10.3
(d)	9.3	32.4	67.6	13.2	88.0	12.0
(e)	12.7	40.5	59.5	15.6	83.9	16.1
(f)	14.4	47.8	52.2	16.3	80.0	20.0

Plait Point 16.0 M. 64.5 W. 35.5 B.

TABLE III

Binodal Curve, Tie Lines, Plait Point and Density Determinations at 30°C.

Binodal Curve

Comp. in grams			Density
M.	W.	B.	
—	92.92	7.08*	0.985
4.71	92.3	7.67	
6.12	92.1	7.94	0.975
7.55	91.1	8.87	0.961
8.23	90.8	9.17	
9.08	90.7	9.34	0.979
11.06	89.1	10.91	0.971
12.3	87.1	12.9	0.958
13.5	83.6	16.4	0.953
14.1	82.0	18.0	
13.9	80.6	19.4	0.946
14.3	79.0	21.0	
14.2	76.1	23.9	0.938

* H. & M.

Comp. in grams			Density
M.	W.	B.	
14.3	75.9	24.1	
14.2	73.1	26.9	
14.2	71.8	28.2	0.928
13.9	67.3	32.7	0.918
13.8	61.9	38.1	0.911
13.4	57.2	42.8	0.904
11.2	48.0	52.0	0.888
11.0	44.4	55.6	0.881
9.50	39.0	61.0	0.874
8.21	35.2	64.8	0.870
6.54	31.0	69.0	0.863
3.97	26.1	73.9	0.854
—	20.6	79.4*	0.842

Tie Lines

	Comp. of system			Phase volume ratio	Phase weight ratio
	M.	W.	B.		
(a)	3.98	71.0	29.0	1.93	2.20
(b)	7.95	71.0	29.0	1.93	2.15
(c)	9.83	68.5	31.5	1.62	1.78
(d)	11.1	68.5	31.5	1.64	1.78
(e)	12.3	68.5	31.5	1.64	1.77
(f)	13.6	68.5	31.5	1.78	1.88

	Comp. upper phase			Comp. lower phase		
	M.	W.	B.	M.	W.	B.
(a)	2.4	23.8	76.2	4.7	92.4	7.6
(b)	5.3	28.4	71.6	9.1	90.7	9.3
(c)	7.5	33.0	67.0	11.2	88.8	11.2
(d)	8.5	35.9	64.1	12.5	86.7	13.3
(e)	10.0	41.5	58.5	13.5	83.8	16.2
(f)	12.3	52.2	47.8	14.2	77.2	22.8

Plait Point 13.9 M. 65.5 W. 34.5 B.

TABLE IV

Binodal Curve, Tie Lines, Plait Point and Density Determinations at 45°C

Binodal Curve

Comp in grams			Density	Comp. in grams			Density
M.	W.	B.		M.	W.	B.	
—	93.5	6.50*	0.982	11.7	60.8	39.2	0.905
.789	93.82	6.18	0.982	10.8	54.4	45.6	0.900
3.89	93.1	6.87	0.978	10.5	51.1	48.9	0.898
8.14	90.3	9.67	0.963	10.1	47.4	52.6	0.895
9.87	87.3	12.7	0.961	9.16	42.9	57.1	0.885
10.7	84.2	15.8	0.949	9.20	40.8	59.2	0.864
11.1	81.3	18.7	0.942	7.94	36.1	63.9	0.859
11.3	78.6	21.4	0.935	5.77	30.7	69.3	0.851
12.0	75.8	24.2	0.930	2.40	24.4	75.6	0.837
11.9	71.8	28.2	0.925	—	21.8	78.2*	0.833
11.8	67.4	32.6	0.918				

* (H. & M. interpolated).

Tie Lines

	Comp. of system			Phase volume ratio	Phase weight ratio
	M.	W.	B.		
(a)	3.10	60.8	39.2	0.930	1.08
(b)	6.25	60.8	39.2	0.850	0.963
(c)	8.25	60.8	39.2	0.768	0.865
(d)	9.86	60.8	39.2	0.670	0.758
(e)	11.0	66.2	33.8	1.00	0.964

	Comp. upper phase			Comp. lower phase		
	M.	W.	B.	M.	W.	B.
(a)	3.4	25.9	74.1	2.7	93.3	6.7
(b)	5.9	30.9	69.1	6.3	91.8	8.2
(c)	7.8	36.1	63.9	8.5	89.5	10.5
(d)	9.3	43.0	57.0	10.5	85.0	15.0
(e)	10.7	52.7	47.3	11.5	79.0	21.0

Plait Point 11.5 M. 66.0 W. 34.0 B.

TABLE V

Binodal Curve, Tie Lines, Plait Point and Density Determinations at 60°C.

Binodal Curve

Comp. in grams			Density	Comp. in grams			Density
M.	W.	B.		M.	W.	B.	
—	93.5	6.52*	0.977	9.64	61.0	39.0	0.877
5.54	90.89	9.11	0.962	8.55	52.8	47.2	0.875
6.12	90.3	9.67	0.960	8.13	45.4	54.6	0.858
6.42	90.2	9.80	0.957	6.78	39.0	61.0	0.847
8.59	86.4	13.6	0.940	4.44	32.0	68.0	0.836
9.05	82.4	17.6	0.936	2.49	28.1	71.9	0.830
9.93	73.7	26.3	0.921	—	23.6	76.4*	0.825
9.80	68.7	31.3	0.894				

* H. & M.

Tie Lines

	Comp. of system			Phase volume ratio	Phase weight ratio
	M.	W.	B.		
(a)	5.36	66.9	33.1	1.32	1.53
(b)	7.41	66.8	33.2	1.22	1.36
(c)	8.37	66.8	33.2	1.18	1.29
(d)	1.91	67.0	33.0	1.34	1.57

	Comp. upper phase			Comp. lower phase		
	M.	W.	B.	M.	W.	B.
(a)	1.5	26.3	73.7	2.2	92.8	7.2
(b)	4.1	31.3	68.7	6.2	90.3	9.7
(c)	6.5	38.3	61.7	8.0	87.7	12.3
(d)	7.7	43.3	56.7	8.8	85.2	14.8

Plait Point 9.71 M. 66.8 W. 33.2 B.

TABLE VI

The Critical Temperatures of Various Series of Systems, Each at Constant Methyl Alcohol Content

Methyl Alcohol $M = 2.0$ when $B + W = 100$

Composition of system			Critical Temperature °C.	% dev. of M. from series unit	Average range of critical temperature °C.
M.	W.	B.			
.105	4.60	.398	82.0	4.4	0.1
.102	4.51	.503	95.6	1.2	0.2
.102	4.42	.587	101.7	1.7	0.4
.101	4.21	.804	109.4	0.3	0.1
.103	3.71	1.29	113.2	3.2	0.2
.102	3.03	1.97	113.3	1.4	0.1
.0885	2.08	2.42	107.2	1.6	0.8
.0709	1.36	2.15	96.8	1.2	0.7
.0700	1.14	2.37	82.2	0.2	0.2

TABLE VI (continued)

Methyl Alcohol M = 2.5 when B + W = 100

Composition of system			Critical Temperature °C.	% dev. of M. from series unit	Average range of critical temperature °C.
M.	W.	B.			
.128	4.20	.800	105.8	2.3	0.2
.126	3.78	1.24	109.9	0.6	0.1
.099	2.60	1.40	110.4	0.9	0.3
.100	2.17	1.83	108.7	0.2	0.1
.132	2.33	2.68	103.3	5.5	0.4
Methyl Alcohol M = 3.2 when B + W = 100					
.161	3.94	1.07	105.0	0.4	0.1
.159	3.36	1.64	105.6	0.4	0.2
.161	2.92	2.08	105.4	0.3	0.7
Methyl Alcohol M = 4.0 when B + W = 100					
.166	3.59	.408	81.5	3.8	0.3
.142	2.93	.556	95.6	1.6	0.2
.160	2.97	1.03	99.8	0.3	0.3
.157	2.41	1.59	100.4	1.7	0.1
.160	1.87	2.13	93.5	0.4	0.4
.179	1.72	2.78	82.4	0.5	0.7
Methyl Alcohol M = 5.0 when B + W = 100					
.177	3.15	.353	74.7	0.6	0.8
.175	2.98	.332	88.8	0.6	0.4
.253	3.77	1.24	92.9	1.1	0.6
.251	3.01	1.99	93.0	0.1	0.0
.251	2.52	2.48	89.6	0.4	0.4
.250	2.00	3.00	78.1	0.0	0.5
Methyl Alcohol M = 5.5 when B + W = 100					
.272	3.85	1.15	89.9	1.1	0.0
.275	3.39	1.61	90.4	0.2	0.0
.274	2.95	2.05	89.6	0.4	0.0
Methyl Alcohol M = 6.3 when B + W = 100					
.313	4.31	.692	77.8	1.0	0.3
.316	2.32	2.68	77.1	0.3	0.4
Methyl Alcohol M = 7.2 when B + W = 100					
.360	4.11	.898	76.5	0.3	0.5
.362	2.70	2.30	76.4	0.5	0.1
Methyl Alcohol M = 7.8 when B + W = 100					
.389	3.69	1.31	77.1	0.6	0.5
.389	3.20	1.80	74.9	0.4	0.1

TABLE VII

Binodal Curves at 75°C., 90°C. and 105°C.

B + W = 100

Temp. 75°C.	Composition M.	Composition B.
	0.0	6.8 and 73.7
	2.0	7.4 " 69.8
	4.0	9.1 " 64.8
	5.0	10.6 " 61.4
	6.3	12.7 " 54.8
	7.2	16.6 " 47.8
	7.8	19.5 " 35.4

Temp. 90°C.	Composition M.	Composition B.
	0.0	7.8 and 69.8 .
	2.0	9.0 " 64.5
	4.0	13.0 " 56.5
	5.0	16.5 " 49.0
	5.5	23.0 " 39.5

Temp. 105°C.	Composition M.	Composition B.
	0.0	9.8 and 64.3
	2.0	13.3 " 56.1
	2.5	15.7 " 52.1
	3.2	21.7 " 42.7

TABLE VIII

Tie Lines at 75°C. and 90°C.

Comp. of system M.	W.	B.	Phase Weight Ratio	Comp. upper phase M.	W.	B.	Comp. lower phase M.	W.	B.
75°C.									
.615	6.66	3.57	.983	6.0	44.8	55.2	6.8	85.0	15.0
.525	6.78	3.59	.830	4.5	36.8	63.2	5.5	88.7	11.3
.268	6.59	3.51	.758	2.1	30.0	70.0	3.1	92.0	8.0
90°C.									
.213	6.54	3.72	.973	2.00	35.4	64.6	2.20	90.8	9.2
.421	6.66	3.68	1.16	4.10	43.9	56.1	3.92	87.8	12.2

TABLE IX

The Plait Points

Temperature °C.	Composition of system M.	W.	B.
0	18.5	63.1	36.9
15	16.0	64.5	35.5
30	13.9	65.5	34.5
45	11.5	66.0	34.0
60	9.7	66.8	33.2
75	7.8	67.0	33.0
90 (interpolated)	5.6	67.3	32.7
105 (interpolated)	3.5	67.4	32.6
(H&M) 125.15	0	67.5	32.5

TABLE X

The Effect of Methyl Alcohol on the Critical Temperature for Systems containing Constant Amounts of Water and N Butyl Alcohol

Temperature °C.	Composition (B. = 35, W = 65) M.	Temperature °C.	Composition (B. = 35, W. = 65)
0	18.5	75	7.8
15	16.2	90	5.5
30	13.8	105	3.5
45	11.8	110.9	2.4
60	9.8	120.6	1.1
		125.15	0 (H & M)

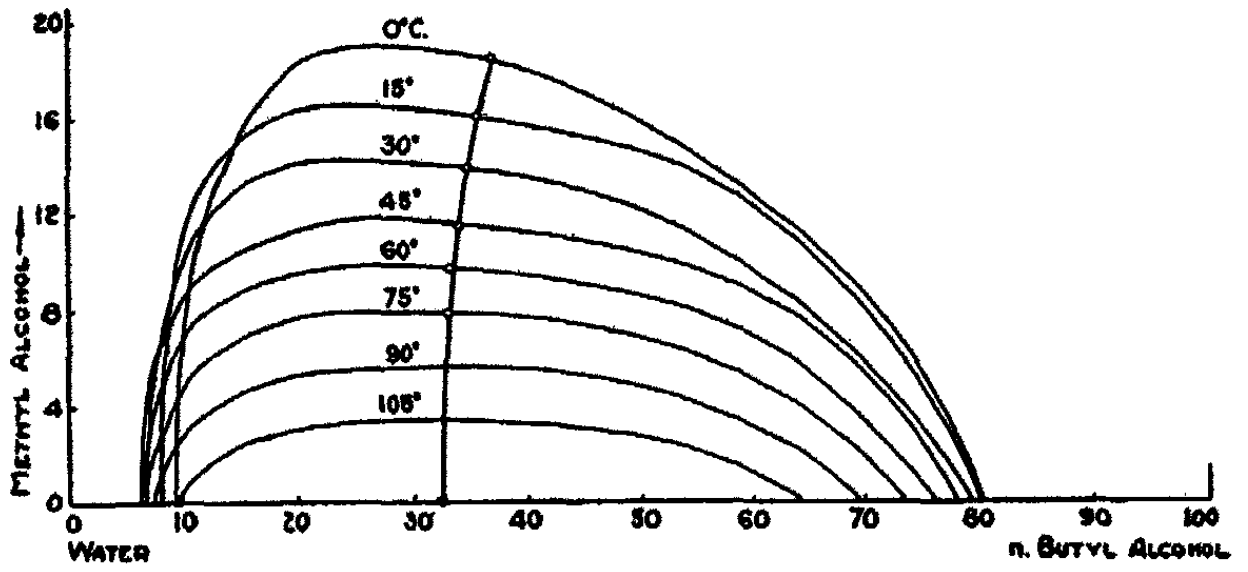

Fig. 1.
Binodal curves and Plait Points

The solubility relations in the binary system n. butyl alcohol-water have been investigated, especially by Jones and by Hill and Malissoff.[8] Their results differ chiefly in the values assigned to the composition of the aqueous phase at low temperatures, the maximum difference occurring at 20°C. When we extrapolated our binodal curves, we obtained a series of values for the composition of this aqueous phase and noted that at 15°C. and 30°C. our values agreed best with those of Hill and Malissoff. At 0°C. and 45°C. where the differences were not so great, our values were a little closer to those of Jones and at temperatures above 45°C., our extrapolation was too inaccurate for us to differentiate between the results of these previous workers. In order to make the comparison, the results of these investigators were plotted and the values taken from the smooth curve drawn. The curve of Hill and Malissoff's results was extrapolated to 0°C. Since our results agreed best with those of Hill and Malissoff at those temperatures where the really significant differences occur, we have used their results for the correlation of our determinations.

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[8] Hill and Malissoff: J. Am. Chem. Soc., 48, 918 (1926).

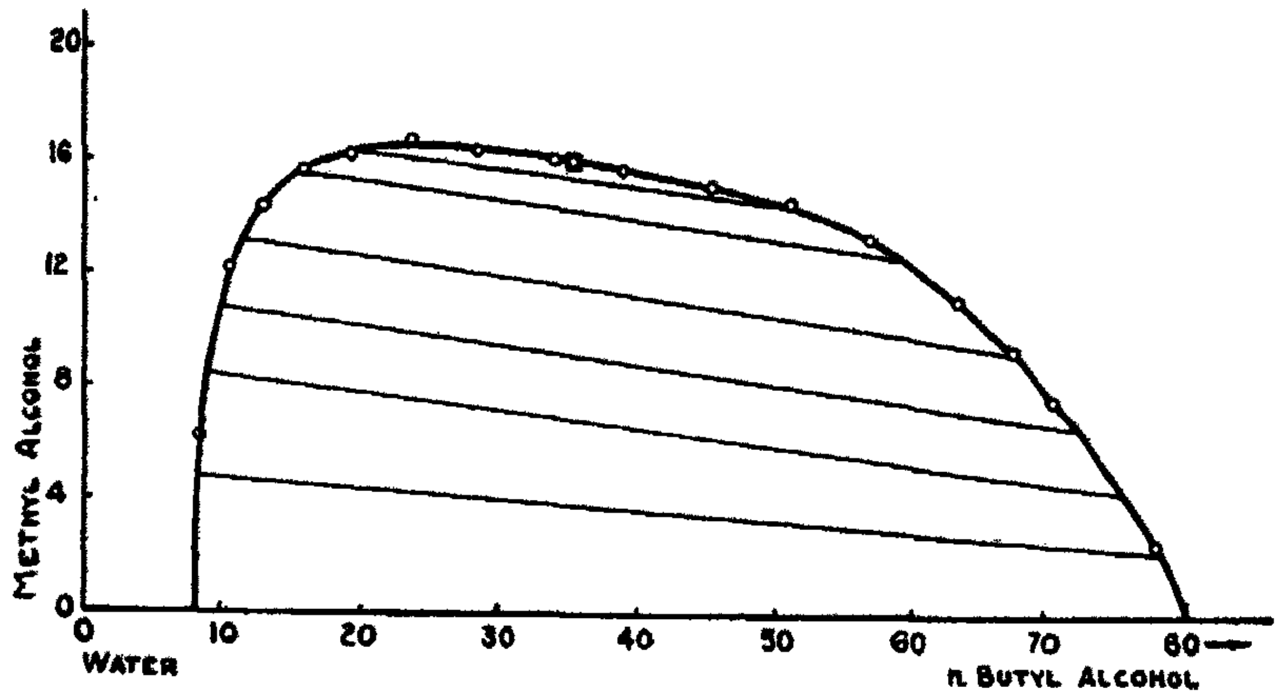

Fig. 2.
Tie lines at 15°C.

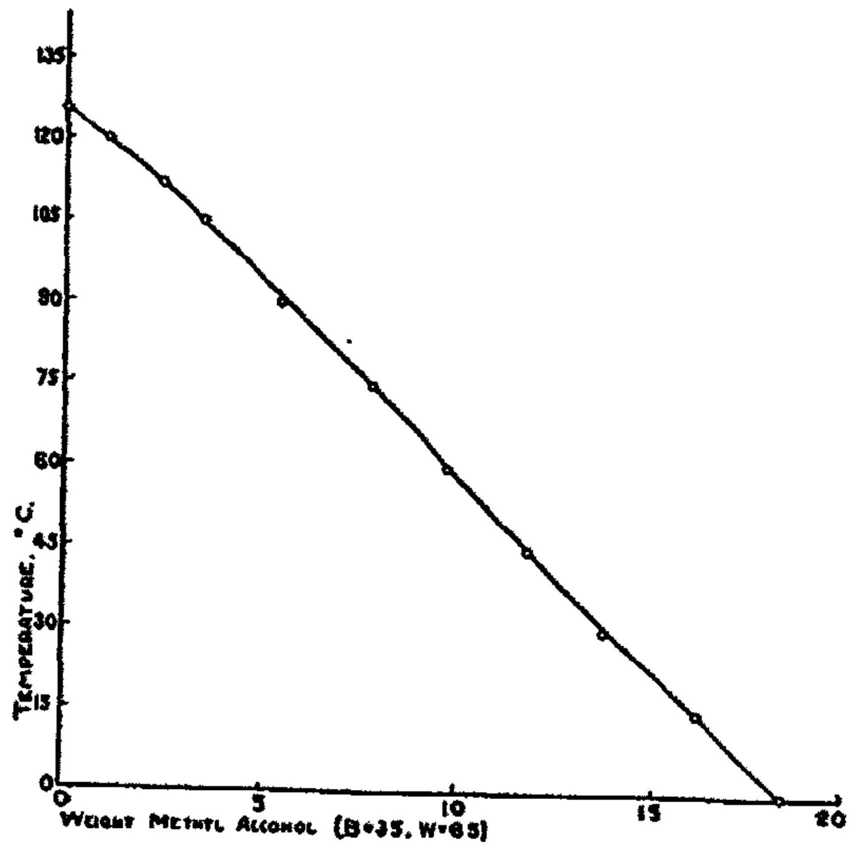

Fig. 3.

In Fig. 1, are given our results for the binodal curves combined with those of Hill and Malissoff for the binary system, n. butyl alcohol-water. An inspection of this graph indicates that the values of the plait points at 90°C. and 105°C. obtained by interpolation cannot be much in error. It seems hardly necessary for us to indicate graphically the various tie lines which we have determined. Perhaps the most useful series would be that obtained at 15°C. which is shown in Fig. 2. The slope of the saturation surface (solid model) at 35 weight percent n. butyl alcohol (B + W = 100) is nearly linear. This is indicated by the plot of the results given in Table X, which is reproduced in Fig. 3.

Summary

The binodal curves, tie lines and plait points of the system n. butyl alcohol-methyl alcohol-water have been determined at temperatures ranging from 0°C. to 105°C. These results have been presented in tabular form and in part graphically.

Certain additional results (particularly densities) which were required for these determinations have been indicated.

Department of Chemistry,
University of Toronto,
January 16, 1931.

A STUDY OF THE REFRACTOMETRIC ESTIMATION OF PROTEINS

I. The Numerical Value of the Refractive Index Constant *a* for Antitoxic Globulins*

BY TILLMAN D. GERLOUGH AND WOODFORD WHITE

The refractive index method for estimating serum proteins, introduced by Reiss,[1] and further developed by Robertson,[2] rests upon a simple linear relationship between concentration and refractive index of the solution. This relationship is expressed by the equation $C = \frac{n - n_1}{a}$, where n and n_1 are the refractive indices of the solution and solvent respectively. C is concentration in grams per 100 cc. of solution, and a is a constant characteristic of a particular protein and is numerically equal to the change in refractive index produced by a change in concentration of 1 gram in 100 cc. When a is expressed in these terms it remains independent of concentration and may, for most purposes, be considered as independent of ordinary temperature changes.

This method has been used extensively in studying serum proteins under normal and pathological conditions, but has received very little attention as a means of measuring accurately the protein content of antitoxins (purified pseudoglobulin solutions prepared from antitoxic horse plasma or serum). It is particularly adapted for such determinations because it is rapid, accurate and entails no loss of material. However, when we first attempted to apply the method to the determination of protein content of antitoxic globulins it did not give results comparable with other reliable methods. We could see no reason why the same general procedure and the refractive index constant employed by many previous workers for the determination of globulin in serum would not give a true measure of the protein content of antitoxic globulin solution. The source of discrepancy was found to be in the value of the constant employed. After the constant was carefully redetermined the results were identical with those obtained by other methods. For instance, in our preliminary work the protein content computed by either of Reiss' constants for pseudo-globulin, 0.00230 or 0.00224, was consistently more than 20 per cent lower than that found by gravimetric, nitrogen, and density determinations. A similar discrepancy was observed by Homer[3] in connection with her work on antitoxins. Miss Homer stated that the protein concentration determined by refractive index through the use of Reiss tables was consistently lower than her gravimetric measurements. Although she apparently made no attempt to check the refractive index constant, it was suggested that the refractive indices of the individual serum proteins required further study.

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*Contribution from the Research and Biological Laboratories of E. R. Squibb and Sons, New Brunswick, N. J.

The purpose of this communication is to present the results of an investigation on the refractive index constant of antitoxic protein as defined by equation $a = \frac{n - n_1}{C}$. The value of *a*, 0.00184, has been established for the following antitoxic globulins: diphtheria, tetanus, scarlet fever and erysipelas.

Purification of the Antitoxins

The antitoxins were first concentrated from horse plasma by a method similar to that described by Banzhaf,[4] and then further purified by removal of remaining euglobulin and denatured protein.[5,6] This was accomplished by diluting the dialyzed* antitoxin with distilled water to 3 per cent protein and adjusting the reaction to pH 5.7 to 5.8. The antitoxin in the clear supernatant liquid was reconcentrated by salting out at pH 7.0 with $(NH_4)_2SO_4$ and the salt removed by pressing the precipitate and dialyzing the solution to a specific conductance of 3 to 5 × 10^{-5}. A portion of each dialyzed preparation was withdrawn at this stage for measurements of refractive index, density, total solids and nitrogen (Tables I-IV). These antitoxin solutions contained 13 to 16 per cent protein and less than 0.10 mg. phosphorus, 1.5 mg. of ash and 3 to 5 mg. of ether-extractable matter per gram of protein. The remaining portion of each dialyzed solution was further treated by the method of Hewitt[7] by precipitating with an alcohol-ether mixture 70:30 (by volume), extracting with ether and finally drying over P_2O_5. These dried antitoxic globulins were used in the preparation of protein solutions of known concentration, upon which a similar series of measurements was carried out.

Experimental Procedure

All measurements of refractive index and density were made at 25°C. A Zeiss immersion refractometer was employed and scale readings converted into refractive indices. The densities were determined with a pyknometer.

The dialyzed antitoxin solutions, as well as those made up from dried antitoxin, were studied in the presence of suitable electrolyte. Refractive indices of the antitoxic globulin solutions were measured in 0.02 N NaCl. The powdered antitoxins were not completely soluble in dilute NaCl, but dissolved readily in 0.036 NaOH, and were examined in this solvent. Solutions of known protein concentration were prepared by dissolving weighed amounts of the powder in known weights of the NaOH solution.

The protein content of the dialyzed antitoxin solutions was determined by evaporating and drying weighed portions. A sufficient sample to yield 400 to 600 mg. of dried solids was placed in weighing dishes and heated for 5 hours at 110°C. The weighing dishes employed were 7 cm. in diameter. Evaporating surface was increased by spreading 8 cc. of washed and ignited sand on the bottom of each dish. Longer heating or higher temperatures up to 130°C gave the same results. Protein content was also checked in a few

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*The solutions were dialyzed to a specific conductance of 2.0 to 2.4 × 10^{-4}.

instances by coagulation with heat. The coagulum was collected in a Gooch crucible, washed once with alcohol and once with ether, dried at 110°C and weighed. This procedure yielded results identical with those obtained by evaporation and drying.

Refractive index measurements on the two preparations, i.e., the dialyzed solutions and solutions of the powdered antitoxin furnished two series of results based on solids determined by independent procedures. In addition to solids obtained by evaporation and by direct weighing, nitrogen determinations by the Kjeldahl method were made on the solutions and dried antitoxins. All gravimetric and nitrogen determinations were made in duplicate and corrected for any added electrolyte.

Experimental Results

These are collected in Tables I to IV. In this connection it may be stated that the protein concentration, in grams per 100 cc. are not recorded directly in the tables. These values may be obtained by multiplying the percentage of protein by the density of the solution. Not all of the densities found in Table I and III were direct determinations. Some were obtained by graphical interpolation of the data in Table IV. The reaction of all antitoxins employed except those made up in dilute NaOH, was between pH 6.2 and 6.6.

(a) *Dialyzed Antitoxin Solutions.*

In Table I are given the results obtained on dialyzed antitoxin solutions. The protein concentration of solutions in sets (A) and (B) of this table was determined by the gravimetric method while those of set (C) were calculated from nitrogen determinations. The average values for the constant, a, obtained from these three sets of determinations are: (A) 0.001834; (B) 0.001839; (C) 0.001834. It should be stated that the solutions of set (B) contained 0.85 per cent NaCl plus 0.5 per cent phenol and that the values of a are corrected for a small amount of phenol which was apparently fixed by the protein during the gravimetric determination by direct evaporation. Separate experiments showed that the presence of 0.5 per cent phenol in the antitoxin solutions containing 14 to 16 per cent protein, increased the total weight of dried solids, i.e., protein and salt, by 1.2 per cent. If the phenol corrections were not allowed for, the average value of a would be 0.001817.

In addition to the data given in Table I other measurements were made to determine whether or not higher concentrations of solvent salt exert any effect on the refractive index of antitoxic globulin. Antitoxin solutions of the same protein content, 6.5 per cent, were compared in 0.02, 0.04, 0.10 and 1.0 M NaCl and in 1.0 M $(NH_4)_2SO_4$. The refractive index due to the protein alone was found to be identical in all NaCl solutions within the limits of accuracy of the instrument. In 1.0 M $(NH_4)_2SO_4$ the increment was low by 1.0 per cent.

TABLE I

Values of the Refractive Index Constant *a* for Antitoxic Globulin Solutions

Globulin in N/50 NaCl	Protein Conc. per cent	$n - n_1$	Density $\frac{25°C}{4}$	$a = \frac{n - n_1}{\text{per cent protein} \times d}$
(A) *Protein Concentration obtained by drying to constant weight*				
Diphtheria (1)	16.15	0.03092	1.0435	0.001835
Diphtheria (2)	8.32	0.01554	1.0210	0.001830
Diphtheria (3)	16.18	0.03093	1.0436	0.001832
Diphtheria (4)	11.71	0.02215	1.0308	0.001835
Diphtheria (5)	3.42	0.00630	1.0072	0.001831
Tetanus (1)	9.32	0.01745	1.0238	0.001829
Tetanus (2)	13.74	0.02616	1.0368	0.001831
Erysipelas (1)	6.46	0.01207	1.0157	0.001839
Erysipelas (2)	13.09	0.02485	1.0348	0.001835
Scarlet Fever (1)	8.74	0.01639	1.0222	0.001835
Scarlet Fever (2)	15.68	0.03002	1.0427	0.001837
				Av. 0.001834
(B) *In Saline Salt and 0.50 per cent phenol*				
Diphtheria (1)	14.62	0.02814	1.0438	0.001844
Diphtheria (2)	15.57	0.02987	1.0466	0.001833
Tetanus (1)	14.91	0.02861	1.0460	0.001834
Tetanus (2)	15.81	0.03042	1.0474	0.001837
Erysipelas	14.49	0.02788	1.0434	0.001844
Scarlet Fever (1)	14.43	0.02774	1.0446	0.001840
Scarlet Fever (2)	14.63	0.02812	1.0439	0.001841
				Av. 0.001839
(C) *Protein Concentration calculated from Nitrogen Determinations*				
Diphtheria (6)	8.33	0.01554	1.0202	0.001830
Tetanus (3)	13.23	0.02507	1.0346	0.001832
Erysipelas (1)	6.46	0.01207	1.0149	0.001838
Scarlet Fever (1)	8.73	0.01639	1.0214	0.001837
				Av. 0.001834

Table II

Influence of NaOH on the Refractive Index of Antitoxic Globulin

(1) Antitoxic Globulin	(2) Normality NaOH	(3) Per cent Protein	(4) $n - n_1$ in Dilute NaCl	(5) $n - n_1$ in Dilute NaOH	(6) $\frac{(4) - (5)}{(4)}$ in per cent
Diphtheria (7)	0.036	14.70	0.02593	0.02564	1.12
Scarlet Fever (3)	0.036	12.30	0.02186	0.02153	1.50
Tetanus (4)	0.036	9.70	0.01747	0.01717	1.71
Diphtheria (7)	0.036	7.10	0.01282	0.01259	1.80
Diphtheria (7)	0.018	7.10	0.01282	0.01272	0.78
Diphtheria (7)	0.018	14.70	0.02593	0.02578	0.58

Table III

Values of the Refractive Index Constant *a* for Solutions of Dried Antitoxic Globulin in Sodium Hydroxide

Globulin in 0.036 N NaOH	Protein Concn. per cent	Density $d\frac{25°C}{4}$	$n - n_1$	$a = \frac{n - n_1}{\text{per cent protein} \times d}$ in NaOH	Correction for Effect of Alkali per cent	*a* (Corrected)
Diphtheria (1)	6.56	1.0163	0.01208	0.001812	1.82	0.001845
Diphtheria (2)	9.25	1.0239	0.01713	0.001809	1.75	0.001841
Tetanus (1)	13.80	1.0367	0.02605	0.001820	1.30	0.001844
Tetanus (2)	7.76	1.0197	0.01435	0.001814	1.79	0.001846
Tetanus (3)	8.92	1.0229	0.01651	0.001809	1.76	0.001841
Tetanus (4)	6.22	1.0154	0.01141	0.001807	1.90	0.001841
Erysipelas (1)	9.65	1.0250	0.01787	0.001810	1.73	0.001841
Erysipelas (2)	7.83	1.0199	0.01443	0.001807	1.80	0.001840
Scarlet Fever (1)	8.92	1.0229	0.01656	0.001815	1.76	0.001847
Scarlet Fever (2)	10.23	1.0265	0.01906	0.001815	1.69	0.001846
					Av.	0.001843

Solutions of Powdered Antitoxin in NaOH

The results obtained on solutions made up with weighed quantities of the powdered antitoxin in a weighed amount of 0.036 N NaOH are shown in Table III. In this table two sets of constants appear, those actually obtained in 0.036 NaOH (Column 5), and the latter values corrected for the decrease in refractive index brought about by the presence of NaOH in the system (Column 7). It will be noted that the observed values are definitely lower than the corrected values. Since this lowering is a function of the concentration both of protein and alkali its magnitude was observed over a range of protein concentrations consistent with working conditions, and the corrections interpolated graphically from calculated deviations in the last column of Table II. In determining these corrections the apparent refractive index of the protein in dilute NaOH was compared with its refractive index in dilute NaCl solution as follows:—Equal weights of the same antitoxin solution were placed in two different flasks. A definite weight of NaCl solution of suitable concentration was added to one flask while an equal weight of NaOH solution of the same refractive index was placed in the other. After mixing, the refractive indices of both solutions were determined under identical conditions. The resulting measurements are set forth in Columns 4 and 5 of Table II.

The average constant of the various dry antitoxins, corrected for the effect of NaOH, is 0.001843. When not so corrected, the average value of this constant is 0.001812.

TABLE IV

Densities of Antitoxic Globulin Solutions at 25°C/4

	Per cent Protein	Density in N/50 NaCl
A. *Antitoxic Globulin Solutions*		
	3.41	1.0072
	5.13	1.0120
	7.71	1.0193
	9.06	1.0231
	9.79	1.0251
	11.71	1.0308
	16.29	1.0441
	0.00	1.00085
B. *Dried Antitoxic Globulin*		
		Density in 0.036 NaOH
	2.73	1.0059
	3.83	1.0089
	6.22	1.0154
	7.18	1.0179
	9.71	1.0251
	13.80	1.0367
	0.00	1.00168

A total of 18 nitrogen determinations were made to ascertain the nitrogen content of the antitoxic globulins. The material used included antitoxic globulins in solution and solid form as well as antitoxic globulin which had been electro-dialyzed to a specific conductance of 6×10^{-6} to remove last traces of $(NH_4)_2SO_4$. The average of all nitrogen values was 15.55 per cent. None of the individual determinations deviated more than 0.25 from the average. Our results are considerably higher than those reported by Banzhaf, Suguira and Falk[8] for the nitrogen content of antitoxins and are in better agreement with the value, 15.85 per cent, recorded by Hammarsten[9] and by others for "normal" serum globulin, i.e., from non-immunized horses.

The average refractive index constant obtained on 10 solutions of dried antitoxins, whose protein content was calculated from nitrogen determinations was 0.001844 when corrected for the effect of NaOH.

The average of all determinations, 42 in number, was selected as the final value for the constant a. This value was 0.001839; when rounded, 0.00184.

Table IV shows the densities of solutions of both types of antitoxin preparations. They agree with those recorded by Chick and Martin[10] and Chick[11] for pseudo-globulin (horse), when compared under the same conditions. Solutions of the powdered antitoxins (B) in dilute NaOH gave densities sensibly lower than those observed for the antitoxic globulin solutions (A) in dilute NaCl. In the absence of electrolyte, the densities may be calculated from the following equations: (A) $d\frac{25^\circ}{4} = 0.99708 + 0.002727C + 0.00000602C^2$; (B) $d\frac{25^\circ}{4} = 0.99708 + 0.002611C + 0.0000101C^2$; where C is protein concentration in per cent by weight. The second and third term coefficients were evaluated by the method of least squares. The densities of solvent and protein were regarded as additive.*

Discussion

According to Robertson the refractive index constant a is independent of solvent salts, dilute acids or alkali; in other words, the refractive index of the protein and solvent are additive. Although we found strict additivity in dilute neutral salt solvents when determined in the proximity of the isoelectric point, small but consistent differences observed in alkaline solution lead us to conclude that the refractive indices of NaOH and antitoxin solution are not additive. The magnitude of the deviations from strict additivity depends on concentration both of protein and NaOH or more probably on the amount of NaOH combined. These deviations were large enough to noticeably affect the constant in the third significant figure and thus be of consequence in measurement of antitoxin solutions which contain 15 to 20 per cent protein. Similar observations concerning the effect of solvents have been made by Thomas and Mayer[12] for gelatin in dilute HCl and by Kondo and Hayashi[13] for casein in dilute NaOH.

Since the constant determined by us is approximately 20 per cent lower than Reiss' value it might be argued that the discrepancy is due to a difference between "normal" and antitoxic pseudo-globulin. Measurements on the globulin and albumin of "normal" horse sera show that *this is not true*. The following values were obtained:—euglobulin,** 0.001845; pseudo-globulin, 0.001843; albumin, 0.001840. Many other measurements were made on the protein fractions separated by various procedures, but in no instance could we detect any significant difference in refractive index between the globulins and albumin of "normal" unheated and heated antitoxic plasmas or serums. Concentrated pneumococcus antibody***also gave essentially the same value, viz., 0.001845.

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*In separate experiments it was found that the densities of protein and alkali are not strictly additive.

**Precipitated by 33⅓ per cent of saturation of $(NH_4)_2SO_4$.

***Precipitated from serum by diluting 1:12 with distilled water and adjusting the reaction to pH 6.8 according to the methods of Felton (14) (15).

The recent work of von Deseö[16] shows that the constant for purified globulin lies between 0.00174 and 0.00189. Our results agree more nearly with his. An interesting observation brought out by von Deseö's measurements and one which has important bearing on the value of the constant if determined in high concentration of $(NH_4)_2SO_4$ solution following fractional precipitation of a serum, was that the precipitate binds water[17] and thus concentrates the salt in the filtrate.* Because of this concentration of salt the apparent constant obtained will vary depending on the amount precipitated, and, in the case of globulin, appear to be larger than when determined in the same solvent salt of concentration insufficient to cause precipitation.

Summary

1. The increment in refractive index corresponding to a change of protein concentration of 1.000 gram in 100 cc. of solution has been accurately determined for four antitoxic globulins and "normal" serum globulins of the horse. The value of this increment (constant *a*) for protein concentrations between 3 and 17 grams per 100 cc. is 0.00184.

2. NaOH produced a small but definite lowering in the refractive index of the protein.

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*We have confirmed this observation.

THE SOLUBILITY OF BARIUM SULPHATE IN SULPHURIC ACID

BY NELSON R. TRENNER[1] AND H. AUSTIN TAYLOR

The high solubility of barium sulphate in absolute sulphuric acid and its marked decrease on addition of water presents a real anomaly when considered from the point of view of modern theories of strong electrolytes whilst realising that the dielectric constant of absolute sulphuric acid is of the same order as that of water. A search of the literature for reliable data on the system revealed a complete lack of concordance among the results of many investigators, not only in the solubility of the salt in the pure acid but more particularly in the solid phases in equilibrium with aqueous sulphuric acid solutions.

Kendall and Davidson[2] attempted to isolate the solid phase by freezing it from solution and drying between porous plates. They find an analysis corresponding to $BaSO_4.3H_2SO_4$. Barter[3] attempted to analyse the wet solids and the saturated solutions deducing the composition of the solid by graphical extrapolation, obtaining two compounds $3BaSO_4.8SO_3.7H_2O$, stable from 85.5 to 93 percent sulphuric acid and $4BaO.5SO_3.6H_2O$ stable in high concentrations. The latter stable at high concentrations of acid having an excess of water, whilst the former stable at lower concentrations, an excess of SO_3 is almost beyond credence. The difficulty no doubt lies in the handling of so viscous and hygroscopic a system where experience shows that exposure to the atmosphere even for a very short period renders an analysis worthless.

An attempt was made therefore to determine the true solubility relationships between $BaSO_4$, H_2SO_4 and H_2O with as reasonable a degree of accuracy as such a system would permit.

Experimental

Preparation of Materials.

1. Sulphuric Acid. Absolute sulphuric acid was prepared by two different methods which gave consistent results. In the first method a pure nitrogen and arsenic free acid was redistilled at a pressure of 1-2 mms. of mercury yielding about a 95 percent acid. To bring this up to absolute acid, purified fuming sulphuric acid was distilled into it until its concentration was correct as determined by specific gravity methods. Careful volumetric analyses were then made. In the second method a slightly fuming sulphuric acid prepared from redistilled acid and sulphur trioxide, was brought down to absolute by addition of water. The change in resistance of the acid at constant temperature, was meanwhile measured. According to Lichty[4] the

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[1] Abstract from a thesis presented in partial fulfillment of the requirements for the degree of Master of Science at New York University.

[2] J. Am. Chem. Soc., 43, 979 (1921).

[3] Trans. Roy. Soc. Canada, 7, 208 (1913).

[4] J. Phys. Chem., 11, 238 (1907); J. Am. Chem. Soc., 30, 1834 (1908).

resistance of absolute acid is a maximum. Subsequent analyses showed the acid to be 100 percent within 0.05 percent.

2. *Barium Sulphate.* Barium chloride recrystallised three times was used to precipitate barium sulphate from pure sulphuric acid. The possible impurities could then be only barium chloride, hydrogen chloride or sulphuric acid. Of these the two latter seem to be strongly adsorbed since after washing continuously with hot water until the wash water showed no acidity to methyl orange, upon roasting, copious fumes of hydrogen chloride and sulphur trioxide were evolved. To remove the first two the sulphate was redissolved in absolute sulphuric acid and maintained at about 200°C. for not less than half an hour. The supernatant liquid was drawn off and cooled, no crystallisation taking place. When cold, this solution was poured into a very large volume of cold distilled water yielding barium sulphate with no other possible impurity than sulphuric acid. Since the decomposition of $BaSO_4$ only becomes apparent above 900°C., the sulphuric acid, admixed or adsorbed, was removed by roasting at about 600°C. for from 18 to 24 hours. Different preparations yielded samples of different particle size. Some fine-grained samples were obtained by pulverising in an agate mortar and required nine days to settle completely from solution as compared with less than twenty-four hours for the usual samples.

Method of Measurement. The solubility determinations were made on various mixtures of barium sulphate, sulphuric acid and water which had been allowed to come to equilibrium in sealed tubes by rotation for seven days in a thermostat at 25 ± 0.05°C. The ternary complexes were prepared by placing a known weight of the salt in the tube which had two openings: one, a fine capillary as an air vent, the other carrying a constricted tube with a ground joint and stopper, also fitting a Lunge pipette from which the acid-water mixtures could be forced with dry air. The acid solutions were made up by drawing into the pipette a calculated amount of absolute acid and water, each being weighed. The weight of the acid-water mixtures run into the solubility tube having been determined, the capillary and constricted side tubes were sealed off, the whole procedure occurring in an atmosphere of dry air. Three weighed samples of acid were taken at each filling for check determinations by titration of the acid concentration.

Equilibrium being established in the tubes the solutions were allowed to settle for twenty-four hours, the supernatant liquid being then drawn into a Lunge pipette for analysis. The titration of the acid in the saturated solution was made using carbonate-free sodium hydroxide with methyl orange as indicator. The titration had to be performed in the presence of solid barium sulphate thrown down by dilution with water. The end-points were matched with a color standard adjusted for opacity by addition of about the average amount of suspended barium sulphate. Weighed samples were drawn from the pipette for titration and also for the gravimetric analyses of the sulphate. Check determinations were made for every measurement.

Experimental Results and Discussion

The results obtained by the above method are given in detail in Table I.

TABLE I

Initial Complex			Saturated Solution			Conc.	Solid Phase
H_2SO_4	H_2O	$BaSO_4$	H_2SO_4	H_2O	$BaSO_4$	H_2SO_4	H_2SO_4
			A				
82.92	—	17.08	84.11	—	15.89	100.00	—
—	—	—	—	—	15.77	99.81	—
74.87	0.14	24.99	84.05	0.21	15.74	99.75	67.33
83.85	0.16	15.99	84.22	0.17	15.61	99.80	—
—	—	—	—	—	15.68	99.70	—
—	—	—	—	—	15.22	99.61	—
—	—	—	—	—	14.79	99.45	—
62.92	0.21	36.87	84.84	0.46	14.70	99.47	—
—	—	—	—	—	13.84	99.07	—
69.78	0.52	29.71	85.27	0.90	13.83	99.95	—
78.94	0.57	20.49	85.49	0.89	13.62	98.97	68.86
62.87	0.61	36.52	85.80	0.95	13.25	98.91	—
84.00	1.12	14.88	85.57	1.26	13.17	98.65	—
73.94	0.60	25.47	86.00	1.21	12.79	98.61	62.09
77.99	1.16	20.84	86.06	1.65	12.29	98.12	58.86
84.10	1.60	14.29	86.54	1.78	11.68	97.99	62.38
80.37	1.60	18.03	87.22	1.83	10.95	97.80	32.70
81.23	2.63	16.15	88.45	3.02	8.53	96.70	32.55
85.06	3.47	11.47	88.86	3.63	7.05	96.08	—
60.55	1.89	37.56	89.13	3.58	7.29	96.14	28.60
73.26	2.84	23.90	89.28	3.86	6.86	95.85	28.68
—	—	—	89.68	4.53	5.79	95.19	—
75.28	3.97	20.75	90.40	4.97	4.63	94.79	15.24
			B				
78.07	3.67	18.26	90.57	5.33	4.10	94.44	50.43
—	—	—	90.58	6.91	2.51	92.91	—
77.69	5.42	16.89	90.75	7.27	1.97	92.58	39.37
69.46	9.07	21.47	87.45	12.06	0.486	87.96	14.87
69.40	9.12	21.49	85.90	13.87	0.230	86.10	37.70
68.10	9.10	22.80	85.50	14.29	0.210	85.63	37.60
73.25	11.26	15.49	84.93	14.87	0.203	85.08	36.80
—	—	—	—	—	0.058	83.62	—
68.98	13.80	17.23	83.21	16.74	0.050	83.25	2.21

The values in the above table are expressed in percent by weight. The concentration of sulphuric acid is expressed as the ratio of sulphuric acid to sulphuric acid plus water in the saturated solution. Fig. 1 shows the solubility of barium sulphate plotted against the concentration of sulphuric acid in the saturated solution.

In the last column in Table I the percentage of sulphuric acid in the solid phase was obtained by a mathematical extrapolation of the tie-line joining the composition of the initial complex with that of the saturated solution which it yields. To this end it was assumed that the solid phase extracts no water from the solution phase, sulphuric acid alone being possibly removed. The assumption appears to be justifiable in the concentration range studied, where the acid actually possesses a sulphur trioxide vapor pressure. The theoretical percentages of sulphuric acid in possible compounds of the formulae $BaSO_4.H_2SO_4$, $BaSO_4.4H_2SO_4$, and $BaSO_4.5H_2SO_4$ are 29.67, 62.72 and 67.79 respectively. An examination of the data would at first sight suggest that all these compounds are present in the solid phase at certain acid concentration but a reference to Fig. 1 shows no apparent transitions as evidenced by a change in direction of the solubility curve. We are led therefore to consider in more detail the accuracy of the data and more particularly the reliability of the extrapolation.

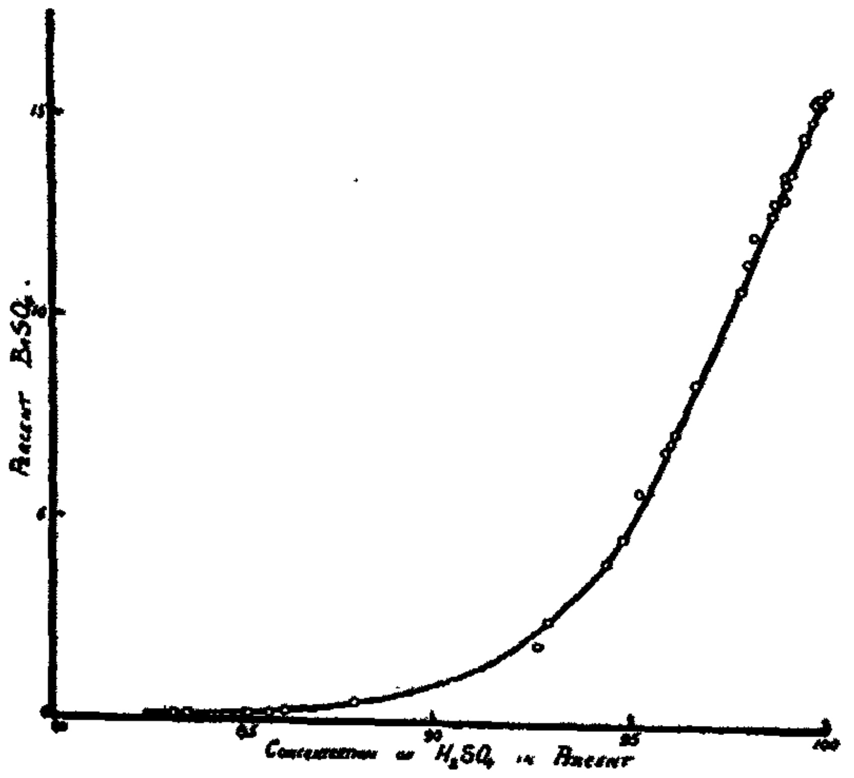

FIG. 1

It is obvious that since the quantity of water both in the initial complex and in the saturated solution is in all cases much less than the quantity of sulphuric acid that the greatest error involved in the extrapolation will be due to an error in these two values for the water. At the higher concentrations of acid this error naturally will be less than at lower acid concentrations and we might expect a greater reliability of the extrapolation under the former conditions. In fact, a complete analysis of the probable error, which need not be detailed here, shows that for acid around 88 percent of the saturated solution the probable error in the extrapolated percentage of acid in the solid phase is of the order of four percent, whereas at 85 percent acid with now only 0.3 to 0.4 percent water the error may be as high as forty percent, despite the previously mentioned care in all volumetric and gravimetric determinations.

In part A of Table I there are four values of the percentage of sulphuric acid in the solid phase in the neighborhood of 30, namely 32.70, 32.55, 28.60 and 28.68 or a mean of 30.6 which might be compared with the 29.67 percent calculated on the basis of $BaSO_4.H_2SO_4$ suggesting a compound of this type as the solid phase. Values below this for example the 15.24 percent quoted might correspond to a mixture of $BaSO_4$ and $BaSO_4.H_2SO_4$. The values above 30 percent as the analysis shows are unreliable and no conclusion can justifiably be drawn concerning compounds with excess sulphuric acid despite the apparent agreement between the extrapolated values and those above mentioned for $BaSO_4.4H_2SO_4$ and $BaSO_4.5H_2SO_4$. If therefore the compound $BaSO_4.H_2SO_4$ should exist a transition from the unsolvated salt should appear in the solubility curve. From the data this would be expected at around 88 percent sulphuric acid which reference to Fig. 1 will show to be on the flat portion of the curve where a break would be very difficult to realise. Its apparent absence cannot be judged then as indicating the non-existence of the compound.

In order therefore to settle definitely the existence of this compound and to determine the exact invariant area in the three-component diagram it was decided to follow the change in a property of the system as the concentration of one of the components was gradually increased. According to the phase rule such a system undergoing a transition of solid phases is invariant and any property of the system will remain constant throughout this process. The limits of constancy of the property then becomes the limits of the invariant area. The property chosen for study was the conductance and the component to be successively increased was water, the determinations of Lichty having shown that as small an amount of water as 0.01 percent gave a measurable change in the conductance of sulphuric acid in the region around absolute acid.

The cell used in these measurements consisted of a pyrex tube carrying electrodes of heavy platinum foil about one square centimeter area and about 40 cms. apart, dimensions chosen to give a conveniently measurable resistance range. Experience showed that for a sharp null point a heavily platinised surface was necessary. The opening in the cell, for the purpose of introducing the various components, carried a wide tube giving free space to allow mixing during tumbling in the thermostat. This tube was closed with a ground-glass stopper and as further protection against water leakage during immersion the whole was covered by a cap ground to fit the outside of the tube.

The resistance of the cell was measured using the usual Wheatstone bridge arrangement, a specially constructed vacuum tube Hartley type oscillator producing a smooth 1000 cycle note being used as source of current. The oscillator was located some ten feet away from the cell and carefully shielded and grounded to minimise extraneous capacity effects. The reliability of the measurements may be illustrated by a comparison of the specific conductivity of absolute sulphuric acid found namely 1045×10^{-6} ohms^{-1} with that found by Lichty, 1040×10^{-6} as the mean of several samples.

The procedure consisted in introducing absolute sulphuric acid, using all the precautions against water absorption mentioned previously, into the weighed conductivity cell and reweighing to show the amount. The conductivity at 25°C was then measured to check the acid concentration. After drying and reweighing, the requisite amount of barium sulphate was added and the whole reweighed. The cap was then secured in place with a rubber jacket and the whole cell rotated in the thermostat until successive conductivity readings gave the same result indicating the establishment of equilibrium, a process requiring not more than 18 hours. The tube was then again dried and reweighed as a check against water absorption, between 0.25 and 0.5 gram conductivity water introduced and the whole reweighed and returned to the thermostat, a process repeated at about 24 hours intervals throughout the entire range of water concentration desired.

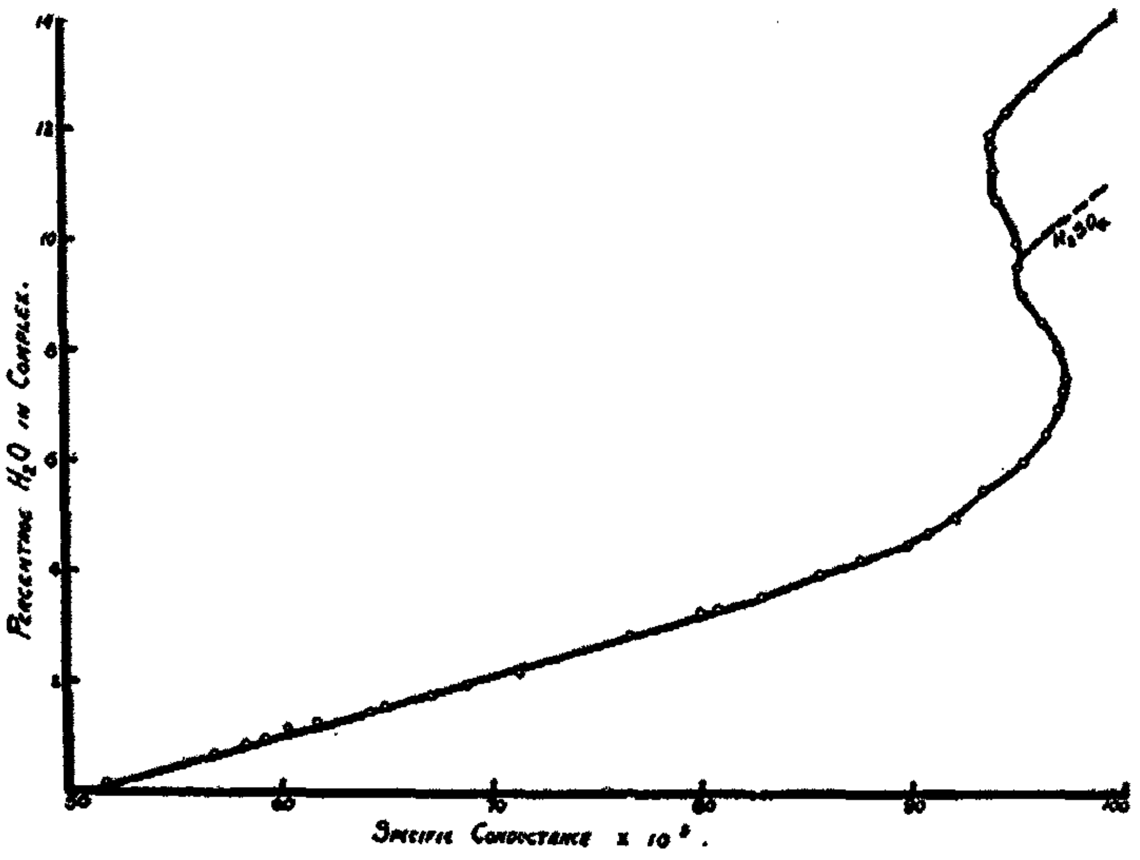

Fig. 2

The values of the specific conductance at various water concentrations are given in Table II, and shown graphically in Fig. 2.

A second cell was also used with a slightly different initial complex which unfortunately developed a leak before the run was completed. The data obtained however checked the above figures when due allowance was made for the slight difference in amount of the solid phase present. The general shape of the curve is in agreement with that for sulphuric acid alone, which has been accounted for by the existence of hydrates. The *S* in the curve occurs at 84.80 percent acid which would correspond to $H_2SO_4.H_2O$. The constancy of the starred values in the Table would indicate an invariance of the system at this point only, since over the remainder of the region covered

TABLE II

Initial Complex		81.54% H_2SO_4, 18.46% $BaSO_4$	
Percent Water	Sp. Cond.	Percent Water	Sp. Cond.
0.000	4889 × 10^{-5}	5.468	9363 × 10^{-5}
0.136	5135	5.992	9535
0.722	5681	6.498	9649
0.897	5831	6.980	9710
0.961	5925	7.280	9725
1.103	6030	7.512	9731
1.241	6161	8.044	9700
1.454	6420	8.528	9645
1.542	6486	9.026	9540
1.777	6719	9.496	9520
1.952	6880	9.988	9520
2.190	7142	10.740	9430
2.806	7663	11.256	9420*
3.328	8081	11.760	9418*
3.584	8300	11.941	9418*
3.982	8585	12.390	9495
4.202	8763	12.834	9608
4.532	8990	13.502	9816
4.698	9092	14.111	10000
4.988	9215		

there is a gradual change in conductance with change in water concentration. This constancy would indicate the presence in the system of another compound besides $BaSO_4$, probably an acid solvated barium sulphate.

The composition of the initial complex used and the quantities of water added, being known, the composition of the invariant complex may be calculated. An analysis of the invariant solution then would yield sufficient data to locate the invariant area and thus by extrapolation, the composition of the solid phases in equilibrium. Fig. 3 shows the graphical extrapolation.

It will be observed that the lower limit of the invariant area does not correspond with pure $BaSO_4$ as the solid phase but gives a solid containing about ten percent acid. This is believed to be due to adsorption which though suspected in earlier work, could not be definitely shown. It is for that reason that the data in Table I were divided into two sections A and B, in the former a coarse grained barium sulphate being used, in the latter an extremely fine grained sample and it was this which was employed in the conductance measurements. The last results in section B of Table I where a somewhat lower acid concentration was used gives an extrapolated solid phase containing 2.21 percent acid indicating clearly a gradual and continuous change in composition of the solid phase below about 85 percent acid, characteristic of adsorption.

Such adsorption would cause a displacement of the invariant area as the diagram shows. The extrapolation of the upper limit of the area gave a solid phase of 36.80 percent acid. This is to be compared with the other values in section B of Table I namely 39.37, 37.70 and 37.60, values which would appear to correspond most closely with $BaSO_4.3/2\ H_2SO_4$. However in section A are found values of 32.70, 32.55, 28.60 and 28.68 percent acid in the solid phase which correspond rather well with 29.60 percent acid in $BaSO_4.H_2SO_4$. Realising that the grain size in the latter is much larger than in the former, and hence that the adsorption is probably much less, it must be concluded that the only compound present is probably $BaSO_4.H_2SO_4$, apparent variations from this being due to adsorption. An analysis of the invariant solution showed it to contain a concentration of sulphuric acid of 85.08 percent. A transition occurs in the system therefore at this point.

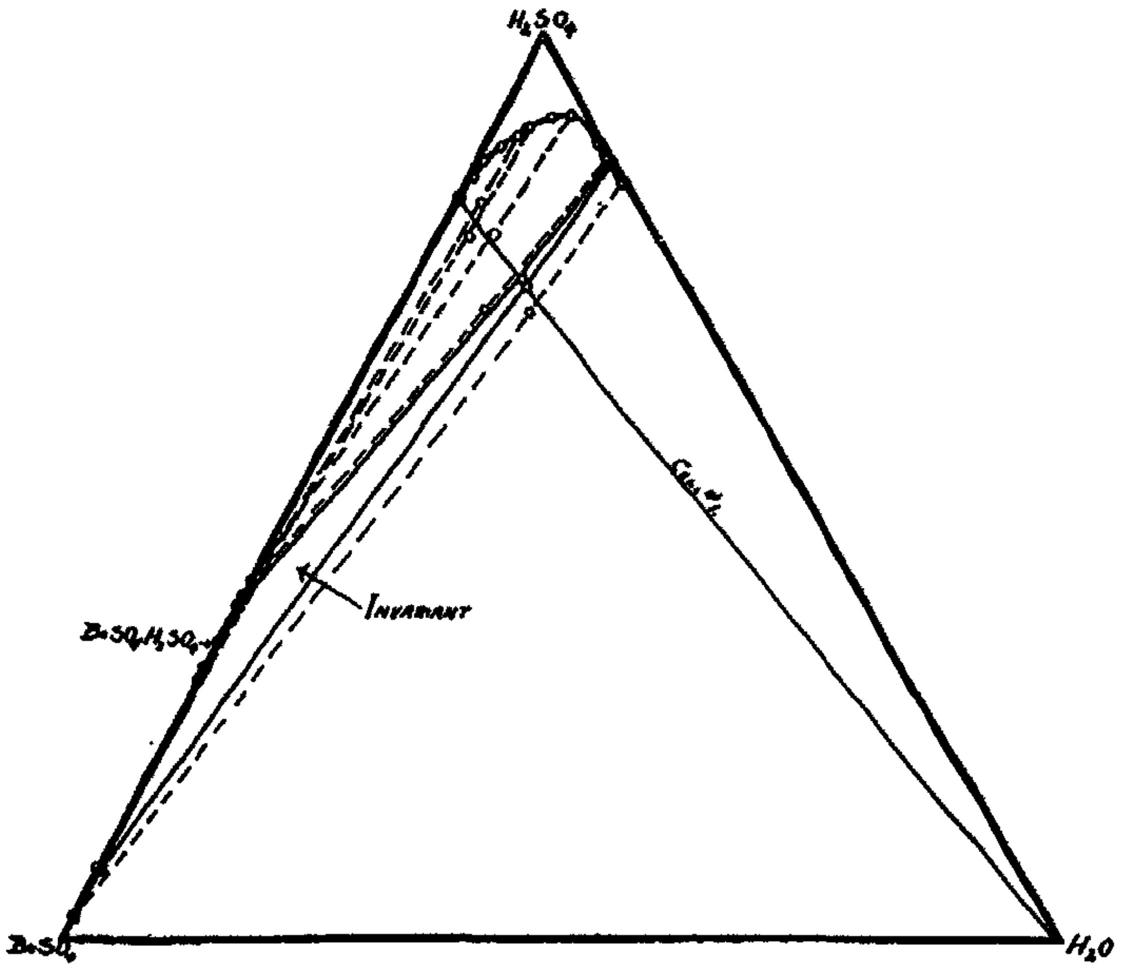

FIG. 3

In conclusion it may be stated that the system shows a marked metastability. In the early stages of the conductance measurements it was observed that in about two hours the equilibrium had reached almost 95 percent completion but that at least eighteen hours were necessary before constant conductance was attained. Furthermore in the data in section B Table I one sample gave an extrapolated value for the acid content of the solid phase of only 14.87 percent. This sample had been agitated in the thermostat for only eighteen hours. The other values shown were obtained from samples agitated not less than five days and show values in the neighborhood of 38 percent. A distinct change also was to be observed in the state of the solid phase after long agitation, the typical opaque white granules of $BaSO_4$ yielding finally well-formed translucent needles. The acid salt therefore would appear to be slow in forming. This metastability together with the complications of adsorption are probably responsible for the lack of a greater concordance than was found in view of the extreme precautions taken throughout the whole work.

Summary

1. The solubility relations for the system $BaSO_4$-H_2SO_4-H_2O at 25°C have been determined over the concentration range 83-100 percent acid. The solubility in absolute acid is 15.89 percent by weight.

2. The system possesses but two solid phases at 25°C $BaSO_4$ and probably $BaSO_4.H_2SO_4$ with a transition at an acid concentration in the neighborhood of 85 percent.

3. The existence of compound formation as distinct from solid solution and adsorption has been demonstrated by the application of a conductance method which might prove convenient and precise in other similar work.

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PHENACETIN HYDROCHLORIDE*

BY IRENE H. SANBORN

Although phenacetin itself is a well known antipyretic, its hydrochloride is rather an elusive substance. Apparently there was no reason to question its accessibility; thus when its existence became a matter of interest in connection with the work on Phase Rule Studies on the Proteins by Wilder D. Bancroft and C. E. Barnett,[1] the author proceeded with the usual methods for such an organic preparation.

Phenacetin is para ethoxy phenyl acetanilide, $C_2H_5OC_6H_4NHC_2H_3O$. From the behavior of the nitrogen atom in analogous compounds, Bancroft and Barnett stated in part that phenyl groups decrease the reactivity of the nitrogen; ethoxy groups increase it; adjacent carbonyl groups decrease it; and alkyl groups increase it. Acetanilide is a weak base but does combine with hydrogen chloride, while diacetanilide, with the diketo linkage, does not. No statement was found in the literature regarding the hydrochloride of benzanilide, $C_6H_5NHCO.C_6H_5$; so Bancroft and Barnett tested it to find that it did form a definite hydrochloride. They concluded that "phenacetin should be at least as positive as acetanilide and therefore must add on hydrogen chloride, although Meyer and Jacobson do not mention the fact."

Accordingly, three attempts were made to prepare the hydrochloride. Phenacetin is a stable, white, crystalline substance of m.p. 135°C, insoluble in cold water, slightly soluble in hot water, and soluble in hot concentrated hydrochloric acid.

A sample was dissolved in hot absolute alcohol, and dry hydrogen chloride gas was passed into the solution. Although the solution was placed in an ice bath, no precipitate appeared. Either the phenacetin hydrochloride was not formed, or else it was dissolved in absolute alcohol.

Another sample was dissolved in an alcohol-ether solution, containing just enough alcohol to keep the phenacetin in solution. The solution was kept cold, and dry hydrogen chloride passed into it as previously. A curdy white precipitate formed, apparently the hydrochloride. In attempting to filter and wash this precipitate, decomposition was evidenced immediately, and phenacetin was recovered on the filter paper.

One other method was tried. Phenacetin was melted, and to the melt concentrated hydrochloric acid was added. The mass was heated, and allowed to stand in a desiccator over stick sodium hydroxide. A white powdery layer formed on the surface of the melt. Probably this was the hydrochloride, for upon exposure to the air it began to fume, and left a residue of phenacetin.

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*This work is a part of the programme now being carried out at Cornell University under a grant to Professor Bancroft from the Heckscher Foundation for the Advancement of Research established by August Heckscher at Cornell University.

[1] J. Phys. Chem., 34, 753 (1930).

From these procedures it appeared rather evident that there is such a compound as phenacetin hydrochloride, and that it is exceedingly unstable. For this reason, other methods, whereby the hydrochloride would not be exposed to the air, were used.

The apparatus used in Phase Rule Studies[1] was employed. Phenacetin was pulverized and dried over concentrated sulphuric acid in a desiccator for several days. A sample was placed in the reaction flask, the system was evacuated, and dry hydrogen chloride was introduced. Our data show conclusively that phenacetin combines stoichiometrically with dry hydrogen chloride mol per mol. See data Fig. 1 and Table I.

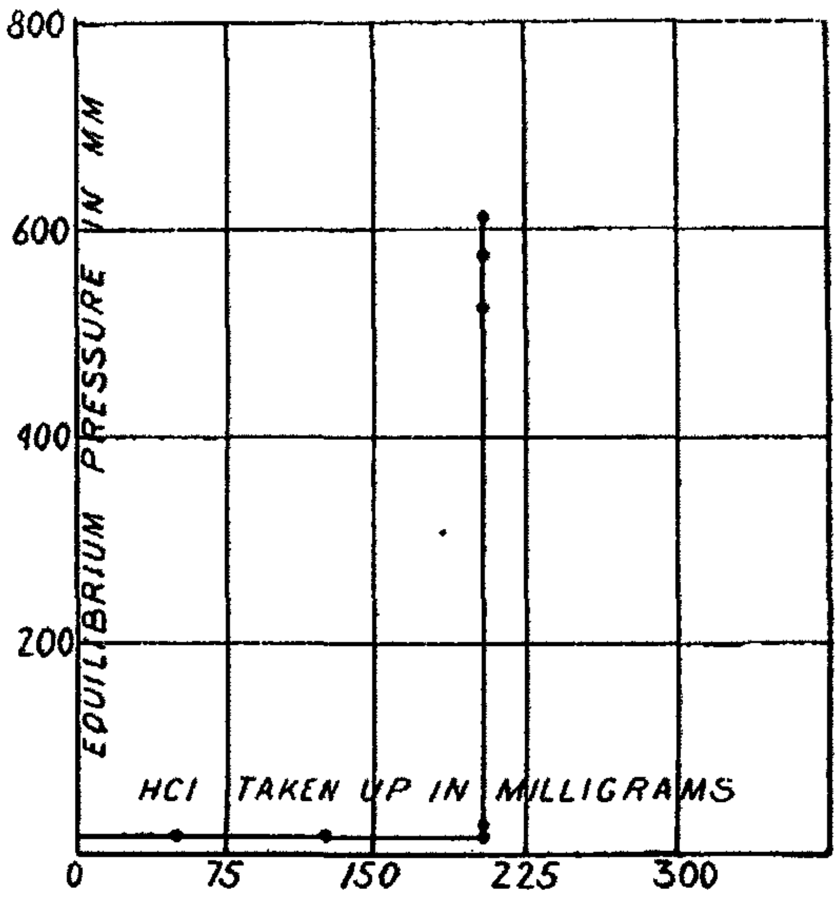

Fig. I
Phenacetin Hydrochloride

Table I
Phenacetin and Hydrogen Chloride

S.T.P. Sample 2.5 grams Dry

Vol HCl added c.c.	Vol HCl removed c.c.	Net volume c.c.	Equilibrium pressure mm.	Vol HCl remaining c.c.	Vol HCl taken up c.c.	Wt. HCl taken up mgm.	Wt. HCl taken per g. mgm.
575.2		575.2	614	262	313.2	512	205
	17.1	558.1	576	246	312.1	508	204
	21.8	536.3	526	224	312.3	508.1	204
	172.4	363.9	25	48	315.9	515	206
	19.2	344.7	17	32.6	312.1	508	204
	1120.4	224.3	17	32.6	191.7	312.3	125
	115.0	109.3	17	32.6	76.7	125	50

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[1] J. Phys. Chem., 34, 449 (1930).

Theoretically one gram of phenacetin should take up 204 mgms. of hydrogen chloride for the formation of phenacetin hydrochloride. We find that it actually does take up that amount. The hydrochloride is a practically colorless fine powder with a dissociation pressure of 17 mm. It melts sharply at 154°C at 741 mm. pressure, and decomposes immediately and completely in water into hydrogen chloride, and the flakey lustrous white phenacetin which gives a m.p. of 135°C. Some of the phenacetin hydrochloride was preserved in a closed tube and its properties tested about five months after its preparation. It was found to be quite stable. Another part was left in an open tube. During this same period this portion slowly decomposed. The surface layer gave a m.p. of 135°C indicating its decomposition into phenacetin and hydrogen chloride.

In order to obtain a separate proof of the existence of phenacetin hydrochloride, a method somewhat similar to the one used by T. W. Richards[1] to establish the identity of $BaCl_2.2H_2O$ was tried. For this experiment a special glass tube was used, so constructed that the sample and solvent could be introduced through A, and into which was sealed a long tube B with a flanged mouth which reached nearly to the bottom of the tube. See Fig. 2. This arrangement made it possible to bring the entire sample in contact with the dry hydrogen chloride. The tube is of such a size that it rests unhampered upon the pan of the ordinary analytical balance.

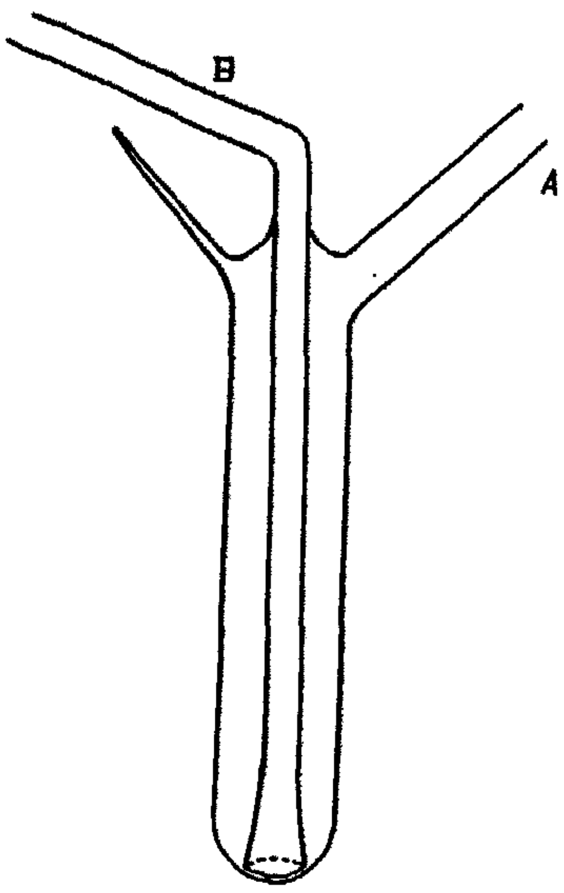

FIG. 2
Glass Drying Tube

TABLE II
Phenacetin Hydrochloride (Curve A)

Sample of phenacetin 0.480 grams.

Wt. HCl taken up mgms.	Time Hours	Days	Equivalence in HCl mol per mol.
351	24	1	3.6
80	48	2	.8
56	168	7	.7
56	192	8	.7
56	240	10	.7

Note: 1 equivalent for this sample is 97 mgms.

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[1] Z. anorg. Chem., 17, 165 (1898).

The sample of finely divided dry phenacetin was placed in the special tube. 25 cc. of freshly distilled dry chloroform was added to the sample. The tube was gently heated to dissolve the phenacetin; after which dry hydrogen chloride was passed through B into the solution. During this process the tube was retained in a bath of warm water until the chloroform had been completely evaporated. The tube was then placed in a desiccator containing concentrated sulphuric acid and stick sodium hydroxide, being removed periodically for the purpose of weighing. The data for two samples are found in Fig. 3 and Tables II and III.

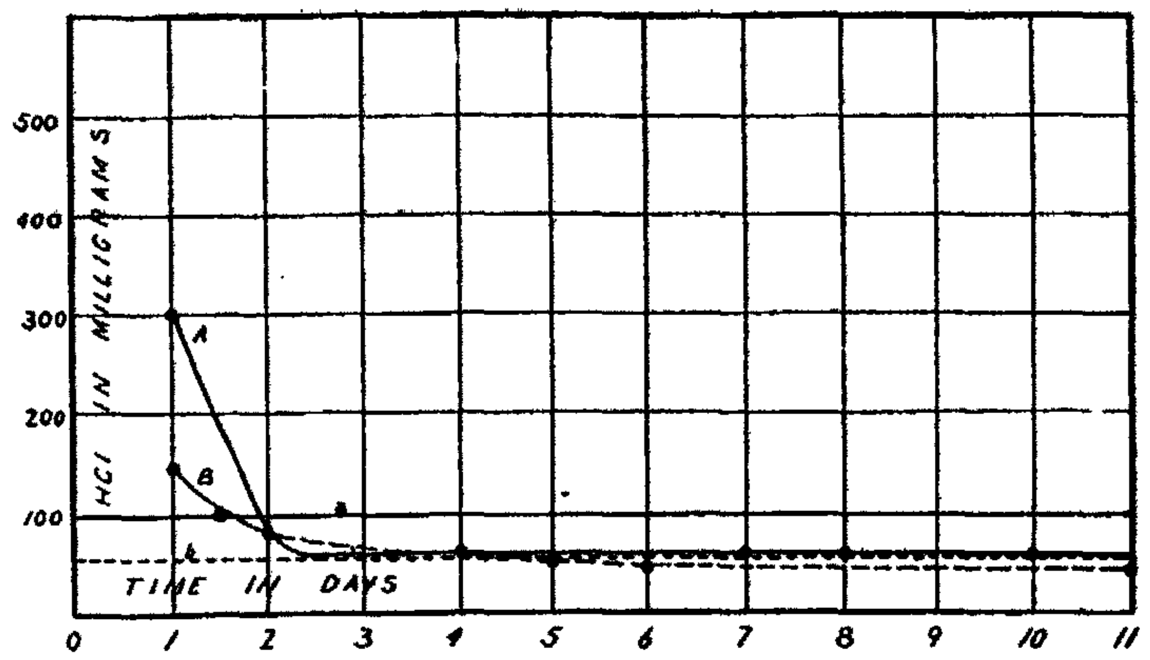

Fig. 3

Dissappearance of HCl from Phenacetin Hydrochloride

Table III

Phenacetin Hydrochloride (Curve B)

Sample of phenacetin 0.265 grams.

Wt. HCl taken up mgms	Time Hours	Days	Equivalence in HCl mol per mol.
147	24	1	2.7
99	36	1.5	1.8
57	96	4	1.05
50	120	5	.92
44	144	6	.80
44	264	11	.80

Note: 1 equivalent for this sample is 54 mgms.

The intersection of the line "a" with the curve A represents the point at which the sample contains one equivalent of hydrogen chloride. There should be a break in curve A at this point. As shown, there is none; but there are no points between one and two days and between two days and four days. Consequently the curve as drawn may not be right. To check this a second experiment was done. The intersection of the line "b" with the curve B represents the point at which the sample contains one equivalent of hydrogen chloride. In this case the break comes pretty fairly well at the right place, the loss being about 17 mg. per day from 1.5 to 4 days and 7 mg. per day from 4 to 5 days. Neither curve A nor curve B becomes theoretically horizontal at any point; but the rate of diffusion happens to be very low. The method is not especially accurate in its present form; but it does show conclusively the existence of a definite chemical compound with a composition pretty close to the monohydrochloride.

Another experiment was devised of a similar nature. A weighed sample of the finely divided dry phenacetin was spread upon a weighed watch-glass, thoroughly moistened with concentrated hydrochloric acid, and placed in a vacuum desiccator containing concentrated sulphuric acid. The desiccator was evacuated, and then filled with dry hydrogen chloride. After allowing the sample to remain in the desiccator long enough to insure the complete removal of any trace of water, the sample was removed and weighed. The amount of hydrogen chloride with which it had combined was calculated. The experiment was done twice, using first a small sample of phenacetin, 0.361 g.; and second a larger sample, 2.954 g. The same watch glass was used in each case. After standing in desiccator for a week, at which time all the water had been removed, sample 1 had combined with 0.062 gms. of hydrogen chloride, an amount equivalent mol per mol to 0.84 mol of hydrogen chloride. Sample 2 remained in desiccator for over a month. Upon removal and subsequent weighing it had combined with 0.555 gms. of hydrogen chloride, an amount equivalent to 0.924 mol of hydrogen chloride. See Table IV.

Table IV

	1	2
Phenacetin samples	0.361 grams.	2.954 grams.
Amount HCl combined after one week.	0.062	
Amount HCl combined after one month.		.555
Equivalence to HCl mol per mol.	0.84	0.924

The results are conclusive as to the existence of a definite chemical compound; but the results are not such as to lead one to prefer this method to the one in which the pressure is studied. The last two methods have the advantage that there are no stop-cocks to leak and spoil the experiment near the end of a run.

Conclusions

1. Phenacetin combines stoichiometrically with hydrogen chloride mol per mol to form phenacetin hydrochloride.

2. Phenacetin hydrochloride exists as a stable compound in the presence of hydrogen chloride gas. It is a very pale yellow powder with a m.p. of 154°C.

3. At room conditions, phenacetin hydrochloride is unstable because of the dissociation pressure of about 17 mm. It decomposes gradually to give hydrogen chloride and phenacetin.

4. In aqueous solution its decomposition is immediate into phenacetin and hydrogen chloride.

5. While it is possible to show the existence of a compound between phenacetin and hydrogen chloride by passing hydrogen chloride into a solution of phenacetin and ether, the compound cannot be obtained both pure and dry in the ordinary way.

6. The phenacetin hydrochloride has been analyzed indirectly in three different ways, just to show how the problem can be solved.

7. The existence of phenacetin hydrochloride is in accordance with the criteria laid down by Bancroft and Barnett.

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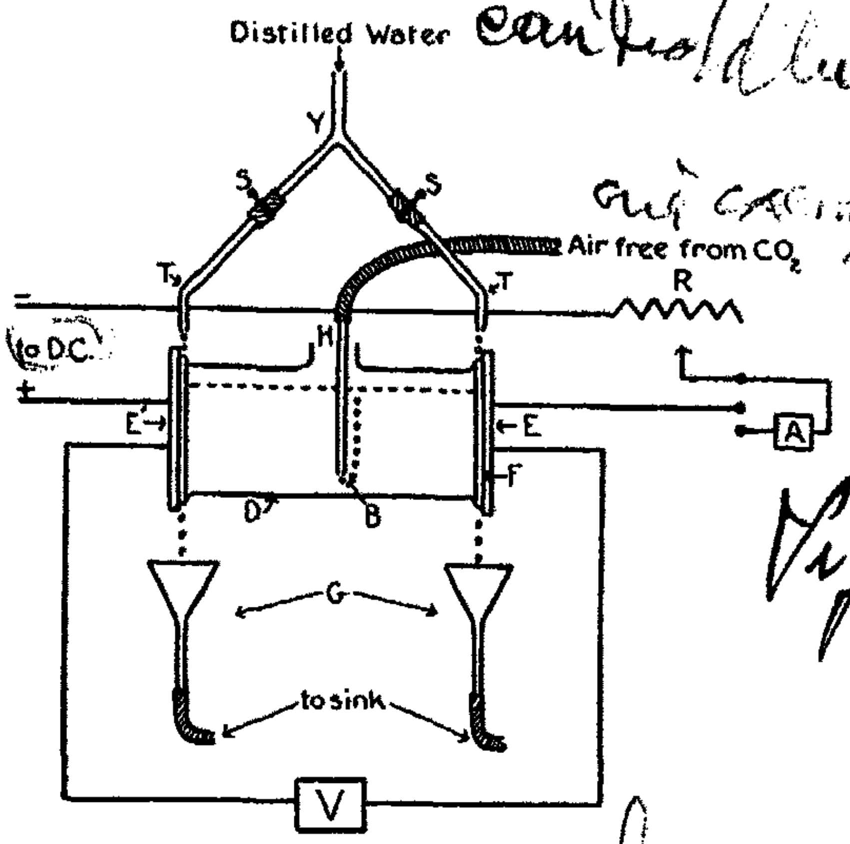
19-106

A NEW CELL FOR ELECTRODIALYSIS*

BY HARRY N. HOLMES AND ALBERT L. ELDER**

The usual apparatus for electrodialysis consists of three compartments, one for the solution to be dialyzed and one for each of the electrodes. The electrode compartments are commonly as large as the center compartment. The apparatus described in this paper, constructed in line with a suggestion by Kruyt that the electrode compartments be as small as possible, has reduced them to a mere moving film of water.



Vig. 1006

Fig. 1

APPARATUS. The apparatus and electrical connections are shown in Fig. 1. D is the dialyzing cell, a cylinder of pyrex 9 cm. in diameter and 13 cm. in length with a hole H at the top. Over the flanged ends of the glass cylinder are stretched pieces of rubber tubing, such as may be used on Gooch crucibles. After these are given a light coating of vaseline, wet parchment papers are stretched over the ends and are tightly secured by means of long strings of rubber bands looped together somewhat like links in a chain. Against each of the membranes are placed six sheets of filter paper (Whatman No. 44, ash content 0.000120 gr.). These are cut to a point at the bottom. The tops are folded over for about 2 cm. and V-shaped holes are cut in the folded edges.

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* Contribution from Severance Chemical Laboratory of Oberlin College.

** The authors are indebted to Mr. Elton S. Cook for some of the quantitative measurements.

The electrodes E are cleaned carbon plates 13 cm. × 13 cm. × 6 mm. These are pressed lightly against the filter papers by means of ring clamps containing rubber stoppers, the clamps being supported by a rod fastened to a ring-stand (not shown in the figure). Distilled water from a 40-liter carboy is led through the tube Y, its rate of flow being regulated by the screw-clamps S, and is allowed to drop through the tubes T, which are drawn to capillary tips, into the V-holes of the filter paper F. This device guarantees the maintenance of a moving film of water the thickness of the filter papers. The electrodes must not be pressed too tightly or the water will tend to go around the ends of the dialyzer. The folding of the filter papers, giving greater thickness at the top, also helps to prevent this. The dialysate drops into the funnels G and is carried to the sink. Through the hole H is led a tube B carrying a stream of CO_2-free air which acts as a stirrer, although some other mechanical stirrer may be used at H. A heating coil C, enclosed in a pyrex tube, may be suspended through H if desired. The electrical connections are self-explanatory, A being an ammeter, V a voltmeter, P a single-pole double-throw switch, R and R′ variable resistances. For greater constancy of temperature, the whole apparatus, exclusive of the electrical instruments, is placed in a glass case.

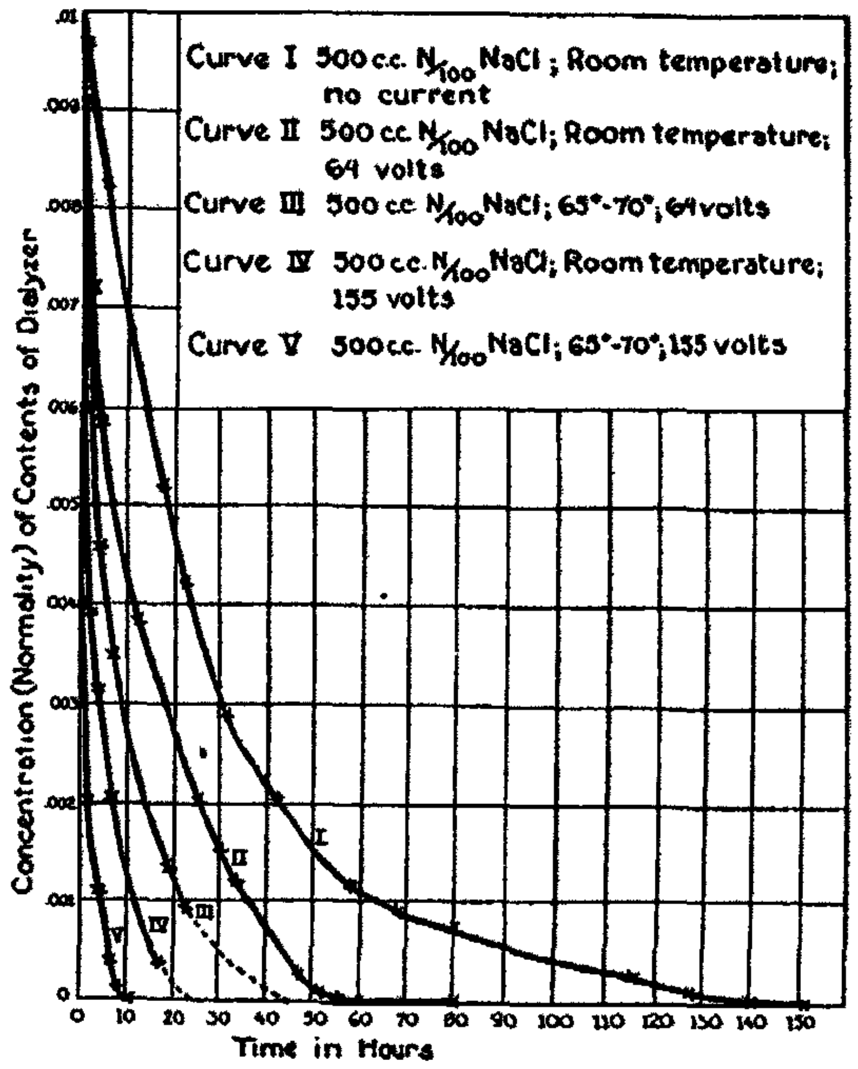

FIG. 2

Experimental

The results obtained with the apparatus are plotted in Figs. 2 and 3. In all determinations the source of current was storage batteries or storage batteries in series with B-batteries. The rate of flow of water over each electrode averaged 15 cc. per minute. Fig. 2, in which concentration of the solution in the dialyzer is plotted against time in hours, shows the removal of sodium and chlorine ions from N/100 NaCl. In each case 500 cc. of the solution was used. Concentration of the solution in the dialyzer was determined by titrating 5 cc. samples with N/100 silver nitrate, using saturated potassium dichromate as the indicator. The legend accompanying the figure explains the curves. It will be seen that, using 155 volts and maintaining the temperature at 55°-60°, no qualitative test for chloride ions could be obtained after 10 hours, while at room temperature and with no current flowing over 150 hours were required for such effective removal of chloride ions.

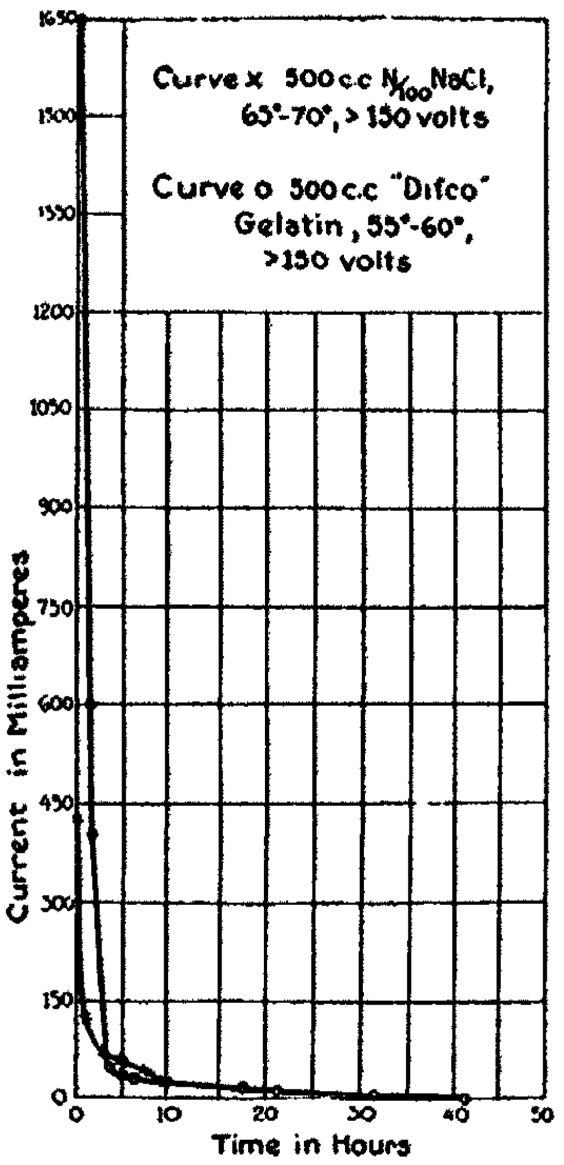

Fig. 3

Fig. 3, giving the results of dialyzing 500 cc. of 6% "Difco" gelatin at 155 volts and 55°-60°. A curve for N/100 NaCl, is included for comparison. In these curves, current in milliamperes is plotted against time in hours. The rapid drop of current during the first four hours of gelatin dialysis will be noted. The gelatin at this point still gave a test for sulfates. To remove this last trace of sulfate ion it was necessary to continue the dialysis in excess of 40 hours.

Experiments were carried out using N/100 HCl. At high voltages and high temparatures it was found that the membranes were attacked with consequent leakage.

The removal of adsorbed chloride ions from silica gel which had been treated with HCl to dissolve out the iron was also tried. This could be accomplished satisfactorily but not in so short a time as by continuous washing with warm water.

Some experiments were tried using platinum electrodes consisting of pieces of fairly coarse gauze, 2.5 cm × 3 cm., backed with glass plates.

The dialysis was not as efficient as with carbon electrodes. However, for the results to be comparable, platinum electrodes of larger dimensions should be used.

Heating the cell with a flame is not quite so good as heating with a resistance coil. Dialysis at 65°-70° is, of course, more effective because ionic movements are more rapid than at room temperatures.

Summary

1. A new, inexpensive and efficient cell for electrodialysis has been described.

2. It has been proved that, using N/100 NaCl, no test for chloride ions can be obtained after 10 hours of dialysis at 155 volts and 65°-70°.

3. The application of the cell to the removal of salts from gelatin has been shown.

PHOTOMICROGRAPHIC STUDIES OF SUCROSE CRYSTALS*

BY SYBIL WOODRUFF AND HELEN VAN GILDER

Introduction

Photomicrographs of fondants make it possible to compare the magnitude of crystals forming in syrups of varying composition. The sucrose crystals present in a fondant type of candy of good quality are of such small size that they cannot be felt by the tongue as distinct particles. A high-grade product is said to be "creamy" or smooth in texture when it is entirely free from the grit of detectable crystals. It is rather surprising that the tongue and roof of the mouth give a tactile response to particles so slightly greater in size as are those of perceptibly coarse fondant compared with the crystals of a finely-textured one. The measurements of crystals accompanying these photomicrographic records show that in two fondants which would be rated as fine and slightly gritty respectively, we are able to sense a difference in crystal dimension of but 6 or 10 microns.

The factors which determine the size of crystals developing in a syrup are then of considerable importance if a difference in size of about 10 microns between two samples represents the difference between a candy of poor and one of good texture. Besides these crystals of maximum size in a fondant there are many others barely visible at a magnification of 360 times and furthermore there are assuredly present still others of colloidal dimensions. The dispersion of these minute crystals of sucrose in a continuous phase of concentrated sugar syrup produces a product which is plastic and one whose consistency depends very largely upon the ratio existing between the two phases, and, therefore, in turn upon the composition of the syrup-phase. Since the presence of other sugars increases the solubility of the sucrose, the relative amount of syrup will be greater and the consistency of the fondant softer and more pliable the greater the amount present of sugar other than sucrose.

The size to which sucrose crystals will grow as the mass of candy "grains out" depends upon physical conditions as well as upon the composition of the syrup. Cooling the syrup to a highly supersaturated state before agitation is permitted, favors crystallization at countless points simultaneously and thereby reduces the opportunity for crystal nuclei to build up to great size. A syrup may contain such a proportion of invert sugar to sucrose that crystals of small size would be expected to form but, due to faulty manipulation, opportunity may be given for the particles to grow to a size exceeding that found in an acceptable product. Examples of manipulative errors which might so hinder the desired graining of sucrose are failure to continue agitating the syrup until crystallization is complete, the accidental seeding of the hot syrup, or the cooling of the syrup in a vessel with rough surfaces. Thus

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syrups containing even 15 percent reducing sugars can form coarse-grained candies under circumstances such as these; on the other hand, fondants of surprisingly fine texture and plasticity can be obtained when no reducing sugar at all is present, providing the physical conditions for crystallization are cleverly controlled.

The only other published photomicrographs of fondants are those by Halliday and Noble,[1] which illustrate only the differences caused by manipulative procedure and not those of different syrup composition. The photomicrographs of our study illustrate the effect upon the size of sucrose crystals of varying amounts of invert sugar produced by boiling sucrose in turn with hydrochloric, tartaric and citric acids, and with acid potassium tartrate; also the action of added glucose or fructose with reference to maximal crystal size. Measurements of the largest and smallest crystals in the micrographic fields have been made in freshly made fondant and in that which had been stored for some time. Variations in the physical conditions attending crystallization were avoided as perfectly as possible.

Experimental Methods

Preparation of fondant. One volume of sugar to one-half volume of water, or 200 grams of commercial sucrose to 118 grams of distilled water, were boiled together in a beaker. A sugar solution of this concentration had a boiling temperature of approximately 103°C and the rate of boiling was always so adjusted that the syrup reached the desired concentration and a boiling temperature of 115° in 20 minutes. Analysis showed about 30 grams of the original 118 grams of water to remain in the final fondant. Such an excess of water at the start was necessary since if much less than this was used there appeared to be an incomplete dissolving of the sucrose, thus making it less possible to control its recrystallization. The syrup boiled to 115° was therefore supersaturated as soon as it began to cool and if permitted to cool to 40° before any nuclei of granulation appeared, agitation produced crystals of small size. The hot syrup was poured immediately into a shallow glass bowl, allowed to cool undisturbed to 40°, then was beaten with a wooden spoon until it had changed to a plastic mass. It was kneaded smooth and stored in air-tight jars.

The procedure was the same when acid was boiled with the sugar and also when other sugars were substituted for a part of the sucrose. It had been found by a preliminary test that 0.2 grams of potassium acid tartrate to 200 grams of sugar which is an amount frequently called for in the home-made article, gave a product of satisfactory grain and contained 7.5 percent of invert sugar on the basis of the moist fondant. Therefore, in substituting glucose or fructose for part of the sucrose, such an amount of each was used as would give this quantity of reducing sugar in the fondant.

Photomicrographic Technique. The chief difficulty in mounting the specimen for microscopic observation was in spreading the fondant on the

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[1] Halliday and Noble: "The Hows and Whys of Cooking," p. 139 (1928).

slide in a sufficiently thin smear. A very small amount of the fondant from the center of the jar was transferred to a drop of Canada balsam on the slide, a cover slip was pressed down upon it and moved to and fro between the thumb and forefinger until a thin layer of the specimen was obtained. A photomicrograph was made using a Leitz "Makam" camera and a magnification of 360 times. It was found that ordinary light with a ground-glass shield over the source, gave a better negative than did polarized light; also that a six-minute exposure under these circumstances was satisfactory. When samples were to be photographed after they had been stored, fresh smears from the center of the jar were prepared.

Determination of hydrogen ion concentration. This measurement was made with a Leeds and Northrup quinhydrone electrode at 25°C upon solutions containing 10 grams of fondant in 50 cc. The freshly boiled, distilled water used in making the dilutions had a pH of 5.83.

Determination of reducing sugar. The method used was the iodine titration modification of the well-known Munson and Walker one. The accuracy of the method for the case in hand was determined by checking the reducing sugar content of known combinations of sucrose with glucose or fructose or mixtures of the two wherein the reducing sugar varied from 7 to 30 percent of the total sugar present. The maximum deviation from the expected result was but 5 percent of the reducing sugar known to have been added. In a fondant containing, as it well may, 10 percent of its moist weight in the form of invert sugar or glucose, an error of 5 percent in the analysis of invert sugar would raise or lower the expected percent of invert sugar in the fondant to but 10.5 or 9.5. The characteristics of fondants do not change rapidly with small variations in the percent of invert sugar present; hence, it is believed that the accuracy obtainable with this method is sufficient for the purpose.

Discussion of Results

Invert Sugar produced by Different Acids. The inverting effect of acids or acid salts other than potassium acid tartrate (cream of tartar) has not been studied in connection with candy making. A paper by Carrick[2] gave 6.28 as the percent of invert sugar formed by boiling for 15 minutes a sugar solution consisting of 210 grams of sucrose and 0.3 grams of cream of tartar; this quantity of invert sugar was said to have given a desirable plasticity to the fondant. Daniels and Cook[3] have reported the invert sugar in a series of fondants containing from none to 1.2 grams of cream of tartar used with 110 grams of sugar and alkaline tap water. Their report did not describe the textures of the resulting candies, however.

Before the days of commercial glucose fondant was made by boiling the syrup with a small amount of "cream of tartar" and many rules for making the candy still suggest the use of acid. A study of this means of controlling crystal size was undertaken in a series of three fondants containing in turn

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[2] Carrick: J. Phys. Chem., 23, 589 (1919).

[3] Daniels and Cook: J. Home Econ., 11, 65 (1919).

0.2 gram (an amount frequently recommended), 0.4 and 0.8 grams of potassium acid tartrate to 200 grams of sugar which served as a means of showing what effect the correspondingly increasing amount of invert sugar would have upon the size attained by the sucrose crystals. It had been expected that when citric, tartaric and hydrochloric acids were used in such amounts as to give the same hydrogen ion concentration as that shown by the "cream of tartar" samples, the same amounts of invert sugar would likewise be produced during boiling and therefore similar effects upon the crystallization of the sucrose. The actual results as they are recorded in Table I do not show this to be the case, however.

TABLE I

Amounts of invert sugar and pH of fondants containing various acids
(Percent based upon moist fondant)

Sample Number	Acid		pH of Fondant Average	Average Invert Sugar Percent
	Kind	Amount Milligrams		
1 b	None		5.33	0.42
4 a	K-H-tartrate	200	4.10	6.49
b	" " "	400	3.82	11.10
c	" " "	800	3.73	15.80
5 a	Citric acid	10	4.72	7.00
b	" "	20	4.20	16.30‡
c	" "	40	3.85	43.43*
6 a	Tartaric acid	10	4.37	13.05
b	" "	20	4.02	23.55‡
7 a	Hydrochloric acid	46 cc.	4.86	6.35
b	" "	69 cc.	4.37	above 50.00*

Note: The period of boiling to a temperature of 115°C. was 20 minutes in each fondant. All syrups were cooled to 40°C. before crystallization was induced. The amounts of acid are for 200 grams of sucrose. The HCl was 0.001 N.

* Syrup did not crystallize.

‡ Syrup crystallized after 50 to 60 minutes of beating whereas others grained in from 7 to 15 minutes.

There was so little relation between the manner and completeness with which sucrose crystallized from the syrup and the pH of the solution that it seemed as feasible a way as any to record results given by 10, 20, and 40 mg. of citric acid, by 10 and 20 mg. of tartaric, and by 46 and 69 cc. of 0.001 N hydrochloric acid. The citric acid and hydrochloric acid fondants contained about 7 percent of invert sugar each, for instance, when their pH was but 4.72 and 4.86 respectively. This was approximately the same amount of invert sugar as that contained in the product carrying 200 mg. K-H-tartrate and pH 4.10. The pH produced by 800 mg. of K-H-tartrate was 3.73 but the invert sugar formed was nevertheless 15.80 percent; contrast this with the 43.43 percent invert sugar induced by a pH of 3.85 with 40 mg. of citric, 23.55 percent by 20 mg. of tartaric (pH 4.02) and more than 50 percent by such an amount of HCl as gave pH 4.37. Neither was there as marked a taste of sourness in citric and hydrochloric acid fondants as there was in that containing 800 mg. of K-H-tartrate even where the three were similar in degree of softness.

As for consistency and ease of molding, the syrups containing 43.43 percent or more invert sugar would not deposit any sucrose crystals even with long beating and long standing. One containing 23.55 percent crystallized to a semi-fluid mass after 60 minutes of continuous beating; one with 16.30 percent crystallized to a very soft product after 50 minutes of beating and one of 15.80 percent invert sugar was plastic but too soft to be molded easily. The 6 to 7 percent of invert sugar always gave a firm, moldable fondant free from detectable "grits" of large crystals. It would appear therefore that from 6 to 15 percent invert sugar for a fondant containing 13 percent moisture, represents the limits of possibilities for convenient molding, the lower figure giving a firm, moldable product and the upper one a softer and still more finely grained candy.

Effect of glucose and fructose upon texture. It has been shown that the invert sugar content of fondant must be kept within the limits of approximately 6 to 15 percent for superior texture and ease of molding. It is not a simple matter so to regulate conditions that this percent can be attained. It is far less complicated as a procedure to add the desired amount of glucose or some other simple sugar at the beginning than to depend upon the formation of invert sugar, the amount of which will be uncertain unless the length of the boiling period and the kind and amount of acid are all under control.

Glucose has commonly been used in the making of a fondant type of candy but usually in the form of corn syrup which contains along with glucose, dextrins and maltose. It seemed desirable to know whether pure glucose used in the same percentage as the invert sugar of the preceding part of the study would control crystal size in the same manner. Fructose was also used in a similar manner. Each sugar, in amounts to correspond to approximately 7.46 percent of reducing sugar in the moist fondant, was boiled with sucrose and water and crystallization induced in the usual fashion. Each gave a product smooth to the tongue and firmly moldable, not showing any of the stickiness upon which the invert sugar products bordered when they were equally fine in texture. The fructose, the purest obtainable, imparted a caramel-like flavor and a visible color to the candy, however.

The moisture content of fondant. The results thus far refer, where softness and plasticity are concerned, to a fondant whose syrup was boiled to a temperature of 115°C. A product, concentrated to this degree and made with no inverting agent or glucose, was found by analysis to contain 13.07 percent (average) moisture. The percents of moisture found for boiling temperatures of 113° and 117° were 15.73 and 11.59 respectively. This shows that a difference of one degree downward from 115° alters the moisture in the fondant by 3 grams per 200 grams of sugar; this much extra water made the consistency markedly softer. The moisture content of fondants containing invert sugar or glucose and boiled to 115° was not significantly different from the figures obtained for plain water fondant. These determinations of moisture were made by drying 2 gram samples, spread out upon the bottom of a shallow, wide, weighing bottle, uncovered during drying in vacuo at 56° to 60°C. for approximately 8 hours. The cover of the weighing bottle was in place during all weighing operations to prevent the hygroscopic material from changing weight.

Photomicrographs and sucrose crystal size. Photomicrographs were made of all the fondants previously described. The average diagonal measurement of six of the largest and of six of the smallest crystals in each microscopic field has been recorded in Table II. The millimeters of length of the crystals at a magnification of 360 times were reduced to microns of actual size; the method of measurement, though crude, gave comparative results of significance.

A micrograph has been included (Plate 1), showing the contrastingly large size of crystals attained in an admittedly coarse product wherein the syrup was beaten at 70°C. and opportunity given for the crystals to grow to large proportions. Plates II to XII inclusive are photomicrographs of the fondants of the composition given in Table II.

TABLE II

Approximate size of sucrose crystals shown in photomicrographs of fondants containing invert sugar and other reducing sugars

		Acid or Reducing Sugar Added			Crystal Diagonal Lengths	
Sample Number	Plate Number	Kind	Weight† Milligrams	Reducing Sugar Percent	Smallest Microns	Largest Microns
1 a*	I	None		—	7.0	45.5
b	II	None		0.42	5.0	25.5
2	III	Glucose		7.46	3.8	19.6
3	IV	Fructose		7.46	3.8	15.2
4 a	V	K-H-tartrate	200	6.49	5.2	15.5
b	VI	K-H-tartrate	400	11.10	3.6	12.5
c	VII	K-H-tartrate	800	15.80	2.8	13.2
5 a	VIII	Citric Acid	10	7.00	3.3	18.8
b	IX	Cirtic Acid	20	16.30	2.7	10.0
6 a	X	Tartaric Acid	10	13.05	3.0	11.3
b	XI	Tartaric Acid	20	23.55	2.7	11.1
7 a	XII	Hydrochloric Acid	46 cc.‡	6.35	3.1	12.2

† Milligrams per 200 grams of sucrose.

* Beaten while syrup was at a temperature of 70°C. All others in the table were beaten at a temperature of 40°C.

‡ Refers to 0.001 N solution.

All the fondants of the series, with the exception of the one made with water alone, were smooth and fine in texture, those containing large percentages of invert sugar being so very fine that they were like soft putty in feel and so plastic that they could be stretched. The ones containing less invert sugar were free from grittiness but were of more solid consistency, and

PLATE I.
Photomicrograph of fondant no. 1a. Crystals of this size make a coarse texture. Syrup was beaten hot.

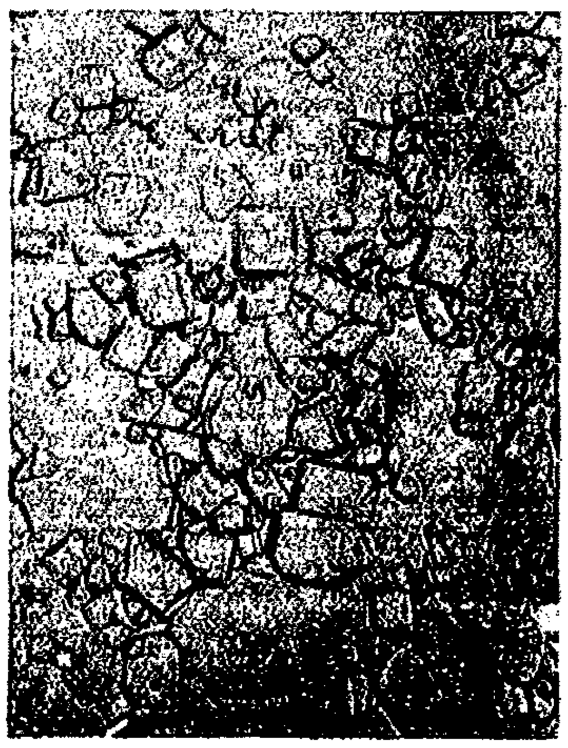


PLATE II.
Photomicrograph of fondant no. 1b. Texture was good except for occasional "grits." Syrup was beaten cold.

PLATE III.
Photomicrograph of fondant no. 2, containing glucose.

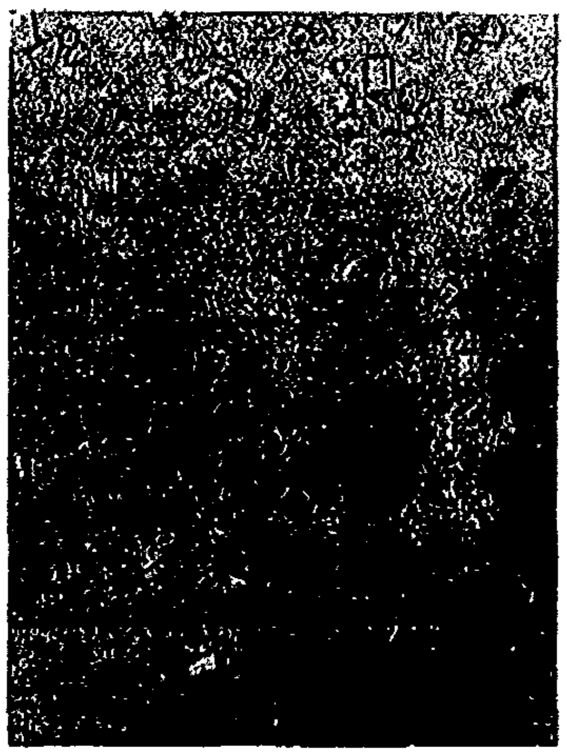


PLATE IV.
Photomicrograph of fondant no. 3, containing fructose.

Magnification × 360

PLATE V.
Photomicrograph of fondant no. 4a, containing 200 mg. of potassium acid tartrate.

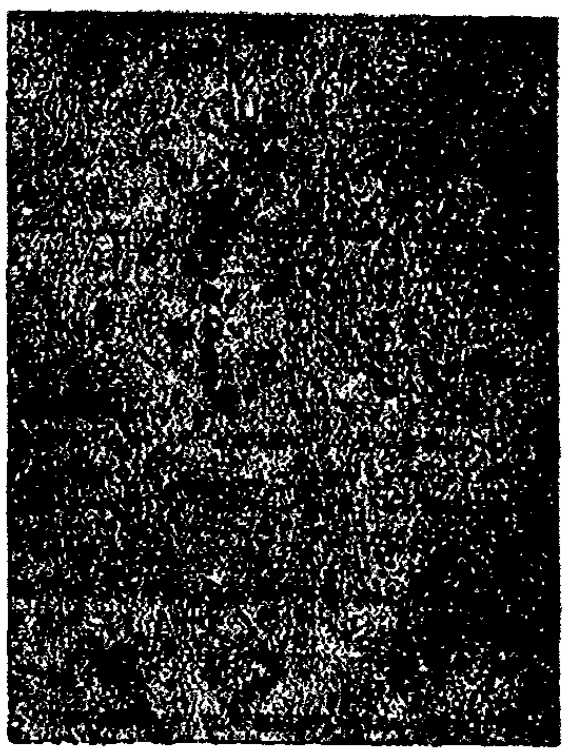


PLATE VI.
Photomicrograph of fondant no. 4b, containing 400 mg. of potassium acid tartrate.

PLATE VII.
Photomicrograph of fondant no. 4c, containing 800 mg. of potassium acid tartrate.

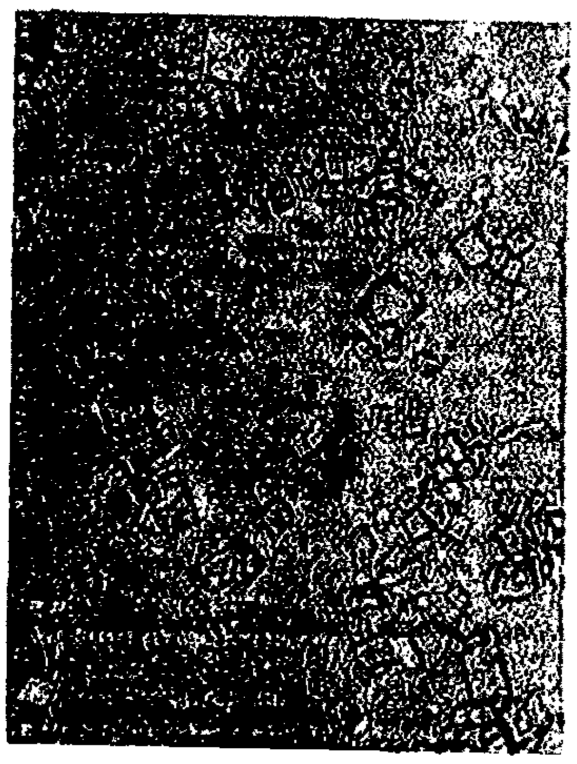


PLATE VIII.
Photomocrograph of fondant no. 5a, containing 10 mg. of citric acid.

Magnification × 360

PLATE IX.
Photomicrograph of fondant no. 5b, containing 20 mg. of citric acid.

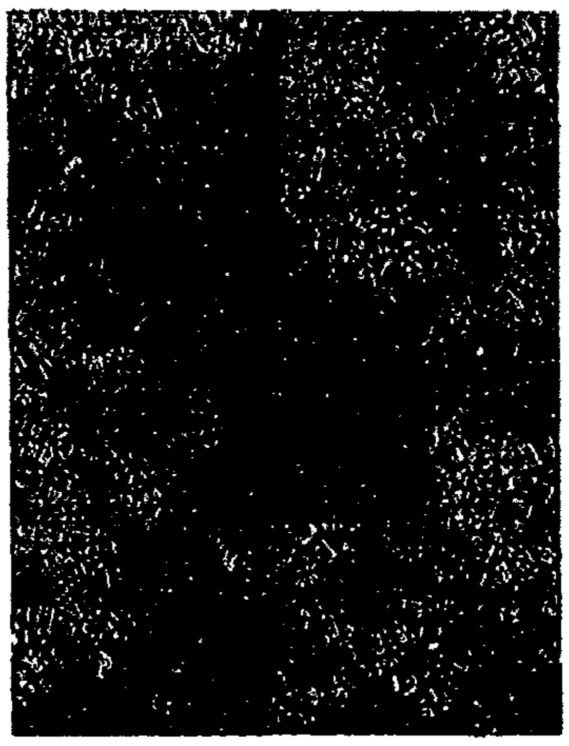


PLATE X.
Photomicrograph of fondant no. 6a, containing 10 mg. of tartaric acid.

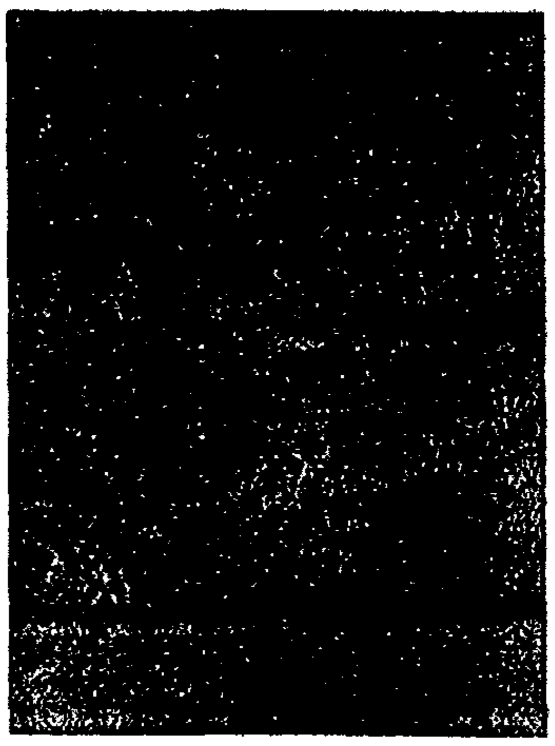


PLATE XI.
Photomicrograph of fondant no. 6b, containing 20 mg. of tartaric acid.

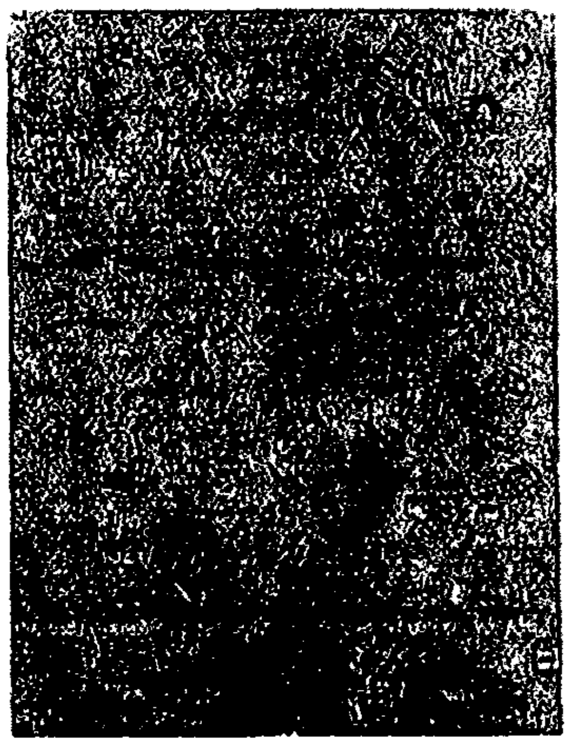


PLATE XII
Photomicrograph of fondant no. 7a, containing 46 cc. of 0.001 N HCl.

Magnification × 360

broke apart when pulled. The fondant made with water alone looked and felt much like those which contained small amounts of invert sugar; but when it was chewed there were noticed occasional grits of either large single crystals or possibly of crystal clusters. An indiscriminating person would have pronounced this a good product and it was, to be sure, superior to many of the home-made candies of questionable quality which are consumed with apparent relish.

It will be noted that there were some crystals but 7μ across even in the coarse fondant, number 1a, though the maximum size attained by them was many times that. There was little variation in the size of the smallest crystals in the different fondants, indicating probably that 3μ approached the limits of visibility. It is conceivable that there were present many crystals which could not be seen even at a magnification of 360 times. The largest crystals in the coarse candy (1a) measured 45.5μ across; the largest ones in number 1b, which also contained no invert sugar but whose syrup was beaten after it had cooled to 40°, were 25.5μ in size. Two other samples, numbers 2 and 5a showed crystals not much smaller than those of 1b, but even though their largest crystals measured 19.6 and 18.8μ there were no grits discernible when the fondants were chewed. This must mean that in a product like this the ability to note particle size by the sense of touch in the mouth, ceases with dimensions which lie some place between 19.5 and 25.5μ. The crystals of all other samples were at least 10μ smaller than the 25.5μ size of the gritty ones. Reducing sugar in quantities of 6.49 to 7.46 percent permitted crystals to grow to a somewhat larger size, 15.2 to 19.6μ, than did 11.10 percent or more invert sugar, in the presence of which the maximum crystals measured but 10.0 to 13.2μ. The odd member of the series was the hydrochloric acid fondant containing but 6.35 percent invert sugar and yet crystals only 12.2μ in length. The crystals of this sample also appeared misshapen and indistinct in outline in comparison with others.

The results show that when the same amounts of each invert sugar, glucose and fructose are present they are equally effective as a means of regulating crystal size. For ease and certainty, the use of known quantities of glucose or fructose is preferred to partial inversion during boiling. The inverting agent may just as well be either potassium acid tartrate or citric or tartaric acids though the two acids act so powerfully in comparison with the acid salt that it is easy to understand the preference for the latter in recipes calling for roughly measured ingredients. It was still less easily possible to limit and control inversion by hydrochloric acid than it was by citric and tartaric.

The size of the largest crystals in the photomicrographic field was roughly inversely proportional to the amount of invert sugar though never less than 10 to 12 microns regardless of the percent of invert sugar present. There was no means of estimating accurately the relative numbers of small and large crystals in products of different composition. There appears to be no point, therefore, in seeking to have larger amounts of invert sugar than about 16 percent for the purpose of keeping the crystals small; more invert sugar

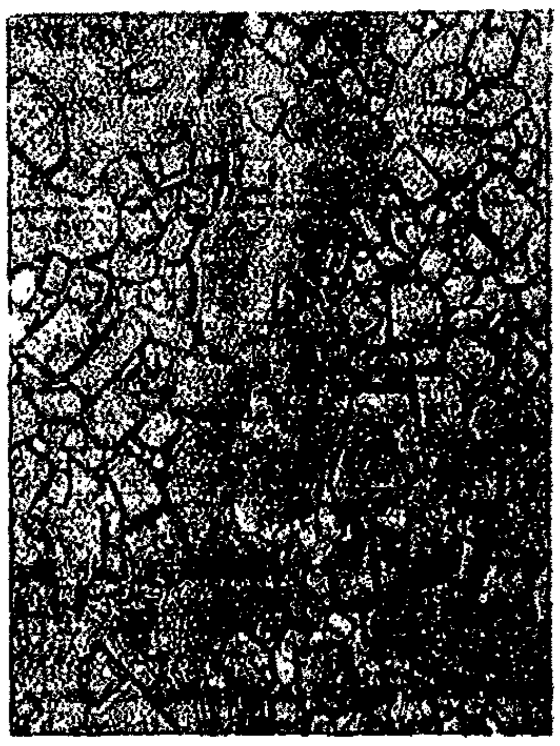
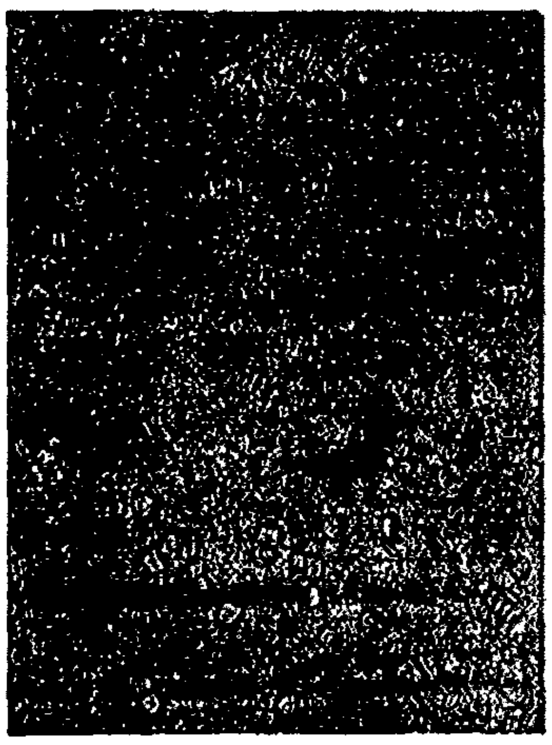


PLATE XIII.
Photomicrograph of fondant no. 1b after stored 7 days. Compare with Plates II and XIV.

PLATE XIV.
Photomicrograph of fondant no. 1b, after stored 21 days. Compare with Plates II and XIII.



PLATES XV.
Photomicrograph of fondant no. 4b (400 mg. K-H-tartrate), after stored 7 days. Compare with Plates VI and XVI. .

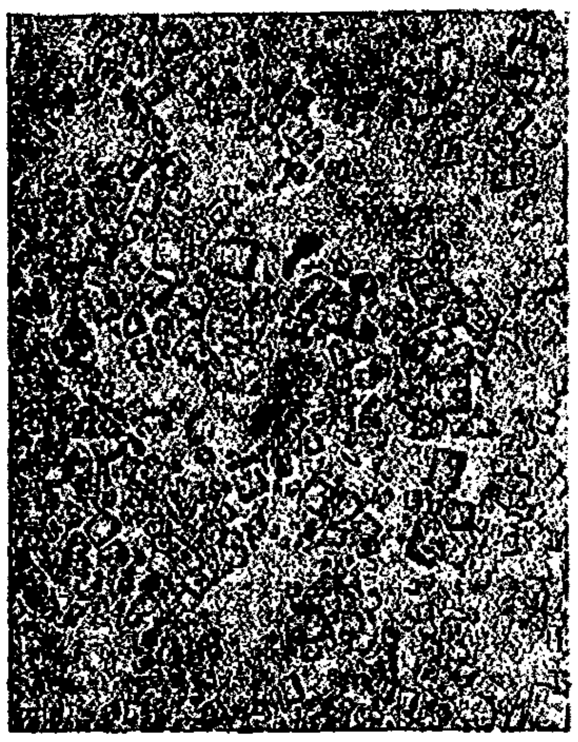


PLATE XVI.
Photomicrograph of fondant no. 4b (400 mg. K-H-tartrate), after stored 21 days. Compare with Plates VI and XV.

Magnification X 360

may act favorably in another direction by increasing the ratio of syrup phase to solid phase and thus enhancing the flowing quality of the cream candy.

Crystal size after storage. It is a common observation that fondants do not tend to become coarser in texture as they age but rather that they ripen to an even smoother and more uniform grain. It is, therefore, of interest to see what alterations occur in microscopic appearance and crystal dimension. The fondants photographed in plates II to XII were afterward all stored for a period of at least 7 days after which new micrographs were made. The sample made with no inverting agent and those made with potassium acid tartrate were photographed again after 21 days of storing. Characteristically the same results were obtained in all cases; therefore, only the photomicrographs of the samples containing none and 400 milligrams of K-H-tartrate and stored for 7 and 21 days are shown in plates XIII to XVI inclusive. The numerical measurements of the smallest and the largest crystals at 1, 7 and 21 days are to be found in Table III.

Table III

Approximate size of sucrose crystals in fondants with and without K-H-tartrate after 7 and 21 days of storage (Size in microns)

Sample Number	K-H-tartrate Milligrams	Average Diagonal Length of Sucrose Crystals					
		Smallest			Largest		
		1st Day	7th Day	21st Day	1st Day	7th Day	21st Day
1 b[*]	None	5.0	5.8	6.1	25.5	28.3	26.1
4 a	200	5.2	5.2	6.1	15.5	18.3	20.0
b[‡]	400	3.6	4.0	3.3	12.5	13.3	14.4
c	800	2.8	3.3	2.8	13.2	15.8	17.5

[*] See Plates II, XIII and XIV for 1, 7 and 21 days, respectively.
[‡] See plates VI, XV and XVI for 1, 7 and 21 days, respectively.

No change in crystal size is casually apparent in the micrographs; any change in the small crystals comes well within the limits of error of measurement. This is more or less true of the largest crystals in the field; the increases found were never more than 4.5μ and usually were even less than this. Therefore, the size of the grains at the time the candy is first made will determine almost entirely their size after the candy becomes several weeks old.

This interpretation of the significance of the change in size of sucrose crystals is different from that given by Halliday and Noble who report a growth of crystals during storage without indicating any actual measurements. Their comment implies to the average reader an increase sufficiently great to alter the character of the grain of the fondant. That this is unlikely is indicated by the measurements given in our report.

Summary

Photomicrographs have been shown of masses of sucrose crystals in fondants containing glucose, fructose and varying amounts of invert sugar. The average diagonal measurements of the largest and the smallest crystals in the micrographic fields have been reported in microns.

Glucose, fructose and invert sugar served equally well in regulating the size of crystals. It was far from easy, however, so to adjust the conditions that the amount of invert sugar arising could be predicted. Inversion was so rapid as to make its control difficult when citric, tartaric or hydrochloric acids were used, though potassium acid tartrate was far slower even at the same pH. Under the conditions of the experiment, no exact relationship between the pH of the syrup and the amount of inversion was noted when different kinds of acids were used.

Syrups containing 43.43 percent or more invert sugar would not crystallize; those containing 16.30 to 23.55 percent formed a semi-fluid mass of crystals. From 6 to 15.80 percent invert sugar permitted a satisfactory proportion of the sucrose to crystallize out to give a plastic, moldable product.

In the presence of 11.10 percent or more invert sugar the crystals of maximum size measured 10.0 to 13.2 microns and the grain was exceedingly fine. Fondants containing about 7 percent reducing sugar of either kind were of agreeably fine texture and in them the largest crystals were 15 to 19 microns across. Candy observed to be coarse in texture contained crystals 45 microns in size. The crystals of all these samples were found not to grow noticeably in dimensions when the fondants were stored for 7 to 21 days.

The sense of touch in the mouth can detect a difference of about 6 to 10 microns in size of crystals as representing the difference between a smooth and a "gritty" texture.

THE MECHANISM OF THE COAGULATION OF SOLS BY ELECTROLYTES. II. HYDROUS ALUMINA SOLS

BY HARRY B. WEISER

In a paper presented before the Eighth Colloid Symposium[1] an adsorption mechanism was outlined to account for the change in composition and nature of the double layer which results in a decrease in the charge on the micelle when electrolytes are added to hydrous oxide sols. The proposed mechanism was the outgrowth of potentiometric observations of the change in chloride ion concentration during the stepwise addition of electrolytes to hydrous ferric oxide sol containing a slight excess of hydrochloric acid or ferric chloride as stabilizing electrolyte. At the same Symposium, Thomas and Whitehead[2] reported on their observations of the change in hydrogen ion activity when electrolytes were added to hydrous alumina sol formed by peptizing precipitated alumina with the minimum amount of hydrochloric acid to ensure stability and centrifuging to remove any unpeptized oxide. Under the condition of their observations, it was found that the pH value of the sol was increased by the addition of approximately neutral electrolytes, the anion order being oxalate > acetate > sulfate > halides > nitrate. To explain the observed increase in pH value Thomas and Whitehead assumed that the alumina sols are Werner complexes resembling the poly-ol basic chromic salts formulated by Bjerrum.[3] Starting with this postulate the increase in pH value on adding salts was attributed to replacement of (OH) groups by the anion of the added salt, followed by the union of the displaced OH radicals with hydrogen ion to form water. The pH value of the sols peptized by HCl was found to increase slightly on standing at room temperature, but on subsequent heating the pH value decreased and the change was irreversible.

In the absence of any independent proof of the constitution of the alumina sols proposed by Thomas and Whitehead, the hypothesis can be regarded only as a suggestive qualitative one for the present. Certainly if alumina sols behave like ferric oxide sols in the presence of electrolytes, the picture will have to be modified to account for the observed fact that chloride ion rather than hydroxyl ion appears to be largely displaced by the added anions.

Although the action of salts on colloidal alumina is not considered by Thomas and Whitehead in its bearing on the coagulation of sols, it is evident from observations with colloidal ferric oxide that the stepwise addition of electrolytes below the precipitation value is accompanied by a gradual decrease in micellar charge with a consequent increase in the tendency of the micelles to agglomerate into larger aggregates. The change in specific surface accompanying this phenomenon has a marked effect on the adsorption

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[1] Weiser: J. Phys. Chem., 35, 1 (1931).

[2] J. Phys. Chem., 35, 27 (1931).

[3] Z. physik. Chem., 59, 336 (1907); 73, 724 (1910).

equilibria. This manifests itself in the form of the chloride displacement curve on adding electrolytes and one should expect it to influence the pH value of the sol.

The decrease in the pH value of alumina sols on heating and their failure to return to the original value on cooling are likewise explained by Thomas and Whitehead by using the postulates of Bjerrum[1] and Stiasny,[2] namely, that aquo groups in the complex radical give up H˙ ions leaving hydroxo groups which then become "olated" forming larger aggregates. These hypotheses do not take into account the well-known decrease in the hydrous character of the colloidal particles on heating and the accompanying change in the extent and nature of the surface of the particles which will markedly influence the adsorption equilibria. The ageing which takes place at ordinary temperatures manifests itself in a similar but much slower change in the surface of the particles. As will be pointed out later, we failed to observe an increase in pH value on ageing sols formed by peptization with $AlCl_3$.

In this paper will be given a report of observations on the change in the chloride ion concentration and in the pH value of alumina sols prepared by two different methods, when electrolytes are added to the sols above and below the precipitation value. In addition, the effect of ageing on the pH value of the different sols will be considered.

Preparation of Sols

(1) *Peptization of "Grown" Alumina.* A method was sought for the preparation of alumina sol by peptization of an alumina which was not formed by the hydrolysis of an aluminum salt. If such could be done there would seem to be no more reason for assuming that the alumina sol is a complex Werner compound of indefinite composition than for assuming that silver halide sols formed by peptization with a slight excess of silver nitrate[3] are complex subhalides of indefinite composition. A method for preparing the alumina sol by peptization of pure alumina was suggested by an earlier observation[4] that "grown" alumina[5] formed by the activation of amalgamated aluminum on water was held in the colloidal state by a trace of HCl. The method of procedure finally worked out for the preparation of the sol was as follows: After burnishing to remove the film of oxide from sheets of aluminum 10 cm x 20 cm in size, they were placed in dilute hydrochloric acid which was allowed to act until the surface was thoroughly cleaned. Following this, they were rinsed and dropped immediately into a solution of mercuric chloride. After a minute the sheets were taken out, washed thoroughly to remove the loose film of mercury, rinsed with distilled water, and each one placed in a liter of approximately 0.015 normal $AlCl_3$ which was stirred continuously

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[1] Loc. cit.

[2] Stiasny and Grimm: Collegium, 691, 505 (1907); Stiasny and Szego: 670, 41 (1926).

[3] Lottermoser: J. prakt. Chem., (2) 72, 39 (1905).

[4] Weiser: J. Phys. Chem., 33, 1713 (1929); Cf. also, Pauli and Schmidt: Z. physik. Chem., 129, 199 (1927).

[5] Wislicenus: Kolloid-Z., 2nd Supplement XI (1908).

with a mechanical stirrer. The action was quite rapid at the start as evidenced by the rate of evolution of hydrogen. The "grown" alumina which was formed was held in the sol state owing to preferential adsorption of aluminum and hydrogen ions. After several hours the action slowed down and the metal was re-treated as previously described. The process was continued until a sol of the desired composition was obtained or until no more of the "grown" alumina was peptized even when a large excess of unpeptized oxide was present. Sol I used in preliminary observations still contained a little unadsorbed aluminum ion and so would have peptized more alumina. Sol II, on the other hand, was almost free from unadsorbed aluminum ion.

(2) *Hydrolysis of Aluminum Chloride.* For the purpose of comparison, a third sol was prepared by the usual method of hydrolysis of $AlCl_3$ followed by dialysis. To a liter of solution containing approximately 100 grams of $AlCl_3.6H_2O$ was added ammonia slowly until the precipitate which was formed just failed to be peptized completely. The mixture was diluted to 3.5 liters and was boiled for 30 minutes after which it was dialyzed at the boiling point in Neidle[1] dialyzers through which water was allowed to flow continuously. The process was continued until an analysis showed a suitable ratio of alumina to chlorine and the sol was then concentrated by evaporation to the desired composition.

The sols were analyzed for alumina content by precipitating with a slight excess of ammonia, washing, igniting, and weighing in the usual manner. The chloride content was determined by adding to a 25 cc portion of sol, an amount of $AgNO_3$ which was found by a preliminary experiment to be slightly in excess of that necessary to react with all the chloride. Nitric acid was then added and the mixture digested on the hot plate in the dark until all the oxide was dissolved. After diluting, the silver salt was collected on a Gooch crucible, dried and weighed. The composition of the three sols is given in the following table.

Composition of Alumina Sols

Sol No.	Method of Preparation	Al_2O_3 grams per liter	Cl mols per liter
I	Peptization of "grown" Al_2O_3	3.01	0.0160
II	Peptization of "grown" Al_2O_3	4.12	0.0156
III	$AlCl_3$ treated with NH_4OH short of precipitation and dialyzed	4.10	0.0164

In order to obviate any marked change in the composition of the sols during the course of the observations on them, they were allowed to age from two to three weeks before using.

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[1] J. Am. Chem. Soc., 38, 1270 (1916).

Observations on Alumina Sol I

The change in chloride ion concentration during the stepwise addition of electrolytes to the sols was determined by the same procedure as given in detail in an earlier paper.[1] It consists essentially of mixing separate portions of sol with gradually increasing amounts of electrolytes making the observations on the separate samples. Twenty-cubic-centimeter portions of sol in which was suspended a small amount of pure calomel, were mixed with a definite volume of standard electrolyte diluted to 5 cc in a mixing apparatus dried each time before use. After transferring the mixture to a 30 cc weighing bottle which had been thoroughly cleaned and steamed, it was placed in a thermostat at 25° and shaken at intervals for 24 hours. It was then placed in the electrode vessel like that shown in Fig. 2 of the paper above mentioned and after standing 24 hours longer, the potential was measured against an $N/10$ calomel electrode. The potentiometer employed was the Leeds and Northrop Type K apparatus in conjunction with a Hartman and Braun moving coil galvanometer sensitive to 0.1 millivolt. From the observed potential the activity of the chloride as potassium chloride was calculated and from this the molar concentration was obtained by dividing by the corresponding activity coefficient as read off from a graph prepared from data given by Lewis and Randall.[2]

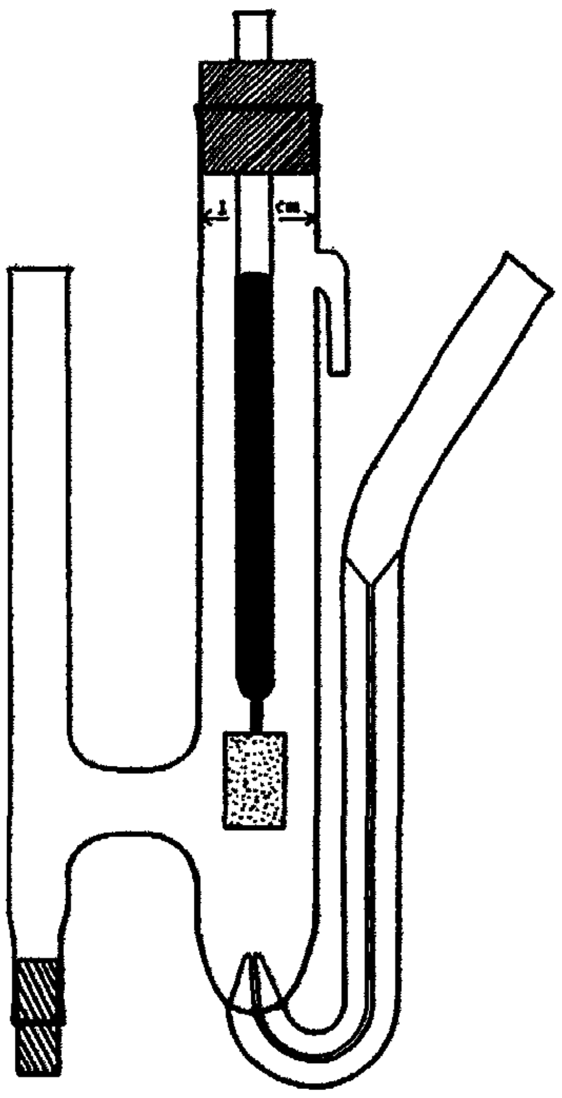

FIG. 1
Diagram of Hydrogen Electrode Vessel

Since the quinhydrone electrode gives erroneous values in unbuffered solutions with a pH value greater than 5,[3] the pH-value measurements were made with the hydrogen electrode in most cases. For this purpose the hydrogen electrode vessel of Pyrex designed by Dr. Everett E. Porter was found to be especially useful. The essential features of the vessel, shown in Fig. 1, are the hydrogen inlet device for giving small bubbles that stir the solution continuously and saturate it promptly; the small capacity, 4 or 5 cc being adequate test solution; the connecting bridge; and the outlet tube near the top through which is discharged the froth likely to form when a gas is bubbled

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[1] Weiser: J. Phys. Chem., 35, 1 (1931).
[2] "Thermodynamics," 344 (1923).
[3] Best: J. Phys. Chem., 34, 1815 (1930).

through a sol. The electrodes were of platinized platinum foil 6 mm × 8 mm in size. The hydrogen from a tank was purified by passing over an incandescent tungsten filament, next over sticks of KOH, then bubbled through sulfuric acid, and finally through water.

The hydrogen electrode can not be used to determine the pH value in the presence of KNO_3. Fortunately in the experiments with this salt the pH value remained in the neighborhood of 5 and the quinhydrone electrode would be expected to give reliable results. A gold electrode as supplied by Leeds and Northrop was employed in the test solution.

The same potentiometer set-up used in making the chloride ion measurements was employed in determining the pH values.

Freshly boiled distilled water and salts of tested purity were used throughout. Sols and solutions were stored in Pyrex vessels.

Titration with K_2SO_4. Since 20 cc of sol was precipitated with less than 5 cc of *N*/20 K_2SO_4, this concentration of salt was used in the experiments. Above the precipitation value all the suspended calomel was carried down by the precipitated oxide. To make sure that the supernatant solution was saturated with calomel, a small amount of paste was added at the time the mixture was transferred to the electrode vessel. Following the determination of the chloride ion concentrations of the several mixtures, the pH value of each was measured. The experimental results are given in Table I and plotted in Fig. 2, the points being represented by dots.

TABLE I

Titration of Al_2O_3 Sol I with K_2SO_4

Cc *N*/20 K_2SO_4 to 20 cc sol. Total volume 25 cc	π volts	αCl^- $\times 10^3$	[Cl] $\times 10^3$	[Cl] displaced $\times 10^3$	½ [SO_4] added $\times 10^3$	pH final
0.0	0.0658	6.12	6.50	0.0	0	4.31
0.5	0.0644	6.46	6.88	0.38	1	4.38
1.0	0.0634	6.71	7.15	0.65	2	4.42
1.5	0.0620	7.08	7.56	1.06	3	4.44
2.0	0.0608	7.43	7.94	1.44	4	4.46
2.5	0.0593	7.93	8.50	2.00	5	——
3.0	0.0570	8.61	9.26	2.76	6	4.47
3.50	0.0552	9.24	9.97	3.47	7	——
3.75	0.0545	9.49	10.25	3.75	7.5	——
4.00	0.0540	9.68	10.47	3.97	8	4.48
4.50	0.0530	10.07	10.90	4.40	9	——
5.00	0.0521	10.43	11.32	4.82	10	4.49

Titration with $K_2C_2O_4$. The same procedure described in the preceding paragraph was repeated with *N*/20 $K_2C_2O_4$ instead of K_2SO_4. The results given in Table II are plotted in Fig. 2, the points on the curves with this salt being represented with circles.

A glance at the form of the chloride displacement curves reveals the S-form which characterized similar curves using ferric oxide sols. As with the latter sols, the amount of chloride displaced is always less than the amount of sulfate or chloride added. Moreover, the total chloride concentration of the

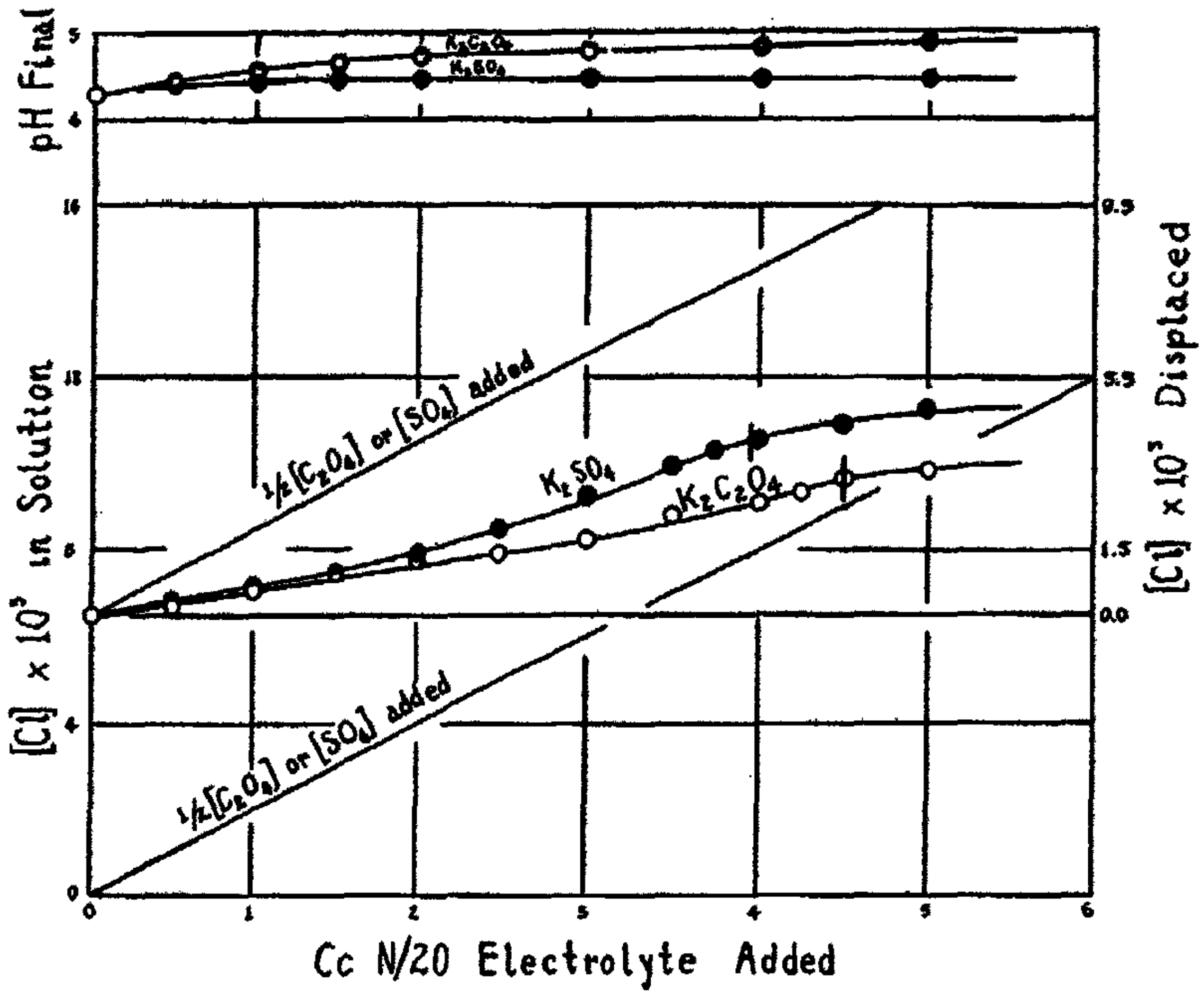

FIG. 2

Titration Curves for Al_2O_3 Sol I with N/20 K_2SO_4 and N/20 $K_2C_2O_4$

TABLE II

Titration of Al_2O_3 Sol I with $K_2C_2O_4$

Cc N/20 $K_2C_2O_4$ to 20 cc sol. Total volume 25 cc	π volts	αCl^- × 10²	[Cl] × 10³	[Cl] displaced × 10³	½ [C_2O_4] added × 10³	pH final
0.0	0.0658	6.12	6.50	0.0	0	4.31
0.5	0.0646	6.41	6.82	0.32	1	4.43
1.0	0.0637	6.64	7.07	0.47	2	4.57
1.5	0.0620	7.08	7.56	1.06	3	4.67
2.0	0.0614	7.25	7.75	1.25	4	4.73
2.5	0.0608	7.43	7.94	1.44	5	——
3.0	0.0600	7.67	8.21	1.71	6	4.80
3.5	0.0583	8.22	8.82	2.32	7	——
4.0	0.0576	8.42	9.06	2.56	8	4.85
4.25	0.0571	8.59	9.24	2.74	8.5	——
4.5	0.0567	8.96	9.65	3.15	9	——
5.0	0.0556	9.10	9.81	3.31	10	4.91

solution at the precipitation value (shown by the vertical line cutting the curve) approximates the concentration of the added salts. The displacement of chloride by sulfate is greater at all concentrations than that of oxalate and the precipitation value of the former is the lower. This is usually true in fairly acid solution since in such cases there is a relatively higher concentration of univalent bioxalate ions than of univalent bisulfate; and in general, the bivalent ions are more strongly adsorbed and so have a more marked displacing power than univalent ions at the same concentration.

The pH values of the sol-sulfate mixtures were but very little more than that of the pure sol; with the sol-oxalate mixtures a somewhat greater increase was noted, as might be expected since solutions of $K_2C_2O_4$ are slightly alkaline.

Experiments with Alumina Sol II

The results of the preliminary experiments with Sol I were sufficiently promising that the investigations were continued with Sol II which was similar in total chloride content to Sol I but contained 35 percent more Al_2O_3. In the preliminary experiments, the mistake was made of using too low a concentration of electrolyte so that but little information was obtained above the precipitation value. With the stronger sol, $N/10$ solutions of the salts with multivalent anions were employed. Moreover, it seemed of value to know the pH value of the electrolytes alone at the same concentration as the sol-electrolyte mixture. Accordingly the pH values were determined for mixtures in which water was substituted for the sol. In the subsequent tables the pH values for sol-electrolyte mixtures and for the pure solutions are labeled respectively "pH final" and "pH initial."

Titration with K_2SO_4. The chloride displacement and pH values on adding $N/10$ K_3SO_4 in gradually increasing amounts to the sol are given in Table III and represented graphically in Fig. 3.

A comparison of the chloride displacement curve with that obtained with ferric oxide sol under similar conditions reveals a striking similarity in behavior. Note the usual upward course before the precipitation value is

TABLE III

Titration of Al_2O_3 Sol II with K_2SO_4

Cc $N/10$ K_2SO_4 to 20 cc sol. Total volume 25 cc.	π volts	$\alpha Cl^- \times 10^3$	$[Cl] \times 10^3$	$[Cl]$ displaced $\times 10^3$	½ $[SO_4]$ added $\times 10^3$	pH final	initial
0.0	0.0635	6.78	7.21	0.9	0	4.20	—
0.5	0.0605	7.52	8.04	0.83	2	4.24	—
1.0	0.0581	8.25	8.85	1.64	4	4.25	7.33
1.5	0.0565	8.78	9.43	2.22	6	—	—
2.0	0.0535	9.87	10.68	3.47	8	4.26	7.43
2.5	0.0500	11.32	12.32	5.11	10	—	—
3.0	0.0485	12.00	13.10	5.89	12	4.32	7.56
4.0	0.0474	12.59	13.79	6.58	16	4.38	7.56
5.0	0.0470	12.72	13.93	6.72	20	4.43	7.56

reached. This is due to the gradual agglomeration of the particles and the consequent proportionately greater displacement of chloride for a given increment in sulfate concentration owing to decrease in the extent of surface. Note also that the curve changes direction in the immediate region of the precipitation value, the upper portion of the curve representing the relatively smaller displacement of chloride from the coagulum for a given increment in sulfate concentration. Again, the amount of chloride displaced is much smaller than the total sulfate added, but in the region of the precipitation value the total concentration is approximately equivalent to the sulfate added, although the variation from equivalence in this case appears to be somewhat greater than usually obtains. The total chloride content of the sol is 1.56×10^{-3} mols per liter. More than ten percent of this remains in the coagulum even in the presence of twice the precipitation concentration of K_2SO_4. From the form of the chloride displacement curve it is apparent that relatively large con-

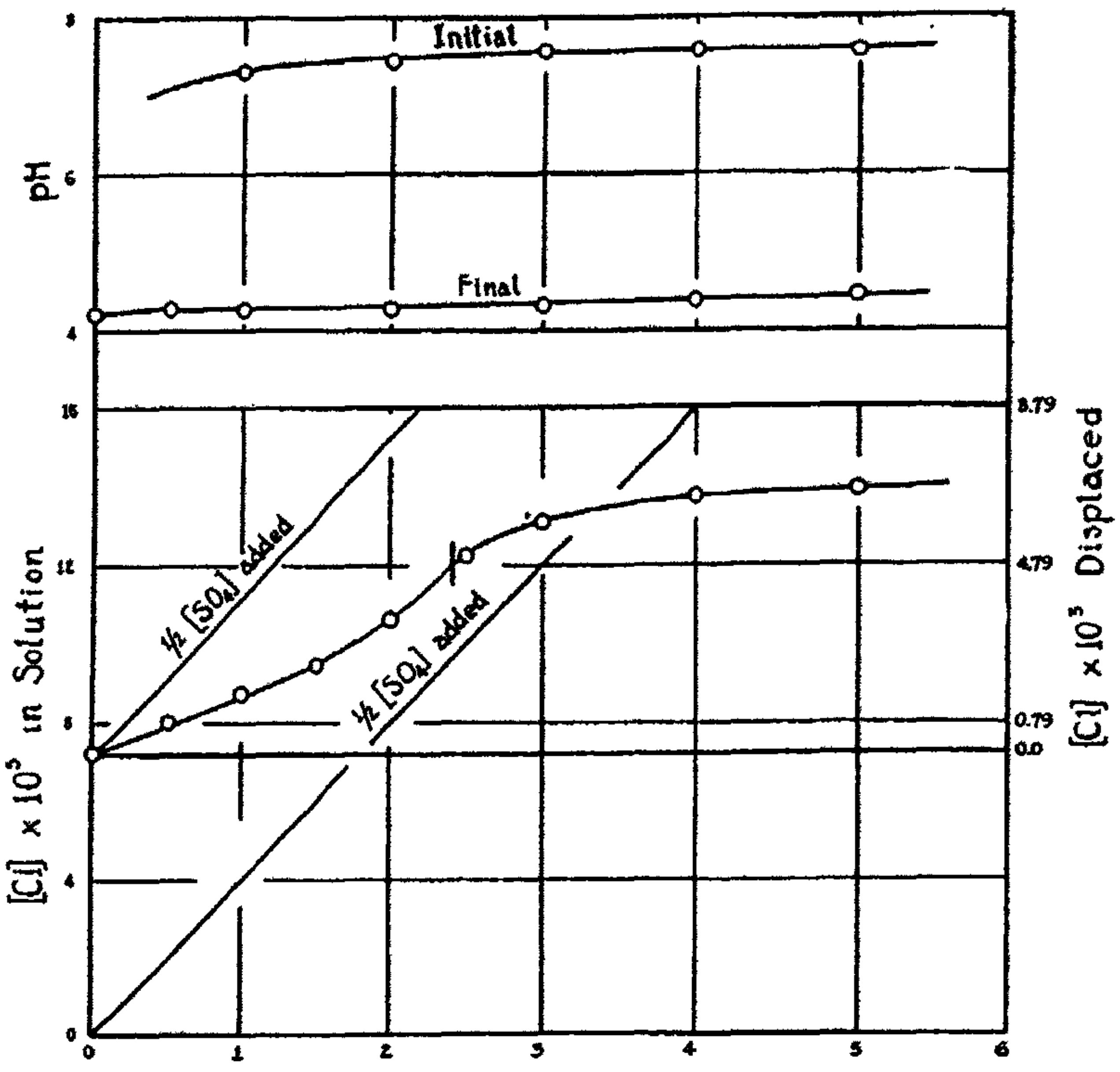

FIG. 3
Titration Curves for Al_2O_3 Sol II with $N/10$ K_2SO_4

centrations of electrolyte would not displace all the chloride from the oxide. The added sulfate is almost completely adsorbed from solutions up to and including the precipitation value.

In accord with the observations on Sol I, the change in pH value during coagulation is quite small, being but 0.06 pH greater at the precipitation value than the value for the sol. Since the form of the chloride displacement curve shows that agglomeration is taking place during the stepwise addition of the electrolyte, one might expect the pH value to decrease slightly. But this is opposed by the adsorption of hydrogen ion to minimize the action of the adsorbed sulfate ion. The net effect is the slight rise in pH value observed. The pH value of the salt is slightly above 7 but this slight alkaline reaction would influence the pH value of the sol but little if at all, since K_2SO_4 possesses little or no alkali reserve.

Titration with $K_2C_2O_4$. The observations with $K_2C_2O_4$ as precipitating electrolyte are given in Table IV and plotted in Fig. 4. In order to show more clearly the form of the chloride displacement curve the chloride concentration is henceforth plotted on a larger scale. The size of the figure is kept approximately the same by eliminating the lower portion between 0 and 6×10^{-3} [Cl] which lies within the chloride ion concentration of the original sol. The curve for "1/2[C_2O_4]added" obviously begins at 0, 0.

TABLE IV

Titration of Al_2O_3 Sol II with $K_2C_2O_4$

Cc $N/10$ $K_2C_2O_4$ to 20 cc sol. Total volume 25 cc	π volts	α Cl⁻ $\times 10^3$	[Cl] $\times 10^3$	[Cl] displaced $\times 10^3$	½ [C_2O_4] added $\times 10^3$	pH	
						final	initial
0.0	0.0635	6.78	7.21	0.0	0	4.20	—
0.5	0.0625	7.00	7.47	0.26	2	4.44	—
1.0	0.0610	7.37	7.87	0.66	4	4.61	7.80
1.5	0.0594	7.84	8.40	1.19	6	4.73	—
2.0	0.0580	8.28	8.90	1.69	8	4.85	7.83
2.5	0.0555	9.14	9.85	2.64	10	5.00	—
3.0	0.0511	10.84	11.78	4.57	12	5.68	7.85
4.0	0.0498	11.41	12.43	5.22	16	7.08	8.03
5.0	0.0496	11.45	12.47	5.26	20	7.16	8.15

It will be noted that the chloride displacement curve falls slightly below that for sulfate and the precipitation value is somewhat higher than for sulfate as was true for Sol I and for the reason already given. However, the curve with oxalate rises more rapidly as the precipitation value is approached so that the amount of chloride displaced at the precipitation value is approximately the same with both electrolytes.

The pH values of the sol-electrolyte mixtures are somewhat greater than that of the sol, increasing gradually to the precipitation value and then rising sharply. This behavior is exactly what would be expected under the circumstances. The electrolyte is slightly alkaline owing to hydrolysis as follows: $K_2C_2O_4 + H_2O \leftrightarrows KOH + KHC_2O_4$. It thus possesses an alkali reserve which neutralizes to a certain extent the acidity of the sol, the effect being more marked as the precipitation value is approached. Above the precipitation concentration, the pH value rises sharply approaching that of

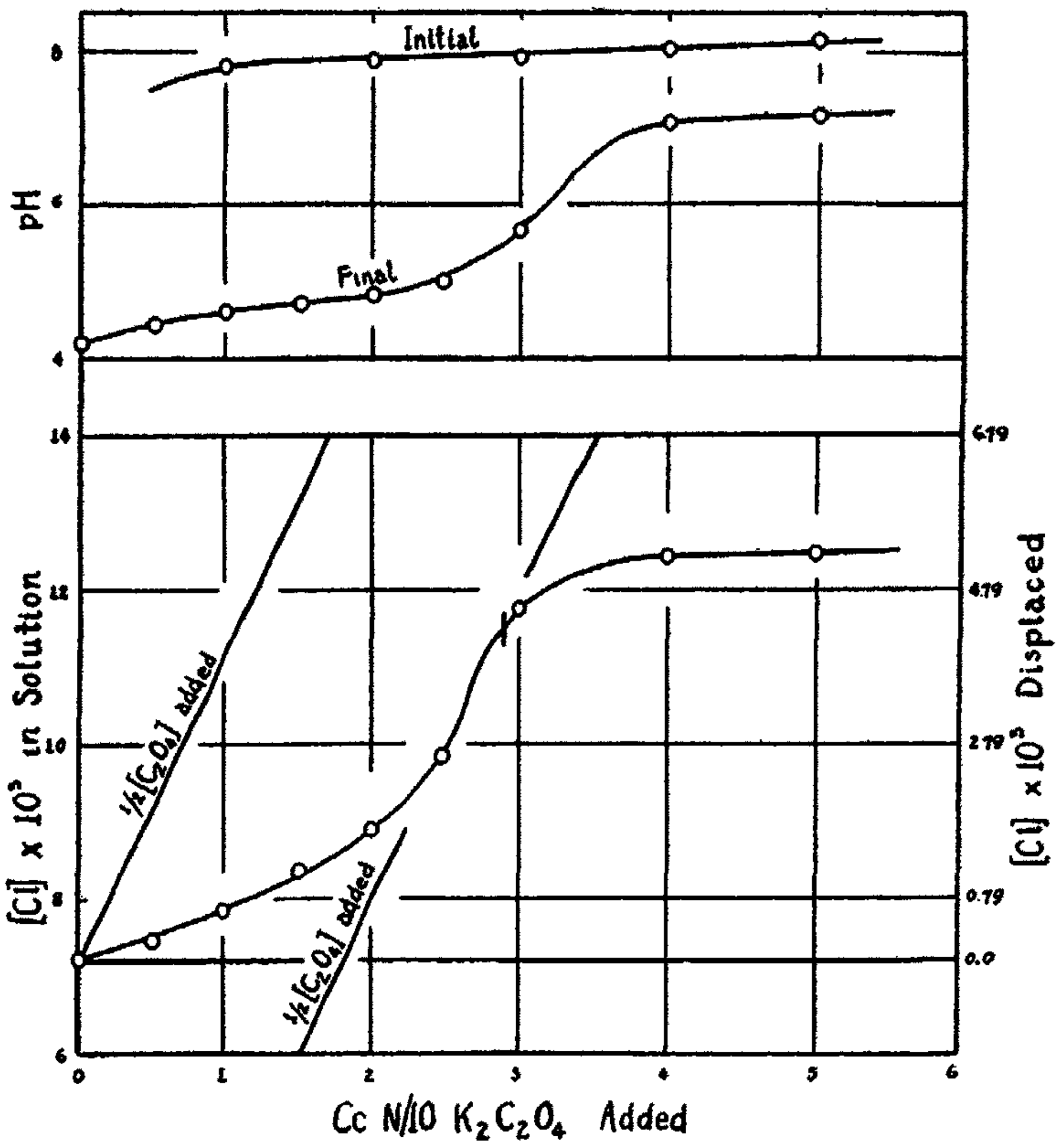

FIG. 4
Titration Curves for Al_2O_3 Sol II with $N/10$ $K_2C_2O_4$

the pure electrolyte. This is what it should do since the neutralized coagulum settles out leaving the supernatant liquid which contains only chloride and the excess oxalate.

Titration with $K_3C_6H_5O_7$. An $N/10$ $K_3C_6H_5O_7$ solution was prepared by taking 1/30 of the molecular weight of the salt per liter. Since such a solution contains relatively few trivalent ions as compared with the number of divalent and univalent ions, it is not permissible to compare the data given in Table V and shown graphically in Fig. 5 with the corresponding data obtained

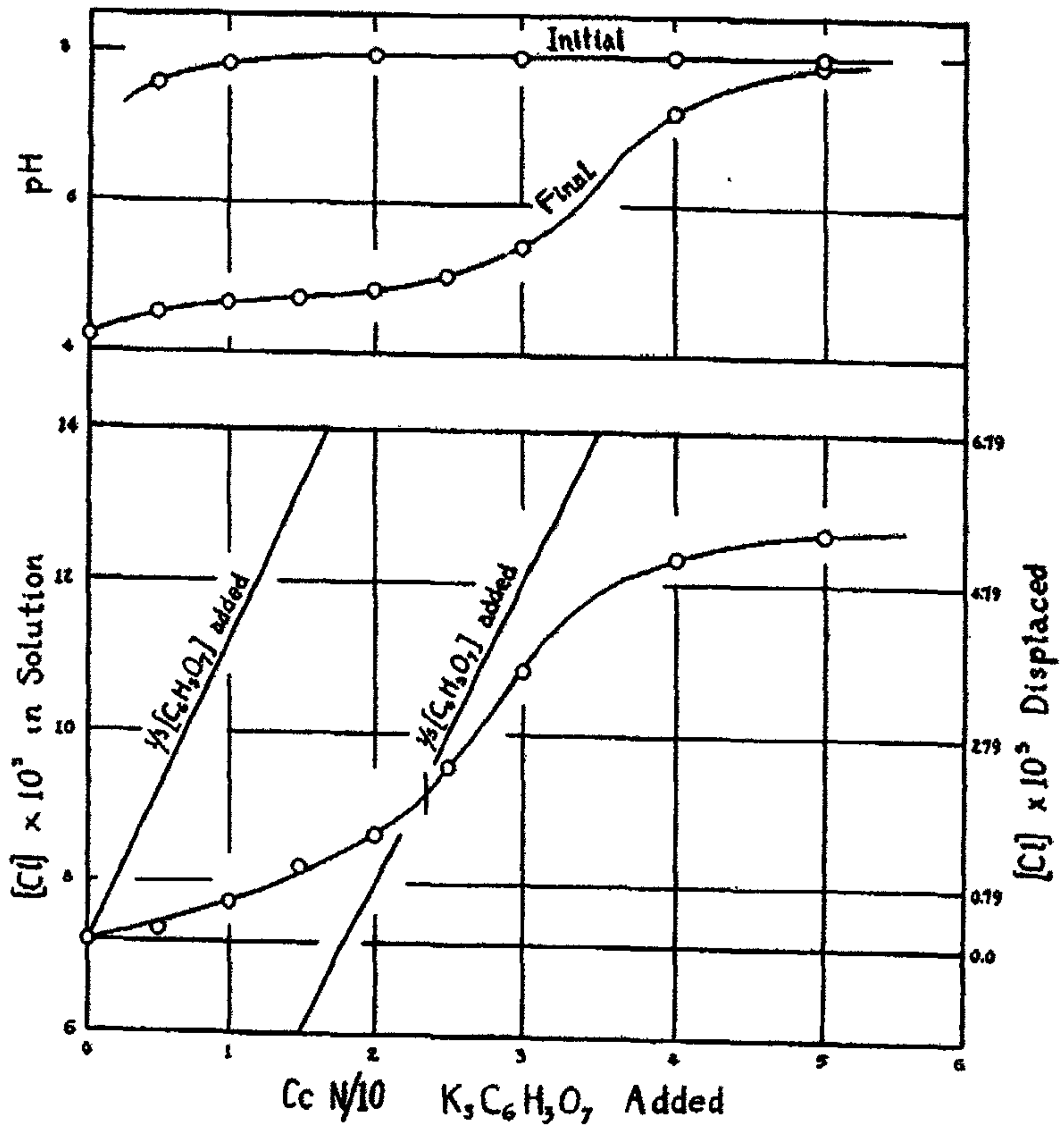

Fig. 5
Titration Curves for Al_2O_3 Sol II with N/10 $K_3C_6H_5O_7$

Table V

Titration of Al_2O_3 Sol II with $K_3C_6H_5O_7$

Cc N/10 $K_3C_6H_5O_7$ to 20 cc sol. Total volume 25 cc	π volts	α Cl^- × 10^3	[Cl] × 10^3	[Cl] displaced × 10^3	⅓ [$C_6H_5O_7$] added × 10^3	pH final	pH initial
0.0	0.0635	6.78	7.21	0.0	0	4.20	—
0.5	0.0628	6.87	7.32	0.11	2	4.51	7.57
1.0	0.0615	7.23	7.72	0.51	4	4.65	7.83
1.5	0.0600	7.67	8.21	1.00	6	4.71	—
2.0	0.0588	8.03	8.61	1.40	8	4.85	7.90
2.5	0.0563	8.85	9.53	2.31	10	5.03	—
3.0	0.0532	10.00	10.82	3.61	12	5.42	7.93
4.0	0.0500	11.32	12.33	5.12	16	7.24	7.98
5.0	0.0494	11.60	12.65	5.44	20	7.89	7.98

with sulfate and oxalate, since the concentration of effective ions in the citrate solution is probably lower than with the other salts.

It will be noted that the precipitation concentration of the $M/30$ citrate is somewhat lower than with either $N/10$ sulfate or oxalate and that the chloride displaced at the precipitation value is less than with either of the above mentioned salts. This is accounted for by the fact that the neutralization of the charge on the particles is due in part to the strongly adsorbed trivalent ion which has a more marked discharging action than either monovalent or divalent anions. Accordingly, to the extent that the trivalent ion contributes to the lowering of the charge on the particles to the point of coagulation, less needs to be adsorbed and correspondingly less chloride will be displaced at the precipitation value. This behavior is similar although much less pronounced than was observed with the trivalent ferricyanide on ferric oxide sol.[1]

The increase in pH value during the titration process is comparable to that of potassium oxalate but is somewhat more pronounced owing to the more marked buffering action of alkali citrate solutions.

Titration with $NH_4C_2H_3O_2$. Since the precipitating power of the univalent acetate ion is relatively weak, it was necessary to use a 2 normal solution of the salt to effect coagulation within 5 cc of electrolyte in 20 cc of sol. The titration data are given in Table VI and plotted in Fig. 6. The chloride displacement curve does not have the S-shape and there is no point of inflexion at the point where coagulation is complete. The reason is obvious to one carrying out the experiments. The addition of as little as 0.5 cc of the 2 N salt in a total volume of 25 cc caused a perceptible increase in the cloudiness of the sol. This cloudiness increased gradually with larger additions of electrolyte until finally the particles grew to a sufficient size to settle out. The form of the chloride displacement curve is a manifestation of this gradual

TABLE VI

Titration of Al_2O_3 Sol II with $NH_4C_2H_3O_2$

Cc $N/10$ $NH_4C_2H_3O_2$ to 20 cc sol. Total volume 25 cc	π volts	$\alpha Cl^- \times 10^3$	$[Cl] \times 10^3$	$[Cl]$ displaced $\times 10^3$	$[C_2H_3O_2]$ added $\times 10^3$	pH final	pH initial
0.0	0.0635	6.78	7.21	0.0	0	4.20	—
0.5	0.0578	8.35	8.97	1.76	40	5.55	6.51
1.0	0.0553	9.20	9.92	2.71	80	5.86	6.57
1.5	0.0526	10.11	10.94	3.73	120	6.06	—
2.0	0.0512	10.80	11.71	4.50	160	6.16	6.63
3.0	0.0491	11.72	12.78	5.57	240	6.30	6.66
4.0	0.0474	12.52	13.71	6.50	320	6.30	6.71
5.0	0.0465	12.97	14.22	7.01	400	6.46	6.74

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[1] J. Phys. Chem., 34, 1 (1931).

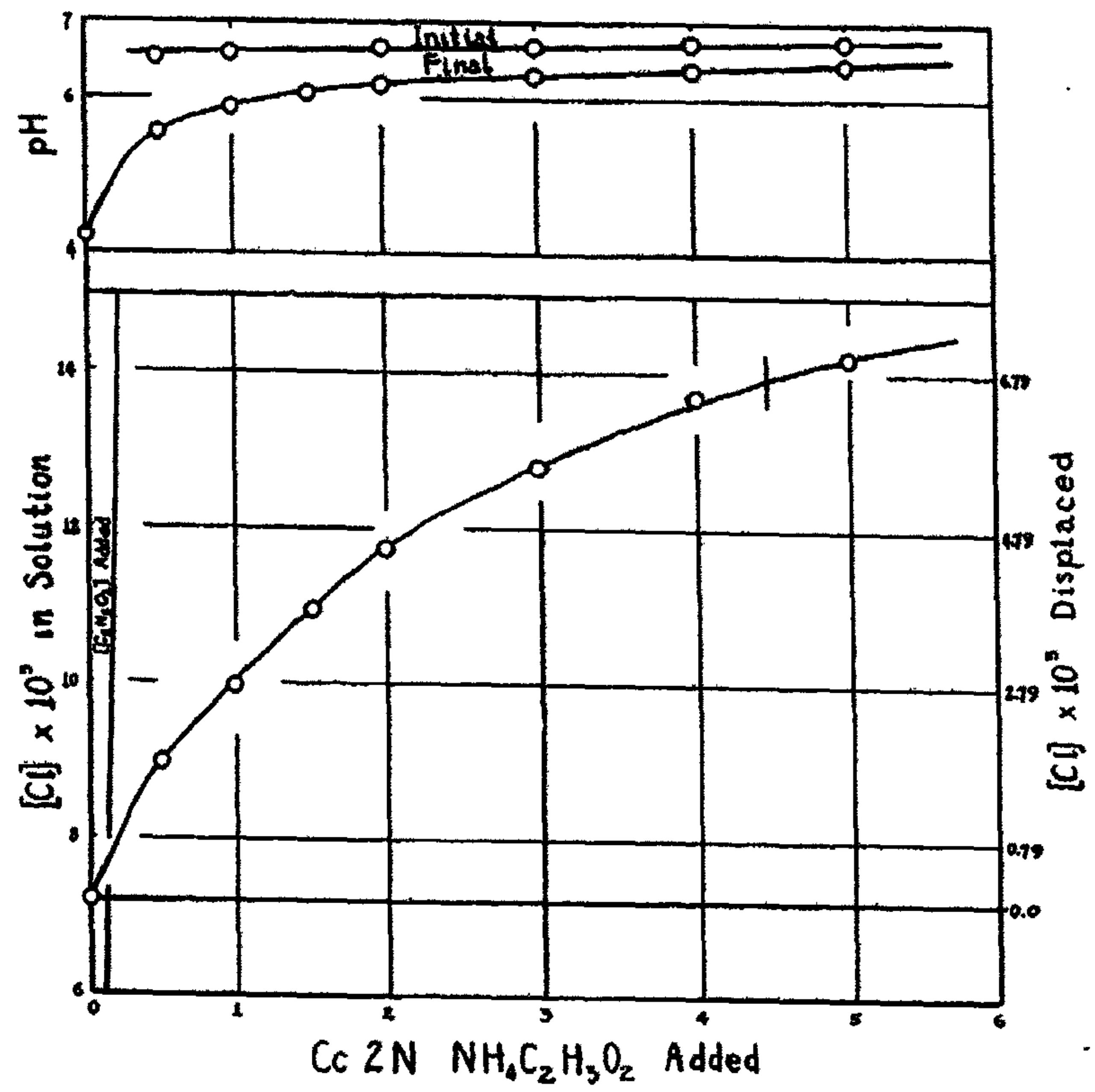

FIG. 6
Titration Curves for Al_2O_3 Sol II with 2*N* $NH_4C_2H_3O_2$

TABLE VII

Titration of Al_2O_3 Sol II with KNO_3

Cc *N* KNO_3 to 20 cc sol. Total volume 25 cc	π volts	αCl⁻ × 10³	[Cl] × 10³	[Cl] displaced × 10³	[KNO_3] added × 10³	pH final	pH initial
0.0	0.0635	6.78	7.21	0.0	0	4.21	——
0.5	0.0608	7.36	7.86	0.65	40	4.32	——
1.0	0.0605	7.52	8.05	0.84	80	4.38	6.19
2.0	0.0605	7.52	8.05	0.84	160	4.44	6.22
3.0	0.0606	7.50	8.03	0.82	240	4.48	6.24
4.0	0.0606	7.50	8.03	0.82	320	4.51	6.27
5.0	0.0605	7.52	8.05	0.84	400	4.52	6.28
5 in 10	0.0668	5.88	6.24		1000	——	——
10 in 10	0.0729	4.64	4.90		2000	——	——

lowering of charge and the consequent gradual increase in particle size without a distinct zone of rapid coagulation such as obtains with multivalent precipitating ions.

The increase in pH value on adding acetate to the acid sol, the value at higher concentrations approaching that of the pure electrolyte, is in entire accord with the well known buffer action of acetates.

Titration with KNO_3. A 2 N solution of KNO_3 was employed in these experiments although the precipitation concentration is higher than 5 cc of 2 N solution in 25 cc of sol. From the data in Table VII which is plotted in Fig. 7 it would appear that the observed chloride displacement rises to a maximum value in the presence of but 1 cc of 2 N solutions. This value remains constant until more than 5 cc of 2 N solution is added and thereafter it drops off. This observed behavior is undoubtedly due in part at least to the limitations of the experimental method. Certainly the apparent falling off in the chloride displaced at higher concentrations cannot be right and is probably the result of an oxidation-reduction reaction involving calomel and KNO_3 which becomes quite pronounced with the more concentrated KNO_3 solutions. The observations show clearly the lower precipitating power and chloride displacing power of univalent nitrate as compared even with univalent acetate which in turn shows a much lower displacing and precipitating action than the multivalent anions.

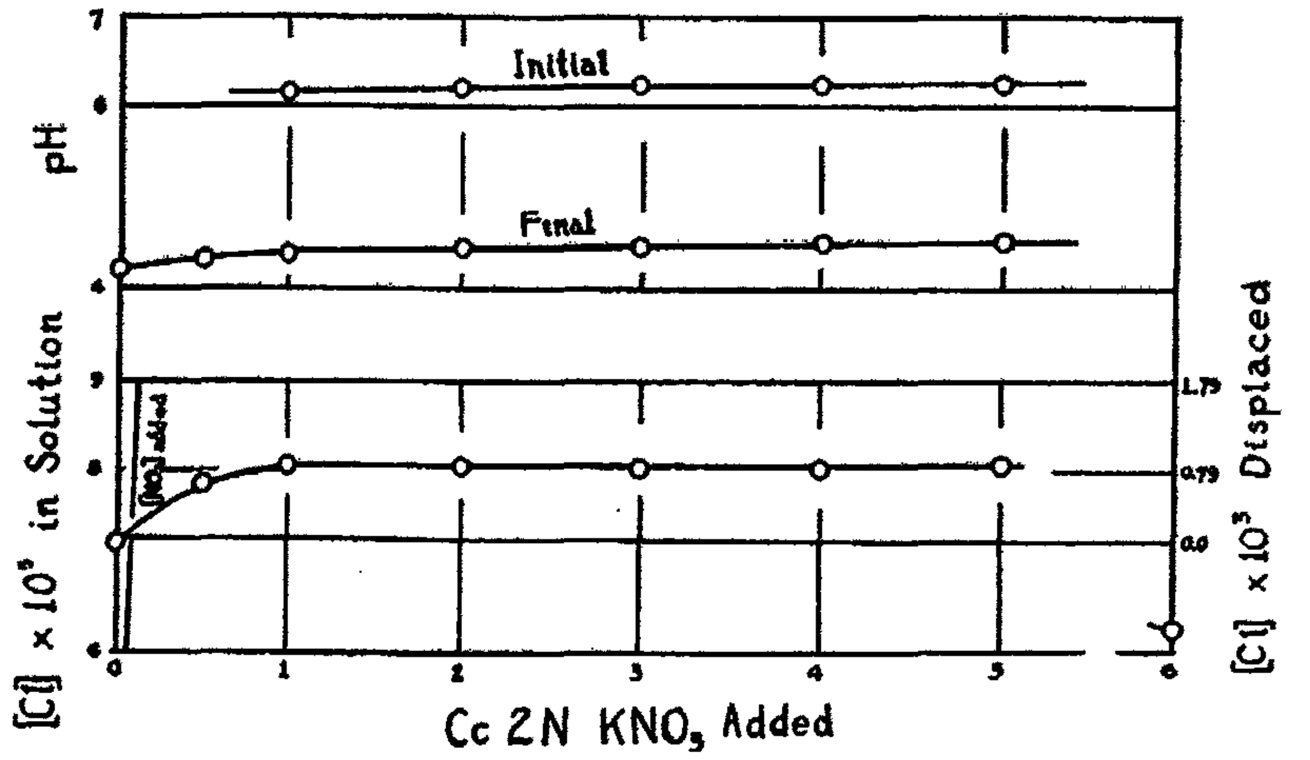

Fig. 7
Titration Curves for Al_2O_3 Sol II with 2 N KNO_3

As would be expected, the change in pH value on adding KNO_3 solution to the acid sol is negligible as compared with acetate, citrate, or oxalate and is of the same order of magnitude as that for the same concentration of K_2SO_4. A test showed that the addition to the sol of 0.1 cc of 2 N KNO_3 in a total volume of 25 cc, which would be almost enough to effect coagulation if it were K_2SO_4, causes a rise in pH value from 4.20 to 4.25.

Observations on Alumina Sol III

It will be recalled that Sol III was prepared by hydrolysis of $AlCl_3$ solution while Sols I and II were formed by peptization of "grown" Al_2O_3 formed by the direct action of water on amalgamated aluminum. If the hydrolysis of $AlCl_3$ under conditions that lead to sol formation gives poly-ol basic aluminum salts of the Werner type as assumed by Thomas and Whitehead and if the change in pH value on adding salts to such sols is due to displacement of OH groups from the complex which unite with H to form H_2O, then one might expect to find some difference in the behavior of the two types of sols toward electrolytes. As the following experiments show there is some difference in behavior but it is in the direction opposite to that which would be predicted on the basis of the Thomas-Whitehead hypothesis.

Titration with K_2SO_4. The results of adding $N/10$ K_2SO_4 to Sol III in gradually increasing amounts are given in Table VIII and plotted in Fig. 8.

TABLE VIII
Titration of Al_2O_3 Sol III with K_2SO_4

Cc $N/10$ K_2SO_4 to 20 cc sol. Total volume 25 cc	π volts	αCl^- $\times 10^3$	[Cl] $\times 10^3$	[Cl] displaced $\times 10^3$	½ [SO_4] added $\times 10^3$	pH	
						final	initial
0.0	0.0640	6.56	7.00	0.0	0	5.20	——
0.5	0.0622	7.02	7.50	0.50	2	——	——
1.0	0.0600	7.67	8.21	1.21	4	5.11	7.33
1.5	0.0582	8.22	8.82	1.82	6	5.06	——
2.0	0.0560	8.96	9.66	2.66	8	5.02	7.43
2.5	0.0539	10.07	10.90	3.90	10	4.01	——
3.0	0.0523	10.31	11.18	4.18	12	4.91	7.56
4.0	0.0516	10.63	11.54	4.54	16	4.86	7.56
5.0	0.0513	10.76	11.70	4.70	20	4.86	——

The form of the chloride displacement curve is essentially the same as that obtained with Sol II. The particles of the sol formed from "grown" alumina are less hydrous and the precipitate less gelatinous than that obtained from Sol III and the precipitation value is slightly higher. Approximately 20 percent of the total chloride content is retained by the precipitate so that it cannot be detected potentiometrically after adding 5 cc of the electrolyte to 20 cc of sol. This is somewhat more than was observed under similar conditions with the less hydrous Sol II.

The change in pH value is significant. It will be noted that there is a slight decrease in pH value during the stepwise addition of electrolyte. In this case it appears that the loss of adsorbed hydrogen ions by the particles during the coalescence which accompanies the lowering of the charge is slightly greater than the opposing tendency to adsorb hydrogen ion from solution to maintain the charge. Obviously, the change is in the wrong direction to account for it by assuming the displacement of OH groups from a Werner complex by the sulfate radicals.

Whatever difference of opinion there may be as regards the explanation of the phenomenon, there appears to be little or no question about the accuracy of the findings. Observations of the change in pH value on adding varying amounts of sulfate solution were repeated three times using both the hydrogen and the "quinhydrone" electrodes. Closely agreeing results were obtained in the measurements and there was always a definite, unmistakable decrease in pH value on adding the electrolyte to the sol. There is of course nothing unusual in this behavior from the standpoint of the adsorption theory. For, as already pointed out, the shifting of the adsorption equilibria on addition to the sol of a neutral salt of a strong acid and a strong base would be expected to increase slightly, decrease slightly, or leave unchanged the pH value depending on the relative magnitude of two opposing tendencies.

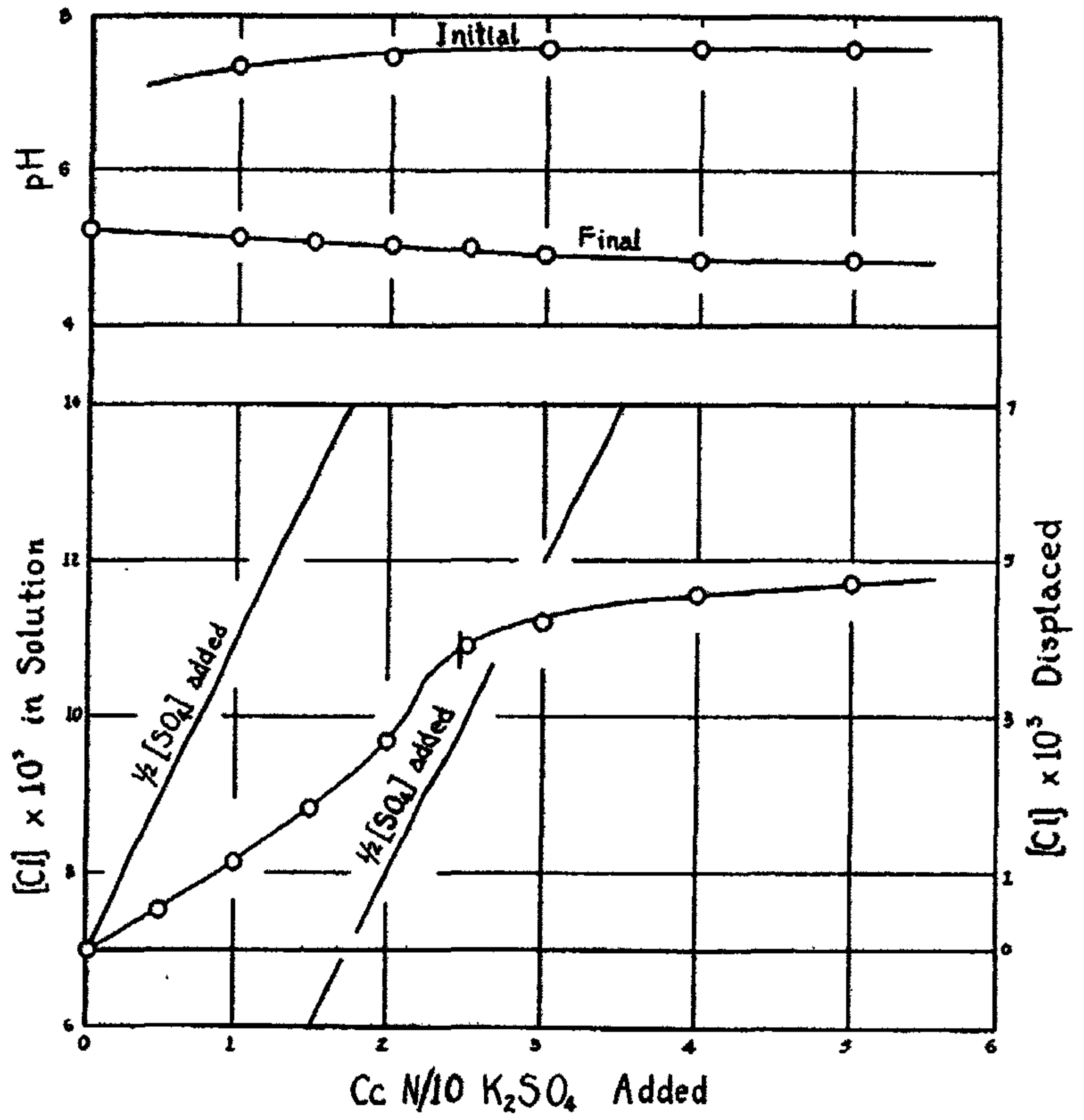

FIG. 8
Titration Curves for Al_2O_3 Sol III with $N/10$ K_2SO_4

From the observed small decrease in pH value on the coagulation of Sol III with potassium sulfate and of a small increase in the pH value on coagulating Sol II with the same salt, one would expect the increase in pH value with a buffering salt like potassium citrate to be proportionately less with Sol III than with Sol II for a given addition of electrolyte. That such is the case will be shown in the subsequent observations.

Titration with $K_3C_6H_5O_7$. The displacement of chloride and the change in pH value on titrating Sol III with citrate are given in Table IX and Fig. 9.

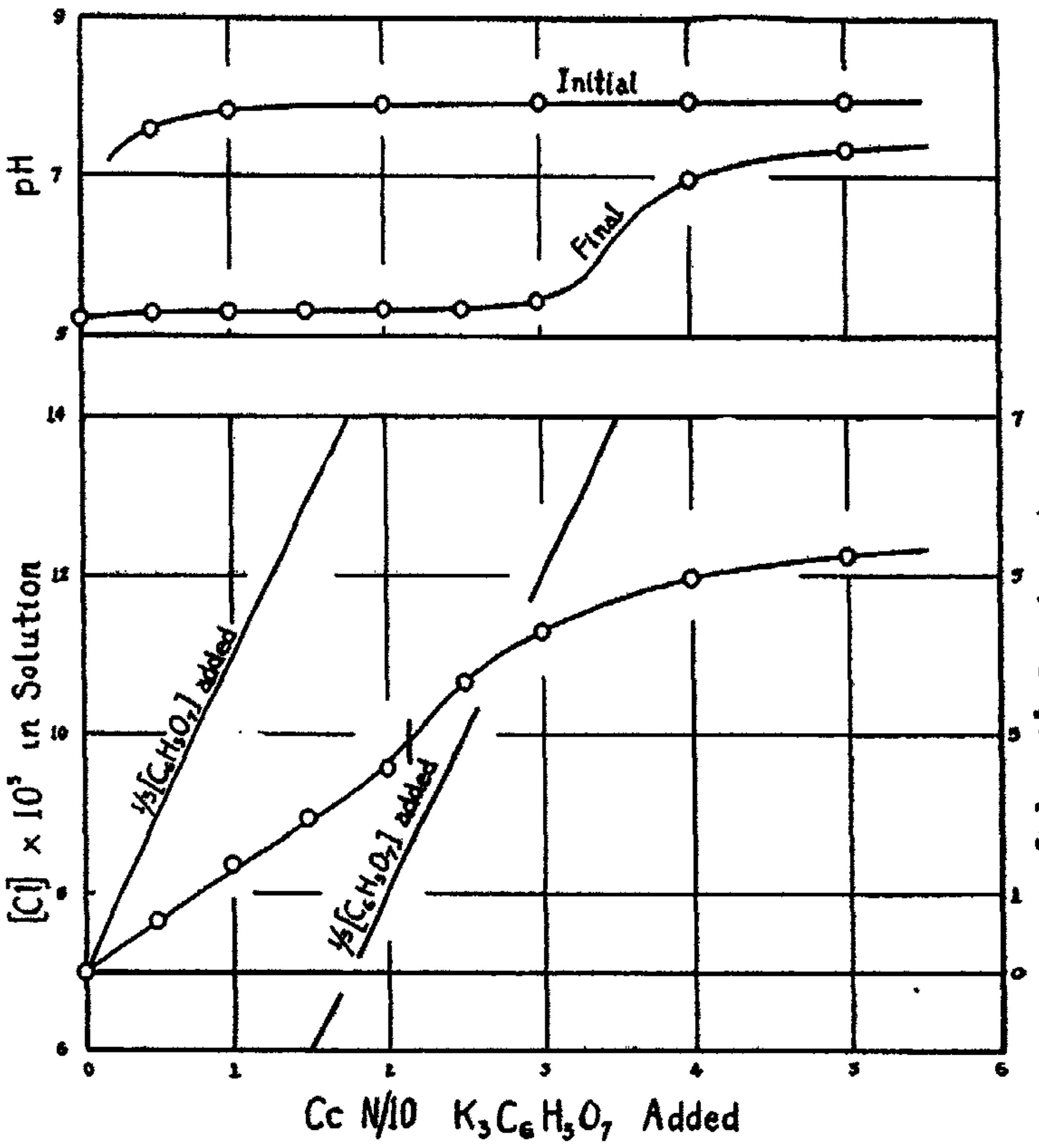

Fig. 9
Titration Curves for Al_2O_3 Sol III with $N/10$ $K_3C_6H_5O_7$

As in the case of sulfate the chloride displacement curve is somewhat lower than that with the "grown" alumina sol.

As predicted, the increase in pH value is less on adding citrate to Sol III than to Sol II. Indeed the increase is but 0.20 pH until the colloid precipitates out whereupon the pH value of the supernatant solution, due in large measure to unadsorbed citrate, approaches that of the pure citrate solution.

Titration with $K_2C_2O_4$. The observations with $K_2C_2O_4$ as precipitating electrolyte are given in Table Xa and Fig. 10, the points being represented

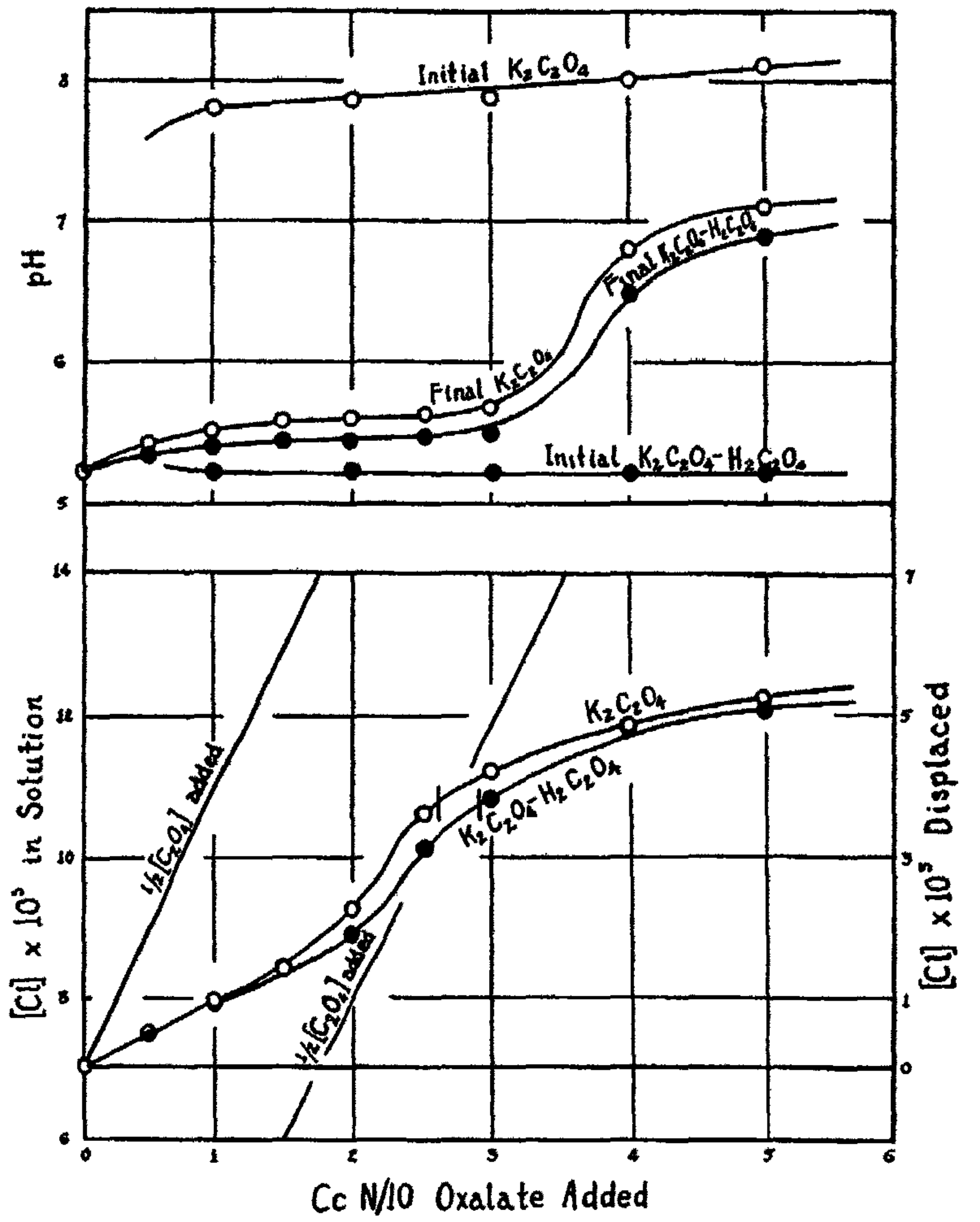

FIG. 10
Titration Curves for Al_2O_3 Sol III with $N/10$ $K_2C_2O_4$ and $N/10$ $K_2C_2O_4$-$H_2C_2O_4$ Mixtures

TABLE IX

Titration of Al_2O_3 Sol III with $K_3C_6H_5O_7$

Cc $N/10$ $K_3C_6H_5O_7$ to 20 cc sol. Total volume 25 cc	π volts	αCl^- $\times 10^3$	[Cl] $\times 10^3$	[Cl] displaced $\times 10^3$	$\frac{1}{3}[C_6H_5O_7]$ added $\times 10^3$	pH	
						final	initial
0.0	0.0640	6.56	7.00	0.0	0	5.20	—
0.5	0.0617	7.17	7.66	0.66	2	5.25	7.57
1.0	0.0595	7.81	8.38	1.38	4	5.28	7.83
1.5	0.0580	8.28	8.90	1.90	6	5.30	—
2.0	0.0564	8.82	9.50	2.50	8	5.32	7.90
2.5	0.0536	9.86	10.64	3.64	10	5.37	—
3.0	0.0522	10.39	11.27	4.27	12	5.43	7.93
4.0	0.0508	10.97	11.93	4.93	16	6.97	7.98
5.0	0.0501	11.27	12.26	5.26	20	7.34	7.98

TABLE Xa

Titration of Al_2O_3 Sol III with $K_2C_2O_4$

Cc $N/10$ $K_2C_2O_4$ to 20 cc sol. Total volume 25 cc	π volts	αCl^- $\times 10^3$	[Cl] $\times 10^3$	[Cl] displaced $\times 10^3$	$\frac{1}{2}[C_2O_4]$ added $\times 10^3$	pH	
						final	initial
0.0	0.0640	6.56	7.00	0.0	0	5.20	—
0.5	0.0622	7.02	7.50	0.50	2	5.42	—
1.0	0.0608	7.45	7.97	0.97	4	5.50	7.80
1.5	0.0594	7.84	8.40	1.40	6	5.56	—
2.0	0.0570	8.62	9.26	2.26	8	5.61	7.83
2.5	0.0537	9.80	10.60	3.60	10	5.62	—
3.0	0.0523	10.31	11.18	4.18	12	5.66	7.88
4.0	0.0510	10.88	11.82	4.82	16	6.81	8.03
5.0	0.0500	11.32	12.32	5.32	20	7.12	8.15

by dots. These data merely confirm previous observations with this salt. Here also the increase in pH value for a given amount of added electrolyte is less than was observed with Sol II.

Since potassium oxalate is alkaline, the question is naturally raised as to what will be the effect of rendering it slightly acid before the titration by the addition of oxalic acid keeping the total oxalate concentration the same.[1] The results of some observations with an $N/10$ oxalate solution brought to about the same pH value as the sol by adding a small amount of $N/10$ oxalic acid to $N/10$ $K_2C_2O_4$, are given in Table Xb and shown graphically in Fig. 10, the points on the curves being represented by circles.

The behavior with the potassium oxalate-oxalic acid mixture is in line with what would be expected from earlier observations of Weiser and Porter.[2] The addition of the mixture supplies a small hydrogen ion reserve which is

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[1] Cf. Thomas and Whitehead: J. Phys. Chem., 35, 27 (1931).

[2] J. Phys. Chem., 31, 1383 (1927).

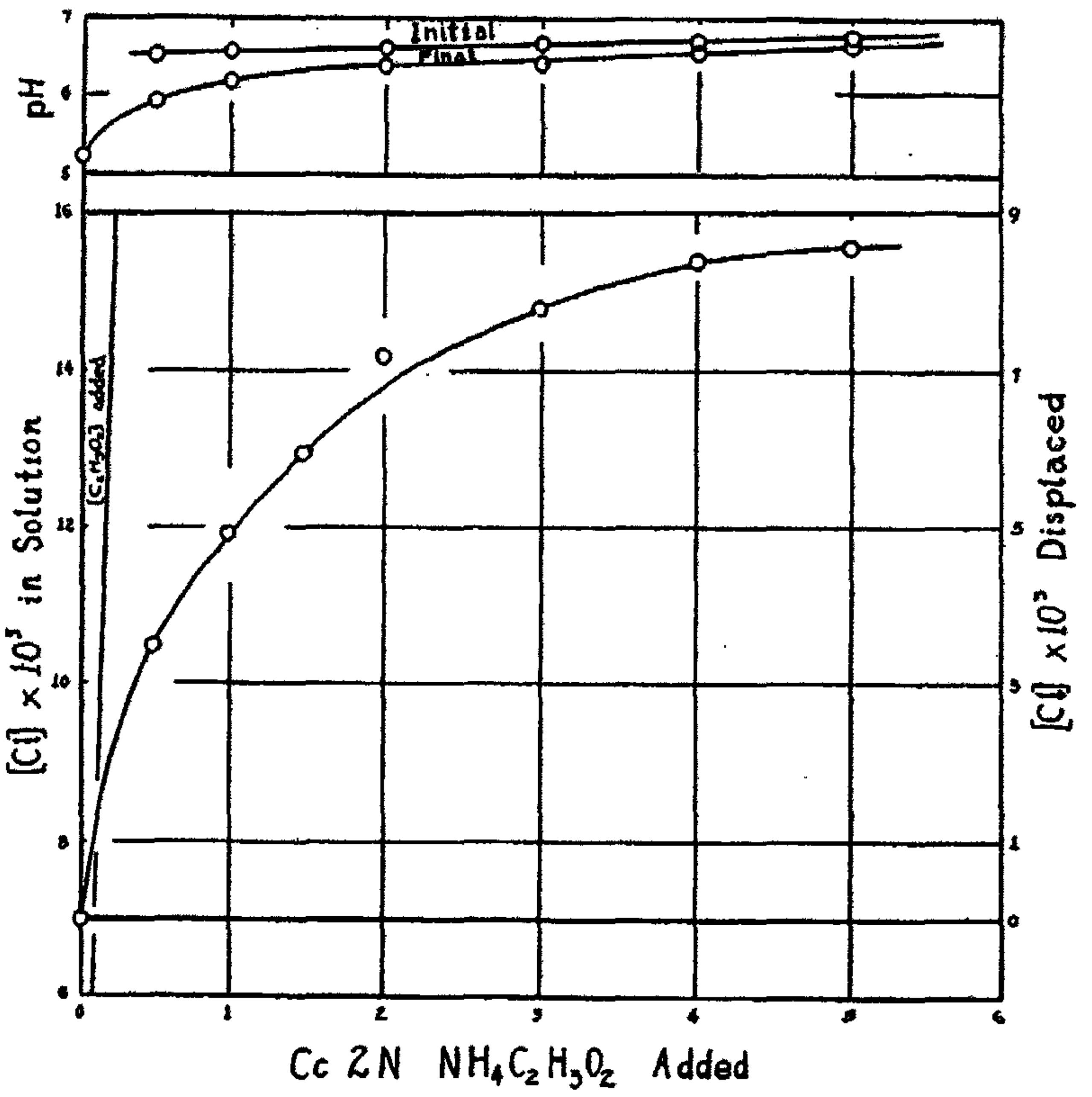

FIG. 11
Titration Curves for Al_2O_3 Sol III with 2 N $NH_4C_2H_3O_2$

TABLE Xb

Titration of Al_2SO_3 Sol III with $K_2C_2O_4$-$H_2C_2O_4$ Mixture

Cc N/10 oxalate to 20 cc sol. Total volume 25 cc	π volts	αCl⁻ $\times 10^3$	[Cl] $\times 10^3$	[Cl] displaced $\times 10^3$	½[C_2O_4] added $\times 10^3$	pH final	pH initial
0.0	0.0640	6.56	7.00	0.0	0	5.20	——
0.5	0.0620	7.09	7.56	0.56	2	5.34	——
1.0	0.0610	7.37	7.88	0.88	4	5.39	5.20
1.5	0.0592	7.94	8.51	1.51	6	5.43	——
2.0	0.0580	8.28	8.90	1.90	8	5.47	5.21
2.5	0.0549	9.35	10.09	3.09	10	5.46	——
3.0	0.0535	9.88	10.80	3.80	12	5.48	5.22
4.0	0.0511	10.85	11.80	4.80	16	6.51	5.22
5.0	0.0505	11.10	12.17	5.17	20	6.91	5.22

promptly adsorbed by the colloidal particles, a phenomenon which results in an increase in the charge on the particles and hence on the stability of the sol. Thus, the sol acts as a buffer owing to its adsorption capacity. This behavior is not unusual, as Bovie[1] has demonstrated in an interesting way the buffer action of charcoal which acts by virtue of its adsorbing capacity.

It is, of course, a mistake to assume that the oxalate concentration remains constant on mixing equivalent solutions of $K_2C_2O_4$ and $H_2C_2O_4$ since the following reaction takes place: $K_2C_2O_4 + H_2C_2O_4 \rightarrow 2KHC_2O_4$. The net result of the increased stability of the sol and the proportionately larger amount of univalent bioxalate ion in the salt-acid mixtures, is a chloride displacement curve that runs under that for $K_2C_2O_4$ and a precipitation concentration for the salt-acid mixture that is distinctly higher than for the salt alone.

The pH value curve on adding the salt-acid mixture to the sol is appreciably lower than that for the slightly alkaline salt as would be expected. But hydrogen ion is so strongly adsorbed by the colloidal particles that above the precipitation value, the pH value promptly mounts toward that of a $K_2C_2O_4$ solution although, here also, the curve runs below that when oxalate alone is used.

Titration with $NH_4C_2H_3O_2$. The data with ammonium acetate as precipitating electrolyte are given in Table XI and represented graphically in Fig. 11.

TABLE XI

Titration of Al_2SO_3 Sol III with $NH_4C_2H_3O_2$

Cc 2 *N* $NH_4C_2H_3O_2$ to 20 cc sol. Total volume 25 cc	π volts	$\alpha Cl^- \times 10^3$	$[Cl] \times 10^3$	$[Cl]$ displaced $\times 10^3$	$[C_2H_3O_2]$ added $\times 10^3$	pH final	pH initial
0.0	0.0640	6.56	7.00	0.0	0	5.20	——
0.5	0.0540	9.68	10.46	3.46	40	5.93	6.51
1.0	0.0508	10.97	11.92	4.92	80	6.19	6.57
1.5	0.0488	11.86	12.92	5.92	120	6.35	——
2.0	0.0465	12.97	14.22	7.22	160	6.40	6.63
3.0	0.0452	13.64	14.82	7.82	240	6.50	6.66
4.0	0.0445	14.02	15.44	8.44	320	6.57	6.71
5.0	0.0443	14.13	15.55	8.55	400	6.62	6.74

The chloride displacement curve follows the same general course as observed with Sol II. By comparison with Fig. 6 it will be seen that the amount of chloride displaced by the same concentration of acetate is relatively greater with the sol under observation than with Sol II.

The pH values of the sol-acetate mixtures are, of course, higher than for the sol alone, approaching that of the pure electrolyte when high concentrations are added.

Titration with KNO_3. The titration data in Table XII which are plotted in Fig. 12, show that the displacing action of nitrate like that of acetate is

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[1] J. Med. Research, 33, 295 (1915).

TABLE XII

Titration of Al_2O_3 Sol III with KNO_3

Cc $N/10$ KNO_3 to 20 cc sol. Total volume 25 cc	π volts	αCl⁻ × 10³	[Cl] × 10³	[Cl] displaced × 10³	[NO_3] added × 10⁵	pH final	pH initial
0.0	0.0640	6.56	7.00	0.0	0	5.20	——
0.5	0.0585	8.14	8.73	1.73	40	5.39	——
1.0	0.0584	8.16	8.75	1.75	80	5.46	6.19
2.0	0.0582	8.22	8.82	1.82	160	5.50	6.22
3.0	0.0575	8.45	9.08	2.08	240	5.51	6.27
4.0	0.0590	7.97	8.54	1.54	320	5.51	6.27
5.0	0.0600	7.67	8.21	1.21	400	5.51	6.28

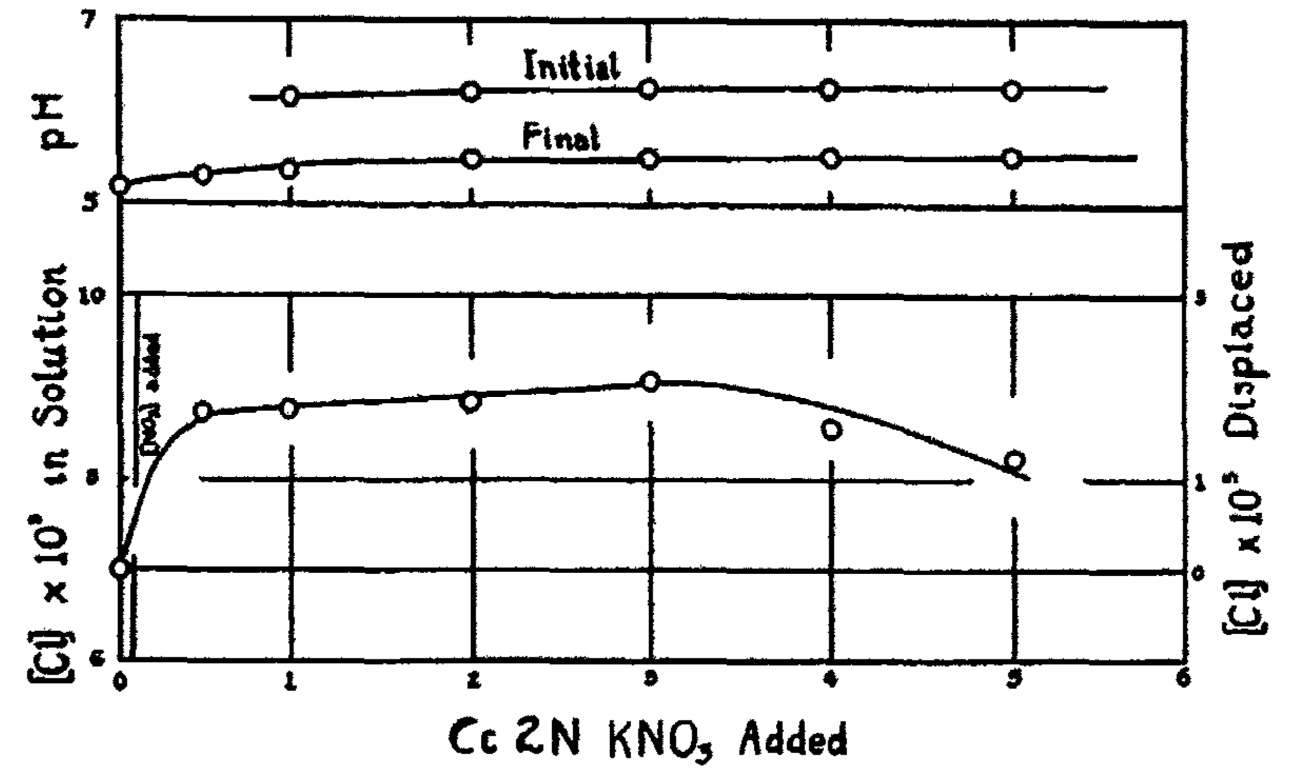

FIG. 12
Titration Curves for Al_2O_3 Sol III with 2 *N* KNO_3

greater for the sol under observation than that for Sol II. Unfortunately the limitations of the potentiometric measurements do not give the true course of the chloride displacement at the higher concentrations of KNO_3. As would be expected the pH value changes but little during the coagulation process.

Summary. A summary of the observations on chloride displacement and pH value for the same normal concentration of KNO_3, $NH_4C_2H_3O_2$, K_2SO_4, and $K_2C_2O_4$ is given in Fig. 13. As already pointed out, the data with $K_3C_7H_3O_6$ are not strictly comparable with those of sulfate and oxalate and so are not included in the figure. If the citrate solution contained largely trivalent ions the first part of the chloride displacement curve with this salt would be appreciably higher than that for the same normal concentration of divalent ions. The order of chloride displacing power below the precipitation concentration for the sol is: citrate > sulfate > oxalate > acetate > nitrate. Above the precipitation value where the supernatant oxalate solution becomes less acid, oxalate and sulfate exchange places. This is due to the fact that the oxalate solution contains relatively more of univalent bioxalate ion in the more acid range and relatively more of the strongly adsorbed bivalent oxalate ion in the less acid range beyond the precipitation value. The displacement curve with oxalate never rose above that for sulfate when the more acid Sols I and II were used.

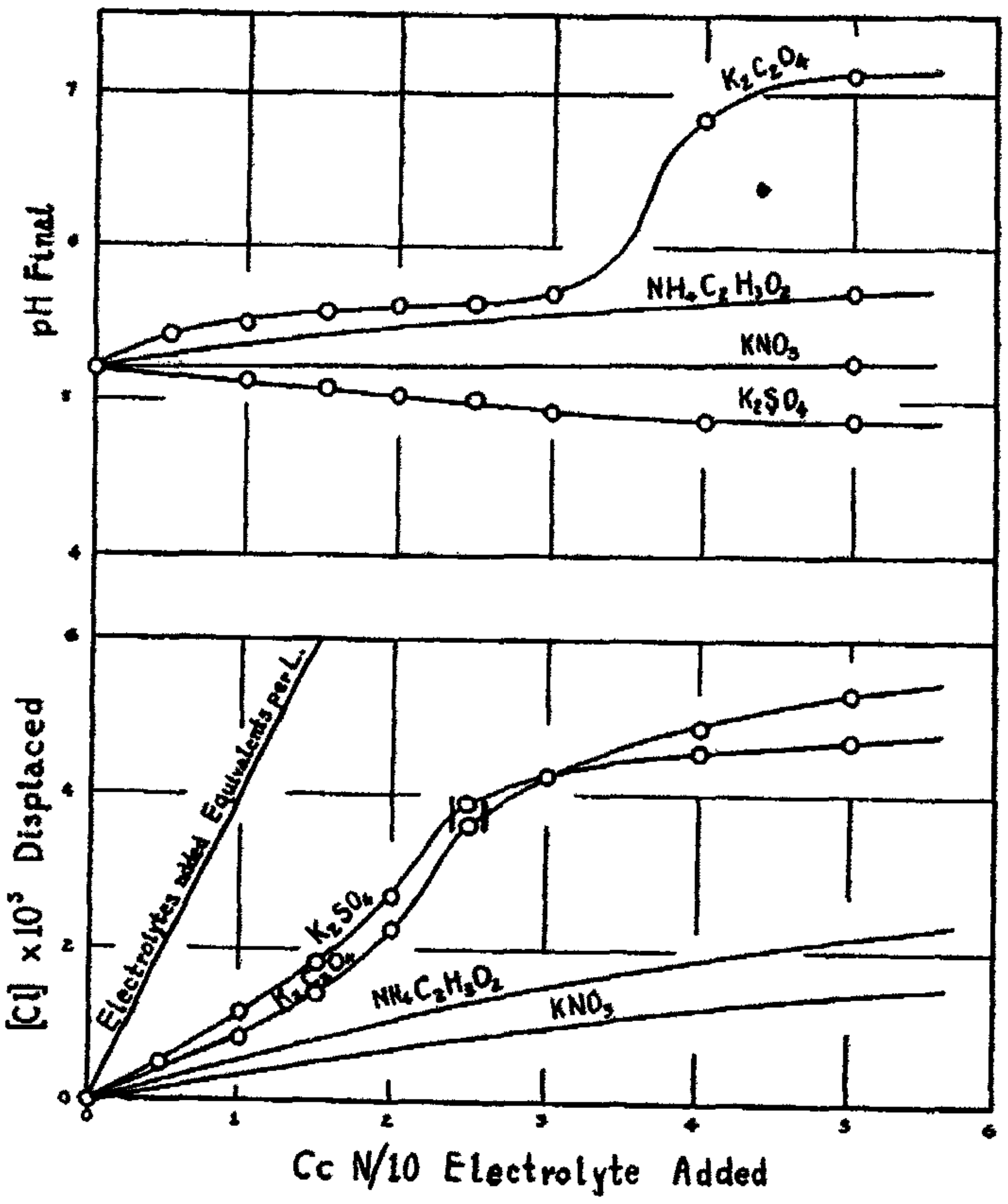

FIG. 13
Comparison of Titration Curves for Al_2O_3 Sol III with Different Electrolytes

The order of precipitating power of the several salts is: citrate > sulfate > oxalate > acetate > nitrate. This order is identical with the order of chloride displacing power.

A comparison of the pH value and chloride displacement curves on adding the several electrolytes to alumina sols reveals a distinct difference in the order. Thus the order in which the alkali salts increase the pH value of the several sols is: citrate > oxalate > acetate > nitrate > sulfate. It will be recalled that the addition of sulfate actually raises slightly the pH value of Sol III and that nitrate has but little effect. As would be expected, the most marked tendency to raise the pH value of the acid sols is manifested by the electrolytes with a buffering action, by virtue of their alkali reserve. It should be pointed out that it is not strictly accurate to compare the pH value curves in the region just above and below the precipitation concentration of salts having multivalent anions with the curves for the same equivalent concentration of the salts of univalent ions, since such concentrations of the latter salts affect the stability of the sol much less than the former and so influence the adsorption equilibria to a much smaller extent. The order at the precipitation concentration is: acetate > citrate, oxalate > nitrate > sulfate.

Effect of Ageing on the pH Value of Sols

In the introductory paragraphs it was pointed out that ageing a hydrous oxide sol leads to some coalescence and agglomeration of particles and a decrease in their hydrous character with a consequent decrease in specific surface. This should result in a falling off in the pH value of a sol stabilized by preferential adsorption of hydrogen ion, owing to the release of some of the adsorbed ions accompanying the decrease in surface. This change should be less in a sol that had been heated in the course of preparation than in one prepared at room temperature. Some observations made in the course of this investigation which have been brought together in Table XVIII support the above conclusions. With none of the sols was there any indication of an increase in pH value on standing such as Thomas and Whitehead observed with sols peptized by HCl. As already suggested it seems probable that the initial increase which they observed resulted from removal of H ions by direct action of the acid with the oxide.

TABLE XVIII

Sol I Peptization of grown Al_2O_3 with $AlCl_3$		Sol II Peptization of grown Al_2O_3 with $AlCl_3$		Sol III Hydrolysis of $AlCl_3$ followed by hot dialysis	
Time	pH value	Time	pH value	Time	pH value
2 days	4.42	1 day	4.35	1 day	5.23
3 weeks	4.31	3 weeks	4.20	2 weeks	5.20
3 months	4.03	2.5 months	4.01	2 months	5.12

Structure of the Alumina Micelles

The experimental results given above confirm and extend the observations made on ferric oxide sols. To account for the behavior of alumina sols, during the process of coagulation by electrolytes, the structure of the colloidal particle may be represented diagrammatically as in Fig. 14. Exclusive of the

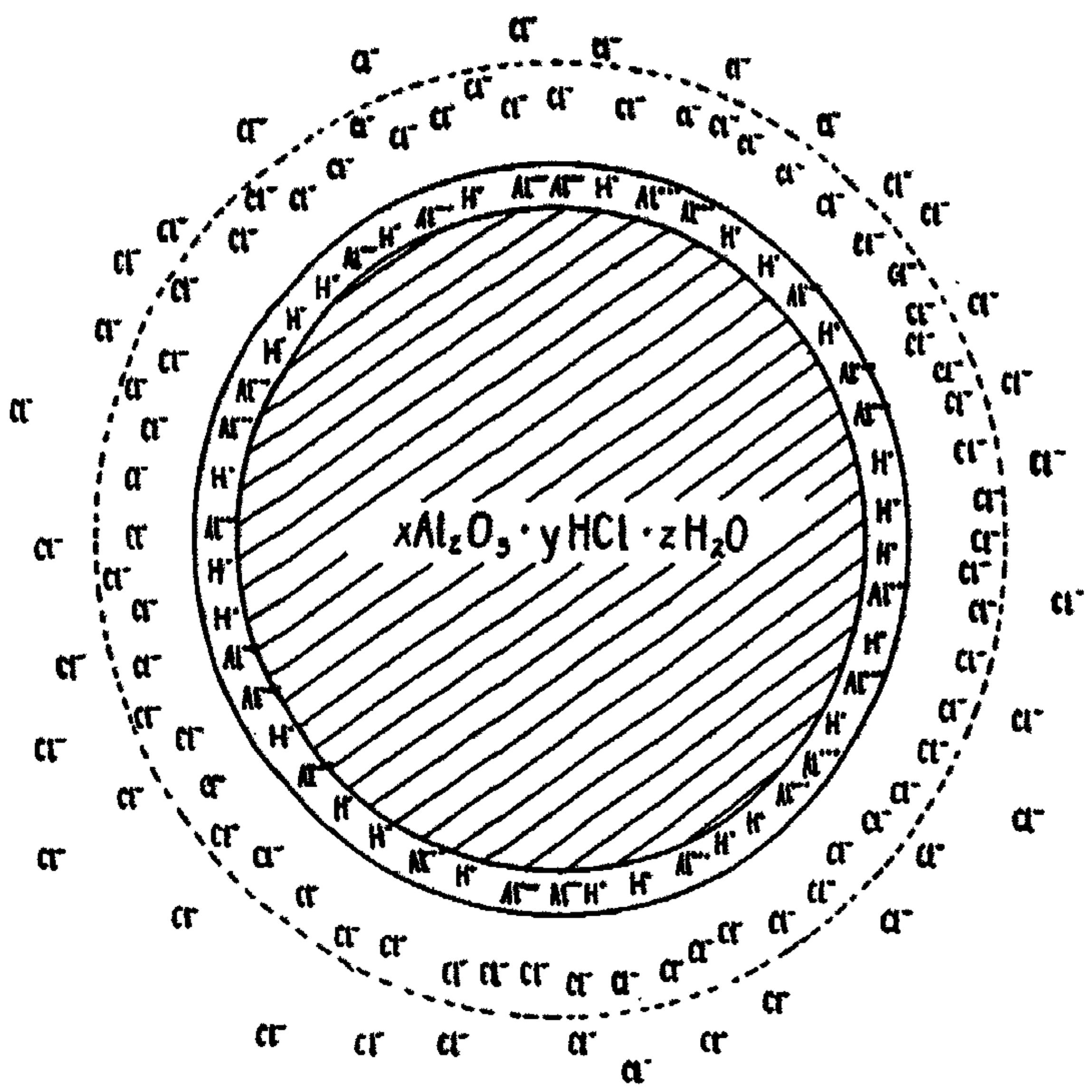

FIG. 14

Diagrammatic representation of the constitution of an alumina micelle stabilized by preferential adsorption of $H^{\cdot}$ and $Al^{\cdot\cdot\cdot}$ ions. The Cl' ions beyond the dotted circle can be estimated potentiometrically.

outer layer the composition can be indicated by some point in the three component diagram $Al_2O_3 \cdot HCl \cdot H_2O$. Since the relative amounts of the several components vary with the conditions of formation, the composition is formulated: $xAl_2O_3 \cdot yHCl \cdot zH_2O$. The outer capsule is an ionic double layer. The inner portion of this layer consists of adsorbed hydrogen and aluminum ions in adsorption equilibrium with the cations in the intermicellar liquid. The outer portion consists of a diffuse layer of chloride ions most of which are held by the electrostatic attraction of the adsorbed positive inner layer; but a part of which, because of a relatively higher kinetic energy, exert sufficient osmotic repulsive force against the attraction of the double layer to influence the calomel electrode and so may be detected potentiometrically. The latter ions are represented in the diagram beyond the dotted line.

This diagrammatic representation of the structure of the micelle indicates the source of its positive charge, its variability in composition, and the fact that not all of the chloride is readily displaced by the addition of other ions. If a salt with a multivalent anion such as potassium sulfate is added to the sol, there is a change in the double layer which is represented diagrammatically in Fig. 15. The strongly adsorbed sulfate ion goes into the double layer closer

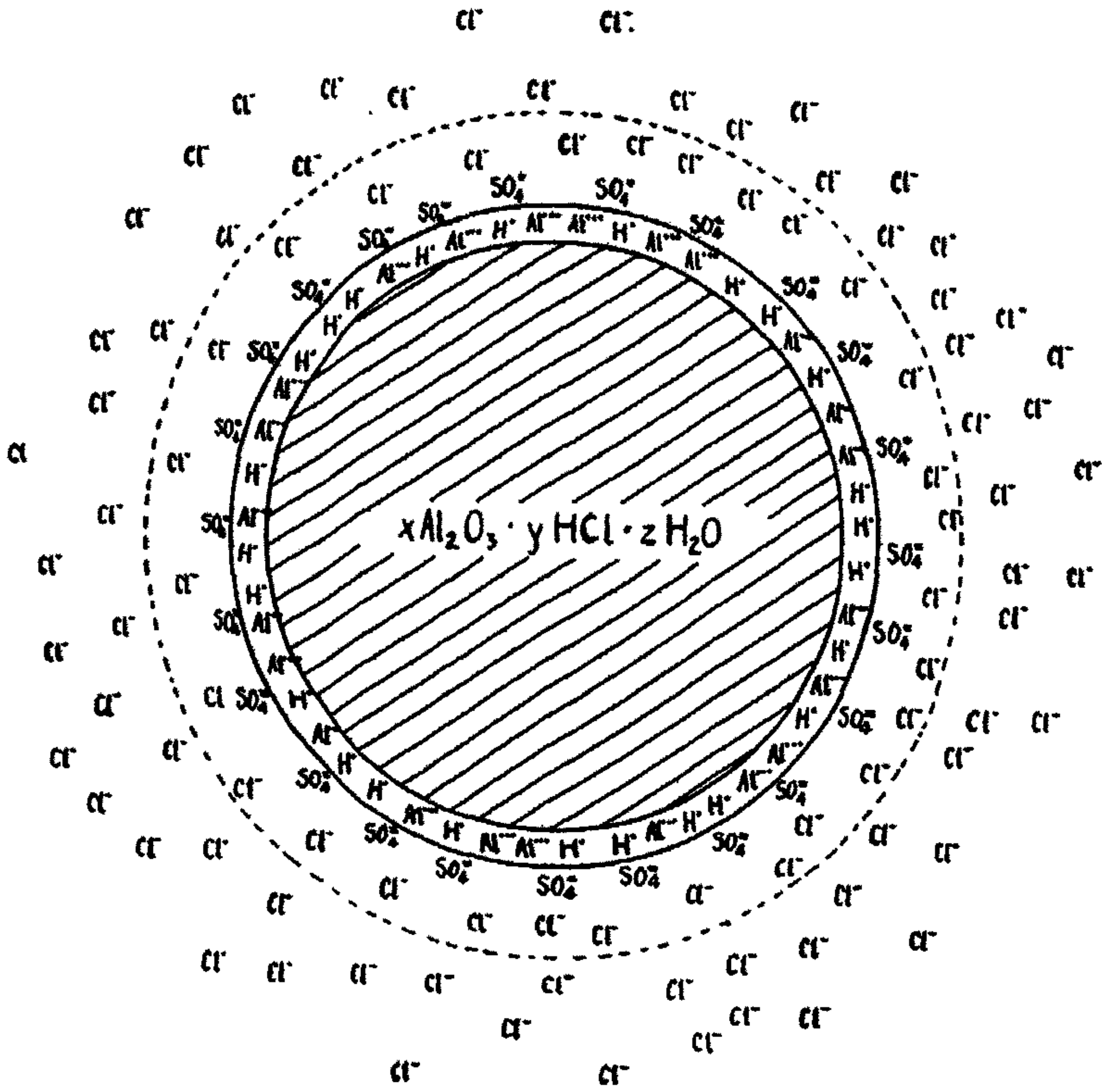

Fig. 15
Diagrammatic representation of the constitution of the alumina micelle shown in Fig. 14 after the addition of sulfate.

to the inner layer and displaces chloride as indicated. The differences between the chloride measured potentiometrically in the original sol and that after the addition of sulfate represents the amount of chloride displaced by sulfate. A glance at the several curves discloses that in all cases the amount of chloride displaced is less than the amount of electrolyte added. Thus in the case of sulfate the displaced chloride is less than one-half the equivalent of sulfate added. Since up to and including the precipitation value most of the sulfate is adsorbed, it may be wondered why an equivalent amount is not displaced. The reason is that a part of the sulfate which enters the layer corresponds to chloride measured potentiometrically in the original sol. At the precipitation value of the strongly adsorbed multivalent ions, the amount of chloride in the supernatant solution approximates that of the multivalent ion adsorbed. But the observed concentration of chloride is the sum of that originally present and that displaced in the adsorption process.

The lowering of the charge on the particles following the addition of small amounts of multivalent ions is due to the much stronger adsorption of multivalent ions than that of univalent chloride. The result is that the adsorbed ions are drawn closer to the inner layer, as indicated in the diagram, thus reducing the thickness of the double layer. Since the potential difference between two layers of opposite sign with constant charge density is directly proportional to the distance between them, it necessarily follows that the thinner layer will have a lower charge. In case the adsorbability of ions is determined by valency alone, multivalent ions will have a stronger discharging action than univalent ions because the larger charge on the former will cause them to be attracted more closely to the inner layer with the consequent lowering of charge. As is well known, a similar discharging action with univalent precipitating ions takes place only at relatively high concentrations.

The lowering of the charge on the particles results in coalescence and agglomeration of the particles with a consequent decrease in specific surface. This manifests itself in an increase in the amount of chloride displaced for a given increment in the multivalent ion added as the region of rapid coagulation is approached. Hence the upward bend in the chloride displacement curve with multivalent ions, which becomes more marked in the region of rapid coagulation. Above the coagulation point, the chloride is displaced from the precipitate by exchange adsorption without any marked decrease in specific surface and the curve follows the usual course of the adsorption isotherm. This combination of conditions accounts for the S-shape of the chloride displacement curve with all electrolytes having a high precipitating power and causing rapid coagulation above a critical concentration.

Electrolytes with relatively low precipitating power which do not cause rapid coagulation, in a critical zone, give chloride displacement curves which follow throughout the course of the adsorption isotherms as a result of exchange adsorption and gradual coagulation.

The adsorption of the added anions by the colloidal particles will tend to increase the adsorption of cations and the agglomeration with decrease in specific surface which accompanies the lowering of the charge will tend to decrease the adsorption of both cations and anions. In the sols under observation, the adsorbed hydrogen ion is in equilibrium with a hydrogen ion concentration between 10^{-4} and 10^{-5} mols per liter. The shifting of the adsorption equilibria which accompanies the addition to the sol of a salt of a strong acid and a strong base will increase slightly, decrease slightly, or leave unchanged the pH value depending, in any given case, on the relative magnitude of the two opposing tendencies, above mentioned. With salts such as potassium citrate and ammonium acetate buffer action always renders the pH value of the sol-electrolyte mixtures higher than that of the sol alone.

There appears to be little justification for the assumption that an alumina sol formed by hydrolysis of $AlCl_3$ and dialysis is an indefinite complex poly-ol basic aluminum salt of the Werner type and that the increase in pH value on adding such salts as KNO_3 and K_2SO_4 to the sol is due to displacement of OH groups which unite with $H^{\cdot}$ to form water. Indeed the addition of K_2SO_4 to one such sol caused the pH value to decrease slightly. Finally, there appears to be no more justification for assuming that alumina sols formed by peptization of "grown" alumina with $AlCl_3$ are indefinite complex poly-ol basic aluminum chlorides than for assuming that AgCl sol formed by preferential adsorption of Ag ions is a complex silver subchloride of indefinite composition.

Summary

A study has been made of the change in chloride ion concentration and in pH value during coagulation by the stepwise addition of electrolytes to aluminum sols prepared (a) by peptization of "grown" alumina with $AlCl_3$ and (b) by hydrolysis of $AlCl_3$ and dialysis. The results confirm and extend those obtained by similar observations on ferric oxide sol. The following summary is therefore limited to results which did not appear in the study of the mechanism of coagulation of ferric oxide sol and so constitutes an addendum to the summary given in the first paper.

1. Titration curves are given which show the displacement of chloride from the micelles on adding potassium sulfate, oxalate, citrate, nitrate, and ammonium acetate, stepwise to the different alumina sols.

2. The form of the chloride displacement curve is S-shaped with electrolytes containing multivalent precipitating ions which cause rapid coagulation above a critical concentration. The amount of chloride displaced for a given increment in multivalent precipitating ion is proportionately greater as the point of rapid coagulation is approached, since the lowering of the charge causes coalescence and agglomeration of the particles with a consequent decrease in specific surface. Above the point of rapid coagulation, the chloride is displaced from the coagulum by exchange adsorption without any marked decrease in specific surface and the curve follows the usual course of the adsorption isotherm.

3. Electrolytes with univalent precipitating ions which do not cause rapid coagulation in a critical zone, give chloride displacement curves which follow throughout the course of the adsorption isotherm as a result of exchange adsorption and gradual agglomeration.

4. The adsorption of anions by the positive sols tends to increase the adsorption of cations from the intermicellar solution and the agglomeration with decrease in specific surface which accompanies the lowering of the charge, tends to decrease the adsorption of both anions and cations. In the alumina sols investigated, the adsorbed $H^\cdot$ ion is in equilibrium with 10^{-4} to 10^{-5} mols per liter of $H^\cdot$ ion. The shifting of the adsorption equilibria which accompanies the addition to the sol of a salt of a strong acid and a strong base will increase slightly, decrease slightly, or leave unchanged the pH value depending on the relative magnitude of the two opposing tendencies. All of these cases have been realized experimentally. With salts such as $K_3C_6H_5O_7$ and $NH_4C_2H_3O_2$, buffer action always renders the pH value of the sol-electrolyte mixture somewhat higher than that of the original sol.

5. Ageing the freshly formed sol releases adsorbed $H^\cdot$ ion and the pH value falls off slightly. This is due to the loss of specific surface which accompanies the gradual agglomeration of the particles and the decrease in their hydrous character.

6. For the same equivalent concentration, the chloride displacing power and the coagulating power of the anions follows the same order which is: citrate > sulfate > oxalate > acetate > nitrate.

7. For the same equivalent concentrations the order in which the several salts increase the pH value on addition to the sols is: citrate > oxalate > acetate > nitrate > sulfate. At the precipitation value the order is: acetate > citrate, oxalate > nitrate > sulfate.

8. An adsorption mechanism has been outlined to explain the effect of the addition of electrolytes to the sol on the chloride displacement, the lowering of the charge, and the change in pH value.

9. The experimental results fail to justify the assumption that alumina sols formed by hydrolysis of $AlCl_3$ and dialysis are indefinite complex poly-ol basic aluminum chlorides of the Werner type and that the increase in pH value on adding salts such as KNO_3 and K_2SO_4 is due to displacement of (OH) groups which unite with $H^\cdot$ to form water. (Thomas) In one such sol the addition of K_2SO_4 decreased the pH value.

10. There appears to be no more justification for assuming that alumina sols formed by peptization of "grown" alumina with $AlCl_3$ are indefinite complex poly-ol basic aluminum chlorides than for assuming that AgCl sol formed by preferential adsorption of silver ion is a complex silver sub-chloride of indefinite composition.

11. A method has been described for the preparation of alumina sol with any desired chloride content from alumina formed by the interaction of amalgamated aluminum and water.

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HEAT OF WETTING OF CHARCOAL AS A MEASURE OF ITS ACTIVITY[1]

BY RUDOLPH MACY[2]

The use of charcoal as a gas adsorbent in the industry and in warfare has led to a voluminous literature on the methods of determining the quality of the charcoal. Probably the most complete bibliography on adsorption by charcoal is that included in the monograph on the subject by Blüh and Stark.[3] A typical discussion of the activity of charcoal is the recent article by Lowry[4] in which it is stated that most investigators use for their measure of activity of charcoal the "adsorptive capacity" of the charcoal under certain arbitrary conditions. In this category he includes the "retentivity" as defined by Chaney[5,6] and later explained more fully by Allmand[7].

The above mentioned paper by Lowry[4] contains a good resumé and bibliography of recent work on the relationship between activation of charcoal, the capacity of the charcoal, and its surface area. It is noteworthy, however, that practically nothing is to be found in any of the English or American journals on the usefulness of the heat of wetting of charcoal as a measure of activity.

A fairly complete historical account of investigations concerning heat of wetting is to be found in the text book by Freundlich.[8] The important names in this early work described by Freundlich are Pouillet (1823), Melsens (1874), Gore (1894), Chappuis (1883) and Gaudechon (1913). More recently, Berl and Andress[9] made a study of a precise method of determining adsorption isotherms of vapors on charcoal and followed this by determination of the heat of wetting in benzene. Their assembled data and curves show that the ether isotherms for various charcoals are practically quantitatively related to the heat of wetting in benzene. Berl and Andress consider the heat of wetting to be a function of both the "saturation capacity" and "intensity factor" of the adsorbent. Herbst[10] obtained the heat of wetting in water and in benzene and found that these data were proportional to the activity of the charcoal, when the activity is based on the adsorptive ability as compared with

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[1] Contribution from the Chemical Warfare Service, Edgewood Arsenal. This problem was suggested in June, 1929 by Captain M. E. Barker, Chief of Research Division, Chemical Warfare Service.

[2] Research Division, Edgewood Arsenal, Maryland.

[3] Blüh and Stark: "Die Adsorption" (1929).

[4] Lowry: J. Phys. Chem., **34**, 63 (1930).

[5] Chaney et al: Trans. Am. Inst. Chem. Eng., **15**, 283 (1923).

[6] Chaney: Trans. Am. Electrochem. Soc., **36**, 91 (1919).

[7] Allmand: J. Soc. Chem. Ind., **47**, 370 (1928).

[8] Freundlich: "Colloid and Capillary Chemistry."

[9] Berl and Andress: Z. angew. Chem., **34**, 369 (1921); **35**, 722 (1922).

[10] Herbst: Kolloid-Z., **38**, 320 (1926).

a standard high grade charcoal. Honig,[11] also, has shown that there is a distinct relation between heat of wetting and adsorptive capacity. Alekseyevskii[12] applied the methods of Berl and Andress (loc. cit.) to discover whether the heat effects could be used to grade the value of absorbent materials for a variety of vapors. Finally, Burstin and Winkler,[13] state that there is a direct proportionality between maximum adsorption of benzene vapor and heat of wetting in benzene.

It is the purpose of this article to show that the heat of wetting in benzene is at once the most rapid and one of the best methods of determining the quality of a charcoal for gas adsorption. The heat of wetting is proportional not so much to the total adsorption capacity as stated by these earlier authors, as it is to the capacity for firmly held vapor, or retentivity. The distinction between these two capacities has been explained by Chaney (loc. cit.) as follows. Adsorption of vapor is due to two forces—

a) *Capillary, or physical, forces.* The vapor held by capillary adsorption practically has the properties of the liquid state, such as relatively high vapor pressure, and is easily eliminated either by application of vacuum or passage of dry air over the sample.

b) *Adsorptive, or chemical, forces.* Part of the vapor is held by secondary forces to the surface of the carbon. Its vapor pressure is extremely low and it can be completely eliminated only by heating. The amount of vapor held by true adsorption forces is the "retentivity."

Experimental Part

The charcoals used were of various types. A large number were obtained from commercial sources, and some were prepared at Edgewood Arsenal. The nature of the samples is described in Table II. The charcoal samples were dry-screened 8-14 mesh on Tyler Standard Screens, and in most cases they consisted of equal amounts of 8-10 and 10-14 mesh. The charcoal was dried for two hours at 150°C. before use.

The adsorption capacity, or saturation value, of the charcoal samples was determined in several ways. In all cases the capacity for benzene vapor was found by placing a weighed sample of two to five grams in a desiccator over the liquid. The temperature was that of the room and did not vary more than two degrees from an average of 25°C. The error introduced by this temperature variation was negligible considering the nature of the material being studied. Constancy in weight of the samples exposed to vapor was usually reached in about two days.

In one series of experiments the capacity of charcoal for chlorpicrin vapor was determined by the method just described for benzene, that is, by exposing weighed samples to the saturated vapor of chlorpicrin at 25°C. In another series of determinations the adsorption capacity of the charcoal was obtained

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[11] Honig: Kolloidchem. Beihefte, **22**, 345-420 (1926).

[12] Alekseyevskii: Zhurnal prikladnor Khimi (Moscow), **1**, 182 (1928).

[13] Burstin and Winkler: Przemysl Chem., **13**, 114 (1929).

at a chlorpicrin concentration in air of 47 mg./liter. This was done by passing the chlorpicrin-air mixture through a 10 cm. layer of the sample contained in a tube of 1.41 cm. diameter according to the usual procedure for measuring the service time of the charcoal. This method of determining service time has been discussed by Lamb, Wilson and Chaney.[14] After the service time had been obtained the passage of chlorpicrin through the charcoal sample at 25°C. was continued until the sample no longer gained weight. The total time required was usually less than two hours.

The retentivity values were determined by placing the saturated charcoal samples in a U-tube of 1.4 cm. diameter and passing dry air through the sample at the rate of 1000 cm. per minute for two hours at 25°C. The amount of vapor retained at the end of this treatment was arbitrarily called the retentivity. Before using this method the retentivities had been measured by a method developed by Dr. Leo Finkelstein in this laboratory, by suspending the saturated samples in a bucket from a quartz fibre spring balance according to the procedure of McBain[15] and evacuating the system to about .002 mm. Hg at 25°C. The loss of weight was followed by a telescope and cathetometer arrangement and the system kept evacuated until no noticeable loss in weight occurred for about three hours. A single experiment occupied about 25 to 40 hours, but practically the same results were obtained by passing dry air over the sample for two hours as already described, and the data were also more consistent and more easily duplicated by the latter rapid method.

As already stated, the retentivities obtained in this work are arbitrary values in that they are measured by weighing the retained vapor after air has been passed over the sample for exactly two hours. In Fig. 3 a set of curves is given which show the rate of loss of vapor under these arbitrary conditions. In two hours all the charcoals give up the loosely held vapor, and then begin to give up the remainder at a slow rate which is nearly the same for all the samples. The two hours desorption period therefore should furnish good relative retentivity values, even though the results obtained are arbitrary ones.

The apparatus required to determine the heat of wetting was found to be very simple. The usual practice in measuring the heat effect when a solid is immersed in a liquid is to use a well insulated reaction vessel, the most common apparatus for such a purpose being a Dewar flask. The preliminary experiments on heat of wetting of charcoal were accordingly made in a 200 cc. Dewar flask, fitted with a Beckmann thermometer and a glass stirrer both of which passed through a rubber stopper to prevent evaporation of the liquid. Measurements made in this way were very accurate, but tedious, and would not be appropriate for the use of routine analysis in plant control work. In order to keep all such heat measurements comparable it is necessary to start each experiment at some common temperature such as 25°C., since the specific heats vary with temperature. Temperature changes in a vacuum flask are so slow that each time fresh materials are placed in the flask a considerable period must elapse before the actual determination can be made.

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[14] Lamb, Wilson, and Chaney: J. Ind. Eng. Chem., 11, 420 (1919).

[15] McBain and Bakr: J. Am. Chem. Soc., 48, 690 (1926).

Although the heat of wetting measurements should begin at some common temperature, this fixed point can vary several degrees without having an appreciable effect on the results obtained. Furthermore, the heat of wetting determination with charcoal is very rapid, the maximum temperature rise when it is wetted being reached often in 30 seconds. Heat transfer to surroundings are therefore very slight. All that is necessary then is to use a test tube for the reaction vessel with an outer test tube to serve as an air-jacket, assembled as in an ordinary freezing-point determination. When a fresh supply of liquid at room temperature is placed in such an apparatus only a few moments elapse before it reaches a fairly constant temperature which will not be far from that of the room and can be taken as the initial temperature of the experiment. The room in which the present work was conducted seldom varied more than 2° from an average of 25°C.

The Beckmann thermometer had to be dispensed with, since it would necessitate starting each measurement at a predetermined fixed temperature, whereas it is more convenient to begin the heat measurement at whatever the temperature in the test tube might be, within a limit of 2 to 3 degrees. In its place a thermometer graduated to 0.02°C. was used, reading from 17° to 31°C.

Benzene was chosen as the wetting liquid after a study of the adsorption curves for several vapors on charcoal showed that it is one of the most highly adsorbed substances. It would therefore be reasonable to suppose that the heat effects would be comparable with other determinations on charcoal in which high adsorptive capacity is a predominant feature. Such tests are the accelerated chlorpicrin tube test, and retentivity. The volumes of charcoal and of benzene used were simply those found by trial to be most convenient in the apparatus employed. The apparatus used can be found in any laboratory. The following method of carrying out the test has been found to be satisfactory.

After pouring 20 cc. of benzene into the tube, the thermometer and stirrer were inserted and the contents stirred a few moments until the temperature was constant, and the temperature recorded to 0.01°C.

About 5 cc. of charcoal was weighed out to 0.001 g. in a slender weighing tube about 1/2 inch in diameter. The thermometer and stopper were partially lifted from the tube, leaving the stirrer loop resting at the bottom, and the charcoal was poured in rapidly. The stopper and thermometer were replaced and then on the first up-stroke of the stirrer the charcoal and benzene were well mixed. Stirring was continued vigorously, the mercury thread climbing rapidly to a maximum position. A little practice is necessary before duplicate results can be obtained. An active charcoal gives a very rapid rise (the maximum reached in less than 30 seconds); less active charcoals are characterized by a slower rise and slower fall in temperature. The maximum rise in temperature is recorded to 0.01°C. After a determination the test tube is rapidly dried by a stream of compressed air. From the weight of sample and rise in temperature the heat of wetting is calculated in °C./g. The apparent density is determined separately, and the heat of wetting is then calculated in °C. cc.

The heat capacity of the apparatus and its contents was calculated from the standard physical constants of its components, assuming an average specific heat for charcoal of 0.2 and an average weight for the sample of 2.0 grams. The water equivalent was found to be almost exactly 10.0, so that it was only necessary to multiply the heat of wetting data by the factor 10 in order to convert it to calories per g. or per cc. of charcoal. This factor is not strictly accurate because of variations in the weight of sample and specific heat of different charcoals.

Summary and Discussion of Results

Heat of Wetting and Particle Size. The effect of the size of the charcoal granules was studied, using a high grade commercial coconut charcoal. This was screened to give fractions with the mesh sizes listed in the following summary:

Mesh	Apparent Density	Sample g.	Heat of Wetting			
			°C./g.	°C./cc.	cal./cc.	cal./g.
6-8	.487	2.318	1.88	0.915	9.15	18.8
8-10	.47	2.257	2.13	1.00	10.0	21.3
10-14	.465	2.322	2.18	1.01	10.1	21.8
14-20	.455	1.827	2.15	0.98	9.8	21.5

Within the range of particle sizes usually employed, that is, 8 to 20 mesh, the variation in size has practically no effect on heat of wetting.

Relation between Heat of Wetting in Benzene, and the Maximum Adsorption and Retentivity of Benzene

The relations between these quantities are shown graphically in Figs. 1 and 2, and the data are presented in Table I. Burstin and Winkler (loc. cit.) claim that the relation between total adsorption of benzene vapor and heat of wetting in benzene is expressed by a straight-line function $A = K\,Q$, where

A is maximum adsorption in percent by weight

Q is heat of wetting in calories per gram

K is a constant, equal to 1.9 percent calories (A being expressed in parts adsorbed per 100 parts of charcoal).

A careful study of their paper indicates that they did not use more than two different commercial samples of charcoal (one made by Bayer and the other by Merck) and these were both of similar characteristics. The work reported in this article, however, is based on a wide variety of types, as shown in Table II.

In Fig. 1 the data have been plotted to agree with the system of units employed by Burstin and Winkler, the broken line representing the constant K as evaluated by these authors. In Fig. 2 the data are given on the more usual volume basis. In both diagrams it is clear that the data are more accurately represented by smooth curves rather than by straight lines, and this is also evident for the corresponding chlorpicrin results shown in Figs. 4 and 5.

Inspection of Figs. 1 and 2 proves beyond doubt that the heat of wetting is a function of the retentivity of the charcoal rather than of its adsorption capacity. This to be expected from the very nature of the experiment. The heat evolved when charcoal is wetted by liquid benzene is due to some surface phenomenon—whether it is considered to be an initial formation of a monomolecular layer or condensation in capillaries of molecular size, or both, is immaterial. It is hardly likely that penetration of the larger capillaries by the liquid would give rise to heat effects of measurable magnitude, since it is simply a sponge effect and not true adsorption.

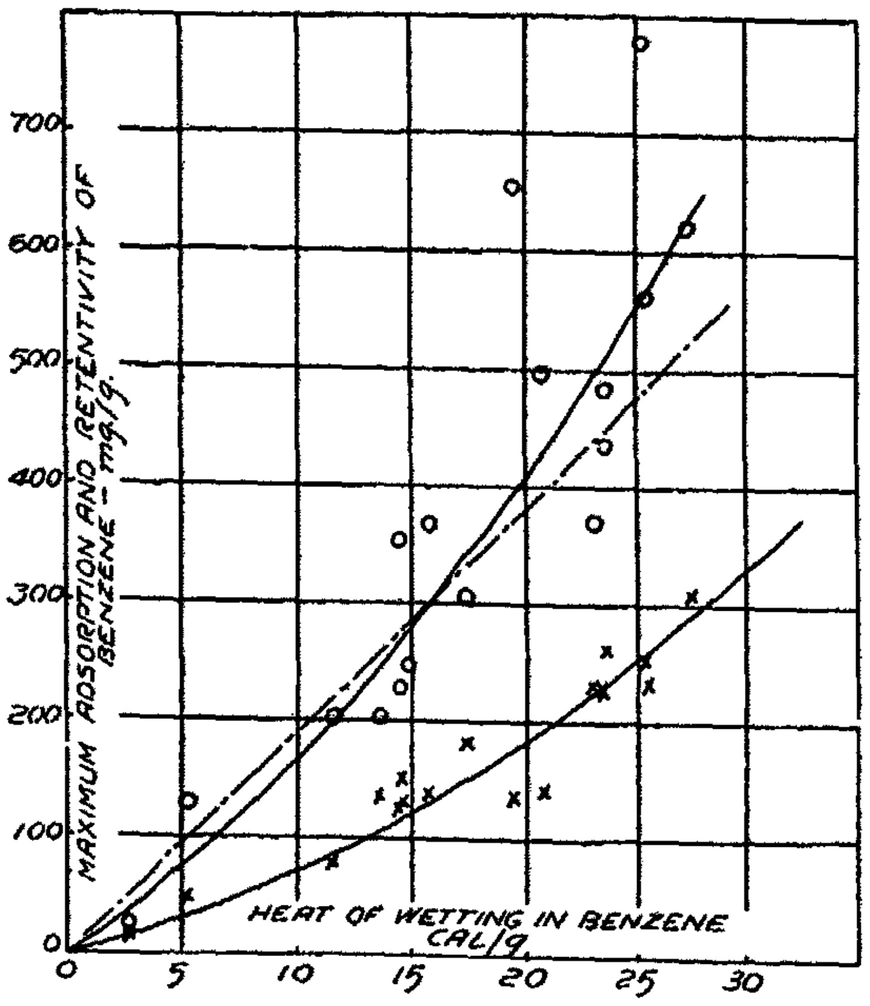

FIG. 1

Adsorption data—circles; retentivity data—crosses.

Thus, the Urbain charcoal and the sample of German charcoal in Table I have very high saturation capacities (this is more readily appreciated from Fig. 2) but these saturation values are out of proportion with their corresponding heat effects. At saturation they probably store up considerable benzene vapor in large capillaries in practically the liquid state. This excess vapor is easily lost, as shown in Fig. 3, when dry air is passed over the charcoal. The amount of vapor firmly held by Urbain and the German charcoal is, however, accurately predicted by the heat of wetting.

It is a logical conclusion, therefore, that the heat of wetting is a measure of the amount of vapor held by true adsorption forces, or retentivity.

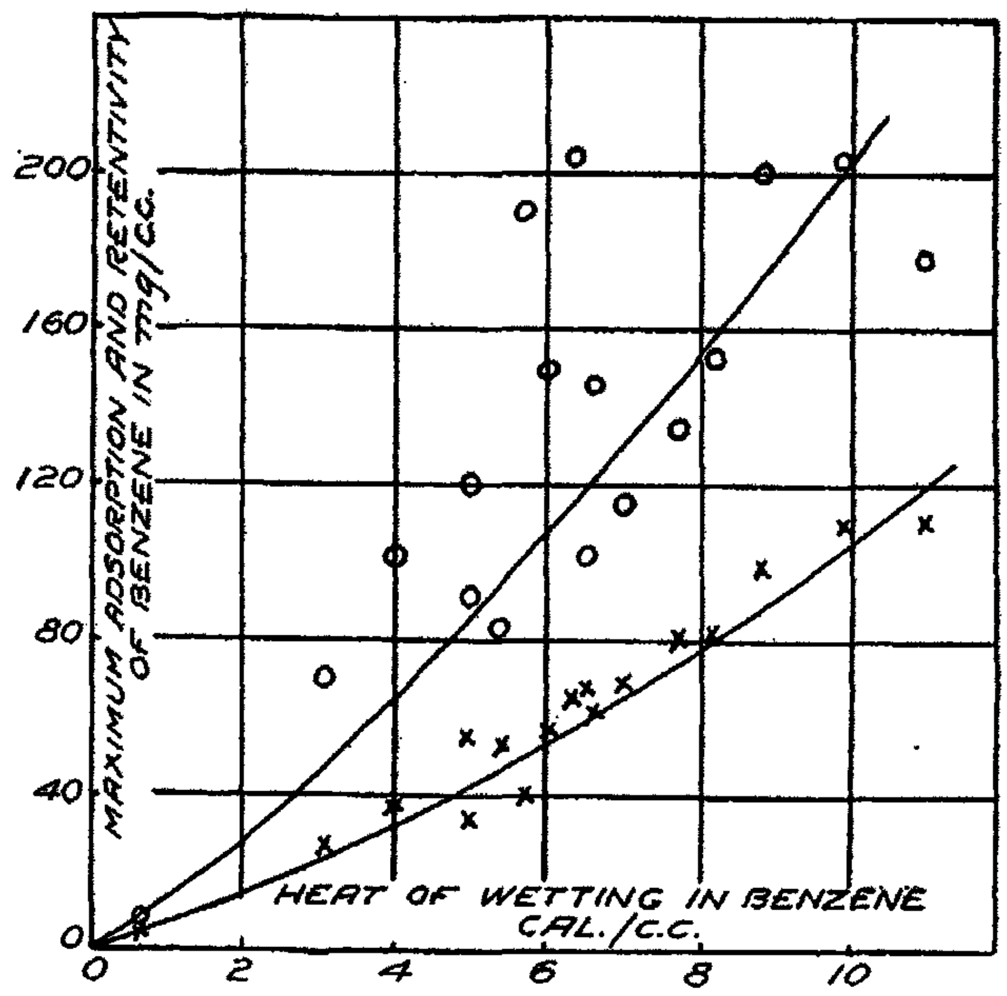

FIG. 2
Adsorption data—circles; retentivity data—crosses.

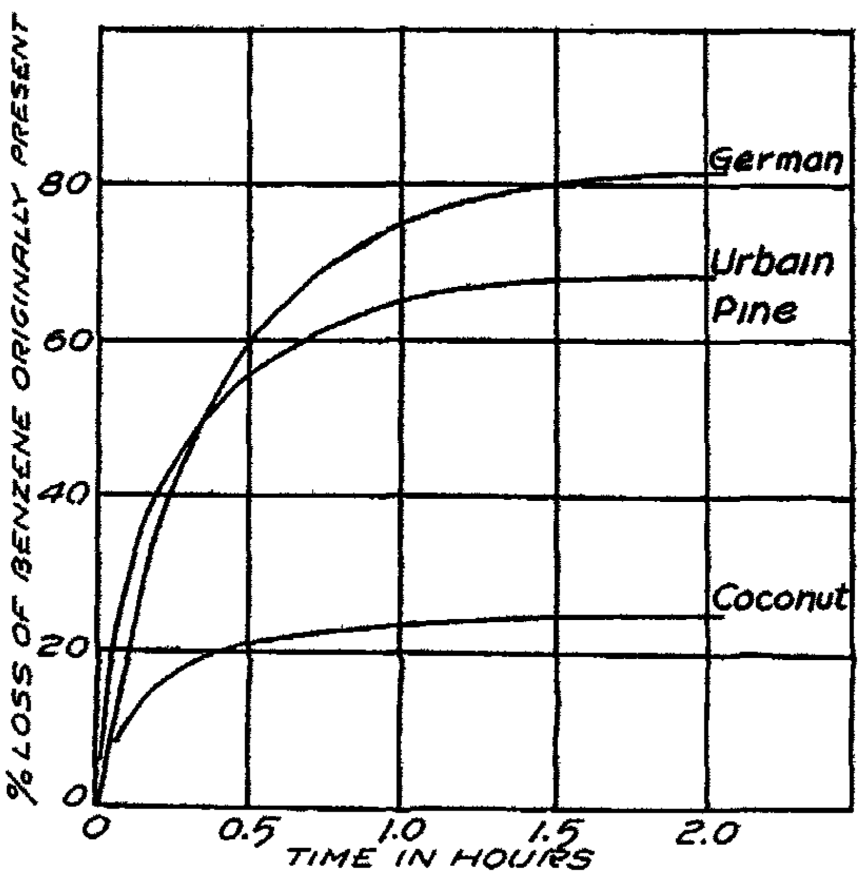

FIG. 3
Rate of loss of adsorbed benzene by charcoal in a current of dry air.

Tryhorn and Wyatt[16] found that a discontinuity occurs in the rate of adsorption of benzene vapor by a coconut charcoal when it has adsorbed 120×10^6 moles per gram, and that its total saturation is 204×10^5 moles. The break in the curve was ascribed to the sudden formation of a liquid layer. The ratio 120/204 is nearly identical with the ratio of the retentivity and saturation data given in Table I for the coconut charcoal. This confirms the assumption that the retentivity value is a measure of the adsorbed vapor which is held firmly by secondary valence bonds, while the part that is loosely held has properties corresponding to the liquid state.

TABLE I

Relation between Heat of Wetting in Benzene,
Maximum Adsorption of Saturated Benzene Vapor,
and Retentivity of Benzene at 25°C.

Sample and Number		Apparent Density	Heat of Wetting		Maximum Adsorption		Retentivity	
			cal./g.	cal./cc.	mg./g.	mg./cc.	mg./g.	mg./cc.
124	Tec-Char	.29	2.4	0.7	26	7	14	4
125	Norit	.19	15.8	3.1	367	70	137	26
108	Batchite	.78	5.1	4.0	129	101	48	37
61	Pine	.24	20.8	5.0	496	120	142	34
56	Oak	.44	11.4	5.0	206	91	128	56
24A	Ironwood	.40	13.5	5.4	206	83	135	54
120	German	.29	19.6	5.7	655	190	136	40
107	Coal Briquets	.42	14.3	6.0	354	149	135	57
101	Urbain	.25	25.2	6.3	780	203	258	65
23	Ironwood	.45	14.5	6.5	227	102	150	68
39	Maple	.26	25.4	6.6	560	146	234	61
126B	Oak	.44	17.5	7.7	307	135	184	81
15A	Ironwood	.47	14.9	7.0	244	115	148	70
38	Oak	.35	23.4	8.2	437	153	233	82
50B	Oak	.32	27.5	8.8	623	200	310	99
51A	Oak	.42	23.6	9.9	486	204	263	110
102	Coconut	.48	23.0	11.0	371	178	231	111

TABLE II

Nature of Charcoals listed in Table I and Figs. 4 and 5

Name	Description
Tec-Char	—A wood charcoal made by the Tennessee Eastman Corporation. Serial No. K-200.
Norit	—A commercial decolorizing charcoal made from wood.
Batchite	—The generic name for steam activated anthracite coal.
Pine	—Made by carbon dioxide activation of yellow pine.
Oak	—Made by carbon dioxide activation of oak.

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[16] Tryhorn and Wyatt: Trans. Faraday Soc., 22, 134 (1926).

Table II (Continued)

Nature of Charcoals listed in Table I and Figs. 4 and 5

Name	Description
Maple	—Made by carbon dioxide activation of maple.
Ironwood	—Made by carbon dioxide activation of ironwood.
Coconut	—Made by steam activation of coconut shells. Commercial samples were obtained from: Barneby-Cheney Engineering Co., Columbus, Ohio. National Carbon Company, Cleveland, Ohio. Carbide and Carbon Chem. Corporation, New York
German	—From a German world-war canister; probably made by zinc chloride impregnation and subsequent activation of wood
Coal Briquets	—Made from a mixture of hard and soft coals, steam activated.
Urbain	—Briquetted lignite coke, made by the Urbain Corporation of Niagara Falls, N. Y.
Lamp Black	—Made by steam activation of lamp black briquetted with a sugar binder.
Aqua Dag Graphite	—Made by neutralizing Acheson's Aqua Dag, filtering, washing, drying, and crushing to 8-14 mesh.

Relation between Heat of Wetting in Benzene, and the Maximum Adsorption and Retentivity of Chlorpicrin Vapor

The discussion of these three factors leads to exactly the same conclusions which have been expressed in the preceding section, that is, the heat of wetting of charcoal is proportional more to its retentive capacity than its adsorptive capacity. The data obtained on the adsorption and retentivity of chlorpicrin are so numerous that it was not thought advisable to use up space by a tabulation of the results when they could be adequately represented diagrammatically. Most of the data obtained are shown in Fig. 4 and Fig. 5, all the results being plotted on a volume basis.

The adsorption capacities in Fig. 4 were all obtained by exposing the samples to saturated chlorpicrin vapor at 25°C. In many cases the capacity was measured in a stream of chlorpicrin vapor, as described in the experimental part; the results obtained showed that condensation of liquid chlorpicrin on the charcoal in saturated vapor probably did not take place since the relative capacities obtained were proportional to the concentration.

In Figs. 4 and 5 the average curves drawn were influenced principally by the data for coconut charcoal since that is the standard type by which the quality of other charcoals is judged. The most striking proof that heat of wetting is a function of retentivity and not of capacity is given by the data on a sample of Acheson Aqua Dag, which is really not a charcoal but a high grade of graphite. The material had been treated as described in Table II.

The heat of wetting of this graphite was very small, yet it had an adsorption capacity equal to that of a fairly good coconut charcoal. Its retentivity, on the other hand, was practically zero, in agreement with the heat of wetting.

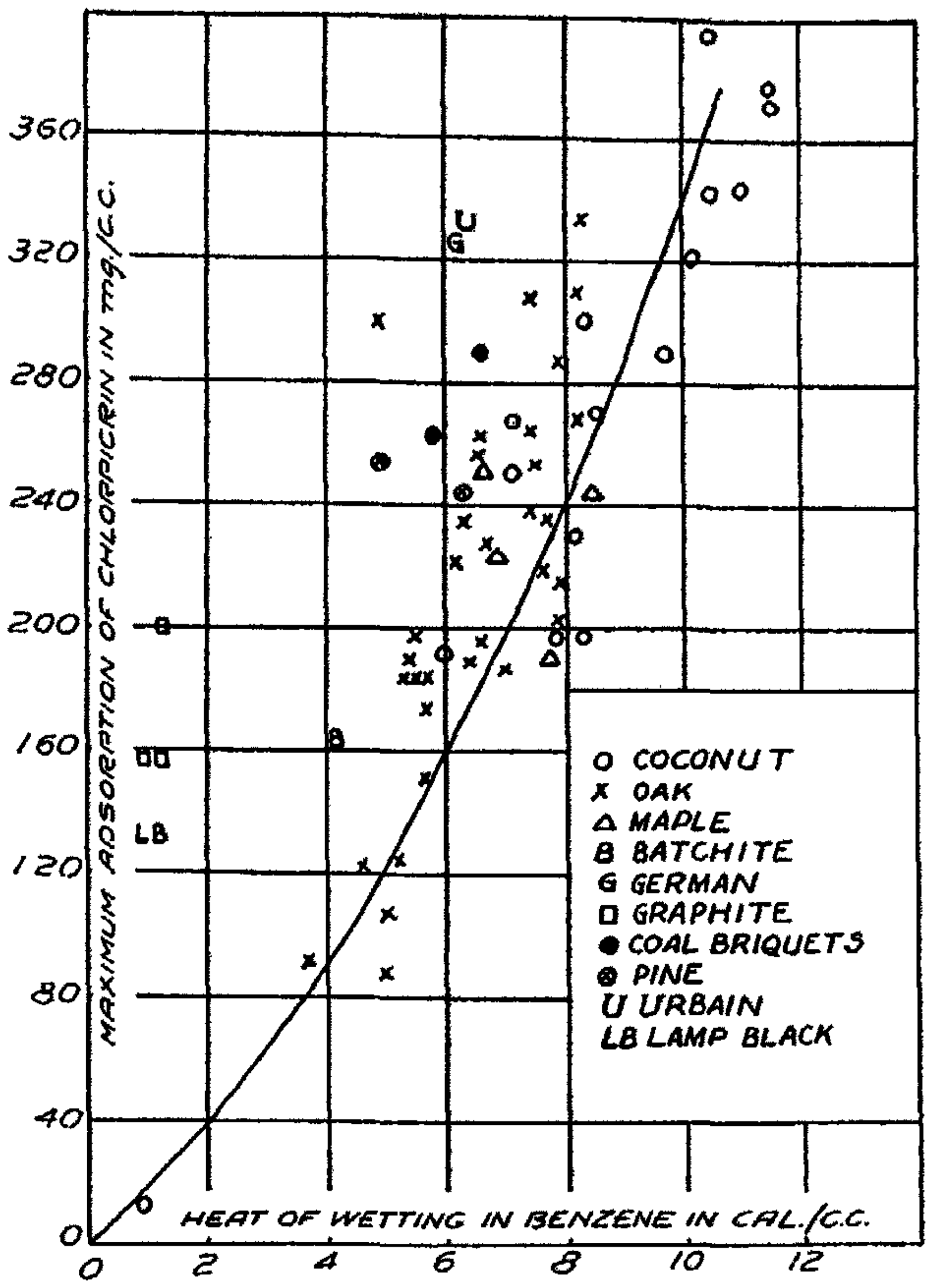

FIG. 4
Relation between heat of wetting in benzene and maximum adsorption of saturated chlorpicrin at 25°C.

Relation between Heat of Wetting and Surface Area of Charcoal

The data presented in this paper show that there is a proportionality between the heat of wetting of charcoal and its retentive capacity. In Chaney's[5,6] definition of retentivity there is the implied assumption that the retentivity of charcoal is determined by the extent of its surface. This idea appears to have a fairly wide acceptance. If this is true then the heat of wetting is a measure of the available surface of the charcoal as well as the retentive capacity. While this article was being written for publication, two other papers have appeared in which the authors also express the opinion that heat of wetting is a function of surface area.

Berl and Burkhardt[17] measured the heat of wetting of a series of activated charcoals, and also measured the adsorption of methylene blue from solution according to the procedure of Paneth and Radu.[18] According to the latter authors methylene blue probably forms a monomolecular film on charcoal and can be used to estimate the surface area of the adsorbent. The heat of wetting and methylene blue adsorption were found to be roughly equivalent; a heat of wetting of 1°C. produced by 1.5 g. of charcoal and 10 cc. of benzene is proportional to a surface area of 60 square meters per gram.

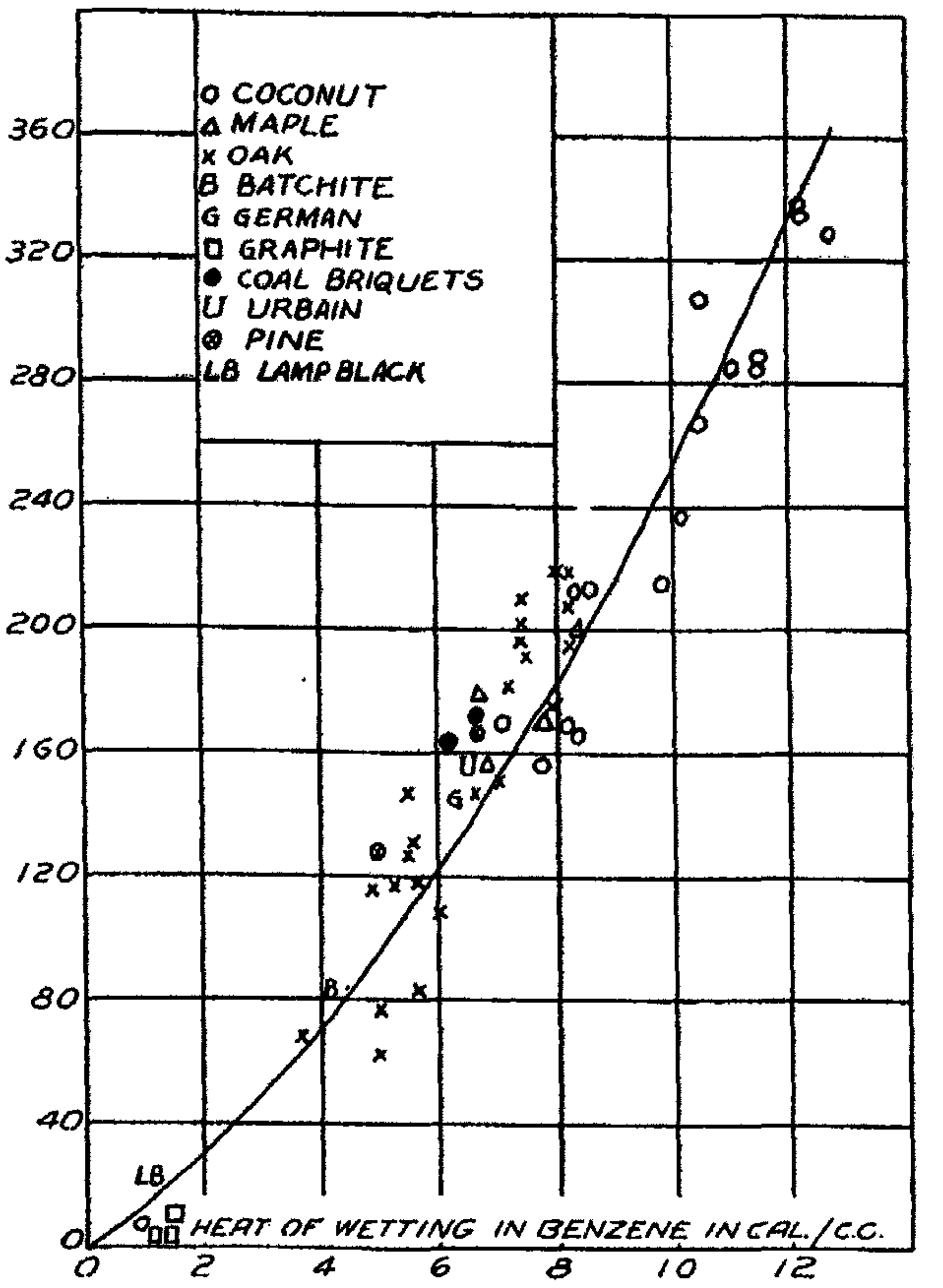

FIG. 5

Relation between heat of wetting in benzene and retentivity of chlorpicrin at 25°C.

Bartell and Fu[19] have made a study of the various methods of measuring the surface area of charcoal and silica gel, and showed that the surface area

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[17] Berl and Burkhardt: Z. angew. Chem., 43, 330 (1930).

[18] Paneth and Radu: Ber., 57, 1221 (1924).

[19] Bartell and Ying Fu: Colloid Symposium Annual, 7, 135.

can be calculated from heat of wetting and adhesion tension. "This method of determining surface area does not depend on the measurement of adsorption from solution; it is, therefore, free from those uncertainties which arise from the use of doubtful assumptions concerning the shape and dimensions of the adsorbed molecules, and the unknown thickness of the adsorbed layers." They obtained a value of 635 square meters for the specific surface of charcoal, which is higher than most values recorded in the literature.

When the above values published by Berl and Burkhardt are recalculated to the same basis on which the heat of wetting was determined in the present work, it is found that a heat of wetting of 1°C. per gram of charcoal is equivalent to a specific surface of 180 square meters. This is in good agreement with the value of 200 square meters calculated from the following data for a high grade commercial coconut charcoal. The calculation is based on the assumption that chlorpicrin retentivity is a measure of the amount covering the charcoal in a monomolecular layer:

Heat of wetting = 2.64°C./g. in 20 cc. of benzene.
Chlorpicrin Retentivity = 330 mg./cc. = 718 mg./g.
Cross-Section Area of Chlorpicrin Molecule = 20 square Ångstrom units (an average figure for molecules in thin films given by Adam, International Critical Tables 4, 476).
Area covered by chlorpicrin = 528 sq. m./g. of charcoal.
Heat of wetting of 1°C./g. is equivalent to 200 sq. m./g.

The above sample of coconut charcoal is one of the best obtainable commercially. Its specific surface area of 528 sq. m. is in fairly good agreement with that found by Bartell and Fu for a sugar charcoal, and the proportionality between heat of wetting and specific surface area is in good agreement with the above-mentioned finding of Berl and Burkhardt. In Table I about six charcoal samples will be found which have a heat of wetting on a weight basis close to that of the above sample of coconut charcoal; these samples include oak, Urbain, and maple charcoals. The heat of wetting in cal./g. in Table I should be divided by 10 to give the corresponding °C./g. values. On a volume basis, however, these charcoals are not so good as the coconut.

Before concluding, it is desired to point out an important factor which has not yet been touched on in this discussion. In the course of this work, after much experience in the manipulation of the apparatus had been acquired, it was found that some charcoals when poured into benzene caused a much more rapid rise in temperature than others. The more active charcoal in this respect usually was found to be better in all other respects. In several cases the time required for the total rise in temperature after mixing was noted with a stop-watch; the following experiment is typical:

Charcoal	Sample cc.	Rise in Temperature			Heat of Wetting °C./cc.	Chlorpicrin Retentivity mg./cc.
		Time Sec.	°C.	°C./cc.		
20 Oak	5.35	21.4	2.66	0.023	0.50	76
43Ab Oak	5.00	14.0	2.46	0.035	0.49	115

These two samples with the same heat of wetting show a much different activity when dropped into the benzene, and the sample which produces a more rapid evolution of heat also has a higher retentive capacity. This and a few similar experiments may be explained by the assumption that the heat of wetting measures the surface area of the charcoal but not the activity of the surface. This explanation is in accord with a statement of Lamb and Coolidge[20] who found that "the heats of adsorption of vapors are very nearly the same on inactive as on active charcoals of the same kind." This is equivalent to stating that the activity of the surface does not affect the total evolution of heat when vapors are adsorbed by charcoal. Unfortunately, further work on this problem was discontinued before the results obtained were sufficient to give any definite conclusions.

Conclusions

The literature has been reviewed on the determination of the heat of wetting of charcoal. Data are presented which agree with statements of other authors that the heat of wetting in benzene is a good rapid test of the value of charcoal as a gas adsorbent. However, it is shown that the heat of wetting is not a function of the adsorption capacity of charcoal, but of the capacity for firmly held vapor, or retentivity. It is probable that the heat of wetting in benzene, and the retentivity of adsorbed vapor, are a measure of the surface area of charcoal.

Edgewood Arsenal,
Edgewood, Md.
August 1, 1930.

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[20] Lamb and Coolidge: J. Am. Chem. Soc., 42, 1146 (1920).

STUDIES IN THE SOLUBILITIES OF THE SOLUBLE ELECTROLYTES

V. An Estimation of the Radii of Ions in Saturated Solutions

BY ARTHUR F. SCOTT

For any given temperature the apparent molal volume φ of a salt in a saturated solution containing one mol of salt is defined by the expression

$$\varphi = V - Nv_1 \qquad (1)$$

where V is the volume of the solution; N is the number of mols of water in the solution; and v_1 is the volume of one mol of pure water.

In a previous paper[1] it was shown that for extremely soluble salts the following relationship between φ and N is presumably valid:

$$\varphi = aN^2 + b \qquad (2)$$

The constants a and b are characteristic of each salt. The latter constant b is particularly important because it is the apparent molal volume of the salt when no water is present. Moreover, if the change in φ with temperature is regarded as the consequence only of a change in the volume of the water present in the saturated solution, b may be looked upon as the volume of the ions of a salt in the saturated solution. In the paper already referred to values of b were calculated for eight alkali salts and in magnitude they were found to be larger than the space occupied by the ions in a crystal lattice and smaller than the effective volumes of the ions in dilute solutions. In the present article these considerations have been extended to permit an estimation of the radii of the individual ions. Such an estimation appears possible by making use of a new empirical relationship from which can be calculated the limiting volume $\bar{v}$ which contains the ions of volume b. Since the ratio $b/\bar{v}$ is of the order of magnitude found for the crystalline state, we can, by assuming that the ions are arranged in a specific lattice, compute definite values for the radii of the ions.

We shall first consider the following empirical relationship between V and N at the same temperature:

$$V^{2/3} = \alpha N + \beta \qquad (3)$$

In order to test this relationship Fig. 1 has been constructed by plotting the experimental data for eight alkali salts. The essential data for this graph are collected in Table I. An examination of Fig. 1 shows that the plotted points for each salt, with very few exceptions, fall directly on a straight line. This method of plotting is, however, not very sensitive to experimental errors in the basic density and solubility measurements. Errors in density measurements will affect only the $V^{2/3}$ term but, since they are much smaller than errors

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[1] Scott and Durham: J. Phys. Chem., 34, 2035 (1930).

TABLE I
$V^{2/3}$ and N Values of Salts at Different Temperatures (Fig. 1)

Temp. °C.	CsCl[1]		RbCl[1]		$NaNO_3$[1]	
	$V^{2/3}$	N	$V^{2/3}$	N	$V^{2/3}$	N
0	27.9	5.76	33.4	8.73	28.07	6.45
20	26.4	5.01	30.7	7.36	25.83	5.36
40	25.3	4.49	28.9	6.47	23.98	4.50
60	24.5	4.08	27.6	5.81	22.41	3.79
80	23.8	3.74	26.5	5.27	21.08	3.20
100	23.2	3.45	25.7	4.84	19.85	2.68

	NaBr[2]		NaI[2]		KBr[2]		KI[2]	
	$V^{2/3}$	N	$V^{2/3}$	N	$V^{2/3}$	N	$V^{2/3}$	N
0	28.82	7.13	25.78	5.20	40.35	12.23	31.56	7.19
25	26.66	6.04	24.42	4.53	35.63	9.68	29.65	6.21
35	25.69	5.60	23.76	4.22	34.25	8.91	29.00	5.84
45	24.67	5.14	—	—	—	—	—	—
50	24.16	4.91	22.50	3.67	32.70	8.09	28.25	5.45
60	24.11	4.85	—	—	—	—	—	—
63	—	—	21.20	3.09	—	—	—	—
68	—	—	20.51	2.81	—	—	—	—
75	24.10	4.78	20.53	2.80	—	—	—	—
92	24.05	4.71	20.56	2.77	29.70	6.51	26.69	4.63

KCl[3]

Temp.	19.6	25[4]	50.0[2]	59.9	68.0[2]	74.8	89.5	92.0[2]	108.1
$V^{2/3}$	39.50	38.58	35.17	33.98	33.35	32.69	31.58	31.49	27.68
N	12.04	11.53	9.68	9.03	8.70	8.35	7.75	7.71	5.66

[1] International Critical Tables.
[2] Scott and Durham: J. Phys. Chem., **34**, 1424 (1930).
[3] Berkeley: Phil. Trans, 203A, 189 (1904).
[4] Scott and Frazier: J. Phys. Chem., **31**, 459 (1927).

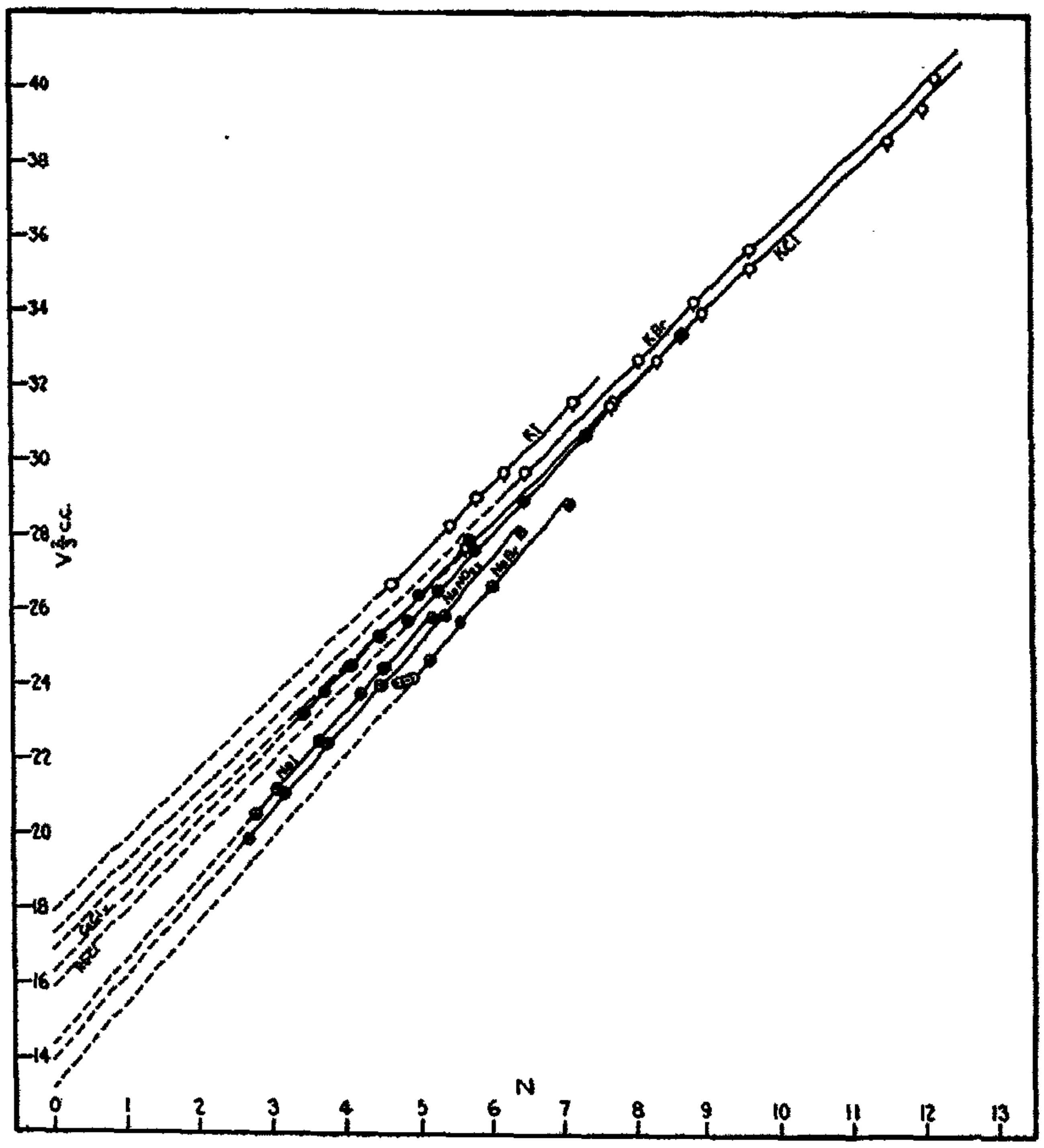

Fig. 1

The Variation of the Volume of a Saturated Solution with its Water Content N.

in solubility measurements, they are probably negligible. Errors in the determination of solubility affect both terms, the value of N somewhat more than the corresponding value of $V^{2/3}$. The few cases in which the plotted points do not fall on the line could all be attributed to errors in the solubility measurements. Nevertheless, until more data are available this means of testing the empirical relationship can not be regarded as decisive.

Indirect evidence in support of the plausibility of equation (3) is to be found by differentiating it with respect to N, as below:

$$\frac{dV}{dN} = \frac{3}{2}\alpha V^{1/3} \qquad (4)$$

If we take the $V^{1/3}$ term to represent the average distance between the ions in a saturated solution, the expression means that the change in volume with N is directly proportional to the separation of the ions. This result is qualitatively what would be expected on the assumptions of the electrostriction theory. If water (N) is added to a saturated solution in which the ions are relatively close, the added water will necessarily come into a region where the ionic forces are stronger and will consequently be more compressed than would be the case if the ions were farther apart. The increase in volume of the solution upon addition of water would be less in the first case than in the second. It is also noteworthy that the constant α turns out to be identical for certain salts, a fact which can be taken to mean that in saturated solutions of these salts the effect of the ions on the water molecules is essentially the same. If the salts of one group are considered, it is seen that they have in common one ion which is relatively stronger and which may be looked upon as the ion influencing the change in volume of the water molecules. In other words we have an additional example of a possible dominant ion effect.[1] Attention should also be directed to the fact that a change in the solid phase is marked by a discontinuity in the linear relationship. For example, in Fig. 1 a dotted line is drawn to indicate the variation of $V^{2/3}$ with N for sodium bromide above the transition temperature. It is at once apparent that the constants of this line (equation 3) are altogether different from those of the solid line, which correspond to the hydrated salt.

TABLE II

Values of β and Related Quantities

	NaBr	$NaNO_3$	NaI	RbCl	CsCl	KCl	KBr	KI
β	13.2	13.9	14.3	15.9	16.3	16.9	17.3	17.9
$\bar{v}$	48.0	51.8	54.1	63.4	65.8	69.5	72.0	75.7
b	31.4	39.2	42.8	40.4	48.4	34.3	41.6	54.7
ψ	0.65	0.76	0.79	0.64	0.74	0.49	0.58	0.72

For our purpose the constant β is particularly important and the values taken from Fig. 1 are given in Table II. In the same table are likewise given figures for $\bar{v}$, which is equal to $\beta^{3/2}$. The quantity $\bar{v}$ is the hypothetical, limiting volume in which one mol of salt is contained when it is in the same state as in a saturated solution but when no water is present. The corresponding values of b (equation 2), which is the space occupied by the ions of an electrolyte under the above conditions, are also presented in Table II and are taken from the paper already mentioned. Finally, we shall find it convenient to introduce the quantity $\psi = b/\bar{v}$ which is termed the space-filling quotient. The values of ψ given in Table II accordingly indicate the fraction of $\bar{v}$ which is occupied by the ions (b).

It will be observed that, although the ψ values vary widely among themselves, they are essentially greater than 0.5. This fact permits[2] the preliminary deduction that the ions in volume $\bar{v}$ must be packed rather closely, in a manner similar to that of ions in a crystalline solid. For any mode of

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[1] Scott: J. Phys. Chem., 33, 1000 (1929).

[2] R. Lorenz: "Raumerfüllung und Ionenbeweglichkeit," page 38.

packing the quotient ψ will vary with the ratio r_1/r_2 of the radii (r_1 and r_2) of the two ions involved. This variation, when the ions are assumed to be perfect spheres, is shown by the two solid lines drawn in Fig. 2. The line marked C.N. = 8 is for the cesium chloride structure where the co-ordination number is eight; the line marked C.N. = 6 is for the simple rock-salt structure. The value of ψ for a tetrahedral mode of packing (C.N. = 4) is indicated only for the one case where the radii ratio equals unity. Furthermore, the extreme limits of the drawn lines are established by the minimum permissible values of the radii ratios.[1] The conditions which determine these minimum values are (1) any sphere (ion) of one sort must be in contact with the number of adjacent spheres (ions) of the second sort given by the co-ordination number and (2) the adjacent spheres must not intersect.

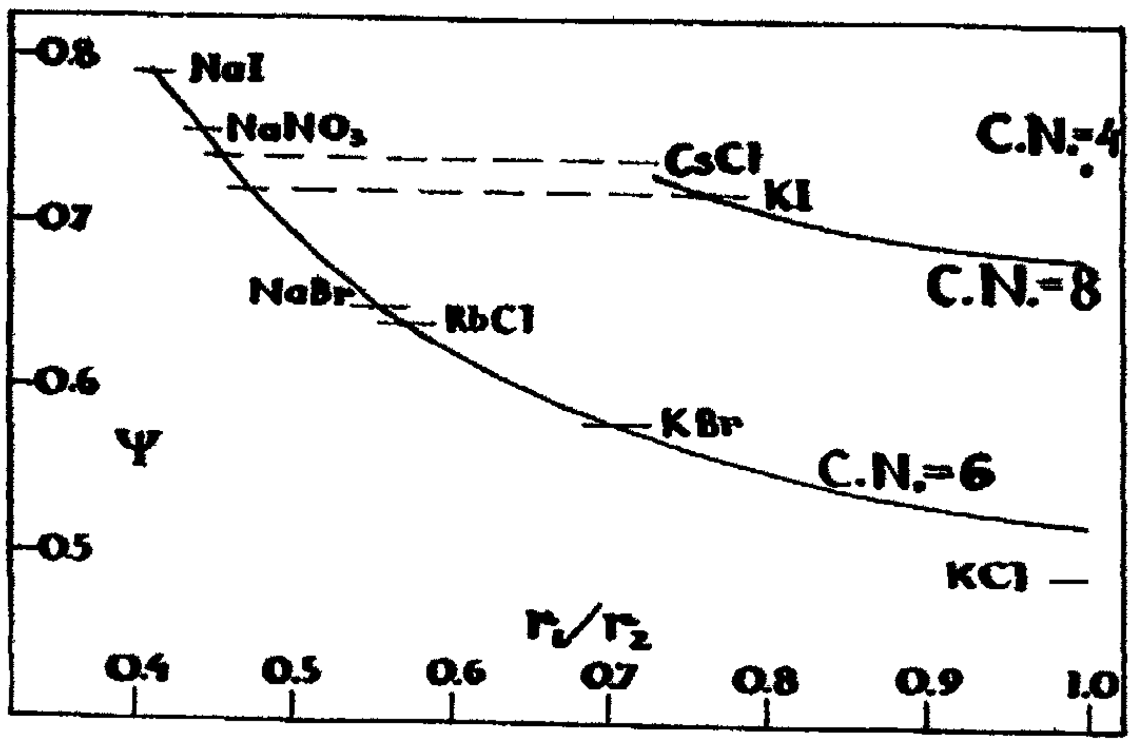

FIG. 2
Variation of Ψ with ratio of ionic radii.

In Fig. 2 are marked the ψ values (Table II) of the different salts. With the exception of the value of potassium chloride the indicated ψ values can be plotted on the C.N. = 6 curve. On the other hand only two salts, potassium iodide and cesium chloride, have ψ values which can also be plotted on the curve drawn for the cesium chloride structure. In considering the significance to be attached to this graph it is important to keep in mind the two assumptions which are involved: first, the domain of the ions is spherical; and second, the oppositely charged ions are in contact. Since the values of b and $\bar{v}$, obtained by extrapolation, are for indeterminate temperatures above 100°C., the above two assumptions are only approximately valid. If, however, we continue to take b to be independent of temperature, a correction for the effect of temperature on $\bar{v}$ would tend to increase the magnitude of ψ. Such a correction, for example, would bring the ψ value of potassium chloride nearer to the drawn curve; but the same correction applied to the ψ value of sodium

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[1] Goldschmidt: "Crystal Structure and Chemical Constitution," The Faraday Society, (1929).

iodide would make it too large. Although no estimation of the magnitude of this temperature correction can be made, one conclusion is worth noting: the effect of a temperature correction will be to decrease the radii ratio, that is, to increase the disparity between the radii of the constituent ions.

With the values of b and $\bar{v}$ at hand it is possible to compute the radii, r_1 and r_2, of the ions constituting each salt by means of the following equations:

$$(r_1 + r_2)^3 = A\,\bar{v}$$

$$N\tfrac{4}{3}\pi\,(r_1^3 + r_2^3) = b$$

Here N is Avogadro's number; A is a constant dependent on the type of crystal structure. For rock-salt structure it has the value 0.938×10^{-8} and for cesium chloride structure its value is 1.02×10^{-8}. The values of r_1 and r_2 obtained by solving these equations, using the $\bar{v}$ and b values contained in Table II, are given in Table III. The radii ratios given in the bottom row are, of course, identical with those which would be obtained from the curves drawn in Fig. 2 by using the appropriate values of ψ. Only for the two possible cases, cesium chloride and potassium iodide, have the radii been calculated for the two types of crystal structure. No values for the radii of the ions in the case of potassium chloride are presented because the solution of the two equations yields imaginary values. This fact means merely, as has already been pointed out, that the oppositely charged ions are not in contact.

TABLE III

Radii of Ions in the Limiting, Hypothetical State

Salt	NaBr	$NaNO_3$	NaI	RbCl	CsCl		KBr	KI	
Structure	NaCl	NaCl	NaCl	NaCl	NaCl	CsCl	NaCl	NaCl	CsCl
$r_1 \times 10^{-8}$cm.	1.21	1.07	1.04	1.37	1.20	1.73	1.59	1.28	1.85
$r_2 \times 10^{-8}$cm.	2.20	2.43	2.51	2.37	2.59	2.40	2.31	2.69	2.47
r_1/r_2	0.55	0.44	0.41	0.58	0.46	0.72	0.69	0.48	0.75

It is of considerable interest to compare these values of the ionic radii with the values obtained in other ways. Although we have no means of knowing which of the two ions is the anion, we shall assume that the one (r_2) with the larger radius is always the anion. The reasonableness of this assumption rests on the fact that practically every estimate of the relative magnitudes of the cations and anions under consideration indicates that the anion is larger than the cations. The values of r_1 and r_2, interpreted according to the above assumption, are plotted in Fig. 3: those values involving the assumption of a rock-salt structure are plotted as circles while those involving the assumption of cesium chloride structure are plotted as triangles. The salt from which each value is derived is also given. As a basis of comparison the ionic radii found by Goldschmidt[1] (line A) and by Webb[2] (line B) are shown in the figure.

The values of the ionic radii portrayed by line A are those found for the ions in crystals; they are in excellent agreement with the values calculated

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[1] Goldschmidt: "Crystal Structure and Chemical Constitution." The Faraday Society, page 282 (1929).

[2] Webb: J. Am. Chem. Soc., 48, 2589 (1926).

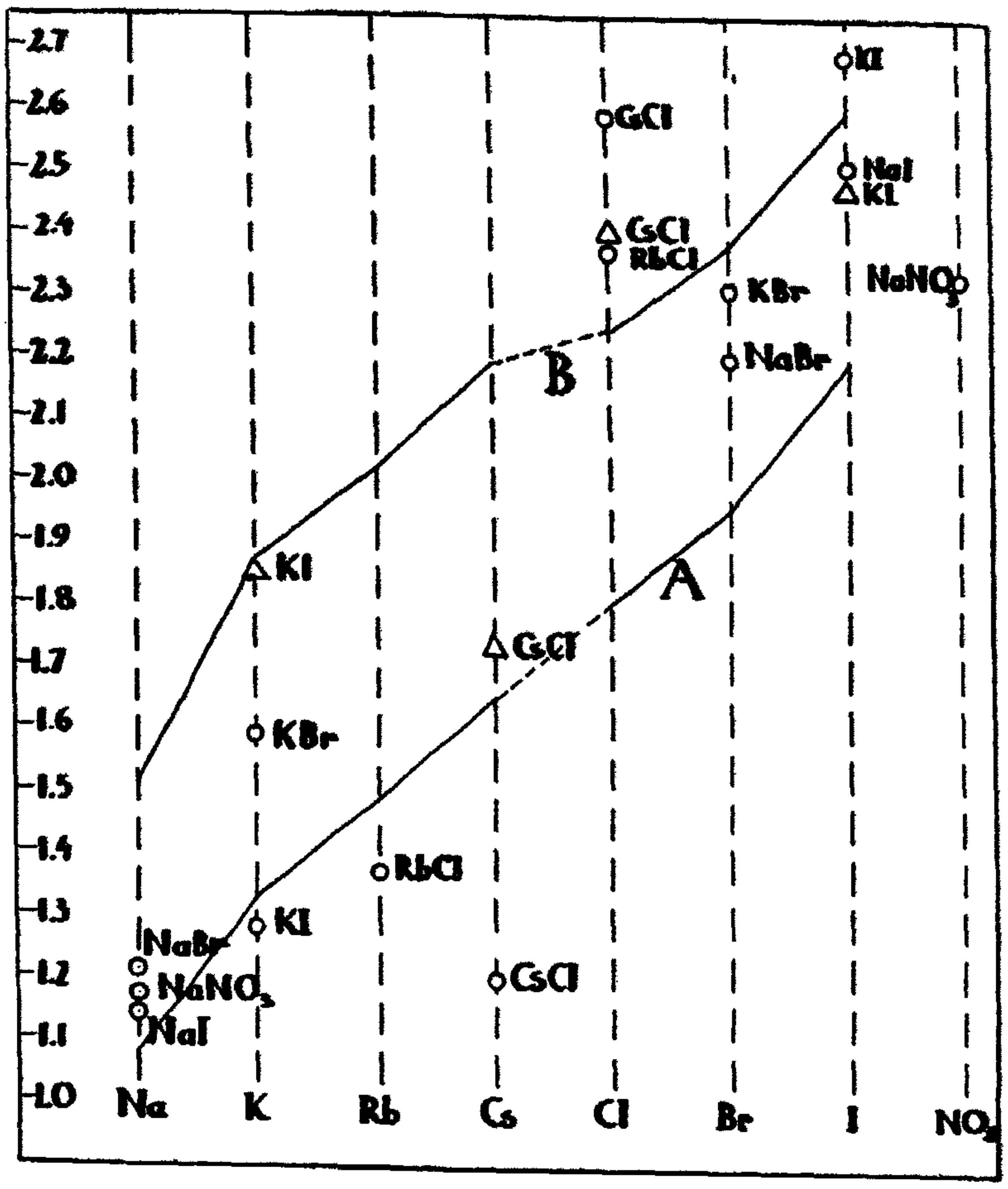

Fig. 3
Calculated radii of ions in Ångstrom units.

from the theory of wave mechanics and with those deduced from the optical data of the crystalline salts. The ionic radii which determine line B are the effective radii of ions invery dilute solutions, calculated from the theory of electrostriction. The effective radius of an ion is understood to be "the radius of a sphere surrounding the center of an ion, inside which there are no water molecules." We may therefore look upon these effective radii as the apparent radii when the ions are in the same state as in very dilute solution but when no water is present. They would thus be comparable to the apparent radii obtained in this paper, provided that the effective volumes do not undergo a change with concentration.

The plotted points in Fig. 3 appear to fall into two distinct groups: the anions have radii approximately the same as the effective radii calculated by Webb; the cations have dimensions very close to those found for the same ions in crystals. This generalization is strengthened by the observation made with respect to the temperature correction, namely, that such a correction would act to increase the ratios of the ionic radii. In other words, a temperature correction would affect the calculated radii in such a way as to emphasize the division of the cations and anions into two groups. Since we have postulated that b is the volume of the salt-ions in the saturated solution, we must regard the calculated radii as approximately the effective radii of the ions in the saturated state. On the ground of this analysis it is allowable to suggest that concentration has no influence on the effective volume of anions whereas it does bring about a diminution of the effective volume of the cation.

The foregoing interpretation is, of course, only tentative because of the limited data on which it is based. A further difficulty in the way of drawing a definite conclusion is the necessity of assuming a specific mode of packing of the ions in the limiting state. An illustration of this difficulty is the case of potassium iodide. Although the face-centered structure (C.N. = 6), which is the structure of this salt in the crystalline state, gives results which agree excellently with the above interpretation, the body-centered structure (C.N. = 8), which is equally possible, gives a quite contrary result. In the latter case, as can be seen in Fig. 3, both ions have radii corresponding to those found by Webb. In this connection it is worth noting that the assumption of a body-centered structure for cesium chloride, which is the normal crystalline structure, yields reasonable figures for the ionic radii, whereas the assumption of the other structure yields abnormal, almost impossible figures. In view of this evidence the conflicting results obtained in the case of potassium iodide on the assumption of an irregular but possible structure might conceivably be disregarded. Unfortunately, however, the evidence is by no means decisive and, as a matter of fact, only tends to emphasize the difficulty in question.

Summary

In the present paper an empirical relationship between the volume (V) of a saturated solution and the solubility (N) of the saturating salt is discussed. From this relationship there is obtained by extrapolation the limiting volume $\bar{v}$ for the hypothetical state where no water is present. The apparent volume (b) occupied by the ions in this limiting state was previously found for eight alkali salts. The space-filling quotient $b/\bar{v}$ for these eight salts is of the same order of magnitude as that of crystalline solids.

By assuming a lattice arrangement of the ions in this limiting state it is possible to calculate the radii of the individual ions. The apparent radii found in this way are, in general, larger than the corresponding radii in the crystalline state and smaller than in dilute solution. Finally, it is pointed out as a possible regularity that in the saturated state the effective volumes of the anions are the same as in dilute solutions while those of the cations are approximately the same as in the crystalline state.

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STUDIES IN PHOTOSYNTHESIS IN TROPICAL SUNLIGHT. PART I

BY G. GOPALA RAO AND N. R. DHAR

Formaldehyde Synthesis

Under the action of sunlight, the green plants absorb carbon dioxide from the air and transform it with the intervention of water into carbohydrates. This phenomenon has been technically called photosynthesis. The reaction $nCO_2 + nH_2O = (CH_2O)n + nO_2$ is endothermic and the quantity of energy absorbed is approximately 110,000 gram calories for each gram molecule of carbon dioxide. Thus in the process of photosynthesis, nature has worked out a method of utilising the enormous floods of solar energy pouring on the earth. According to Warburg, no other endothermal photochemical reaction shows such a high utilisation factor. The green plant is thus an efficient converter of the inexhaustible supply of solar energy into potential energy in the shape of food materials, fuel, etc.; coal and petroleum are likewise the product of photosynthetic activity produced ages ago. Thus it becomes evident that all life on this planet and our gigantic industrial developments of the modern era depend on this phenomenon of photosynthesis, which in the ultimate analysis is the prime mover of civilisation.

Because of its fundamental importance carbon assimilation early attracted the attention of scientific workers. Since the time of Stephen Hales (1707), this has been the subject of numerous researches by such brilliant workers as Priestley, Ingenhousz, Senebier and de Saussure. In spite of countless suggestions the mechanism of the reaction is still obscure. The theory which has held the attention for over half a century and is still the pivot of the modern investigations, is the formaldehyde hypothesis of Baeyer given out in 1864. The general consensus of opinion is in favour of the view that formaldehyde is photochemically synthesised from carbon dioxide and water, and that the formaldehyde is then polymerised to form carbohydrate. The mechanism of the formation of formaldehyde from carbon dioxide and water will be discussed in Part II.

Evidence for the substantiation of Baeyer's theory has been sought from more than one direction. These are:

(1) Attempts to find in the plant the intermediate product, formaldehyde. Evidence on this head would not be of much value as the presence of formaldehyde in the leaves is not a sure indication of its being an intermediate product, especially in view of the work of Spoehr[1] and Moore and Webster[2] who showed that many substances of vegetable origin yield formaldehyde on exposure to ultraviolet light or sunlight. However, recent experiments of Klein and Werner[3] seem to indicate that the existence of formaldehyde in

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[1] Biochem. Z., 57, 95 (1913).

[2] Proc. Roy. Soc., 90, 168 (1918).

[3] Biochem. Z., 169, 361 (1926).

leaves is not due to the photolysis of certain substances existing in plants as has been suggested by the above-mentioned workers, but is really an intermediate product of assimilation.

(2) Another direction in which evidence is sought for the above theory is the feeding of plants with formaldehyde. According to Grafe[1] and Miss Baker[2] plants can utilise small amounts of formaldehyde in light, though large amounts prove toxic. Sabalitschka and Riesenberg[3] have reported that certain plants assimilate formaldehyde in the dark with the formation of sugar and starch. However, from the fact that a substance can serve as food for plants, it need not be concluded that it should be produced in the assimilation process. A more fruitful piece of evidence is furnished by the synthesis of formaldehyde "in vitro" under conditions simulating those obtaining in the plant. This phase of the problem has received new stimulus by the use of the quartz mercury vapour lamp and of fluorescent substances, which are capable of absorbing light of one wavelength and giving out light of another wavelength.

Usher and Priestley[4] obtained positive tests for formaldehyde by exposing quartz tubes containing water and carbon dioxide to ultraviolet light. Baly, Heilbron and Barker[5] claim to have obtained direct synthesis of formaldehyde from carbon dioxide. These experiments have been contradicted by Spoehr,[6] Baur and Rebman,[7] and Porter and Ramsperger.[8] Still recently Baly and coworkers[9] seem to contradict their earlier results. They say that carbohydrate and not formaldehyde is the primary product of the action of ultraviolet light on a mixture of CO_2 and water, and that the formaldehyde results from secondary photochemical action, the photolysis of the carbohydrate. On the other hand Mezzadroli and Gardano[10] have obtained formaldehyde and small quantities of sugar by exposing solutions of bicarbonates of different metals. This work is confirmed by the later experiments of Mezzadroli and Vareton[11] and Mezzadroli and Babes.[12] There is unfortunately little agreement in the results of the various workers on the reduction of carbon dioxide in ultraviolet light.

The question may well be asked of what significance for the natural process of photosynthesis are experiments on the action of ultraviolet light on carbon dioxide and water. That the ultraviolet part of the solar spectrum plays a very insignificant rôle in photosynthesis is almost certain. So at-

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[1] Ber. bot. Ges., 27, 431 (1909); 29, 19 (1911).
[2] Ann. Bot., 27, 411 (1913).
[3] Biochem. Z., 144, 545 (1924).
[4] Proc. Roy. Soc., 84B, 101 (1911).
[5] J. Chem. Soc., 119, 1025 (1921).
[6] J. Am. Chem. Soc., 45, 1184 (1923).
[7] Helv. Chim. Acta., 5, 928 (1922).
[8] J. Am. Chem. Soc., 47, 79 (1925).
[9] Proc. Roy. Soc., 116A, 212 (1927).
[10] Atti Accad. Lincei, 6, 160 (1927).
[11] Zymologica, 3, 165 (1928).
[12] Gazz., 59, 305 (1929).

tempts have not been wanting to obtain formaldehyde and carbohydrates in visible light in the presence of coloured organic and inorganic substances. Moore and Webster[1] claimed to have obtained formaldehyde by exposing solutions of colloidal uranic hydroxide through which carbon dioxide was passed. Similar results are obtained by Baly and collaborators.[2] On the other hand, entirely negative results were obtained by Baur and Rebman, and by Spoehr. Dhar and Sanyal[3] have made an extensive investigation in this line. They find the formation of formaldehyde by passing carbon dioxide through suspensions of methyl orange, methylene blue, chlorophyll, ferric chloride, uranyl salt, chromium salt etc. These experiments of Sanyal and Dhar were recently contradicted by Burk.[4]

The object of the present investigation is to see how far valid are the objections raised by Burk. As will be discussed in the following pages, some of the experimental conditions of Burk differ from those of Dhar and Sanyal and are such as would not be conducive to photosynthesis. So we are constrained to modify one or two of his experimental conditions. Otherwise the procedure is just the same, and it may be mentioned here that in most cases positive results were obtained. Thus a comparison of the present investigation with that of Burk will clearly bring into prominence the importance of experimental conditions, and shows how a change in one or more of the conditions produces altogether contrary results. The present investigation consists of:

(a) the reduction of carbon dioxide to formaldehyde in the presence of organic and inorganic photocatalysts;

(b) the reduction of carbon dioxide to carbon monoxide in the presence of light and chlorophyll.

Experimental

In nearly all the work on photosynthesis repeated previously, with a few exceptions, the experimental conditions have not been described with the detailed precision which the subject demands. In the present investigation, the experimental methods and conditions have been carefully laid down with studied care, and the points of adverse criticism have been met with.

I. *Reduction of carbon dioxide to formaldehyde.*

Carbon dioxide prepared from marble and dilute hydrochloric acid and purified by passage through two or three wash-bottles containing distilled water was passed through a two-way tube into pyrex beakers, one containing conductivity water and the other containing conductivity water to which the photosensitiser has been added. Both the beakers were covered over and exposed to the bright sun for three hours. The object of keeping a blank was to avoid the question of formaldehyde being attributed to impurities.

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[1] Proc. Roy. Soc., 87B, 163 (1913); 91B, 196 (1920).

[2] Loc. cit.

[3] J. Phys. Chem., 29, 926 (1925).

[4] J. Phys. Chem., 31, 1338 (1927).

Porter and Ramsperger (loc. cit.) in their criticism of the work of Baly and collaborators attribute the origin of formaldehyde found to the impurities present such as stopcock grease, rubber tubing, sealing wax, etc. In view of this criticism, we had to cut down the use of rubber tubing to the level of unavoidable requirements and, to prevent the action of light on rubber, it was coated over with black paper. Not content with this, we had resort to a very efficient method of proving the non-interference of impurities and it is that of putting a blank. The gas was passed through a two-way tube simultaneously into two beakers, one containing the reaction mixture and the other pure conductivity water. After three hours' exposure to bright sunlight, both the solutions were tested for formaldehyde. In every case formaldehyde was detected in the reaction mixture and never in the conductivity water kept as a blank. If any formaldehyde were to arise from stopcock grease or rubber, it should have been found in both the beakers. The entire failure to detect formaldehyde in the blank solution effectively removes the question of the impurities and clearly brings about the prominence of the photocatalysts.

The organic photocatalysts employed were: (1) methylene blue; (2) malachite green; (3) methyl orange; and (4) chlorophyll. Baur and Rebman[1] and Baur and Büchi[2] showed that formaldehyde is formed when various dyestuffs such as malachite green, eosin, rhodamine and phosphine are exposed to ultraviolet light. That aldehyde is also produced from chlorophyll and other aniline dyes in sunlight has also been shown by Osterhout.[3] In view of this work, in the experiments in which chlorophyll and other aniline dyes were used as photocatalysts we always exposed a blank solution of the dye under exactly identical conditions but no carbon dioxide was passed through it. The blank solution as well as the solution through which carbon dioxide was passed, were distilled and distillates tested for formaldehyde with Schryver's or a modified Schiff's reagent described by Déniges.[4] Comparative experiments showed that in every case in which carbon dioxide was passed considerably larger quantities of formaldehyde were produced than in the absence of carbon dioxide. These experiments repeated several times leave no doubt that carbon dioxide is reduced to formaldehyde in the presence of light and such dyestuffs.

All the tests employed for the detection of formaldehyde were first critically studied starting with dilute solutions of the substance itself. The modified Schiff's reagent was prepared as follows:

One gram of rosaniline hydrochloride was dissolved in 500 c.c. of water and to this solution 25 grms of sodium sulphite and 15 c.c. of HCl (sp. gr. 1.124) are added and the whole diluted to one litre. The solution is slowly decolorised and can be used after a few hours. In pure solution formaldehyde can be detected in a concentration of 1:500,000. Tests are carried out by

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[1] Helv. Chim. Acta, 5, 1828 (1922).

[2] Helv. Chim. Acta, 6, 959 (1923).

[3] Am. J. Bot., 5, 511 (1918).

[4] Compt. rend., 150, 529 (1910).

adding 1 to 2 c.c. of hydrochloric acid (sp. gr. 1.124) to 10 c.c. of the solution to be tested and then 1 c.c. of the reagent. Formaldehyde produces a blue to red violet coloration. With dilute solutions, several hours are required to develop the colour, which sometimes does not attain maximum intensity until after 20 hours. Other aldehydes give only a temporary coloration.

The inorganic catalysts employed were colloidal ferric hydroxide, uranyl nitrate, and chromium sulphate and copper sulphate. In these cases also the solutions were distilled and distillates tested for formaldehyde. In every one of these cases formaldehyde was detected in appreciable amounts.

II. Reduction of carbon dioxide to monoxide.

The decomposition of carbon dioxide in the extreme ultraviolet light was studied by Herchefinkel[1] and later by Coehn and collaborators.[2] Berthelot and Gaudechon[3] state that the reaction

$$CO_2 \rightleftarrows CO + (O)$$

is facilitated by the presence of reducing substances. We have now shown that such a decomposition takes place in visible light from a 500-watt gas-filled tungsten filament lamp by virtue of the reducing power of methylene blue or chlorophyll.

The test employed for the detection of carbon monoxide is the well-known iodine pentoxide method of C. de La Harpe and Reverdine. Great precautions had to be taken in employing this test; for iodine pentoxide decomposes in light. So the U-tube containing iodine pentoxide was protected from all light both during and after preparation. All the joints were of glass, as iodine pentoxide is a notorious oxidising agent acting on cork, rubber and the usual lubricants. Blank experiments were always done. Traces of CO were always found in the carbon dioxide issuing out of a chlorophyll suspension exposed to light. The important bearing of this fact on the photosynthetic mechanism will be discussed in another paper.

From the experimental results recorded in Section I, ample confirmation is afforded for the work of Dhar and Sanyal, and the other workers in the field. We can now say, with a great degree of assurance that the experimental conditions of Burk were not conducive to successful photosynthesis; and hence the negative results. The distinctive feature of Burk's experimental technique was the use of condensed light. By a curious process of reasoning, Burk arrives at the conclusion that the use of lenses was found indispensable. Many of the reasons assigned are hypothetical and the arguments unconvincing. To use his own words, "the plant leaf is a veritable nest of lenses; there is no question in my mind that these natural lenses do actually increase considerably the intensity of light inside the plant." Therefore Burk used such lenses as would enable the intensity of sunlight to be increased to a maximum of five thousand fold. As against this, let us con-

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[1] Compt. rend., **149**, 395 (1909).

[2] Z. physik. Chem., **91**, 347 (1916).

[3] Compt. rend., **150**, 1690 (1910).

sider the common experience in photosynthesis *in vivo*, as well as *in vitro*. Falling off of photosynthesis was observed by Reinke in "Elodea" when the intensity of illumination surpassed sixty times that of sunlight and by Pantanelli when the light intensity was greater than that of sunlight. As regards experiments *in vitro*, Baly and coworkers[1] report that with increasing intensity of light (using visible light from 100-watt lamps and using coloured substances like nickel and cobalt carbonates as photosensitisers) the quantity of carbohydrate synthesised per unit quantity of light decreases. The same writers report that P. F. R. Venables, in his experiments on the quantities of organic materials, soluble in alcohol, synthesised in presence of aluminum powder and light from CO_2 and water, found that the amount synthesised decreases as the light intensity increases. In the light of such extensive and unequivocal evidence, we have no doubt in asserting that the high intensities used in Burk's experiments were harmful to photosynthesis.

Summary

I. Formaldehyde has been obtained from carbon dioxide and water in the presence of the following photosensitisers and sunlight:

(1) Chlorophyll, (2) methylene blue, (3) malachite green, (4) methyl orange, (5) ferric hydroxide sol, (6) uranyl nitrate, (7) chromium sulphate and (8) copper sulphate.

' Great precautions were taken in view of the adverse criticism.

II. Small quantities of carbon monoxide were obtained from the photochemical reduction of carbon dioxide by chlorophyll.

Chemical Laboratories,
University of Allahabad,
Allahabad, November 18, 1930.

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[1] Proc. Roy. Soc., 116A, 197, 212-219, (1927).

STUDIES IN PHOTOSYNTHESIS IN TROPICAL SUNLIGHT. PART II.

BY G. GOPALA RAO AND N. R. DHAR

Photosynthesis of Formaldehyde and Carbohydrates from Alkali Bicarbonates in the Presence of Coloured Insoluble Substances

In a previous paper we have recorded our results on the photosynthesis of formaldehyde in tropical sunlight. The present paper deals with:

(1) Photosynthesis of formaldehyde and carbohydrates from alkali bicarbonates.

(2) The polymerisation of formaldehyde to reducing sugars.

(3) Discussion of results recorded in both the papers.

The exposed solutions were made up with water twice distilled, the second distillation being carried out in silica vessels; the water had a conductivity not greater than 3×10^{-6} ohm^{-1} at 30°. Merck's or Kahlbaum's chemicals were used, usually without further purification. Most of the solutions were exposed in glass bulbs blown at the end of common soft glass tubes about one and one half feet in length and 10-15 mm. in diameter. The bulbs had a capacity ranging from 50 to 150 cubic centimeters and were very transparent. The tubes were always cleaned first with hot chromic acid, then with plenty of distilled water and finally with conductivity water and dried at 100° and kept away until used. The bulbs were always sealed with a little air space above the solution. The tubes were held dipped under water in beakers and exposed to the sun for periods varying from 10 hours to 60 hours extending over several days. In tropical countries like India, the sunlight on bright days consists of light of wavelengths extending up to 2900 Å; that is, a considerable portion of the ultraviolet spectrum from 3800–2900 Å is thus represented in sunlight. But as ordinary glass transmits wavelengths only up to 3400 Å, it can safely be asserted that not much ultraviolet light takes part in our experiments.

2% solutions of Merck's sodium bicarbonate were exposed with the following catalysts:

(i) Colloidal ferric hydroxide.
(ii) Cobalt carbonate.
(iii) Nickel carbonate.

Saturated solutions of carbon dioxide in conductivity water with the above catalysts were also exposed.

After filtration, since the solutions still contain appreciable amounts of the bicarbonates of nickel and cobalt in solution, they were concentrated on a water bath. The precipitated carbonate was removed and the solutions evaporated to dryness. Part of the solution, however, was tested with Molisch carbohydrate reagent as described in Mulliken's "A Method for the Detection of Pure Organic Compounds".[1] The rest of the solution was evaporated to dryness and the residue extracted with methyl alcohol which on evaporation leaves a small residue. This residue charred on heating with concentrated sulphuric acid and did not reduce Benedict's solution until after hydrolysis with dilute hydrochloric acid at 100° and subsequent neutralisation.

In the case of colloidal ferric hydroxide, the sol was coagulated by the addition of a little potassium sulphate, filtered and the filtrate treated as above.

Sometimes, parts of the original solution were also tested for formaldehyde with Schryver's and modified Schiff's reagents. The following results were obtained:

1.	CO_2 and conductivity water sealed in glass tubes and exposed for 60 hours to sunlight.	Extremely small quantities of formaldehyde.
2.	CO_2 and conductivity water and ferric hydroxide sol exposed for 60 hours.	Small quantities of formaldehyde and carbohydrate.
3.	2% solution of sodium bicarbonate little cobalt carbonate, 45 hours' exposure.	Small quantities of formaldehyde.
4.	2% solution of sodium bicarbonate little nickel carbonate, 45 hours' exposure.	Appreciable quantities of formaldehyde and carbohydrate.

Similar tubes were kept in the dark in each case for the same length of time. On examination, the unexposed solutions yielded negative results. It may be mentioned here that results similar to the above have also been obtained by Baly and collaborators.[2]

Polymerisation of Formaldehyde to Reducing Sugars

Butlerow first observed the condensation of "dioxymethylene" (trioxymethylene) to a sugar like substance by means of alkalis. This phase of the subject has been further studied by Loew[3] and by Lobry de Bruyn and van Ekenstein[4] and lately by Nef[5] who showed that the substance so obtained is a mixture of 24 hexoses and about an equal number of pentoses. That the condensation is affected by light has been observed by various workers. Inghilleri[6] reported that by exposing sealed tubes containing formaldehyde

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[1] "A Method for the Detection of Pure Organic Compounds," **1**, 26 (1904); "Practical Organic and Biochemistry" (1915).

[2] Proc. Roy. Soc., **116A**, 212 (1927).

[3] J. prakt. Chem., **33**, 321, (1886); **34**, 51.

[4] Rec. Trav. Chim., **18**, 309 (1899).

[5] Ann., **376**, 1 (1910); **403**, 204 (1914).

[6] Z. physiol. Chem., **71**, 105 (1911).

to sunlight, he obtained 'methylenitan' a sugar like substance. Recently, Baly, Heilbron, and Barker[1] reported the formation of sugars from a solution of formaldehyde exposed to ultraviolet light. Dhar and Sanyal (loc. cit.) report the formation of reducing sugar from formaldehyde solutions exposed with little ferric chloride or methyl orange.

Aqueous solutions of formaldehyde prepared by diluting Merck's pure formalin were exposed in sealed tubes to sunlight for periods extending over several hours, usually 10 to 30 hours. Similar tubes were kept in the dark in every case. The exposed and unexposed ones were examined simultaneously. As Fehling's solution is reduced by formaldehyde, it was never used in testing for reducing sugars. Benedict's solution which is reduced by sugars and not by formaldehyde was always used. The following results were obtained:

Formaldehyde + water	No reducing sugar
Formaldehyde + water ferric hydroxide sol	No reducing sugar
Formaldehyde + MgO	No reducing sugar
Formaldehyde + ZnO + water	Small quantities of reducing sugar.
Formaldehyde + methyl-orange + water.	do.
Formaldehyde + water ferric chloride	do.

In this last case the ferric chloride was photochemically reduced to ferrous salt; as it was found that ferrous salt itself reduces Benedict's solution, the ferrous salt was first removed by adding just the requisite amount of a dilute solution of potassium ferricyanide, filtering of the precipitated ferrous ferricyanide and then tested for reducing sugar.

Discussion of Results:- In Part I we have recorded evidence for the formation of formaldehyde from carbon dioxide and water exposed to tropical sunlight with small quantities of photocatalysts e.g. chlorophyll, methylene blue, malachite green or methyl orange; and inorganic substances like ferric hydroxide sol, uranyl nitrate, chromium sulphate, and copper sulphate, all coloured substances having strong absorption in the visible portion of the solar spectrum. The analogy between chlorophyll and dyestuffs like methylene blue is not far to seek. At any instant, the amounts of formaldehyde detectable is small, presumably due to the fact that the photo-synthesised formaldehyde rapidly polymerises to sugars. From an analogy with these experiments *in vitro*, it can be said with a certain amount of confidence that in the green plants too, the primary product of photosynthesis is formaldehyde, which then polymerises to sugars. The reaction therefore might be

$$CO_2 + H_2O \rightarrow HCHO + O_2$$

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[1] J. Chem. Soc., 119, 1025 (1921).

which takes place with an absorption of energy equivalent to 110,000 calories. The light energy absorbed by chlorophyll is in some mysterious way converted to chemical energy. On account of the readiness with which photo-synthesised formaldehyde polymerises to sugars, Baly and Barker differentiate it from ordinary formaldehyde by assigning a different structural formula:

$$HCHO \text{ (ordinary)} \rightarrow HCOH \text{ (active)}$$

It is generally believed that chlorophyll plays the rôle of an optical sensitiser. But the mechanism of sensitisation is not yet clear. Chlorophyll in the leaves exhibits fluorescence, and is capable of sensitising photographic plates. Tswett[1] suggests that chlorophyll like all fluorescent substances undergoes a peculiar reversible change associated with intake of energy; when this reverts to the original molecular form, the energy taken up is radiated out as phosphorescent light, which is specifically absorbed by carbonic acid. On the other hand, Weigert considers that the absorption of light by chlorophyll results in an internal photoelectric effect, which finally results in the break-down of water into hydrogen peroxide and hydrogen, which then react with carbon dioxide according to the equation:

$$H_2 + CO_2 + H_2O_2 = HCHO + H_2O + O_2$$

Besides these theories, where an essentially physical function is assigned to chlorophyll, there are some which give it an active part in the chemical reactions. Of these, mention should be made of the theory of Willstätter and Stoll. They think that carbonic acid forms a complex with chlorophyll, which with absorption of energy passes into an isomeric peroxide type of compound. This breaks up thermally, probably due to the action of an enzyme, with the formation of formaldehyde, elimination of oxygen and regeneration of chlorophyll.

The experimental results recorded in the foregoing pages show that chlorophyll besides being an optical sensitiser, also acts as a reducing agent under the influence of light. It has been shown that chlorophyll photochemically reduces carbon dioxide to carbon monoxide. In the light of these results, we suggest the following mechanism for the photochemical synthesis of formaldehyde. According to this hypothesis, the photosynthesis consists of three stages:

(i) In the first stage, chlorophyll reacts with carbonic acid under the influence of light, with the formation of chlorophyll peroxide and carbon monoxide.

The change can be represented by

$$\text{Chlorophyll} + H_2CO_3 + \text{light energy} = \text{chlorophyll peroxide} + CO$$

The interaction of the nascent carbon monoxide with water to give instantaneously

$$H_2O + CO \rightarrow HCHO + (O)$$

The occurrence of this step in the photosynthesis mechanism is also supported

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[1] Ber. bot. Ges., 29, 744 (1911).

by the experiments of Berthelot and Gaudechon[1], who were able to obtain formaldehyde from carbon monoxide and water in presence of light. Under the action of ultraviolet light the carbon monoxide is activated and this active carbon monoxide interacts with water to give

$$H_2O + CO = HCHO + (O)$$

The carbon monoxide obtained in photosynthesis, according to the present scheme, is in the active state at the moment of its formation and hence it readily reacts with water, as in the experiments of Berthelot and Gaudechon[2] This is further supported by the experiments of Bottomley and Jackson, who showed that carbon monoxide can, to a measure at least, replace carbon dioxide in photosynthesis. Here only half of the oxygen is given off.

(ii) The other half of the oxygen comes from the decomposition of the peroxide which takes place with regeneration of chlorophyll. The decomposition of peroxide is probably thermal and due to an enzyme present in the chloroplasts.

(iii) The last stage consists in the polymerisation of formaldehyde to sugars. Thus the oxygen evolution takes place in two stages. Half the amount of oxygen corresponding to the equation (final)

$$CO_2 + H_2O \rightarrow HCHO + O_2$$

is evolved when the photochemically produced carbon monoxide reacts with water giving formaldehyde and oxygen. The other half of the oxygen comes when the photochemically produced chlorophyll peroxide decomposes thermally giving oxygen and regenerating chlorophyll.

That the evolution of oxygen probably takes place in two stages is indicated by the experiments of Kostytschew[3] and confirmed by Spoehr and McGee[4] that the ratio CO_2/O_2 during illumination varies with time. Kostytschew found that during photosynthesis the leaves absorb initially a great deal more of carbon dioxide than oxygen is given off; about one third the absorbed carbon dioxide is fixed without oxygen emission. After a short time these conditions are reversed and finally CO_2/O_2 ratio attains the constant value of 1.

According to our theory of the photosynthetic process, there are two important stages. The first is the photochemical interaction of chlorophyll and carbon dioxide, giving chlorophyll peroxide and carbon monoxide. The carbon monoxide produced is very active being in the nascent condition, so it interacts with water giving formaldehyde and oxygen. The second important stage is the thermal decomposition of chlorophyll peroxide giving a further quantity of oxygen. The whole process of photosynthesis is considered to be complete when both these reactions are complete and the whole amount of oxygen is given off:

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[1] Compt. rend., 150, 690 (1910).

[2] Proc. Roy. Soc., 72, 130 (1903).

[3] Ber. bot. Ges., 39, 319 (1921).

[4] Am. J. Bot., 11, 493 (1924).

i. (a) Chlorophyll + H_2CO_3 + light energy
= Chlorophyll peroxide + CO (active)

(b) CO (active) + H_2O = HCHO + (O)

ii. Chlorophyll peroxide = Chlorophyll + water + (O)

Most workers have followed the kinetics of photosynthetic reaction in plants by measuring the total volume of oxygen evolved from time to time. So if the oxygen is evolved in two processes, the first reaction followed by the second, it is clear that the whole process will be limited by any one of these reactions. Suppose one of the reactions is fast, the other comparatively slow and since the whole process is measured by the total oxygen evolved in the two reactions combined, the photosynthesis will be controlled by the slower of the two reactions.

That there are two stages in photosynthesis, a photochemical and a thermal one is indicated by the work of Blackman and Miss Matthaei,[1] Warburg[2] and of Willstätter[3] on the temperature coefficient of the photosynthesis. As light is necessary for the whole process, it is clear that a photochemical reaction is involved. But photochemical reactions are characterised by low temperature coefficients; while Miss Matthaei and subsequent workers have found a temperature coefficient of 2, characteristic of thermal and enzymic reactions. That the whole process consists of two stages would explain the fact that some workers have found under certain conditions a temperature coefficient of less than 2; for if there are two stages with different temperature coefficients, the temperature coefficient of the whole process will depend upon the rate of the process which proceeds relatively more slowly—if the photochemical stage is relatively slower, the temperature coefficient of the whole process will be low; while if the purely thermal or enzymic reaction is relatively slower the temperature coefficient would be high, about 2. This different behaviour towards temperature was observed by Willstätter in the case of the green and yellow varieties of the same species,—it was found that the rate of photosynthesis of normal green leaves of "ulmas" exposed to strong light and in an atmosphere containing excess (45%) of carbon dioxide, was more influenced by temperature than that of the yellow varieties of the same species. We are of the opinion that in the yellow leaves, the chlorophyll being present in comparatively small quantities and being concerned with the photochemical reaction will determine the rate of the whole process; while in the green leaves chlorophyll will be in excess but substances participating in the thermal reaction, say enzymes, will be in relatively smaller quantity and will therefore determine the whole process. The photosynthesis in the yellow leaves being determined by the photochemical reaction, and that in the green leaves limited by the thermal reaction, it is clear that the temperature coefficient in the former case will be

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[1] Phil. Trans., **197**, 47 (1905).

[2] Biochem. Z., **100**, 259 (1919).

[3] "Untersuchungen über die Kohlensäure Assimilation" (1918).

of the order of the temperature coefficient of a photochemical reaction, and that in the second case will be of the order of a thermal reaction; that is, the temperature coefficient in the former case will be smaller than that in the latter.

The experiments of Warburg on the relation between light intensity and temperature coefficient also support the hypothesis of the two stages. All conditions remaining the same, the temperature coefficient is unity when the light intensity is low and the temperature coefficient is greater than unity when the light intensity is high. In the first case, because the intensity of light is low, the photochemical reaction will be slow and hence it will limit the whole process. In the second case the intensity of light being sufficiently high the photochemical reaction will be fairly rapid; but the thermal reaction is comparatively slow. So the thermal reaction will control the whole process. Hence from the considerations already put forward, it is clear that in the former case, the process being limited by the light reaction, and in the latter by the thermal reaction, the temperature coefficient in the former case will be smaller than that in the latter case.

That an internal factor, like the content of chlorophyll with which carbon dioxide interacts, is limiting the whole process is evident from the researches of Warburg on the effect of carbon dioxide concentration on the rate of photosynthesis. With increasing carbon dioxide concentration, above a certain amount, Warburg found that the increase in the rate of photosynthesis rapidly falls off until a certain concentration of carbon dioxide; further increase in the latter produces no effect. It is clear that the rate of photosynthesis depends not only on the concentration of carbon dioxide, but on that of some other substance as well, with which carbon dioxide reacts. The experimental findings of Warburg are satisfactorily explained on the present hypothesis. According to this hypothesis, carbon dioxide interacts with chlorophyll.

$$\text{Chlorophyll} + \text{carbon dioxide} + \text{water} = \text{chlorophyll peroxide} + \text{CO}.$$

At low concentrations of carbon dioxide, when the chlorophyll is in comparatively greater quantities, it is clear that the photosynthesis will increase with increasing concentration of carbon dioxide. But this will not proceed *ad infinitum*. The content of chlorophyll being limited, a certain stage will be reached where the content of chlorophyll is no longer in excess but is just sufficient to interact with the carbon dioxide present at any instant; if the concentration of carbon dioxide is further increased, there will be no further increase in the reaction velocity, as the chlorophyll with which carbon dioxide interacts is in limited quantities. The surplus carbon dioxide finds no chlorophyll to interact with. Hence Warburg found that by increasing the concentration of carbon dioxide above a certain maximum, no further increase in the rate of photosynthesis takes place.

Influence of Chlorophyll Content

According to the present hypothesis, chlorophyll takes part in the chemical reaction and as such, the content of chlorophyll should have a profound influence on the rate of photosynthesis. Mention would be made only of the great advance made by Willstätter and Stoll in this line. The conditions under which the experiments were carried out were such that neither temperature, carbon dioxide concentration nor light intensity were determining the rate of photosynthesis. This is of course, necessary in order to emphasise or demonstrate the influence of chlorophyll content. In most of the cases, excised leaves were used. Willstätter and Stoll introduced as a measure of the ratio of chlorophyll content to the rate of photosynthesis the term "Assimilationszahl" or photosynthetic number. This is a measure of maximal synthesis expressed in grams of carbon dioxide absorbed per hour by a leaf mass containing 1 gram of chlorophyll under favourable conditions of temperature or briefly, it is the number of grams of carbon dioxide absorbed per hour per gram of chlorophyll; this is the photosynthetic number, which for the sake of brevity, we shall designate by P_o.

$$P_o = \frac{\text{hourly photosynthesis, grams } CO_2}{\text{Grams chlorophyll}}$$

5 % CO_2, about 48,000 lux

Species.	Temp.	Value of P_o
Aesculus hippocastanum	25°	6.4
Acer negundo	25°	7.7
Acer pseudoplatanus	25°	5.2
Ampelopsis quinquefolia	25°	6.2
Hydrangia opulodes	30°	6.5
Pelargonium zonale	30°	7.4
Sambuscus nigra	25°	6.6
Tilia cordata	25°	6.6
Ulmus	25°	6.6
Cucurbita pepo	25°	12.1
Clerodendron trichotonum Thumb	25°	12.3
Fragaria vesca	25°	10.6

In the foregoing table approximately constant values of P_o for a given temperature are obtained, the value being about 6.5. This constant value of P_o would indicate that under these conditions, the rate of photosynthesis was determined by the chlorophyll content. There is a rough parallelism between rate of photosynthesis and chlorophyll content.

In the lower part of the table are given the values of P_o for plants which have a notably rapid growth and high photosynthetic rate. In these, P_o is higher, about 12; nevertheless constant for a number of cases. The results of Willstätter and Stoll on the photosynthetic activity of leaves in different stages of development show that although the chlorophyll content of the leaves increases with age and that the photosynthetic activity also increases, the two are by no means parallel.

These results show that the photosynthetic rate depends to a large extent on the chlorophyll content.

That the thermal reaction is of the type of the decomposition of a peroxide is indicated by the work of Warburg and Uyesugé.[1]. They find that temperature, hydrocyanic acid, and urethane act in the same way on the the release of oxygen from hydrogen peroxide by "chlorella" in the dark, as on the photosynthesis in strong light.

The present theory thus accounts for most of the facts of photosynthesis in plants: firstly for the fact that the ratio of CO_2/O_2 changes; secondly for the variation of temperature coefficient with intensity; thirdly for the considerable difference in temperature coefficient of the photosynthetic reaction with yellow and green leaves of the same species; fourthly, for the observations of Warburg on the influence of carbon dioxide concentration on the rate of photosynthesis and lastly for the effect of chlorophyll content on the rate of photosynthesis.

Chemical Laboratories,
University of Allahabad,
Allahabad,
November 18, 1930.

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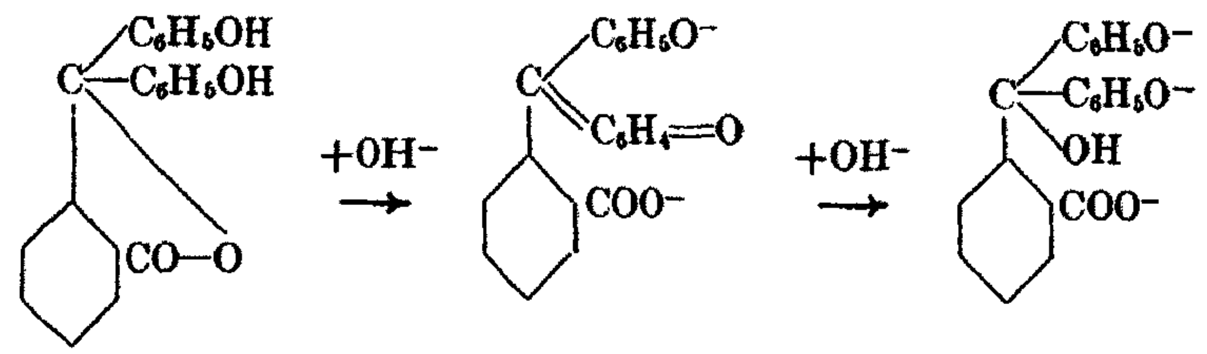
[1] Biochem. Z., **146**, 486 (1924).

THE COLOR CHANGES OF SULFONPHTHALEINS, BENZEINS, AND PHTHALEINS

BY I. M. KOLTHOFF

1. The Phthaleins in the Alkaline Range

Previously it has been shown,[1] that there is no conflict between the chromophoric theory and the ionization theory of the color change of an indicator. For a quantitative interpretation of the color equilibrium in an indicator solution the classical dissociation theory of Wilhelm Ostwald has to be used. The scheme given for the changes in structure and color of phenolphthalein for example:



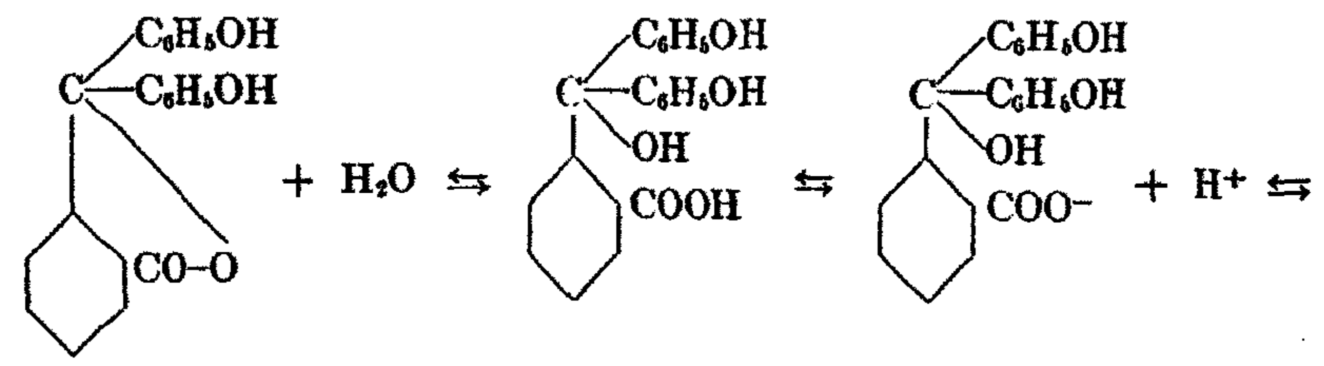
acid form; lactone; colorless

quinone-phenolate weakly alkaline form red violet

carbinolform strongly alkaline form; colorless

does not account for the influence of hydrogen or hydroxylions upon the equilibrium between the various forms. A colorless solution of phenolphthalein is mainly present in the lactone form, though the latter must be in equilibrium with other forms, the concentration of which may be extremely small.

The following scheme represents the various equilibria which have to be considered in the quantitative interpretation of the color change of phenolphthalein and similar compounds:



I Lactone Colorless

II Colorless

III Colorless

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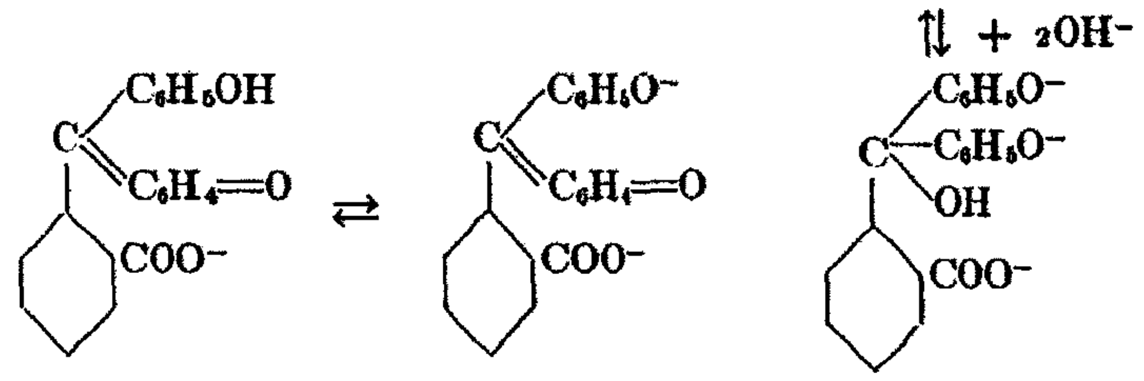
[1] I. M. Kolthoff: "Indicators," p. 239; also W. D. Bancroft and H. L. Davis: J. Phys. Chem., 34, 1797 (1930), where the literature is discussed.



IV Quinoid (probably weakly yellow) V Quinolphenolate red violet VI Carbinol colorless

It is known that the monovalent anions of phenolphthalein (form III) are colorless. One finds for example in the titration of an alcoholic solution of this indicator with sodium hydroxide a considerable amount of sodium hydroxide consumed before the color turns pink. According to measurements of L. Rosenstein,[2] the apparent first ionization constant of phenolphthalein is equal to 1.15×10^{-9}; the second one to 2.8×10^{-10}. Therefore:

$$\frac{[H^+]\,[III]}{[I]} = K_1 = 1.15 \times 10^{-9} \tag{1}$$

The equilibrium between the forms I and II is reversible:

$$\frac{[I]}{[II]} = K \tag{2}$$

or:

$$\frac{[H^+]\,[III]}{[II]\,K} = K_1 \tag{3}$$

II represents an ordinary carboxylic acid. All these acids like benzoic acid, have an ionization constant of 10^{-5} or larger. Assuming that the ionization constant of II is also of the order of 10^{-5}, it is found from equation (3) that:

$$\frac{[H^+]\,[III]}{[II]} = 10^{-5} = K\,K_1 \tag{4}$$

and K is of the order of 10^4.

Therefore in an aqueous solution of phenolphthalein the concentration of the lactone form is of the order of 10,000 times larger than that of the hydrated compound.[3] The concentration of the quinoid form IV (carboxylic group dissociated or undissociated) must be extremely small with respect to those of the other configurations as the solution is colorless. Addition of hydroxylions displaces the equilibrium from II to III over IV to the quinolphenolate V.

In the particular case of phenolphthalein the conditions are such that the equilibrium can quantitatively be expressed by considering the reactions:

$$I \leftrightarrows III + H^+ \qquad\qquad III \leftrightarrows V + H^+$$

$$K = 1.15 \times 10^{-9} \qquad\qquad K_2 = 2.8 \times 10^{-10}$$

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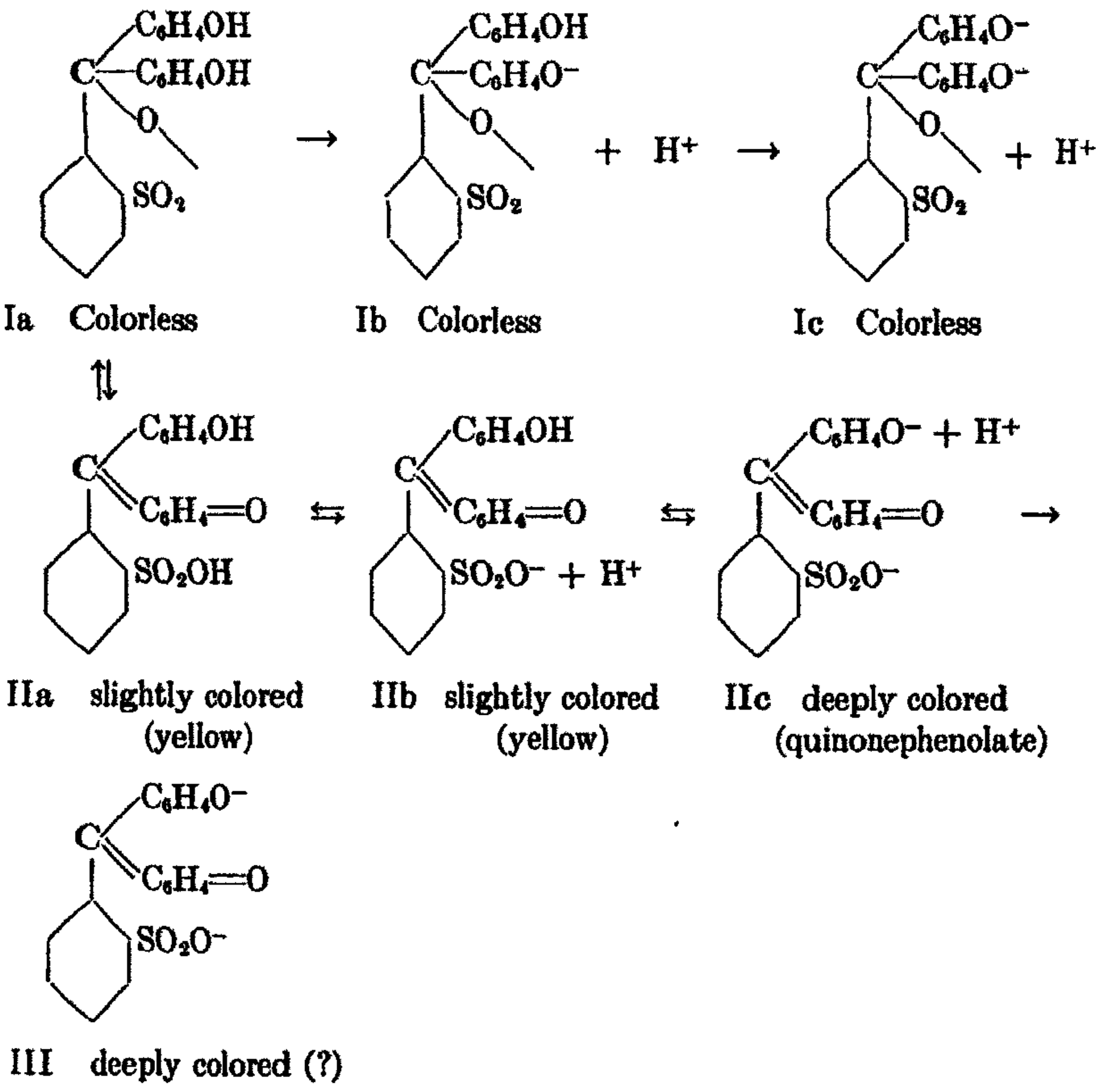
[2] L. Rosenstein: J. Am. Chem. Soc., **34**, 1117 (1912).

[3] Comp. also R. T. Birge and S. F. Acree: J. Am. Chem. Soc., **41**, 1031 (1919.)

The decolorizing effect of an excess of alkali can only be explained by assuming that even in strongly alkaline medium there is some of III left, which is transformed into the colorless configuration VI (equilibrium III ⇆ VI. From the above it is evident that the conditions governing the color change of the phthaleins are extremely complicated. It is of interest to compare the phthaleins with the corresponding sulfonphthaleins.

2. The Sulfonphthaleins in their Alkaline Range

Whereas the (weakly) acid form of most phthaleins is colorless the sulfonphthaleins all are yellow in solution. The structures of all sulfonphthaleins are analogous to that of phenolsulfonphthalein (phenolred) whose various tautomers are given by H. A. Lubs and S. F. Acree[4] in the following scheme:



Even assuming that part of a sulfonphthalein in aqueous solution is present in the colorless form (compare below) it is still questionable whether it is there in the sultone form (I_a: I_b and I_c).

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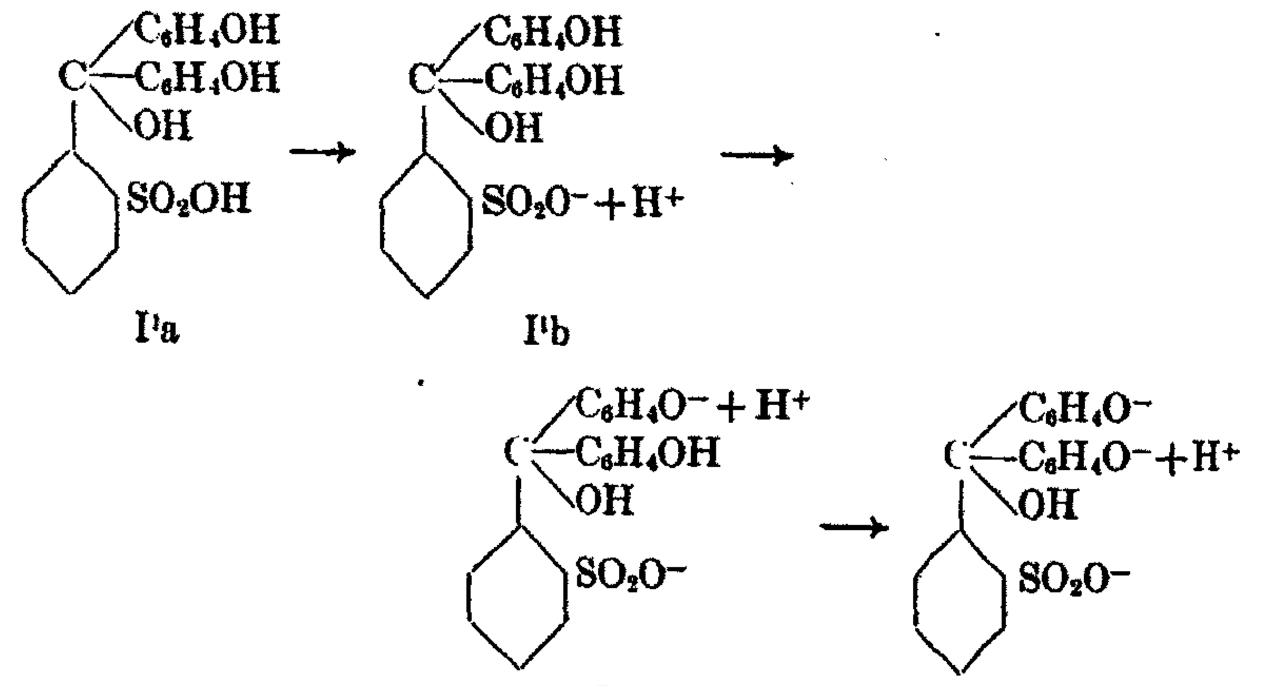
[4] H. A. Lubs and S. F. Acree: J. Am. Chem. Soc., 38, 2772 (1916); comp. also E. C. White and S. F. Acree: 39, 648 (1917) 40, 1092 (1918).

Although the sulfonphthaleins are much more stable towards an excess of alkali than the corresponding phthaleins are, they still can be partly transformed into colorless ions with carbinolstructure as Thiel[5] has shown.

These ions must be derived from the colorless configuration:



I'a I'b

I'c I'd (colorless ion in strongly alkaline medium)

I'_a corresponding to the hydrated form of phenolphthalein (II). Therefore instead of the scheme I_a, I_b and I_c (Lubs and Acree) the above scheme I'_a I'_b I'_c I'_d can as well be written instead. From conductance measurements White[4] has concluded, that in an aqueous solution of phenolsulfonphthalein approximately 65% of the indicator is present in the quinoid (yellow) form, and the remainder in the colorless sultone form. This however seems quite doubtful. If the above statement were true it might be expected that the intensity of the yellow color would increase upon neutralization of the strongly acid sulfonic acid group, as the equilibrium is displaced from II_a to II_b and hence from I_a to II_b. However it was found by the author that phenolred has practically the same color intensity at a pH of 3 and 5. Similarly it was observed, that the intensity of the yellow color of thymolsulfonphthalein practically did not change between a pH of 4 and 7. Therefore if any of the indicator were present in the sultone (I_a) or carbonium form (I'_a); (the latter must be present to account for the decoloration by a large excess of alkali) their quantities must be negligibly small with respect to those of the quinoid configurations II_a and II_b. Therefore from the quantitative point of view the color change from the yellow to the alkaline form can be represented by only considering the equilibrium between II_b and II_c. Actually it has been shown that the indicator constant K_i:

$$\frac{[II_b]\,[H^+]}{[II_c]} = K_i$$

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[5] A. Thiel: Monatsheft, 53-54 1008 (1929).

is constant in the color change from yellow to the alkaline form, and that in this range there is no indication of the formation of a compound like III. The concentration of the carbinolform is so small that it need not be considered in this range of color change. It should be emphasized that the above considerations hold for aqueous solutions of the sulfonphthaleins; in other solvents the conditions may be much more complicated. The color change of the sulfonphthaleins in the alkaline range is completely comparable with that of the corresponding benzeins, where no sultone can be formed. It may be mentioned that some benzeins in strong alkali (33% potassium hydroxide) also form colorless salts, which must have a carbonium configuration.[6] The author has determined the color change interval of some benzeins.

Aurin; (Phenolbenzein) (Product of Eastman Kodak Co.) Indicator solution 0.1% in alcohol.

The color change from yellow to red takes place between pH 6.0 to 7.6; the indicator has almost the same interval as the corresponding phenolsulfonphthalein; the indicator constant of benzein is about two times larger than that of phenolred.

o. Cresolbenzein[7]; 0.1% solution in alcohol.

Color change interval from yellow to deep red between pH of 7.2-8.6.[8] This is about the same interval as found for the corresponding o cresolsulfonphthalein.

Dibromo o.cresolbenzein (Preparation Orndorff[7]).

Again the indicator has the same color change interval as the corresponding sulfonphthalein. Some difficulties were encountered with thymolbenzein and dibromothymolbenzein (both Orndorff[9] preparations.[7] 0.1% solutions of both indicators in alcohol were used.

Thymolbenzein: The indicator is extremely slightly soluble in water; at a pH of 9.0 the solution has a brownish color and shows an opalescence caused by the precipitated benzein. At a pH of 10.2 a bluish tinge is observed, the intensity of which increases at higher pH. The corresponding thymolsulfonphthalein has a color change interval between 8.0 and 9.6, and therefore is completely present in the alkaline form at a pH where thymolbenzein still shows its yellow color. From the above experiments one is not justified in concluding that the ionization constant of the phenolic group in thymolsulfonphthalein is much larger than that of the same in thymolbenzein. The difference in behavior is caused by the extremely slight solubility of thymolbenzein in water. The latter behaves like an indicator acid HI:

$$\frac{[\mathrm{I}^-]}{[\mathrm{HI}]} = \frac{K_I}{[\mathrm{H}^+]} \quad \text{and} \quad [\mathrm{I}^-] = \frac{K_I}{[\mathrm{H}^+]}[\mathrm{HI}]$$

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[6] Comp. W. R. Orndorff, R. C. Gibbs and S. A. McNulty: J. Am. Chem. Soc., 47, 2767 (1925).

[7] Product prepared and used by the late Prof. W. R. Orndorff; obtained from the department of organic chemistry of Cornell University, Ithaca. The author expresses his sincere appreciation for this courtesy.

[8] Comp. W. R. Orndorff and S. A. McNulty: J. Am. Chem. Soc., 49, 992 (1927).

[9] Comp. W. R. Orndorff and H. T. Lacey: J. Am. Chem. Soc., 49, 818 (1927). Attempts to make a salt of the colorless carbinolform have failed.

If K_I is equal to H^+ the indicator is 50% transformed into the alkaline form; $[I^-] = [HI]$. However if the saturation value of HI is extremely small, then $[I^-]$ will be very small also, so that the color of the alkaline form cannot be perceived. The ratio $K_I/[H^+]$ has to decrease much more before the blue color of the alkaline form can be detected.

That the above explanation is correct could be shown by making experiments in buffer solutions containing 50% alcohol. (comp. also Orndorff and Lacey.[9]) In this medium the benzein is much more soluble than in water. By comparing thymolbenzein and thymolsulfonphthalein in the same buffer solutions it was found that the indicator constant of the former is about 2 to 2.5 times larger than that of thymolsulfonphthaleins. (instead of being about 100 times smaller as one might conclude from the experiments in aqueous medium). This could be expected; the color change of the benzein and the corresponding sulfonphthalein is governed by the same type of equilibrium; the ionized sulfonic group in thymolblue has a negatively inducing action upon the ionization of the phenolic group and therefore the indicator constants of the benzeins should be slightly larger than that of the corresponding sulfonphthaleins.

Dibromothymolbenzein: In aqueous buffer solutions:

Color at pH of 9.0 yellowish brown; at 9.2 slightly green, at 9.8 distinctly green; 10.2 bluish, at 10.6 dark blue. The corresponding dibromothymolsulfonphthalein has a color change interval between 6.0-7.6 (yellow to blue). Again the difference in behavior between both indicators is explained by the slight solubility of the benzein in water. In 50% alcohol the benzein and the sulfonbenzein show about the same behavior; the ionization constant of the former being again about two times larger than that of bromthymolblue.

It may be mentioned that the benzeins which are not too slightly soluble in water may have distinct advantages as indicators over the corresponding sulfonphthaleins. In preparing the solutions of the benzeins a strong sulfonic acid group need not to be neutralized. Moreover the color change takes place from the neutral form to the monovalent anion, and it can be expected that the "salt error" of the benzeins will be much smaller than that of the corresponding sulfonphthaleins.

A few words should be said of the derivatives of α Naphtol. α Naphtolphthalein is an indicator, used by S. P. L. Sörensen[10] in his pioneer work. The alcoholic and aqueous solutions of the indicator are not colorless as those of most other phthaleins are, but have a brownish color. α Naphtolphthalein changes its color in aqueous buffer-solutions between pH 7.8 to 8.8 (bluish green). The corresponding α naphtolsulfonphthalein has a color change interval between pH 7.5-9.0 from yellow to blue. α Naphtolbenzein (Eastman Kodak Co. product) again is very slightly soluble in water. In aqueous buffer solutions it changes its color between pH 10.0-11.6 (approximately) from yellow to greenish blue. In buffer mixtures made up in 50% alcohol however it shows the same behavior as α naphtolphthalein. α Naphtolsulfonphthalein

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[10] S. P. L. Sörensen: Compt. rend., Lab. Carlsberg 8, 1 (1909).

and α naphtolbenzein have an indicator constant of about the same magnitude. From this and the yellow-brown color of α naphtolphthalein in acid medium it may be concluded, that in aqueous solution the latter indicator is mainly present in the quinoid form (comparable with form II_a of the sulfonphthaleins, but write in the scheme instead of the phenolgroups 2 α naphtol groups and instead of the sulfonic group the carboxylic group). The above view is supported by another fact, namely that α naphtolphthalein in its color change behaves like a monobasic acid. In this respect it is also of interest to mention, that A. Thiel[5] found the colored alkaline form quite stable in strongly alkaline solution; a behavior quite different from that of other simple phthaleins but more comparable to that of sulfonphthaleins. For the organic chemist it is an interesting problem to find out why the structure of α naphtolphthalein is different from that of phenolphthalein, o cresolphthalein, thymolphthalein etc.; or better why in solutions of the former the equilibrium between the various forms is shifted so much to that of the quinoid configuration.

3. The Sulfonphthaleins in their Strongly Acid Range

In their classical paper Clark and Lubs (1916) already stated that thymolsulfonphthalein has two ranges of color changes, one between pH 1.2 to 2.8 (red to yellow) and the other from 8.0 to 9.6 (yellow to blue). B. Cohen observed that m. cresolsulfonphthalein shows a similar behavior (acid range 0.5 to 2.5; alkaline range 7.6-9.2). This color change in strong acid medium is not restricted to thymolblue and m. cresolpurple but all sulfonphthaleins show a color change in strong acid medium. In monographs on indicators no interpretation of the structural change accounting for this color virage is given, nor is it stated to which group this effect is to be attributed. These points will be further discussed below.

In the following table the colors of various sulfonphthaleins is given at different concentrations of hydrochloric acid and in concentrated sulfuric acid.

The color changes of phenolsulfonphthalein and its dichloroproduct (C.P.R.) in strongly acid medium are not very pronounced. The colors reported (orange) have been observed in transmitted light; the reflected light being nicely pink. From the table it may be inferred that all sulfonphthaleins have two ranges in acidity at which they change their colors. Again it is of interest to compare the behavior of the benzeins to that of the corresponding sulfonphthaleins.

It has been mentioned in §2 that thymolbenzein and its dibromo derivative are extremely slightly soluble in water. In aqueous medium the color changes of these benzeins is observed at a much higher acidity than those of the corresponding sulfonphthaleins. In a medium of 50% alcohol they approach those of the sulfonphthaleins, though the change still takes place at a higher acidity. Phenolbenzein does not show a distinct color change in strongly acid medium; it has been mentioned already that the colors of the strongly acid forms of phenolsulfonphthalein and chlorphenol red are not very pronounced either. o. Cresolbenzein and its dibromo derivative show the same behavior as the corresponding sulfonphthalein.

TABLE I

Color of Sulfonphthaleins in Strongly Acid Medium

Concentration HCl	T.B.;	P.R.;	C.P.;	C.R.;	B.T.B.;	C.P.R.;	B.P.B.;	T.B.P.B.;	B.C.P.;	B.C.G.
0.001 N	yellow	yellow	yellow	yellow	yellow	yellow	yellow	yellow	yellow	yellow
0.01 "	orange-red	brownish-yellow	orange	orange	"	"	"	"	"	"
0.1 "	red-*violet*	*orange*	red-*pink*	orange-*pink*	"	"	"	"	"	"
1 "	"	"	"	red-pink	"	"	"	"	"	
4 "	"	"	"	"	orange-red	orange	"	"	orange	orange
6 "	"	"	"	"	*violet*	red-*orange*	"	"	orange-red	"
12 "	"	"	"	"	"	"	orange-pink	weakly yellow	*violet-red*	*violet*
H_2SO_4	"	"	"	"	purple	"	violet-red	weakly violet	"	intensely violet

T.B. = thymolsulfonphthalein;
C.P. = m. cresolsulfonphthalein;
B.T.B. = dibromothymolsulfonphthalein;
B.P.B. = Tetrabromophenolsulfonphthalein;
B.C.P. = dibromocresolsulfonphthalein;

P.R. = Phenolsulfonphthalein;
C.R. = o cresolsulfonphthalein;
C.P.R. = dichlorophenolsulfonphthalein;
T.B.P.B. = Tetrabromophenoltetrabromosulfonphthalein;
B.C.G. = Tetrabromo o. cresolsulfonphthalein;

TABLE II

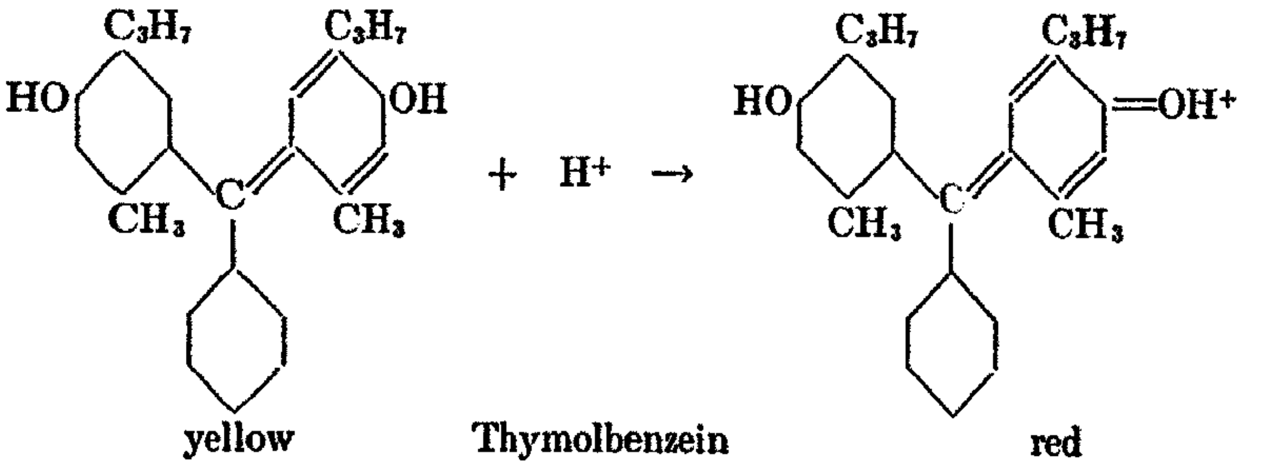
Color Change of Benzeins in Strongly Acid Medium

Concentration HCl	T.Bz.	P.Bz.	o C.Bz.	B.T.Bz.	B.C.Bz.
0.01 N	yellowish	yellow	yellow	yellow	yellow
0.1 "	pink	"	orange-pink	"	"
1 "	pink-red	"	*pink*	"	"
4 "	"	"	"	"	orange
6 "	" "	"	"	orange	*pink*
12 "	"	"	"	*red*	red
H_2SO_4	"	"	"	violet	violet-red

T.Bz. = Thymolbenzein;
o.C.Bz. = o.cresolbenzein;
B.C.Bz. = Dibromo o.cresolbenzein.
P.Bz. = Phenolbenzein (Aurin);
B.T.Bz. = Dibromothymolbenzein;

It is known that the benzeins have a weakly basic character. A. von Bayer[11] prepared the sulfate of benzaurin in the solid state; W. R. Orndorff and H. T. Lacey[9] obtained the sulfate, chloride and perchlorate of thymolbenzein.

Therefore it is evident that the color change of the benzeins is governed by the basic character of the quinoid group:



It is not easy to decide whether this strongly acid form (red) is an oxonium (as given above) or carbonium compound. On the basis of the work carried out by M. Gomberg and Cone,[12] one would be inclined to favor the quinocarbonium configuration.

It is peculiar that the ionization of the quinone group has such an enormous influence upon the absorption spectrum of the compound. The free quinone has a yellow color, its cation is red to red-violet, whereas (in alkaline

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[11] A. von Bayer and R. Hallensleben: Ber., 36, 2791 (1903).

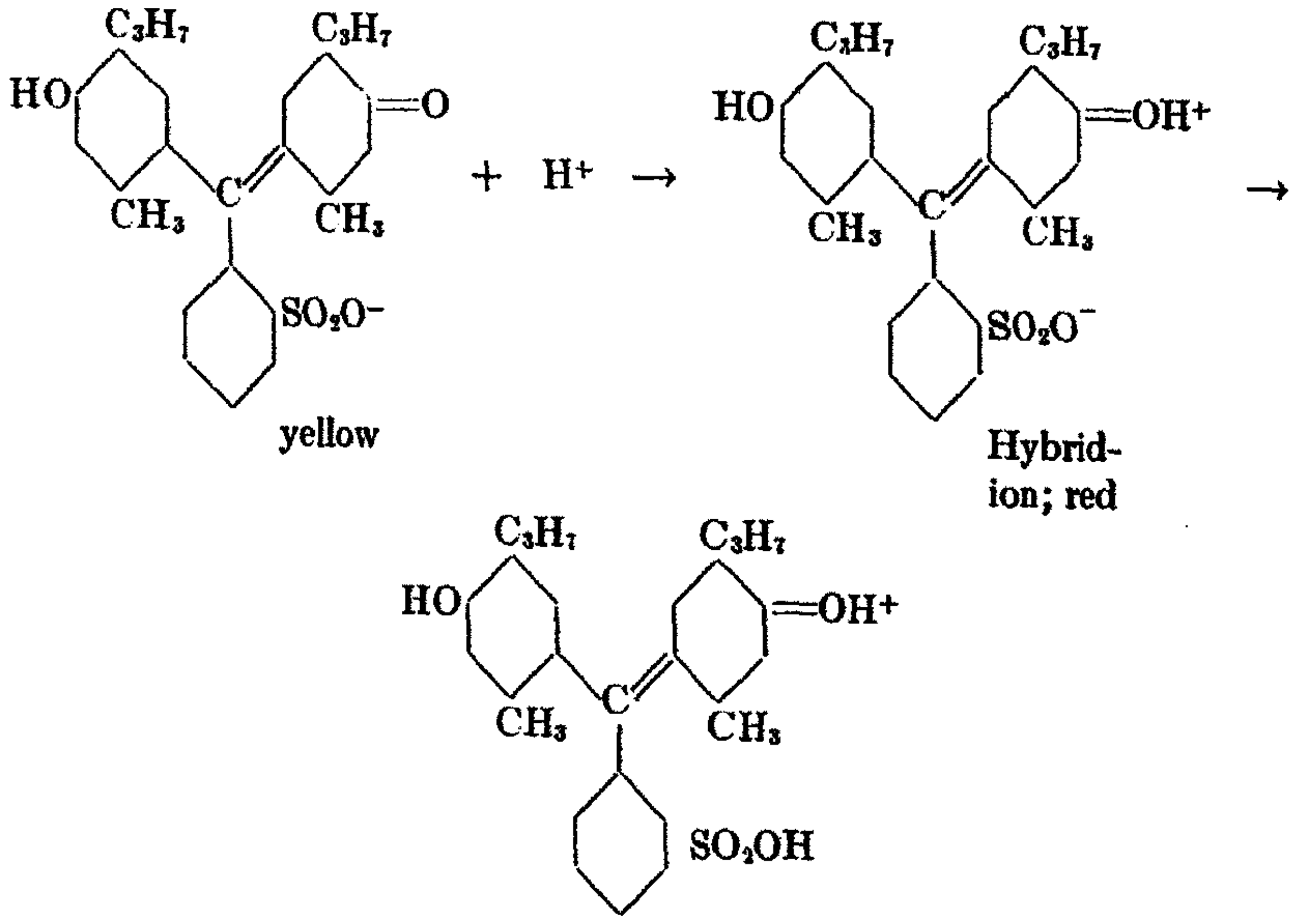
[12] Gomberg and Cone: Ann., 370, 192 (1909); comp. also H. Lund: J. Am. Chem. Soc., 49, 1346 (1927); L. C. Anderson and M. Gomberg: 50, 203 (1928); Anderson: 51, 1889 (1929); 52, 4567 (1930).

medium) the quinonephenolate has an intense blue color. The maximum in the absorption band shifts with this color change to higher wave lengths. From the studies made by W. R. Orndorff and collaborators[13] it may be concluded that a similar shift to longer wave lengths takes place when the yellow form is transformed into the strongly acid configuration, although the maximum is found at a shorter wave length than in alkaline medium.

Moreover in these studies it is shown that the absorption coefficient of the alkaline form is greater than that of the acid form (alkaline color more intense than that of acid form).

From the analogous behavior of the benzeins and the sulfonphthaleins it may be concluded, that the color change of the latter in strongly acid medium is also caused by the ionization of the quinoid group:

Therefore it can be represented by the following scheme: (thymolsulfonphthalein).



cation, red

There are various reasons for assuming that in the color change of thymolsulfonphthalein in the acid range the red hybrid ion is formed, though in stronger acid medium part of the sulfonic group will be present in the undissociated state.[14] However the colors of the hybrid ion and cation will be the same.

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[13] W. R. Orndorff and S. A. McNulty: J. Am. Chem. Soc., 49, 992, 1588 (1927); Orndorff, Gibbs and McNulty: 47, 2767 (1925) Orndorff, Gibbs, McNulty and Shapiro: 49, 1545 (1927).

[14] Comp. the analogous behavior of dimethylaminoazobenzene sulfonic acid (methylorange acid); I. M. Kolthoff: Rec. Trav. chim., 44, 68 (1925).

The salt error of thymolblue in its acid range is very small;[15] the solubility in aqueous medium reaches a minimum at a hydrochloric acid concentration of about 0.1 N.

The solubility of thymolsulfonphthalein was determined in water and in solutions of hydrochloric acid of various strengths (at 25° ± 1°). The solubility seems to depend relatively much upon the size of the fine powder present as a solid body. If a solution of thymolblue was precipitated by hydrochloric acid a much higher solubility was found than if the solution of the same acid normality was saturated by shaking it with solid thymolblue. The supersaturated solutions are stable for a long time; it takes more than a month before equilibrium is attained. In the experiments described below a sample of thymolsulfonphthalein obtained from Hynson, Westcott and Dunning, Baltimore, Md. was used.[16]

The product was shaken with water, and finally washed a long time with conductivity water. Part of the finer particles went into colloidal solution. Though the solubility of thymolblue is very small, it still took 30 to 90 hours shaking before the solutions were saturated. The solid particles are difficultly wetted by water. The saturated solutions were filtered and the solubility determined colorimetrically in 2-3 N hydrochloric acid. Comparison was made with solutions of thymolblue of known concentration at the same acidity.

TABLE III

Solubility of Thymolsulfonphthalein in Water and Hydrochloric Acid

Solvent	Mg. thymolblue per liter	Molarity of saturated solution
Water	110	2.3×10^{-4}
0.01 N HCl	7.2	1.55×10^{-5}
0.05 " "	2.6	5.6×10^{-6}
0.1 " "	1.8	4×10^{-6}
0.2 " "	1.8	4×10^{-6}
0.5 " "	1.6	3.5×10^{-6}
1 " "	1.8	4×10^{-6}
6 " "	5.0	1.1×10^{-5}
0.1 N HCl + 0.9 N KCl	0.8	1.8×10^{-6}

The solubility reaches a minimum in about 0.1 N hydrochloric acid. In 0.5 N acid a slightly smaller solubility is found, but probably this is due to the salting out effect of the electrolyte. In 0.1 N acid and 0.9 N, potassium chloride a solubility about half of that in 0.1 N hydrochloric acid was found. At higher acidities than 0.5 N the solubility increases slightly with the acid concentration, probably on account of the formation of the undissociated sulfonic acid group (cation).

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[15] Comp. I. M. Kolthoff: J. Phys. Chem., **32**, 1820 (1928); **34**, 1466 (1930).

[16] The author expresses his sincere appreciation to this concern for its kindness in furnishing him with a sample of their purest product. According to the conductimetric titration with sodium hydroxide it was 98 to 99% pure.

The solubility of thymolblue in water corresponds to 2.3×10^{-4} molar. Assuming that the red hybrid ion dissociates completely into hydrogen ions and the yellow anions, we have: $[H^+][I^-] = (2.3 \times 10^{-4})^2 = 5.3 \times 10^{-8}$ = solubility product of the hybrid ion.

From the indicator function in acid medium (comp. Kolthoff[15] 1930) we know that the indicator constant

$$\frac{[H^+][I^-]}{[^+I^-]} = 2.2 \times 10^{-2}$$

$[I^-]$ represents the concentration of the yellow form; $[^+I^-]$ the same of the red hybrid ion. From these two equations it is found, that a solution saturated with the hybrid ion contains $\frac{5.3 \times 10^{-8}}{2.2 \times 10^{-2}}$ = approximately 2×10^{-6} moles of the latter per liter. This figure is of the order of the solubility which was found in 0.1 N hydrochloric acid.

That the sulfonphthaleins in strongly acid medium behave like cations could be shown by their behavior as adsorption-indicators.[17]

From the studies of Fajans and collaborators it is known, that a silver halide negatively charged by an excess of halide ions has a tendency to adsorb cations. If these adsorbed ions are colored they usually impart to the precipitate a characteristic color. The following experiments have been made with silver thiocyanate freshly precipitated from the solution containing the dyestuff. In presence of an excess of silver ions the precipitate is positively charged, with an excess of thiocyanate ions it has a negative charge.

Methylred in neutral solution (yellow):

With an excess of silver ions red precipitate; change to yellow with an excess of thiocyanate. The positively charged precipitate adsorbs the (yellow) anions of methylred and forms a red compound at the surface.

Methylred in about 1 N sulfuric acid (red):

With an excess of thiocyanate the precipitate is brick red, and almost colorless, when positively charged. Therefore in acid medium we find the reverse behavior from that in neutral solution, owing to the fact that methylred in strongly acid medium is present in the cation form.

Methylorange shows a behavior exactly analogous to that of methylred. At its isoelectric point the presence of anions of methylorange can also be detected by its behavior as adsorption-indicator.

Tropeolin 00 behaves like methylorange; in acid medium the negatively charged silver thiocyanate assumes a blue color by the adsorption of the

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[17] The following experiments are not important from analytical point of view. The adsorption indicators described in the literature for argentometric titrations are preferable to those mentioned in this paper.

indicator. In a similar way the cations in a red solution of pentamethoxytriphenylcarbinol can be detected if silver-iodide is used as an adsorbent.

Thymolsulfonphthalein in about 1 N sulfuric acid is only slightly adsorbed by positively charged silver thiocyanate, with an excess of thiocyanate ions the precipitate turns deep violet, indicating the cation function of the indicator.

In neutral solution (yellow) thymolblue does not color the precipitate, neither with an excess of silver nor with thiocyanate.

Phenolsulfonphthalein shows qualitatively a similar behavior. In 1 N sulfuric acid the precipitate has a pink color with an excess of thiocyanate, and it is decolorized by an excess of silver ions.

From the above it is evident that the color change of the sulfonphthaleins in strongly acid medium has to be attributed to a cation formation of the basic quinone group. From the experiments listed in Table 1 and other observations the following conclusions could be drawn:

1. The basic character of the quinone group decreases with the introduction of halogens in the phenolic group:

K_{Base} Phenolred > K_{Base} Chlorophenolred > K_{Base} Bromophenolblue > K_{Base} Tetrabromphenolblue..

2. The maximum absorption of light by the quinone cation shifts to longer wave lengths with the introduction of halogens (for example in strongly acid medium: phenolred is orange; dichlorphenolred red orange; tetrabromphenolsulfonphthalein violet red (H_2SO_4). Qualitatively therefore the introduction of halogens has a similar influence upon the absorption of light by the alkaline form as it has upon the strongly acid configuration.

3. The same similarity holds when light absorptions by the alkaline and strongly acid forms of phenol, thymol, cresolsulfonphthaleins are compared.

Many of the sulfonphthaleins in the solid form are strongly colored dark crystals or powders, like thymolblue, phenolred etc.[18]

Orndoff attributes this color to an inner salt between the quinone and sulfonic group (not ionized). There seems more reason to consider these strongly colored compounds as hybrid ions. In agreement with this view is the fact which Orndoff and Cornwell[8] found that thymolsulfonphthalein forms an ammonium salt with dry ammonia, but it does not give a salt with hydrochloric acid. Ammonia liberates the extremely weak basic quinoid group in the undissociated state, whereas dry hydrochloric acid is not able to replace the sulfonic acid ion. In own experiments it was observed that the darkly colored solids are difficultly wetted by water, which fact also seems to be in harmony with the hybrid ion view.

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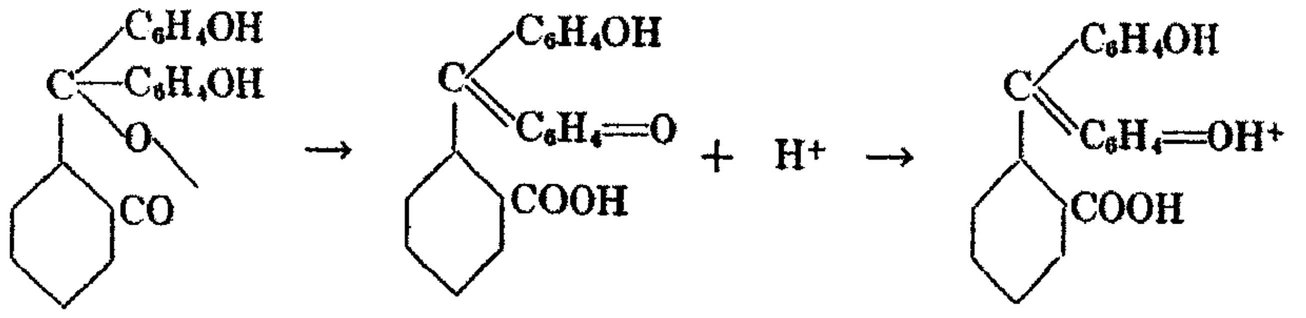
[18] Comp. the interesting and important studies of W. R. Orndorff and collaborators (lit. ref. 8, 9, and 13) also: W. R. Orndorff and F. W. Sherwood: J. Am. Chem. Soc., **45**, 486, 495 (1923); **48**, 2212 (1926); Orndorff and A. C. Purdy: **48**, 2212 (1926); Orndorff and C. Wang: **47**, 290 (1925); **49**, 1284 (1927); Orndorff and R. T. K. Cornwell: **48**, 981 (1926); Orndorff and I. T. Beach: **50**, 1416; Orndorff and C. V. Shapiro: 1730 (1928); Orndorff and M. L. Willard: **51**, 1466 (1929), R. T. K. Cornwell and A. J. Esselstyn: **49**, 826 (1927).

4. The Color Changes of the Phthaleins in Strongly Acid Medium

It has been known for a long time that phenolphthalein has a pink color in extremely strong acid solution. Other phthaleins show a similar behavior. Attributing this color change again to the basic character of the quinone group it may be expected that the change takes place at much higher acidities than at which the corresponding sulfonphthaleins or benzeins change their colors.



Lactone Quinoid Strongly acid form; colored

In §1 it has been shown that phenolphthalein and thymolphthalein are practically completely present in the lactone form, and therefore we may expect a similar difference between the "apparent" basic strengths of thymolphthalein and thymolbenzein in strongly acid medium as there is between the "apparent" acid strengths of the thymolgroup in both indicators in their color change at the alkaline range. So it was found that thymolphthalein is still colorless in 6N hydrochloric acid; it is weakly pink in 9 N hydrochloric acid; and dark violet in concentrated hydrochloric acid and sulfuric acid. Thymolbenzein is completely transformed into the acid form in 1 N hydrochloric acid. Phenolphthalein shows a weakly pink color in 9 N and 12 N hydrochloric acid and assumes a brown orange color in sulfuric acid. In reflected light a pink color is observed, similar to that of phenolsulfonphthalein in the same medium (see 3).

α Naphtolphthalein again behaves like α naphtolbenzein. Both indicators are colorless in 6 N hydrochloric acid, slightly green in 9 N acid, darker green in concentrated hydrochloric and sulfuric acid. On standing a green precipitate settles out. This similar behavior again is a proof that α naphtolphthalein in solution has a quinoid structure.

Summary

1. In an aqueous solution of phenolphthalein the concentration of the lactone form is of the order of 10,000 times larger than that of the carboxylic acid configuration.

2. The color change of the sulfonphthaleins in their alkaline range is quantitatively governed by the equilibrium between the quinone and the quinone phenolate (anion) forms.

3. Benzeins which are not too slightly soluble in water have advantages over the corresponding sulfonphthaleins as indicators.

4. α Naphtholphthalein in aqueous solution is mainly present in the quinoid form.

5. The color change of sulfonphthaleins, benzeins and phthaleins in acid medium is to be attributed to the weakly basic character of the quinone group. Thymolblue forms a hybrid ion in its color change in the acid range.

6. By examining the behavior of dyestuffs as adsorption indicators it is possible to decide whether they are present in the form of cations or of anions.

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THE ACTION OF IMMISCIBLE ORGANIC LIQUIDS ON COLLOIDAL GOLD

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Introduction

The most important paper concerning the behaviour of gold hydrosols when shaken with immiscible organic liquids is one published by Zsigmondy[1] in 1916. In the first place Zsigmondy examined the effect of purifying the liquids, which had apparently not been done by Reinders,[2] the first to study the subject at all extensively. It was found that pure benzene, toluene, ether, carbon disulphide and amyl alcohol had no action upon the alkaline sols obtained by the Zsigmondy methods of preparation. Further, that pure benzene, toluene, and ether produced no change in the acid sols prepared by Donau's method (reduction of gold chloride by carbon monoxide) or in Zsigmondy sols acidified by the addition of hydrochloric acid, provided the concentration of hydrogen ion did not exceed about 10^{-3} grm. ion litre. On the other hand if the sols were shaken with an impure liquid, e.g. ether which had stood in the laboratory for a prolonged period, all the gold collected in the form of a blue film at the liquid-liquid interface, as had been observed by Reinders.

Zsigmondy discovered that the presence of exceedingly small quantities of protein also caused the gold in the acid sols to be shaken out by the organic liquid. In searching to explain this and the fact that excessive acidity led to the same result, experiments were carried out on suspensions of coarse gold, prepared by coagulating sols by ultrafiltration, evaporation, or the addition of electrolyte. Whether the coagulum was washed free from electrolyte prior to suspension or not, the gold particles always accumulated at the junction of the two liquids. Finally a grey-violet sol was prepared by the electrical disintegration of gold wire (Bredig's method) in pure water contained in a quartz vessel, and shaken with purified benzene. It was found that the colloidal gold was unaffected, whereas the coarser material again adhered to the organic layer.

Zsigmondy concluded that the tendency of gold particles to go to the boundary between the aqueous and organic phases was primarily a function of the degree of dispersion of the gold. He suggested that attractive forces existed between the droplets of emulsified organic liquid and the gold particles, which increased as the latter became larger. Wiegner's[3] observation that coarse ultramicrons appear to act as coagulation centres in unstable sols could be interpreted in a similar fashion. Zsigmondy thus considered that the primary particles of a gold sol were unaffected by shaking with a pure organic liquid and that the effect of added substances was due to the coagulation of the sol to form the coarser secondary complexes. To quote from his paper "Die in Wasser gelösten Verunreinigungen (bei sauren Goldlösungen

z. B. Eiweisssubstanzen) bewirken zünachst Koagulation des Goldes, dass dann in Form gröberer Teilchen stets an die Grenzfläche geht, daselbst ein metallschimmerndes Häutchen bildend. . . ."

With regard to other possible factors Zsigmondy was not very definite. He points out that the presence of (a) negative electrical charges and (b) water sheaths (Wasserhüllen) at the surfaces of the gold particles and of the benzene droplets will oppose the tendency of these bodies to unite. He also says "—die in der organischen Flüssigkeit (Aether, Benzol, Amylalkohol—) enthaltenen Verunreinigungen können, falls sie an der Oberfläche sich anreichern, wie flüchtige Fettsaüren u.dgl, auch direkte Vereinigung der Flüssigkeitströpfchen mit dem Gold und damit Koagulation veranlassen."

Freundlich[4] has remarked that it is difficult to account for the absence of effect in the case of the small colloidal particles, since these were not necessarily in a more highly charged condition than the larger ones, for the difference was shown by particles belonging to the same system (Zsigmondy's experiment with the Bredig sol.)* Viewing the problem as essentially a question of preferential wetting, he suggests that the interfacial tension between gold and water decreases as the particle becomes smaller, which makes it more difficult for the organic liquid to displace the water from the gold surface. In other words, the water sheath is more firmly bound, the smaller the particle.

The present authors commenced an investigation with the object of determining the "critical" size which, according to the views outlined above, a particle must possess if it is to be removed from the aqueous phase to the liquid-liquid interface. Preliminary experiments, however, indicated that in certain systems at least, the influence of particle size is of minor importance. The following is an account of a study of these systems.

Preliminary Experiments

Nordenson[5] has shown that the reduction of gold chloride by hydrogen peroxide is accelerated by ultraviolet light, the size of the particles in the resulting sol or suspension decreasing as the exposure is made longer. Advantage was taken of this circumstance to prepare a series of sols of different degrees of dispersion. On examining the behaviour of these systems when shaken with purified amyl alcohol (see below) it was found that in every case the whole of the gold collected immediately at the water-alcohol interface. This result was surprising since, judging from their appearance, the finer grained sols were quite comparable, in regard to particle size, with those studied by Zsigmondy. It was noticed however that Zsigmondy (see Introduction) had not observed the action of *amyl alcohol* on *acid* sols, with which we are here concerned. The possibility of the existence of specific differences between organic liquids was thus indicated and it was decided to investigate the action of a considerable number of organic liquids on both Nordenson and Zsigmondy sols.

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* See however, Freundlich and Loebmann.[11]

Examination of a Variety of Organic Liquids

Preparation of the Sols.—The Nordenson sol (Au_NA) was prepared as follows. Two c.c. of 0.6 percent Merck's gold chloride ($HAuCl_4.4H_2O$) and 0.6 c.c. of 0.1 M anhydrous potassium carbonate (Kahlbaum) were mixed with 120 c.c. conductivity water in a large porcelain basin, 0.4 c.c. of "perhydrol" (Merck) added, and the contents of the basin immediately subjected to direct radiation from a mercury vapour lamp. The exposure lasted for 25 sec. and the reduction mixture was constantly stirred during the reduction. It was found that the addition of potassium carbonate, though in quantities insufficient to produce a neutral or alkaline sol, ensured a high degree of dispersion. (cf. Beaver and Muller[6]). To prepare the Zsigmondy sol (Au_2A), 2.0 c.c. of the same gold chloride solution were diluted with 120 c.c. conductivity water, heated in a Jena glass beaker and 3.0 c.c. of 0.1 M potassium carbonate (as above) added. When the solution was just boiling the flame was removed and 3.0 c.c. of 0.4 percent pure formaldehyde (prepared in this laboratory by Dr. Coutie) added drop by drop with vigorous stirring. Water of spec. cond. $= 0.4 - 0.8 \times 10^{-6}$ mhos, prepared in a Bourdillon still, was used in the preparation of the sols and the solutions were made up with distilled water of particularly good quality (spec. cond. $= 1 - 2 \times 10^{-6}$ mhos.).

It will be noted that the concentration of the gold was the same in the two sols. Both preparations were of a deep cherry red colour and neither showed a trace of opalescence. They were stored in well-cleaned Jena glass-stoppered bottles and proved to be very stable.

Distribution Experiments.—Three c.c. of sol and 1 c.c. of organic liquid were pipetted into a tube closed with a glass stopper and the mixture shaken vigorously by hand. The tube was given 400 shakes except when all the gold was removed from the aqueous phase by less shaking.*

In order to obtain reproducible results it was found necessary to clean the tubes and stoppers very thoroughly. After washing with hot water and rectified spirits, they were immersed in aqua regia to dissolve any gold left from a previous experiment, and then placed in chromic acid overnight. Finally they were well washed with distilled water and dried in an air oven. When first used the tubes were subjected to a prolonged steaming-out. The use of tubes closed with corks was found to be unsatisfactory, at least in the case of alcohols. Apparently the irregularities observed could be traced to material dissolved from some of the corks by the organic liquid. While reproducible results were obtained by selecting new corks which presented an unbroken surface to the contents of the tube, it was considered advisable to get glass-stoppered tubes made for the investigation.

The majority of the organic liquids as obtained were either commercially pure or else had been purified in the department for research work. Finally the following were found to have absolutely no action upon either type of sol: *benzaldehyde, benzene, bromo-benzene, carbon disulphide, carbon tetrachloride, chloroform, o. m.* and *p.chlorotoluene, ether, ethyl benzene, paraffin, salicylalde-*

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*This rule was adopted throughout the work.

hyde, toluene and *m.xylene.* In some instances fractional distillation was necessary in order to obtain a negative result. To avoid contamination of the liquids a distillation apparatus with ground-glass joints was constructed. It was provided with a column of Raschig rings and an Anschütz thermometer was suspended above the column by means of platinum wire.

Even after distillation the toluene and xylene still possessed a slight but quite definite influence upon Au_NA, which however was eliminated by the following methods of purification. The toluene was boiled with aluminium chloride and the black product distilled, the distillate washed with sodium bicarbonate and water and allowed to stand overnight in contact with sodium wire. The organic liquid was now shaken with twelve changes of pure concentrated sulphuric acid, then repeatedly washed with distilled water, and after drying over sodium wire, fractionally distilled. The xylene was shaken with an equal volume of concentrated sulphuric acid and then treated with saturated sodium chloride. After several hours the crystals of sodium xylene sulphonate were filtered off, dried, and boiled with absolute alcohol, the sodium chloride removed by filtration, and the solution evaporated to dryness. The xylene was recovered by steam distillation with superheated steam, separated from the water in the distillate, dried with anhydrous potassium carbonate, and fractionally distilled.

Several immiscible alcohols were now examined. A. R. *amyl alcohol*, "nitrogen and pyridine free", (by B.D.H.) was shaken with four lots of caustic soda solution, well washed with distilled water and dried with anhydrous potassium carbonate. The bulk distilled over between 130.8° and 131° (B.P. iso-amyl alcohol = 131°) and this was used in the experiments. While Au_ZA was not affected in the slightest by this organic liquid (after 400 shakes) Au_NA underwent immediate change, the whole of the gold accumulating to form a blue film at the water-alcohol interface in about 5 shakes. Exactly the same results were obtained with *n-butyl, iso-butyl, hexyl* and *heptyl alcohols.* In these instances A.R. materials (by B.D.H.) were distilled and the fraction boiling over a range of 0.2°C. at the correct boiling point employed.

The Action of the Alcohols

Experiments were now carried out to ascertain the cause of the difference in behaviour of Au_ZA and Au_NA when shaken with an immiscible alcohol. As indicated above the two sols were identical in appearance. They moreover were seen to closely resemble one another when examined in the slit ultramicroscope: in both cases the majority of the particles were green, there being only a small proportion of red or orange ones.* The only obvious difference between the sols was that Au_ZA contained a larger amount of potassium carbonate than Au_NA. Hence the effect of adding this salt to a Nordenson sol was next studied.

For the reason given later a sol, Au_NB, prepared with 0.8 c.c., 0.2 N K_2CO_3 instead of 0.6 c.c. was used. A series of tubes were set up, each tube containing

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*See later for determination of particle sizes.

a mixture of 3 c.c. Au_NB + 1 c.c. K_2CO_3 (Kahlbaum), the concentration of the latter increasing from tube to tube. After standing for 24 hours, the mixtures were carefully examined for any colour change, and then each was shaken with 1 c.c. amyl alcohol. As far as the action of potassium carbonate alone was concerned, no change could be detected in the sol, provided the final concentration (C) of the *added* carbonate did not exceed about 30 m.equivalents/liter. As will be seen from the following summary, within limits potassium carbonate prevented the shaking out of the sol. The values of C are approximate.

C	0.0	0.0-0.5	0.5-3.0	3.0-12.5	12.5 & over
Film formation	complete	decreasing	none	increasing	complete

That portion of the gold which did not go to the interface in any given case appeared to be quite unaffected.

It will be noted that at the higher concentrations of carbonate the sol became unstable again. To complete the comparison, the effect of adding potassium carbonate to a Zsigmondy sol was investigated. The following results were obtained with a sol, Au_ZB,* prepared with 1.5 c.c. 0.1 M,K_2CO_3 instead of 3.0 c.c.

C	0.0-5.0	5.0-15.0	15.0 & over.
Film formation	None	increasing	complete.

The concentration of carbonate required to produce the first sign of coagulation in 24 hours (i.e. in the absence of the alcohol) was about 35×10^{-3}M, which, as in the case of Au_NB, was well above the value at which film formation commenced.

Formation of Red Films.—Since the stabilising action of potassium carbonate might well be due to its alkalinity, the influence of sodium hydroxide (solution prepared from "pure" sticks) on Au_NB and Au_ZB was investigated in exactly the same fashion as above. Table I contains the results for typical series.

The occurrence of *red* films, which does not appear to have been observed by previous workers, is of particular interest since it shows that coagulation to form secondary particles (blue gold) is not essential for removal to the interface. We may therefore reasonably assume that the apparent immediate formation of a blue film from a red sol is also the result of coagulation of the gold *after* it had reached the interface, the aggregation of the gold being extremely rapid in such a case. A change from red to blue *at the interface* could actually be observed with Au_NB and Au_ZB and K_2CO_3. Immediately after shaking, the surfaces of the drops of emulsified amyl alcohol were seen to be covered with red gold, which changed to blue or bluish violet as the drops coalesced.

Other considerations made it appear very unlikely that the action of amyl alcohol on a Nordenson sol was due primarily to coagulation of the

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*Au_NB and Au_ZB had exactly the same appearance as Au_NA and Au_ZA. The former were made to more closely resemble one another than was the case with the latter, by decreasing the difference in the amounts of K_2CO_3 used in their preparation.

TABLE I

Effect of adding Sodium Hydroxide

Nordenson sol (B)

C	Distribution Interface	Aqueous layer
0.00	10BBl	0
0.08	4B	6R
0.25	1B	9R
0.49	+B	10−R
0.66	0	10R
0.82	0	10R
2.51	0	10R
5.02	0	10R
7.53	+R	10−R
10.04	1R	9R
12.55	3R	7R
15.06	7BP	3R
20.08	10−BP	+R
25.10	10BP	0
30.70	"	"
33.21	"	"
35.72	"	"

Zsigmondy sol (B)

C	Distribution Interface	Aqueous layer
0.00	0	10R
2.51	0	10R
5.02	+R	10−R
7.53	+R	10−R
10.04	1R	9R
12.55	3R	7R
17.57	5R	5R
20.08	7R	3R
25.10	9RP	1R
28.19	10RP	0
33.21	10BP	"
35.72	"	"
38.35	"	"
51.35	"	"

R = red B = blue BBl = blue black P = purple
BP = bluish-purple RP reddish-purple

The number indicates approximately the proportion of gold at the interface or in the aqueous layer. 10 represents the whole of the gold. The first fourteen Nordenson sols were red after twenty-four hours; the 15th and 16th had a tinge of purple and the 17th was bluish-purple. The first eleven Zsigmondy sols were red; the 12th and 13th had a tinge of purple; and the 14th was purple.

latter by water-soluble impurities in the former, the coagulum then being brought to the interface. It was established by experiment that methyl, ethyl, n-propyl and iso-propyl alcohols, obtained by the distillation of A.R. materials, had absolutely no effect upon Au_NA (or Au_ZA). The sharp distinction between miscible and immiscible alcohols can hardly be due merely to the absence in the one case and the presence in the other of ionising impurities. The matter was also put to the test in another way. A Nordenson sol was prepared from conductivity water which had been thoroughly shaken with a *large* quantity of purified amyl alcohol. The product, though purplish red in colour, proved to be very stable, showing no change in colour or sign of sedimentation after standing for several months. Viewed in the ultramicroscope it was seen to contain about equal proportions of green and red particles. There are two objections to the assumption that the larger particles were the result of coagulation by impurities in the alcohol. In the first place a very high rate of coagulation must necessarily be assumed, and rapid coagulation usually means complete coagulation. Secondly, the dissolved alcohol may quite well have decreased the rate of nuclei formation during the reduction, which would lead to coarsening of the gold. Even supposing, however, that coagulation had taken place, half the gold was still in the form of primary particles and these showed no tendency to aggregate. The sol was immediately shaken out with amyl alcohol, using the routine procedure.

The Influence of Electrolytes

As shown in the preceding section potassium carbonate and sodium hydroxide were found to oppose or promote film formation, depending upon the concentration. A number of other electrolytes were now tested to see how far these effects were general, exactly the same procedure being employed as formerly. The results are given in Tables II, III, and IV.

TABLE II

Nordenson sol (B)

Electrolyte	x	Distribution	y
KCl	2.4 –26.8	At all concentrations gold completely removed to interface as blue, blue-black or blue film	7.3– 9.8
$BaCl_2$	0.05– 0.40		0.1– 0.15
$LaCl_3$	0.0005– 0.0049		0.0034– 0.0039
HCl	1.4 –14.3		5.7– 7.2
KH_2PO_4	1.7 –16.7		8.3–10.0
NaAc	4.2 –41.9		12.6–16.7
$Na_2HPO_4/2$	5.0 –50.0		25.0–30.0
$Na_3Cit/3$	7.5 –75.0		30.0–37.5

The figures under x are the limits of concentration between which the action of the electrolyte was studied, and those under y, the concentration limits between which there appeared the first sign of change (blue tinge) in the sol, produced by the electrolyte alone in 24 hours. The concentrations are expressed in millimols per litre.

TABLE III

Zsigmondy Sol (B)

Electrolyte	Conc.	Film	y
KCl	2.4	1B	12.2–14.6
	4.9	8B	
	7.3	10B	
$BaCl_2$	0.1	1B	0.3
	0.2	3B	
	0.3	8B	
	0.4	10B	
$LaCl_3$	0.001	9B	0.0029–0.0039
	0.0018	10B	

TABLE IV

Zsigmondy Sol (B)

Electrolyte	Conc.*	Film	y
HCl	2.75	10BBl	5.51– 8.25
KH_2PO_4	1.70	10B	8.3 –10.0
Na Acetate	4.2	9B	20.8 –25.0
Na_3 Citrate/3	7.5	10B	22.5 –30.0
Na_2HPO_4/2	5.0	10B	20.0 –25.0

*Lowest concentrations employed.

These tables show that electrolytes in general promote film formation and that the concentration of electrolyte at which separation of the gold commences is always less, often very much less, than that (y) necessary to bring about a detectable change in the colour of the sol in 24 hours.

The influence of certain electrolytes was now more closely investigated employing an *acid* sol prepared by a modification of Zsigmondy's method. It was found possible to obtain perfectly clear, stable, yellowish-red sols by using tri-sodium citrate in place of potassium carbonate.** The following

TABLE V

Sol Au_{Cit}

	Distribution of gold					
	Na_3 Citrate		Na_2 phosphate		NaOH	
Conc. of electrolyte*	Interface	Aqueous layer	Interface	Aqueous layer	Interface	Aqueous layer
0.00	5B	0	5B	0	5B	0
0.25	3B	2R	+B	5-R	0	5R
0.50	2B	3R	+B	5-R	"	"
0.75	3B	2R	+B	5-R	"	"
1.00	5-B	+R	1B	4R	"	"
1.25	5B	0	1B	4R	"	"
1.50	"	"	2B	3R	"	"
1.75	"	"	4B	1R	"	"
2.00	"	"	5-B	+R	"	"
2.25	"	"	5B	0	"	"
2.50	"	"	5B	0	"	"
5.0					+R	5-R
7.5					3R	2R
10.0					5B	0
12.5					"	"
15.0					"	"
17.5					"	"
20.0					"	"

NaCl, HCl and KH_2PO_4 from 0.25 to 2.50: all gold went to interface at every concentration.

*Concentration of added electrolyte (in millimols per litre) after mixing with the sol.

**Anderson has prepared sols by using sodium citrate alone. Formaldehyde was employed in the present instance in order to approximate as closely to the Zsigmondy method as possible.

quantities proved satisfactory: 1 c.c. 0.6 percent chlorauric acid, diluted with 123.6 c.c. Bourdillon water, + 0.4 c.c. 0.1 M sodium citrate (Kahlbaum) + 3.0 c.c. 0.4 percent formaldehyde. On shaking 3 c.c. of this sol (Au_{cit}) with 1 c.c. of amyl alcohol the gold immediately collected at the interface, forming a blue film.

Table V summarises the results obtained by adding the various electrolytes. In these instances the sol + electrolyte mixtures did not stand for 24 hours but were treated after a few minutes. In no case was there any change in colour of the sol between mixing with the electrolyte and shaking with the alcohol. It will be seen from the table that, after sufficiently low concentrations, sodium citrate and secondary phosphate, as well as NaOH, exerted a stabilising influence upon the sol, whereas the other substances showed no tendency to prevent the gold from accumulating at the interface.

Determination of Particle Size

The average particle sizes of the sols Au_ZA and Au_NA were determined by a counting method which differed in some respects from the methods generally employed. The particles were fixed with gelatine. *accurate allowance being made for the optical heterogeneity of the latter (cf Tuorila[8]).*

Pieces of Coignet's "Gold Label" gelatine were cut from sheets chosen at random from a batch of thirty, and a 0.75% solution prepared from each piece, using optically empty conductivity water. Such solutions become very viscous at room temperature but do not set. On examination in the slit ultramicroscope they were found to contain a quantity of bright white particles, the number of which in a definite volume* was determined when the Brownian movement had been sufficiently reduced (by the cooling of the gelatine) to make counting easy. The field was effectively changed after each count by running out a drop of the solution from the ultramicroscope cell. The last column of Table VI gives the average number of particles contained in 3.09×10^{-6} cubic millimeters.

TABLE VI

Experiment	No. of counts	Av. no. of particles	
1	50	8.2	8.2
2	30	8.0	
3	50	8.3	
4	50	8.5	
5	50	8.0	

For counting experiments with a gold sol, 10 c.c. of the latter were mixed with 10 c.c. of 1.5 percent gelatine. Judging from their appearance to the naked eye and in the ultramicroscope neither Au_ZA or Au_NA was affected

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*Deliminated by means of a calibrated micrometer net. The dimensions of the net and the depth of the light beam were found by using a solution of fluorescein in the cell.

by this treatment. The gold particles were counted under the previous conditions of light intensity, etc. A fresh sample of gold-gelatine mixture was used for each experiment, and each count made on a different portion of the sample. The average radius of the particle was calculated by adopting the usual assumptions. Table VII contains the results.

TABLE VII

Sol	Sample	No. of counts	Average number of particles			Av. radius of gold particles
			Total	In gelatine	In gold sol	
Au_ZA	1	15	40	8.2	31.8	30μμ
	2	22	41	"	32.8	30
Au_NA	1	35	19.6	"	11.4	42
	2	40	19.0	"	10.8	43
	3	40	19.5	"	11.3	42

The above method was used because when the sols were diluted for counts of the usual type, the background was found to be so dark, (indicating the absence of amicrons) that it was extremely difficult to distinguish the micrometer net. On the other hand if this difficulty was avoided by employing the sols at a sufficiently high concentration, it was impossible to make counts with any degree of accuracy unless the Brownian movement was considerably diminished. The method has also the advantage that the number of counts necessary is less than in the ordinary method.

Discussion

In agreement with the work of Zsigmondy, it was found necessary to purify carefully an organic liquid in order to ascertain with certainty if it possessed any action upon gold sols.* Employing organic liquids of the requisite quality, a pronounced specific action of the immiscible alcohols was shown to exist. Of all the liquids examined, they alone were found to affect Nordenson sols. Hence Zsigmondy's conclusion that acid sols are stable when shaken with organic liquids requires modification. It seems probable that this view was based on insufficient experimental material, since the only liquids mentioned as having been studied by him with regard to their influence upon acid sols, are benzene, toluene and ether.

The behaviour of a Nordenson sol when shaken with an immiscible alcohol is also obviously not in accord with Zsigmondy's statement that "Man kann allgemein sagen: reines kolloidales Gold ist stabil gegen Ausschütteln, koaguliertes** dagegen instabil." Moreover, as has already been indicated, the formation of red films provides very direct evidence that the primary

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*Reinders[2] and Yanek[9] neglected to take this precaution and their results are correspondingly limited in value.

**i.e. aggregates (secondary particles) formed by the fusion of the original (primary) particles of the sol, which give a blue coagulum and appear red in the ultramicroscope.

particles of a sol may be attracted to the liquid—liquid interface without loss of individuality. It may however be argued that the contrast between e.g. Au_NA and Au_zA is due to a difference in primary particle size. While the actual size determinations appear to support this contention it is not possible without a closer study of the influence of electrolytes, to arrive at a definite conclusion as to the exact importance of the factor of particle size. Under certain circumstances at least, variations in the composition of the dispersion medium of the sol outweigh any effect of size. For example Au_NB was converted by suitable additions of alkali into a system closely resembling Au_ZB, which can hardly be due to an increase in the degree of dispersion.

In a recent paper Deutsch[10] suggests (1) that solid particles lower the interfacial tension between water and an organic liquid, (2) that the larger the particle the greater the capillary activity and therefore, (3) that the tendency of the particles to aggregate will be greater at a gold sol—organic liquid interface than in the sol itself, since this process reduces the free energy of the system. Thus, according to Deutsch, when a gold sol containing sufficient sodium chloride to produce minimum turbidity is shaken with hexane, the gold collects at the liquid-liquid interface because the coagulation is accelerated by the great increase in interfacial area created by the emulsification of the hexane, and since the coagulation is irreversible, the aggregated gold remains as a film between the two liquid phases after they separate. The absence of effect when a stable gold sol is shaken with hexane is explained in the following words: "die stärker geladenen, innerlich weniger abgesättigten Kolloidteilchen stärker durch das Wasser zurückgehalten werden als die durch Zusammentritt mehr abgesättigten aggregierten Teilchen" and "hier die Abstossungskräfte noch so stark wirksam sind, dass sie selbst an der Grenze noch zum Stabilisieren ausreichen, oder anders ausgedrückt, dass der Zuwachs an Capillaraktivität der durch Zusammentreten zweier Teilchen entstandener Aggregate noch immer zu klein ist, um eine Vergrösserung der Aggregationsgeschwindigkeit zu bewirken". There appear to be a number of difficulties in applying these views to the results of the present investigation. As has been repeatedly shown, a sufficiently acid sol is coagulated by amyl alcohol, although very stable in the ordinary sense. It might be assumed that the tendency to coagulate, while slight, was sufficient for the purpose, but the evidence suggests that the particles first collect at the interface and then coagulate. At least it is certain that in some cases the aggregation of the particles at the interface is, at the most, only of a loose nature (formation of red films). However it might still be assumed that such a species of aggregation constituted coagulation, or even that the electrical condition of the primary particles was not such as to counterbalance their capillary activity. Even supposing this to be the case, however, we have still to account for the absence of effect in the case of, for example, paraffin, which necessitates the further assumption that gold particles diminish the interfacial tension of water-alcohol to a greater extent than that of water-paraffin.

Moreover the coagulation, if such, resulting in the formation of a red film is in all probability reversible, as Whitney and Blake[12] have shown that precipitated red gold may be peptised.

It may be questioned, in any case, whether Deutsch is justified in assuming that the influence of the particles in the liquid-liquid interfacial tension is the factor of primary importance in the distribution of solid particles between two liquid phases. Apart from the difficulty of proving that such an effect exists, it does not seem reasonable to ignore the solid-liquid interfaces, even when dealing with the small particles of a gold sol. Regarding the problem as essentially one of "preferential wetting" the observations described in the preceding sections may be interpreted as follows. The alcohols are more strongly adsorbed at the surface of a gold particle than are the other organic liquids: this is concordant with the pronounced capillary activity of the alcohols. Hence the particles are more easily wetted by the alcohols and made to adhere to the organic layer. It is, however, to be expected that the adsorption of the alcohol molecules will be influenced by the electrical condition of the solid surface. As a rule organic substances depress the electrocapillary curve of mercury, their action being greatest in the neighbourhood of its maximum. This is ascribed to the effect of the electric field at the interface upon the adsorption of the organic molecules. That is to say, the adsorption is greatest when the field has some small value and decreases as the field becomes more positive or negative.[13] In this way it is possible to account for the influence of the nature of the dispersion medium upon the distribution of the gold particles when a gold sol is shaken with an immiscible alcohol, i.e. the effect of any electrolyte may be attributed to its influence upon the electrical charges of the particles.

If this view is correct we would expect to find much the same relationships holding as in the direct coagulation of a negative sol. This proves to be the case. In the first place the order of efficiency of the chlorides in promoting accumulation of the gold at the alcohol-water interface is La $Cl_3 > BaCl_2 > KCl$ (Table II1). Secondly, those electrolytes (NaOH, K_2CO_3, Na_2HPO_4 and Na_3Cit) which oppose the action of the alcohol, have high coagulation values compared with potassium chloride (Tables I, II and IV).

It will be observed that the gold is not necessarily either completely brought to the alcohol-water interface or else left quite unaffected. All degrees of distribution are possible. This may be a size effect but another possible explanation is that the gold particles are not all equally charged, since Anderson[7], Garner and Lewis,[14] and Garner[15] found that they could account satisfactorily for the behaviour of gold sols when slowly coagulated by electrolytes, if they assumed that the primary particles carried unequal charges.

Since, of the salts examined only those which give alkaline solutions possessed the power of "protecting" a sol, the question arises as to whether this effect is due simply to decrease in the hydrogen ion concentration or is partly produced by adsorption of the salt anions. This problem is being investigated.

Summary

1. A considerable number of immiscible organic liquids have been examined with respect to their action on certain gold hydrosols.

2. Zsigmondy's conclusion that unambiguous results are obtained only if very pure liquids are employed has been confirmed.

3. It has been established that the immiscible alcohols exert a specific influence, since they may cause the gold of a stable sol to collect at the liquid-liquid interface.

4. The formation of red interfacial films under certain conditions has been observed.

5. The influence of various electrolytes upon the action of amyl alcohol has been studied.

6. It is suggested that the action of an immiscible alcohol is due to its strong tendency to be adsorbed at the surfaces of the gold particles and that the degree of adsorption depends upon the electrical condition of these surfaces. An electrolyte thus promotes or opposes accumulation of the gold at the interface according as it decreases or increases the particle charge.

References

[1] Zsigmondy: Nachricht. kgl. Ges. Wiss. Göttingen, Math-Phys. Kl., **1916**, 38. Also:—Z. anorg. Chem., **96**, 265 (1916); Z. Elektrochemie, **22**, 102 (1916); Zsigmondy-Thiessen: "Das kolloide Gold," 168 (1925).

[2] Reinders: Kolloid-Z., **13**, 235 (1913).

[3] Wiegner: Kolloid-Z., **8**, 227 (1911).

[4] Freundlich: "Colloid and Capillary Chemistry," 484 (1926).

[5] Nordenson: "Über die Bedeutung des Lichtes für die Bildung und Stabilität kolloider Lösungen." Diss. Upsala, 123 (1914). Also:—Svedberg "The Formation of Colloids," 70 (1921).

[6] Beaver and Muller: J. Am. Chem. Soc., **50**, 305 (1928).

[7] Anderson: Trans. Faraday Soc., **19**, 623 (1924).

[8] Tuorila: Kolloidchem. Beihefte, **22**, 191 (1926).

[9] Yanek: Ann. école mines Oural, **1**, 45 (1919).

[10] Deutsch: Z. physik. Chem., **136**, 353 (1928). See also:—Freundlich and Loebmann.[11]

[11] Freundlich and Loebmann: Z. physik. Chem., **139**, 368 (1929); Kolloidchem. Beihefte **28**, 391 (1929).

[12] Whitney and Blake: J. Am. Chem. Soc., **26**, 1339 (1904).

[13] Butler: Proc. Roy. Soc., **122A**, 399 (1929).

[14] Garner and Lewis: J. Phys. Chem., **30**, 1401 (1926).

[15] Garner: J. Phys. Chem., **30**, 1410 (1926).

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CATALYTIC EFFECT OF SOLVENTS. DECOMPOSITION OF MALONIC ACIDS

BY ROBERT E. BURK AND WILHELMINA DAUS

While numerous instances of the influence of solvents upon the velocities of chemical reactions have been investigated, some of those which have been most carefully worked through[1] have been addition reactions, e.g. the formation of substituted ammonium salts by the reaction of amines with alkyl halides, etc. In this type of reaction the possible factors which may contribute to the rate are not a minimum, e.g., there must be a third body present to carry off the heat of reaction[2] in order for reaction to occur, and the possibility that the heat of reaction would be dissipated internally in the case of complex molecules is not indicated in Menschutkin's work, since the more complex the molecules were, the slower the rates. That this factor is not the whole rate controlling one in these instances, is shown by the fact that Norrish and Smith found a discrepancy between the bimolecular collision rate of active molecules and the observed velocity, of 10^{-8} for the reaction between nitro-benzyl chloride and trimethyl amine in benzene, whereas the factor involving dissipation of heat of reaction could not in all probability lead to any such value, although it would be in the proper direction. Norrish and Smith consider every such collision between active molecules to involve at least one solvent molecule, and if this molecule were efficient in dissipating the energy of reaction, this required dissipation would not have to be considered at all. They attribute the discrepancy in collision and reaction rates to division of activation energy with solvent molecules at the moment of collision between active molecules.

Certain workers[3] on oxidation reactions in solution, however, in applying Christiansen's theory of negative catalysis[4] to such reactions, consider it not improbable that energized molecules of products may undergo of the order of 10^{-4} or 10^{-5} collisions with solvent molecules without losing their energy, and can transfer it specifically to "cold" reactant molecules at the moment of collision with them, without interference from solvent molecules of the type considered by Norrish and Smith.

With addition reactions of the above type, then, the solvent could affect the probability of loss of energy of activation at the moment of collision between active molecules, could lower the energy of activation, could dissipate energy of reaction, etc. Norrish and Smith were inclined to consider the effect of different solvents in altering the reaction rate as due to an effect

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[1] Menschutkin: Z. physik. Chem., **5**, 589; **6**, 41 (1890); Norrish and Smith: J. Chem. Soc., **130**, 129 (1930).

[2] Born and Franck: Ann. Physik, (4) **76**, 225 (1925).

[3] e.g. Bäckström: J. Am. Chem. Soc., **49**, 1460 (1927).

[4] Christiansen: J. Phys. Chem., **28**, 145 (1924).

upon the first factor. It seemed desirable to study a simpler reaction, such as a decomposition, in order that the factors influencing reaction rates in solution could be investigated more closely.

The thermal decomposition of malonic acids was chosen because they fulfill this requirement, because they are important in themselves to organic synthesis, and because the influence of substitution of the active hydrogens on the decomposition rate could be compared with the influence of solvents. Work on the decomposition of acetone dicarboxylic acid has appeared[5] since the present research was started, and the decomposition of malonic acid itself has been investigated kinetically by Lindner,[6] by Hinshelwood,[7] and together with substituted malonic acids by Bernoulli and Wege,[8] by Bernoulli and Jakubowicz,[9] and by Jakubowicz.[10]

Experimental Procedure

The apparatus consisted of a thermostat containing a small reaction vessel of approximately 14 c.c. capacity. Temperature control to ±0.5°C. was obtained. Above the reaction bulb was sealed a vessel of 41.87 c.c. capacity, which was kept immersed in ice. This bulb was followed by a manometer, then a stopcock. All connecting tubing to this point was capillary. The stopcock led to an evacuating system with a discharge tube to indicate when a sufficient vacuum had been produced in the system. The reaction rate was followed manometrically by the pressure changes caused by the evolution of carbon dioxide due to the reaction:

$$RHC(COOH)_2 = RH_2CCOOH + CO_2$$

Due account was taken of the temperature differences of the two bulbs. When a solvent, which was somewhat volatile at the temperature of the reaction, was used, it distilled into the cold bulb and refluxed therefrom to the small bulb. Thus only its vapor pressure at 0°C. affected the manometer, and this was always too small to measure.

The sample was weighed out accurately before sealing on the reaction bulb, using the bulb as a weighing bottle. The amount of acid was so chosen that complete decomposition would not bring the pressure of carbon dioxide in the system above atmospheric. After the sample was weighed, (and the solvent added), the bulb was sealed onto the apparatus, and the system evacuated in order to evolve any dissolved or occluded inert gases.

The materials used were Kahlbaum's benzyl malonic acid (m.pt. 120.0°C.), ethyl malonic acid from E. Merck, Darmstadt (m.pt. 111.5°C.), and solvents the purest obtainable from Eastman Kodak Co. The oleic acid used was from Eastman Kodak Co. and was redistilled twice. The dimethyl aniline was also redistilled, but a redetermination with the distilled product showed no change in rate.

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[5] Wiig: J. Phys. Chem., **32**, 961 (1928); **34**, 596 (1930).

[6] Monatsheft, **28**, 1041 (1908).

[7] J. Chem. Soc., **117**, 156 (1920).

[8] Helv. Chim. Acta, **2**, 511 (1919).

[9] Helv. Chim. Acta, **4**, 1018 (1921).

[10] Z. anorg. allgem. Chem., **121**, 113 (1922).

Order of the Reaction

The kinetic order of the decomposition of benzyl malonic acid was determined by investigating the influence of initial concentration upon the time of half life using as a solvent palmitic acid, which was found to be without appreciable catalytic influence. Table I shows the independence of the time of half life and initial concentration for benzyl malonic acid.

Table I

Concentration (gms. in 5 cc. of acid)	Molality	Time for half change (min.)
1. 0.1046	0.1078	35
2. 0.2013	0.2075	31
3. 0.2516	0.2594	30
4. 0.3004	0.3097	29

The reaction is quite accurately monomolecular.

Influence of Various Solvents

Table II shows the half life for the decomposition of benzyl malonic acid in various solvents.

Table II

Decomposition of Benzyl Malonic Acid

Solvent	Half life (minutes)	
	125°C.	135°C.
None	75	(28.4)*
Oleic Acid	72	32.1
Palmitic Acid		31.0
ortho Nitrochlorobenzene		25.0
meta " "		22.5
para " "		26.0
Dimethyl Aniline	7	4.3

* This value is low, according to the temperature coefficient graph.

A remarkable independence of reaction rate and nature of solvent is evident. Determinations made with ortho, meta, and para nitrochlorobenzene indicate that the position of substitution in the benzene ring has no effect on the velocity, although accompanied by large changes in the electric moments of these molecules.[11]

One experiment was repeated in which about 100 mm. of carbon dioxide were added at the beginning to determine the effect of its presence on the rate of decomposition. It was found that the time of half life in this case was not appreciably different from the others.

All of this is in line with other monomolecular homogeneous reactions, which in the few cases investigated have been found to be less susceptible to catalytic influence than bimolecular reactions.[12]

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[11] Physik. Z., 30, 391 (1929).

[12] This was pointed out by one of us (R.E.B.) at the Minneapolis meeting of the American Chemical Society, September 1929. Examples are the maintenance of decomposition rate of N_2O_5 (Lueck: J. Am. Chem. Soc., 44, 757 (1922)), the racemization of pinene (Smith: J. Am. Chem. Soc., 49, 43 (1927)), and the decomposition of acetone (Taylor: J. Phys. Chem., 33, 1793 (1930)). For exceptions see Clusius and Hinshelwood: Z. Elektrochemie, 36, 748 (1930).

It is to be observed that solvents having a considerable electric moment such as fatty acids and nitrochlorobenzenes have no catalytic influence. The malonic acids were not soluble in completely non-polar solvents such as purified mineral oil.

Dimethyl aniline was the only solvent of those investigated to show marked catalytic properties. Salt formation was indicated by a sharp rise in temperature when malonic acid was stirred with dimethyl aniline. However, reasons are given later for thinking that decomposition of the salt to free base and acid precedes the decomposition of the acid. The catalytic influence of this solvent was accompanied by a pronounced decrease in the temperature coefficient.

Effect of Substituting for the Active Hydrogens in Malonic Acid

This phase of the work was not investigated thoroughly because of its divergent nature, and of good correlation between such experiments as were made and previous rather extensive work. [10]A summary of results is given in Table III. Other comparisons will be made in discussing temperature coefficients.

TABLE III

Acid	Velocity Constant $\times 10^4$	Temperature (Centigrade)	Solvent	Observer
Phenyl malonic	104,921	100	water	Bernoulli and Wege
Benzyl malonic	1,968	100	water	" " "
Allyl malonic	1,321	100	water	" " "
Malonic	755	100	water	" " "
Malonic	477	100	glacial acetic acid	Linder
Diallyl malonic	649	100	water	Bernoulli and Wege
Methyl malonic	598	100	water	" " "
Ethyl malonic	508	100	water	" " "
Methyl ethyl malonic	322	100	water	" " "
Dimethyl malonic	297	100	water	" " "
Diethyl malonic	281	100	water	" " "
Monochlor malonic	1855	100	water	Bernoulli and Jakubowicz
Dichlor malonic	585	100	water	" " "
Tartronic	820	100	water	Jakubowicz
	half life (min.)			
Malonic	174	125	none	Hinshelwood
Ethyl malonic	148	125	none	Daus and Burk
Benzyl malonic	75	125	none	" " "

See Table II for benzyl malonic acid in various solvents.

Temperature Coefficients

Fig. 1 shows the results of plotting the reciprocal of the absolute temperature versus time of half life for the decomposition of benzyl malonic acid at various temperatures, without a solvent, in oleic acid, and in dimethyl aniline. The temperature coefficient determined by Hinshelwood[7] for malonic acid and that determined by Bernoulli and Jakubowicz[9] for malonic acid in water solution are also shown.

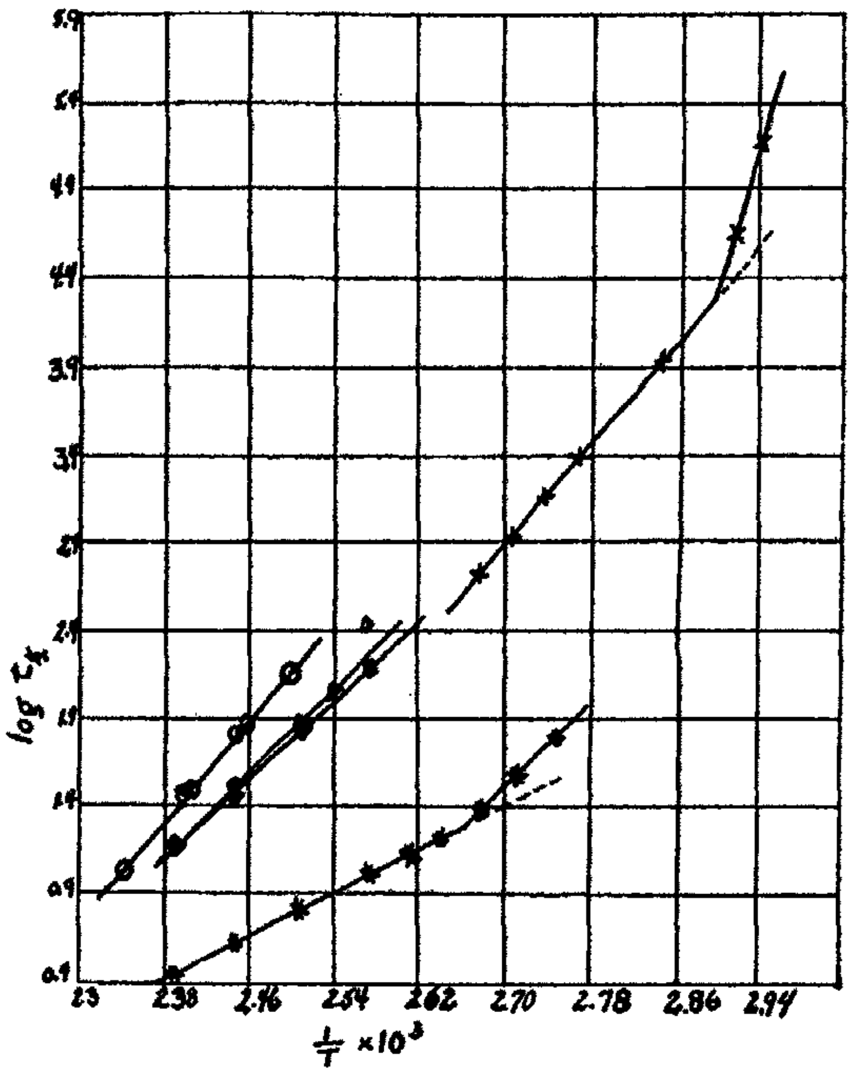

FIG. 1

△ Benzyl malonic acid, no solvent. Daus and Burk.
□ Benzyl malonic acid, solvent-oleic acid. Daus and Burk.
* Benzyl malonic acid, solvent-dimethyl aniline. Daus and Burk.
⊙ Malonic acid, no solvent. Hinshelwood.
× Malonic acid, solvent-water. Bernoulli and Jakubowicz.

It is to be observed that the point at 115°C. ($1/T = 0.002577$) for the decomposition of benzyl malonic acid without solvent is off the straight line in the sense of being too slow. This temperature was below the melting point of the acid. There was a marked induction period in the pressure change-time curve, there being a sharp acceleration when hydrocinnamic acid began to form in quantities sufficient to effect appreciable solution of the benzyl malonic acid. Thus the solid acid has a velocity constant of a lower order. A similar phenomenon was found by Hinshelwood[7] for the decomposition of solid malonic acid.

The energies of activation calculated graphically from the slopes are: 11,270 calories for the decomposition of benzyl malonic acid alone, 10,360 calories for the decomposition in oleic acid, which did not cause a marked increase in rate over the temperature range investigated, and 6,090 calories for the decomposition in dimethyl aniline between 105° and 145°C., which did have a marked catalytic effect. (The value calculated for the lower temperature range was 11,400 calories.)

The graphs leave no doubt that the marked catalytic effect of dimethyl aniline is accompanied by a definite decrease in the temperature coefficient.

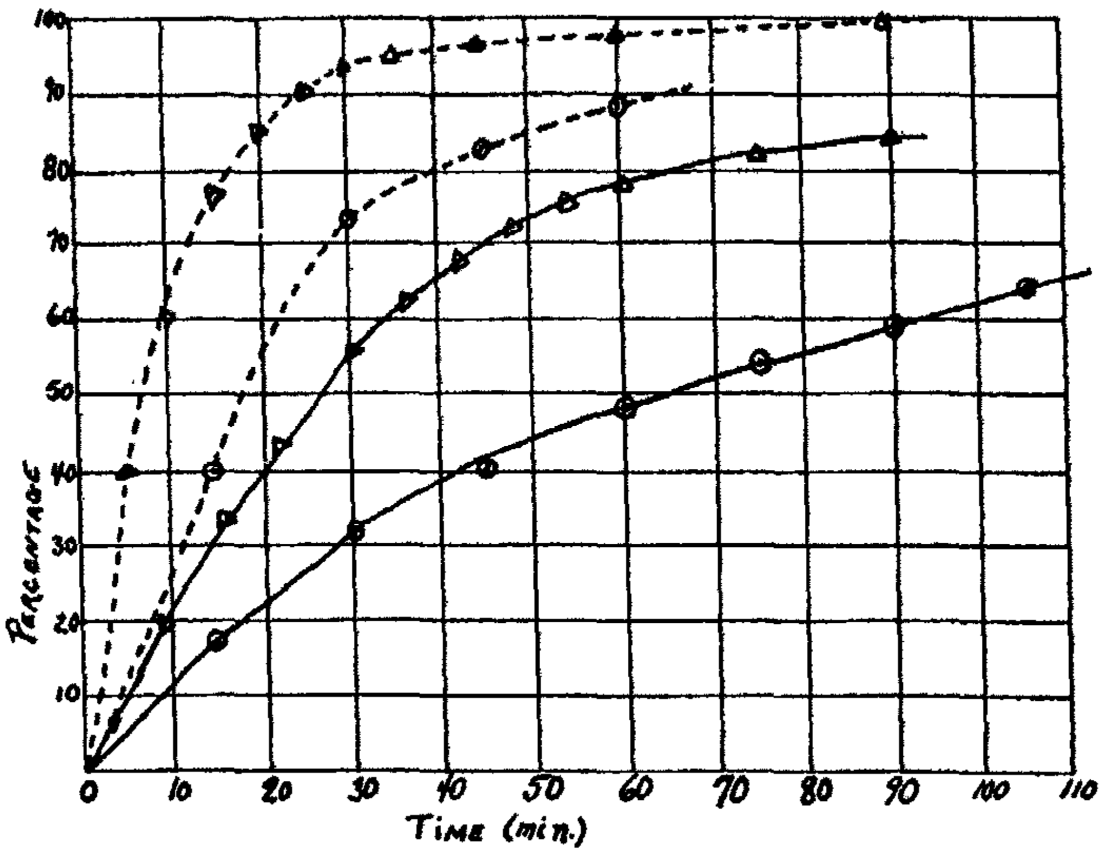

Fig. 2

—— ⊙ Percentage change of pressure with time at 90°C.
—— △ Percentage change of pressure with time at 100°C.
- - - ⊙ Percentage change of conductivity with time at 90°C.
- - - △ Percentage change of conductivity with time at 100°C.

It is seen that there is a change in slope in the sense of the reaction being too slow at the lower temperatures, beginning about 105° for benzyl malonic acid in dimethyl aniline. It was suspected that this was due to a dependence upon dissociation of the salt to free base and acid, which would lead to lower concentration of free acid and consequent diminution in rate.

In order to investigate this point conductivity measurements were made, using a small cell with platinum electrodes, and a Wheatstone bridge. Both high frequency alternating current with phones and electron tube amplification in the detecting arm, and direct current with a galvanometer in the detecting arm were used.

Fig. 2 shows the percent change in conductivity plotted against time at 90° and 100°C. The percent pressure change is also plotted against time for benzyl malonic acid in dimethyl aniline at the same temperatures. The fact that the conductivity would approach a value so small as to be immeasurable with our equipment shows that the end product, hydrocinnamic acid, has a negligible conductivity under these conditions. That the conductivity should drop to one percent of its original value at 90 minutes and 100°C., while the pressure change curve indicated that sixteen percent of the original benzyl malonic acid remained, showed that this acid also has a very small conductivity in dimethyl aniline under these conditions. These facts justify the conclusion that the observed conductivity is due almost entirely to the salt. The assumption of direct proportionality between conductivity and concentration of salt should also be justifiable as a first approximation.

TABLE IV

Temperature (°C.)	Half life in minutes		Temperature (°C.)	Half life in minutes	
	Salt decompn.	Acid decompn.		Salt decompn.	Acid decompn.
80	65.3	—	110	(1.85)	—
90	19.0	73.5	115	(1.084)	10.2
95	(10.24)	38.5	125		6.8
100	7.5	26.0	135		3.9
105	(3.236)	17.2	145		2.6

Table IV shows a comparison of half lives of decomposition of the salt to free base and acid and of the acid to hydrocinnamic acid and carbon dioxide. The values in brackets are calculated from the temperature coefficient as determined from the measured points, which lay on an excellent straight line when log $t_{1/2}$ was plotted against $1/T$.

Fig. 3 shows the values of the time of half change in conductivity plotted against the reciprocal of the absolute temperature with the corresponding half pressure change values for the decomposition of benzyl malonic acid in dimethyl aniline as solvent and without a solvent. It is clear from the table and graphs that the rate of salt decomposition becomes very rapid compared with the acid decomposition at a point corresponding to that at which the temperature coefficient of the acid decomposition settles out to new and lower, but constant value. Furthermore the temperature coefficient for this reaction at low temperatures tends to assume the corresponding value for the salt decomposition.

With concurrent reactions, that reaction having the higher temperature coefficient may predominate at higher temperatures in case it is homogeneous, and that with the lower temperature coefficient is heterogeneous.[13]

This phenomenon depends upon the reaction with the lower temperature coefficient being heterogeneous, in which case but a small proportion of the total reactants is undergoing heterogeneous reaction at a given instant.

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[13] This type of composite reaction is discussed by Hinshelwood: "Kinetics of Chemical Change in Gaseous Systems," 2nd edition, p. 45. Examples are the combination of hydrogen and sulfur (Norrish and Rideal: J. Chem. Soc., **123**, 696 (1923)) and the decomposition of hydrogen iodide in pyrex (H. A. Taylor: J. Phys. Chem., **28**, 984 (1924).)

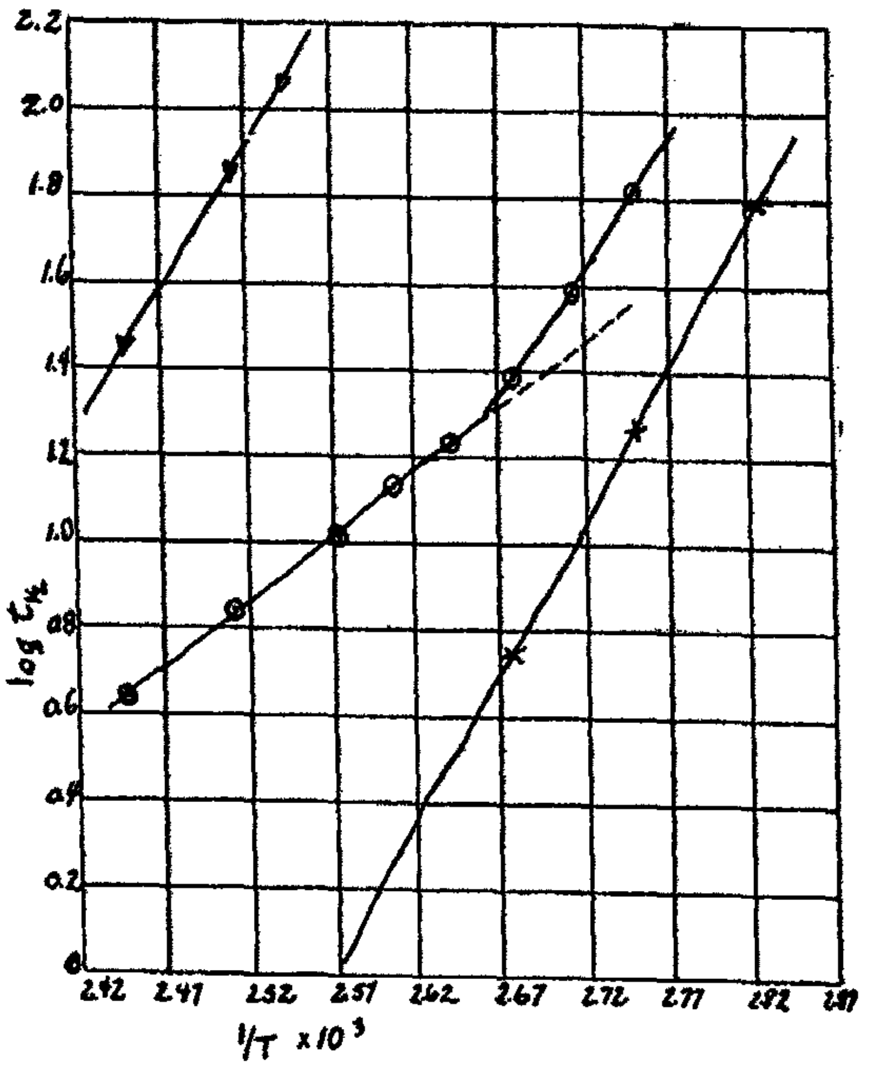

Fig. 3

△ Benzyl malonic acid, no solvent.
⊙ Benzyl malonic acid in dimethyl aniline.
× Conductivity due to salt.

This behavior would not be found with two homogeneous reactions of the same type, for if their velocity expressions were:

$$1.\quad k_1 = p_1\, e^{-A_1/RT} \qquad\qquad k_1 = p_1 n_1 e^{-A_1/RT}$$
$$\text{or}$$
$$2.\quad k_2 = p_2\, e^{-A_2/RT} \qquad\qquad k_2 = p_2 n_2 e^{-A_2/RT}$$

where p is a probability factor
k is the velocity constant
n is the number of collisions per second
A is the energy of activation.

If p_1 and p_2, and n_1 and n_2 are not greatly different, then if $A_1 < A_2$, reaction (1) will always exceed reaction (2) in speed in spite of a relative increase in the speed of (2).

With consecutive reactions, as in our case, the reaction with the lower temperature coefficient not only increases in speed relative to the other, but likewise predominates as the temperature is increased.

It is seen in Fig. 1 that in the results of Bernoulli and Jakubowicz, there is likewise a falling off in the rate of decomposition of malonic acid in water at the lower temperatures. Here salt formation is out of the question. However, since these temperatures are far below the melting point of malonic acid, association of these molecules may occur, leading to a diminished reaction rate for the complexes, as was found for the solid malonic acid by Hinshelwood, and for benzyl malonic acid by us.

Any residual effect due to incomplete salt decomposition at the higher temperatures could only make the temperature coefficient appear higher than its true value, so that the conclusion that the temperature coefficient is lowered by the catalyst cannot be jeopardized. Such demonstrations of temperature coefficient lowering with catalysis, though suspected, are not frequent in the literature.[14]

Interpretation of the Lowering of the Temperature Coefficient

A great deal of evidence has been accumulated to indicate that a major action of catalysts is a lowering of the energy of activation, the dominant factor governing reaction rates.[15] An interpretation which has been given to this is that it may be brought about under proper conditions by the stretching of bonds by a particular kind of association between catalyst and reactant involving more than one point of contact, a point of view which has been shown to be in excellent agreement with those phases of catalysis previously most difficult to explain, namely specificity, and promoter action.[16] The preponderance of evidence was in favor of this type of distortion rather than the atomic distortion mechanism[17] for the influence of a catalyst upon a bond. Recent work on band spectra,[18] and particularly upon Raman Spectra,[19] tends to minimize the possibilities of the atomic distortion mechanism. Some new suggestions arise from Quantum Mechanics, according to which the principal component of non-polar bonds is the resonance or exchange force arising from a coupling of the spin moments of unpaired electrons in the respective atoms making up the bond, such a force being demanded by one of the solutions of Schrödinger's wave equation, resulting from an exchange of the two electrons which potentially can form a bond.[20]

According to London[21] the following notions regarding chemical activation result. If we have a pair of atoms forming a non-polar bond and a third

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[14] Some new cases, e.g., the decomposition of ethers catalyzed by halogens and organic halogen compounds have recently been reported. (Clusius and Hinshelwood: Z. Elektrochemie, 36, 748 (1930) Summarizing paper.).

[15] See e.g., Hinshelwood: "Kinetics of Chemical Changes in Gaseous Systems," 2nd Edition; Burk: Sixth Report of the Committee on Contact Catalysis, J. Phys. Chem., 32, 1601 (1928).

[16] See Burk: J. Phys. Chem., 30, 1134 (1926); 32, 1601 (1928); Balandin: Z. physik. Chem., B2, 289 (1929).

[17] See, e.g., Langmuir: Trans. Faraday Soc., 17, 610 (1922).

[18] See Burk: Sixth Report (Loc. Cit.) for a partial summary.

[19] See e.g., Smekal: Z. Elektrochemie, 36, 618 (1930); Andrews: Phys. Rev. (2), 36, 546 (1930).

[20] Heitler and London: Z. Physik, 44, 455 (1927); Rouark and Urey: "Atoms, Molecules and Quanta," p. 684 (1930); Heitler: Physik. Z., 31, 186 (1930); Mulliken: Chem. Rev., 6, 536 (1929). This relatively simple concept seems, however, to be growing more complex, because of a "degeneration" of orbital momentum of electrons as well as of the spin moments leading to binding forces of the same order of strength. (Heitler: Naturwissenschaften, 17, 546 (1929)).

[21] Z. Elektrochemie, 35, 552 (1929).

atom approaches which is capable of "resonance" combination with either of the two atoms forming the bond, the bond will be weakened, and if the potential reaction is exothermic the new combination will be effected, and the second atom which was a part of the original bond ejected. However, the third atom experiences a repulsion before approaching sufficiently closely to cause the phenomena just described. The energy of activation would thus be that necessary to overcome this "potential wall" in the case of exothermic "atom" reactions, and has been found by Polanyi and co-workers[22] to be vanishingly small for reactions of the type:

$$AB + C = AC + B + \text{energy}$$

London then says, p. 553, "If the distance between the atoms of the original bond is increased, as by increase in vibration or through the influence of a nearby catalyst, the resonance repulsion against the approach of the third atom will be weakened, and the height of the potential wall lowered."

This, in common with previous concepts,[23] attributes the activation process to increasing the distance between the atoms of the bond concerned. However, in contradistinction, the energy of activation as seen by London is external, i.e., the energy necessary to overcome the potential wall rather than the remaining energy necessary to break the bond (for exothermic reactions).

In case the reaction is endothermic, the heat of reaction per molecule must be added to that necessary to overcome the potential wall in order to have a successful elementary act of reaction.

The small activation heats of atomic reactions are attributed by London to the existence of "sensitive spots" on the diatomic molecule easily reached by the approaching atom. For a reaction of the type:

$$XY + ZW = YZ + XW$$

both X and Y cannot reach the sensitive spot of ZW, etc., so activation heats of higher order result, which London says should be close to the energy requirements of:

$$(1)\quad XY + ZW = YZ + X + W$$

or

$$(2)\quad XY + ZW = XW + Y + Z.$$

This works out excellently with the homogeneous bimolecular reaction:

$$2HI = H_2 + I_2 \quad \text{Energy of activation, 44,000 calories}^{24}$$

$$H_2 = 2H - 98{,}100 \pm 2{,}300 \text{ calories}^{25}$$

$$I_2 = 2\,I - 35{,}600 \pm 70 \text{ calories}^{25}$$

$$HI = H + I - 66{,}000 \text{ calories (spectroscopic data)}^{26}$$

$$HI = H + I - 69{,}300 \text{ calories (thermal determination)}^{26}$$

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[22] Beutler and Polanyi: Z. physik. Chem., B1, 3; Bogdandy and Polanyi: 21; Polanyi and Schoy: 30; Outuka and Schoy: 62 (1928).

[23] Burk: J. Phys. Chem., 30, 1134 (1926).

[24] Lewis: J. Chem. Soc., 113, 471 (1918).

[25] Franck: Z. Elektrochemie, 36, 587 (1930).

[26] Sponer: Z. Elektrochemie, 34, 488 (1928).

$2HI = H_2 + 2I - 34{,}900$ calories if the spectroscopically determined heat of dissociation of HI is used, and 40,500 calories if the thermally determined value is used

$2HI = I_2 + 2H$ gives the wrong order of values for the heat of activation.

Polanyi[27] in applying these principles to activation at surfaces, considers again that activation involves stretching of bonds, and in still closer analogy to pre-quantum mechanical concepts, considers that activating adsorption of a molecule AB involves two surface atoms; surface complexes are formed in which the bond AB is either stretched or broken, and the bonds catalyst-A and catalyst-B must of course be of such strength that they lead to increased reaction rates. The correlation with London's "sensitive spot" concept is not so lucid. If the catalyst atoms are spaced somewhat farther apart than the atoms of AB, and we have two point adsorption, then clearly the resonance weakening of the bond would be assisted by mechanical stretching.[28]

The most recent contribution of quantum mechanical theory to the concepts of factors participating in catalytic activation is due to Born and Franck,[29] and has been but very superficially revealed. Referring to the association of energy of activation with that required to overcome a potential wall, they say that if on a catalyst the reacting molecules can be held at a distance from each other comparable with the distance reached in a gaseous collision, and for a time long compared with the duration of a gaseous collision, there is a certain probability of reaction although the energy necessary to overcome the potential wall is not present. This probability depends upon the height and breadth of the potential wall, and upon the mass of the atoms, and is exceedingly sensitive to distance apart at which the atoms find themselves as a result of adsorption and to the time during which they are held in this position. This point of view emphasizes once more the correlation between the spacing of catalyst atoms and their specific action, which various chemists have sought to bring out.[30] However, the energy of activation which is found for catalytic reactions from this viewpoint presumably would be due to the energy requirement for the adsorption of the reactants in the sensitive configuration, in case the reaction probability is itself independent of temperature, although the previously described processes could go on simultaneously and involve temperature coefficients.

The energy of activation may thus be: (1) that which is required for the heat of reaction in the case of endothermic reactions (including in this class the first step of exchange reactions, e.g., $XY + ZW = XZ + Y + W$), (2) that required to overcome a potential wall, (3) that required to produce a sensitive configuration on a surface. In catalysis, then, either (1) or (2) (principally (1)?) is lowered as compared with the homogeneous values, or (3) is substituted.

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[27] Z. Elektrochemie, 35, 561 (1929).

[28] Cf. Burk: J. Phys. Chem. 30, 1134 (1926).

[29] Z. Elektrochemie, 36, 588 (1930).

[30] e.g. Emil Fischer in his lock and key concept of the specificity of enzymes; Adkins and coworkers: J. Am. Chem. Soc., 45, 809 (1923); 46, 130, 2291 (1924); Burk: Loc. cit.; Balandin: Loc. cit.

Just what the activating mechanism is, for dimethyl aniline on benzyl malonic acid, is a matter of speculation. The principles developed for heterogeneous catalysis may be used in the main for homogeneous catalysis, and a large organic molecule as a catalyst, gives plenty of opportunity for spacing effects, etc. The catalytic action is probably dependent, however, upon the "free valencies" of the nitrogen in the present case. Furthermore, since the salt has been found to be less reactive than the free acid, the carboxyl hydrogen atom is probably involved in the first elementary act. The activation may consist in a mild excitation of the electron taken up from the hydrogen atom by the carboxyl group leading to dissociation of the carboxyl into neutral hydrogen and free RCHCOOH COO radicals;[31] this would be a still different type of activation. This may be catalyzed by dimethyl aniline if the nitrogen of the aniline gives up an electron to the hydrogen ion, and then takes one again from the carboxyl ion, in case these two energy steps are appreciably smaller.

There are no evident unpaired electrons in dimethyl aniline available for quantum mechanical coupling which might loosen the OH bond of a non-ionic form of the free acid through resonance action, although a collision with an acid molecule might render them available for coupling so that the dimethyl aniline could fulfill its catalytic duty of bond loosening in the quantum mechanical sense. That there is a type of quantum mechanical perturbation which does not depend on unpaired electrons is indicated in London's new interpretation of van der Waals' forces.[32]

That secondary valence forces have much to do with the present case is, however, not indicated since most solvents, including some which are quite polar, have little influence.

With respect to the effect of replacing the hydrogen atoms alpha to the carboxyl groups by other groups, there is no certain evidence of a lowering of the heat of activation, though a slight lowering is indicated when one benzyl group is introduced, and the rate is certainly increased. A plot of Bernoulli and Jokubowicz' values showed that only their work on malonic acid gave a good straight line when 1/T was plotted against log k, the data for the other acids being erratic.

It has been said that on account of results from investigations of band spectra and Raman spectra, effects corresponding to a distortion carried through the chain should be minimized. This is confirmed by the observation of Bernoulli and Jakubowicz[9] that when both alpha hydrogens are replaced by like substituents the decomposition rate is less than for malonic acid alone, in all cases. Whereas when only one is substituted, the decomposition rate is greater, for phenyl, benzyl, allyl, chlorine and hydroxyl. This would scarcely follow if the effect of substitution on decomposition rate were due to distortion carried through the chain. Furthermore, the halogen substituted acids did not decompose particularly rapidly. This is contrary to

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[31] See Franck: Loc. cit., for such processes of dissociation induced photochemically in polar unions.

[32] Z. Physik, 63, 245 (1930).

the effect of halogen substitution on the strength of acids. This, however, may be a space effect rather than a chain effect.[33]

Since in solution there would always be enough activating collisions to maintain the Maxwellian distribution of energy between acid molecules, the reaction rate would not fall off with diminished concentration and the number of participating internal degrees of freedom cannot be calculated. The heat of activation, reaction rate, and temperature coefficient do, however, fall into line fairly well with other monomolecular reactions.[34]

Summary

The decomposition rate of malonic acids, especially benzyl malonic acid, have been determined both for the acid alone and in various solvents.

Dimethyl aniline was the only solvent, of those investigated, to show marked catalytic action. This was accompanied by a definite lowering of the temperature coefficient. The effect was shown not to be due to salt formation.

Possible mechanisms for activation by the catalyst have been discussed.

Morley Chemical Laboratory,
Western Reserve University,
Cleveland, Ohio.
December, 22, 1930.

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[33] This is suggested by the work of McInnes: J. Am. Chem. Soc., 50, 2587 (1928).

[34] See Hinshelwood: "Kinetics of Chemical Changes in Gaseous Systems, 2nd. Ed., p. 159. The reaction rate of N_2O_5 in Hinshelwood's table would be too high for the purposes of the table if a chain mechanism applied to this case.

LIESEGANG RINGS

BY OLIN F. TOWER AND EDNA E. CHAPMAN

In 1928 Hedges and Henley[1] published a paper, in which they showed that in many cases Liesegang rings can be obtained by a process of coagulation. For example, they prepared a colloidal solution of silver chromate in gelatin, covered it with silver nitrate solution, and thereby obtained rings of silver chromate very similar to those of the original Liesegang experiments. They also found that it was not necessary for the diffusing electrolyte to possess an ion in common with the salt to be coagulated. By allowing a solution of aluminium sulfate to diffuse into a colloidal solution of arsenious sulfide in gelatin, rings of arsenious sulfide were obtained.

Rings of cadmium sulfide and zinc sulfide had already been prepared in this laboratory by the usual method.[2] Experiments were therefore undertaken to see whether rings of these substances could be obtained by the method described by Hedges and Henley. Colloidal solutions of cadmium sulfide were prepared by mixing a tenth-normal solution of cadmium chloride in agar-agar solution with a tenth-normal solution of ammonium sulfide. On standing, these give a very good colloidal solution of cadmium sulfide. More concentrated solutions than these could not be used, as a precipitate of cadmium sulfide was then obtained. Above several of these colloidal solutions of cadmium sulfide in agar-agar were placed cadmium chloride solutions of 0.5% concentration and regularly increasing concentrations up to 20%. These were allowed to stand for several days, but no rings of cadmium sulfide were obtained. Neither were rings obtained when the supernatant liquid contained ammonium sulfide, ferric chloride or aluminium sulfate. The method described by Hedges and Henley is, therefore, not a general one, and only appears to yield rings in certain special cases.

In continuation of the work referred to above by Daus and Tower, we here wish to report the results of experiments of preparing Liesegang rings of manganese, nickel and cobalt sulfides. In all these cases a method similar to that used before was followed. The electrolyte containing the sulfide ion was placed in the gelatinous medium, which consisted sometimes of gelatin, and sometimes of agar-agar, and the electrolyte containing the metallic ion was placed in the supernatant liquid. With gelatin the sulfide ion was furnished by ammonium sulfide, as the gelatin did not set when containing sodium sulfide. With agar-agar either ammonium sulfide or sodium sulfide could be used. The best concentrations of sulfide ions were found to be between 0.2 and 0.5 normal, and for the manganese ion between 0.1 and 2 normal. It

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[1] J. Chem. Soc., **130**, 2714 (1928).

[2] Daus and Tower: J. Phys. Chem., **33**, 605 (1929).

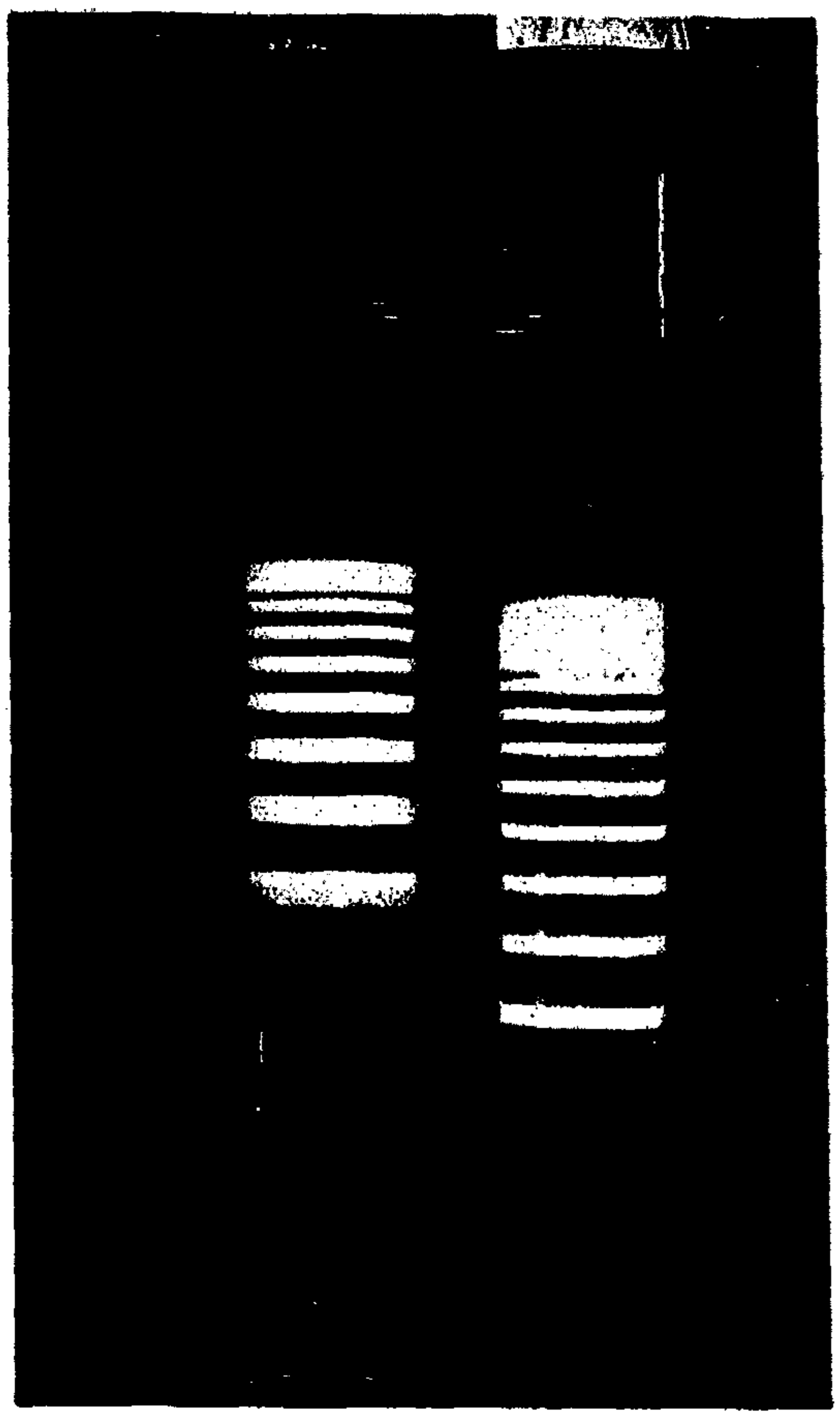

Fig. 1

0.3N $MnCl_2$ 0.9N $MnCl_2$
0.4 $(NH_4)_2S$ 0.9N $(NH_4)_2S$

made no difference whether manganese chloride or sulfate was used. Rings obtained with manganese chloride and ammonium sulfide are shown in Fig. 1.

In attempting to form rings of nickel and cobalt sulfides, it was found that no bands were obtained when ammonium sulfide was present in the gelatinous medium. The only bands that were obtained were, therefore, with sodium sulfide in agar-agar, and the supernatant liquid containing either the chloride or sulfate of either nickel or cobalt. The best concentrations for the sodium sulfide were 0.4 to 0.6 normal, and for the nickel or cobalt salt 0.7 to 2.0 normal. These rings were much finer and closer together than those with manganese sulfide, as is seen in Fig. 2.

Assumptions as to the way in which these rings are formed have already been given in the previous article, and we find no reason to modify them here.

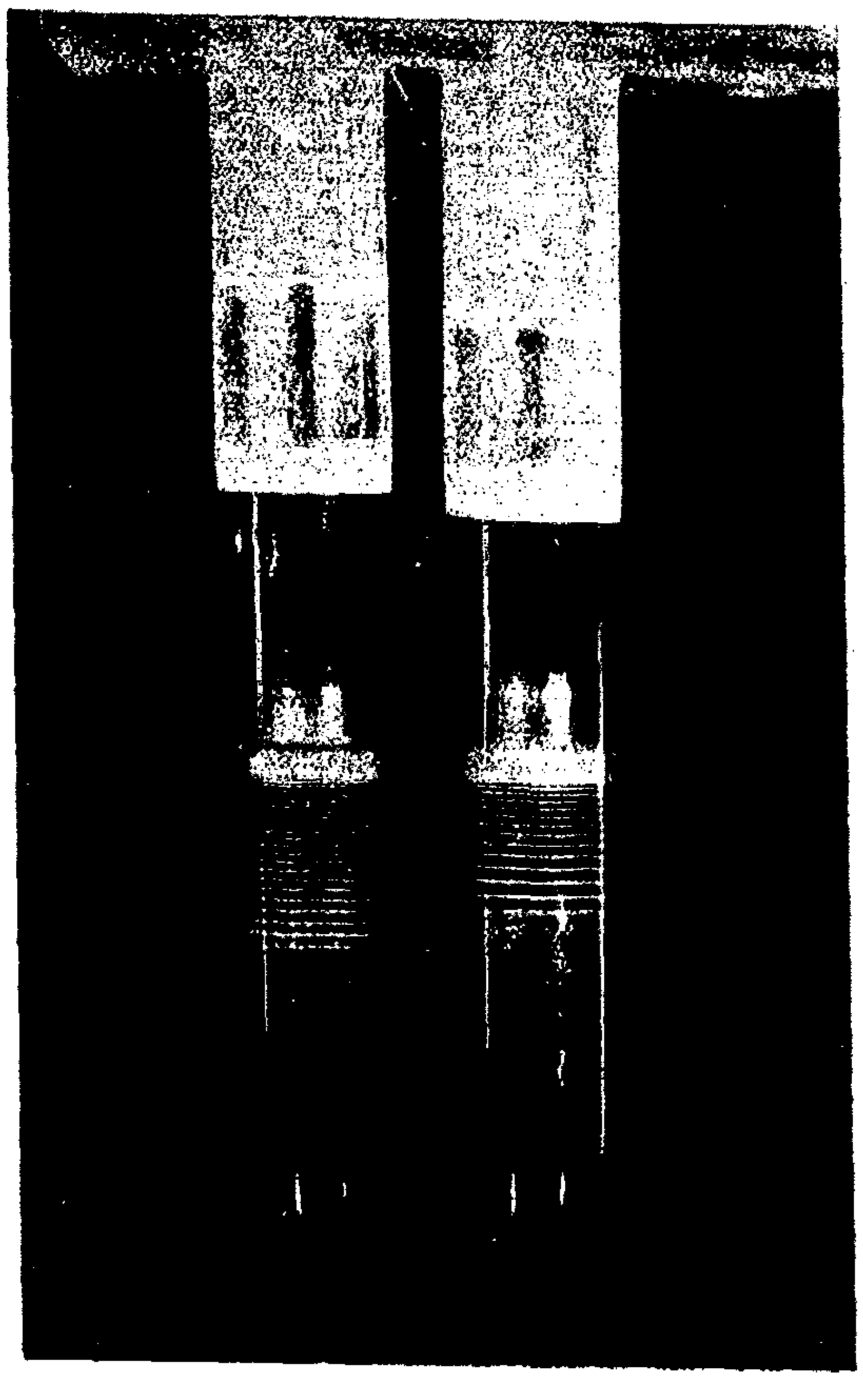

Fig. 2

0.19N $NiCl_2$ 0.7N $NiCl_2$
0.6N Na_2S 0.6 Na_2S

Summary

This paper records experiments to show that the method of forming Liesegang rings by coagulation, as recorded by Hedges and Henley, does not apply in all cases.

Methods for preparing Liesegang rings of manganese, nickel and cobalt sulfides are given.

Western Reserve University,
Cleveland, Ohio.

ON THE COMPOSITION OF ACID BORIC ACID-DIOL COMPOUNDS

BY J. BÖESEKEN AND N. VERMAAS

Introduction

For some time the Boric Acid Problem has been studied according to different physical methods in the Laboratory of Organic Chemistry at Delft. The article by Wilder D. Bancroft and Herbert L. Davis,[1] whose conclusions depart entirely, not only from the results obtained at Delft during the last few months, but also from all that had already been attained before by one of us and his pupils and by several other investigators, induces us to publish some of our results now.

Before proceeding to the discussion of the cause of the variation of acidity, we may be allowed to draw attention to a few passages of this paper which are, in our opinion, incorrect, or which, through their incompleteness, leave room for an erroneous conclusion.

On the significance of the preparation of optically active BR_2-anion (R = diol radical) by which the proof is furnished not only of the *existence* of these complexes, but also of their configuration, no more is said than the sentence: "One of the most recent developments in this field is the isolation of substances which appear to be compounds in which boron must be assumed to have a coordinated valence of four and to possess optical activity," while on p. 2482 it is stated that "the isolation of these compounds seems to be attended with some difficulties," whereas in reality a number of these compounds has been isolated without any difficulty, if in the polyols the hydroxyl groups are favourably situated, and the salts are not too readily soluble in water or in salt solutions.

When we consider that these salts are obtained from aqueous solutions it is natural to assume that the anions BR_2 are also present in aqueous solutions and to ascribe the increase of the conductivity of boric acid by the polyols to the formation of complex acids.

Referring to what will follow presently, where we have also furnished the proof of the existence of these anions in aqueous solution we may point out that these complex acids will be *very strong* acids, because they are formed by absorption of the electron of the H-atom, through which in the completely formed compound the hydrogen will be present entirely as proton; in aqueous solutions these acids will, however, be hydrolysed for an important part; hence it is to be expected that the free acids HBR_2 could be isolated from their aqueous solutions only if they should be much less readily soluble than boric acid or the other component, and there is not much chance of this, exactly with these strong acids.

We meet here with analogous circumstances as with the ammonium-bases, which must cede an electron to the hydroxyl group and which are in consequ-

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[1] J. Phys. Chem., 34, 2479 (1930).

ence very strong bases. These can, indeed be isolated, if no H-atom is bound to the N; if this *is* the case they are dissociated for the greater part in aqueous solution, making the impression of being weak bases.

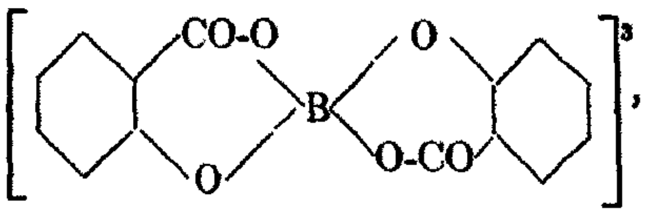
It is, accordingly, not astonishing that Bancroft and Davis have not succeeded in isolating complex acids, and notably not with glycerine, where the acid is almost completely hydrolysed (p. 2486).

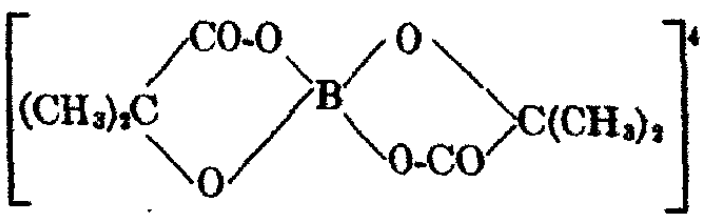
As here the formation of strong acids is in question, the reactions, just as when the equilibrium amine + $H_2O \rightleftarrows$ ammonium base is established, will bear the character of ion reactions, hence take place practically instantaneously. We may, therefore, by no means compare the establishment of the equilibrium: 2 diol + boric acid $\rightleftarrows$ complex + H_2O with the formation of esters of alcohols with weak organic acids (p. 2468 and conclusion 6 pp. 2505-2506).

In consequence of the fact that these complexes and notably glycerine boric acid, remain almost entirely hydrolysed, the heat effect will be slight (2486). Glycerine happens to be a very unfavourable object to prove the formation of compounds by another way than by the increase of the conductivity.

Meulenhoff[2] has succeeded in preparing free dipyrocatecholboric acid by heating its dry aniline salt in vacuo; in this it is noteworthy that the acid itself is very little volatile, as may be expected from such a molecule with polary bonds; it carbonizes at 200°.

We have succeeded in splitting up *three* types of these compounds into optical antipodes, viz. the anions:


[3],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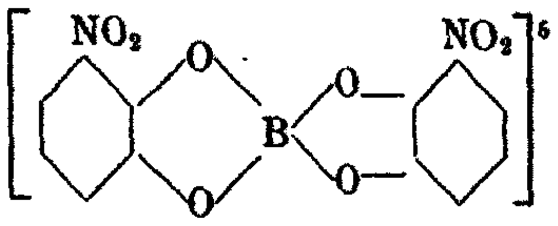
[5]

by precipitating them from *aqueous* solutions with optically active bases.

The spirane configuration of these compounds and the presence of these complexes also in aqueous solutions can, therefore, hardly be called in question. As we have exactly proved the existence of the anions BR^-_2 (as well as of BR^-) in aqueous solutions, as will be set forth presently we will pass by Bancroft and Davis's other considerations in silence.

We will only point out that the tartaric acids form a complicated case, because compounds of boric acid are possible both with the two α-hydroxy-

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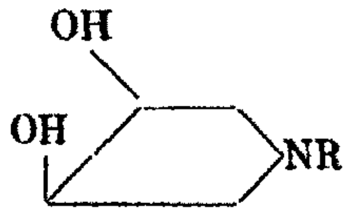
[2] Doctor thesis, Delft, pp. 35-36 (1924).

[3] Meulenhoff: Z. anorg. allgem. Chem., **142**, 377-379 (1925).

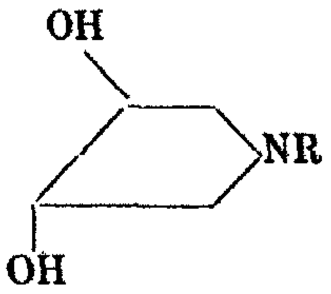
[4] Böeseken, Müller and Jap Hong Jouw: Rec. Trav. chim., **45**, 919 (1925).

[5] Böeseken and Mijs: Rec. Trav. chim., **44**, 750 (1925).

carbonic parts of the molecule, and with the middle glycol part. This is one of the reasons why the esters and the amides of the tartaric acid have been examined, where we have only to do with the glycol part of the acids. Here, too, it was found that the active compounds had a greater influence on the conductivity than the inactive ones, which can be explained by the stronger mutual repulsion of the COOR ($CONH_2$) groups than that of the OH-groups, owing to which these latter will lie closer together in the active acids than in the inactive acids. We may add to this that in the imides, where in consequence of the formation of the 5-atomic ring, the position of the OH-groups is fixed, the very reverse is to be expected, and has also been found by J. Coops.[6]



Anti-tartaric-imide



act-tartaric-imide

The anti-tartaric acid imide causes a considerable increase of the conductivity of the boric acid, the act-tartaric acid imide *absolutely* none. We do not see very well, how this difference can be accounted for in another way than by the formation or non-formation of compounds with boric acid. If Bancroft and Davis should rest satisfied with "the fact that the boric acid *dissolves* preferentially in the activating substance and is therein more highly dissociated than in water" this purely physical formulation does not seem satisfactory to us, and the assumption of a compound with the favourably situated hydroxyl groups of strongly acid character in the first case, the formation of which is impossible in the second case, seems very much more rational.

As regards the tartaric acids themselves, the separation of the potassium boro tartrate KBT_2 with two tartrate groups by Lowry[7] is so important, because it shows so convincingly how easily, with a favourable position of the hydroxyl groups, a compound of the spirane type is formed; accordingly we readily leave it to the readers to decide whether they will accept this formula given by Lowry, or that given by Bancroft and Davis on p. 2502.

In conclusion we will point out, that the summary given on pp. 2495-2496 of investigations of one of us and his pupils, is very incomplete for which reason we may lay aside their opinion on the small value of our investigations with a view to configuration determinations.

Let us now proceed to the closer examination of aqueous solutions of boric acid and polyols.

Bancroft and Davis hold the view that "the activation of boric acid in the presence of sufficient glycerine or mannite or certain other substances, is not

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[6] Doctor thesis, Delft, pp. 62-67 (1924).

[7] J. Chem. Soc., 1929 II, 2853.

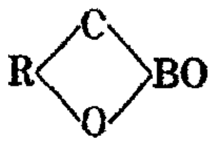
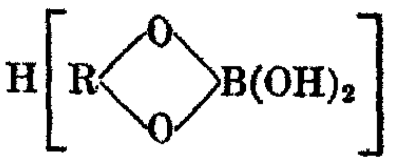
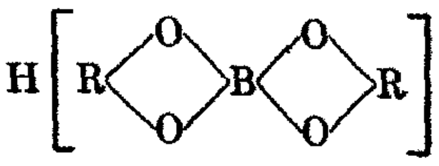
due to compound formation, but to the fact that the boric acid dissolves preferentially in the activating substance, and is therein more highly dissociated than in water".

Among other things the writers also make the following remarks: "The phenomena studied by Böeseken do not require such a ring structure as he adopted, but may more probably be due to a kind of complex formation involving only one hydroxyl group, the adjacent carboxyl, hydroxyl, or keto groups being required to activate the one reacting with the boric acid.

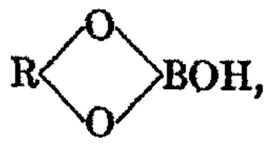
As evidence against the hypothesis of compound formation in these systems is the fact that there is no indication of the existence of a solid compound in the phase study of their aqueous solutions. This is true of the mannite system as well as of the tartaric acid systems, although mannite is one of the most effective activators of boric acid, and should give a compound if one exists."

It will now first be briefly discussed to what the acidity of boric acid diol solutions is to be attributed, after which in the conclusion Bancroft and Davis's views will be tested by the obtained results.

General Remarks on Boric Acid Diol Complexes

When a "favourable" diol (α-oxy-acids etc. included) is added to a solution of boric acid in water, the ring compound  is primarily formed, which, on account of the tendency of boric acid to assume the pentavalent condition, can pass into resp. the monobasic acids H  and H  with water or with a new molecule of diol.

These acids are comparatively strong, and as regards structure perfectly analogous to the acid $H[B(OH)_4]$ to which at present the acidity of a boric acid solution is ascribed.[8,9]

With less favourable diols the position in space of the OH-groups will render the transition of boron to the tetrahedric valence arrangement almost impossible; hence the complex formation will go no further than the , and no increase of acidity will be observed (2-4 dimethyl pentane -2-4 diol boric acid.)[8]

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[8] Hermans: Z. anorg. allgem. Chem., 142, 83 (1925).

[9] Böeseken and Coops: Rec. Trav. chim., 45, 407 (1925).

With absolutely unfavourable diols no complex formation will take place at all.

Combining all the undissociated complex compounds under HBR and HBR_2, the course of the reactions may be represented as follows:

$$\text{HB (boric acid)} + \text{R (diol)} \rightleftarrows \text{HBR} \rightleftarrows \text{H}^+ + \text{BR}^-$$

$$\text{HBR} + \text{R} \rightleftarrows \text{or}$$

$$\text{HB} + 2\text{R} \rightleftarrows \text{HBR}_2 \rightleftarrows \text{H}^+ + \text{BR}^-_2.$$

On the assumption that HBR and HBR_2 are strong acids, HBR and HBR_2 may be neglected with respect to their ions in the case of favourable diols in diluted solution.

The condition of the solution is then determined by the following equilibrium constants:

$$k_1 = \frac{(\text{H}^+) \times (\text{BR}^-)}{(\text{HB}) \times (\text{R})} \text{ and } k_2 = \frac{(\text{H}^+) \times (\text{BR}^-_2)}{(\text{HB}) \times (\text{R})^2}$$

These constants are analogous to those of carbonic acid and ammonia.

If for less favourable diols HBR and HBR_2 may possibly not be neglected, very certainly these equations cannot be used for more concentrated solutions, because then on one side tetra-boric acid[10] on the other side the undissociated HBR and HBR_2 may begin to play a part also for the favourable diols.

By division of the equilibrium constants we get:

$$1) \ldots\ldots\ldots\ldots\ldots\ldots \frac{[\text{BR}^-_2]}{[\text{BR}^-]} = \frac{K_2}{K_1} \times [\text{R}]$$

If now K_2/K_1 is $= \pm 10^3$ and the diol concentration is ± 0.1 mol., then (BR^-_1) may be neglected with regard to (BR^-_2) and the acidity of such a boric acid diol solution is governed by the di-complex.

Poly-alcohols

For poly-alcohols this has been proved in the Rec., **49**, 711, to which we refer here, as also to the theoretical derivations. Inversely it has appeared from this, that actually $K_2/K_1 = \pm 10^3$ or $> 10^3$. To the measurements mentioned in Rec., **49**, 711 only some results are added calculated from measurements of others:

I. Rimbach and Ley[11] measured the hydrogen-ion concentration of boric acid with different quantities of mannitol. From these data the following values were calculated by the methods described in Rec., **49**, 712 (1930). Boric acid = 0.1 mol.

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[10] Kolthoff: Rec. Trav. chim., **45**, 501 (1925).

[11] Z. physik. Chem., **100**, 393.

Boric acid: polyol	pH	ΔpH	n
1 : 6	3.08		
		0.78	2.0
1 : 1	3.86		
		0.75	2.1
1 : 5	3.11		
1 : 4	3.27		
		0.59	2.0
1 : 1	3.86		
		0.46	1.9
1 : 3	3.40		

Boric acid = 0.25 mol.

Boric acid: polyol	pH	ΔpH	n
1 : 2	2.93		
		0.49	2.0
1 : 6	2.44		
		0.74	1.9
1 : 1	3.18		

There is, therefore, no doubt but n is = 2 for these solutions but on the other hand it is easy to understand that for more concentrated solutions, where, moreover tetraboric acid appears, also the remaining OH-groups of the mannitol play a part through which the difficulties that arose in the separation of these acids, find a natural explanation.[12]

II. Years ago van Liempt (Rec., **39**, 358) titrated boric acid diol solutions potentiometrically with alkali. One of his measurements (on fructose) can be used for the calculation mentioned in Rec., **49**, 711 on account of the proportion boric acid : diol = 1 : 5.

In view of the irregular intervals of the pH his measurements appeared to be not very accurate, among other things for the reason that he made use of a very concentrated boric acid and fructose solution, which he greatly diluted with sodium hydroxide during the titration. According to Rec., **49**, 714.

$$K_3 = \frac{[H^+] \times [BD_2^-]}{[HB] \times [D]^2}$$

hence if the initial concentration of boric acid = a, and of the fructose = 5a, and if xa mol of alkalies have been added, then:

$$K_3 = [H^+] \times \frac{xa}{(a - xa)\,(5a - 2xa)^2}$$

The final point of the titration being reached at 15 cc, x is = y/15 if y is = the number of added cc's of NaOH, hence:

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[12] Hermans: Z. anorg. allgem. Chem., **142**, 111 (1925); Fox and Gauge: J. Chem. Soc., **99**, 1075 (1911).

$$[H^+] \times \frac{y}{(15 - y)(75 - 2y)^2} = \frac{a^2K_2}{225} = \text{constant} = c.$$

For the middle part of van Liempt's titration curve, where the error in $(15 - y)$ and in y is slight, and the electrolyte content not too great, and where also the dilution does not vary too much, the following values were calculated:

cc's NaOH	pH	$c \times 10^6$
5	3.21	7.3
6	3.42	6.3
7	3.56	6.5
8	3.69	6.7
9	3.83	6.8
10	4.09	5.5

Accordingly the K_2 appeared to be constant even under these comparatively unfavourable circumstances.

α-oxy-acids

1. In the first place a small orientating calculation will be given in connection with Rimbach and Ley's measurements[11] on α-oxy-acids. They measured the hydrogen-ion concentrations in oxy-acid solutions of different concentrations with and without boric-acid.

If it is assumed that, just as it has appeared with the poly-alcohols, the mono-complex acid may be neglected with respect to the bi-complex acid in these solutions, the following calculation may be made: Let a be the (H^+)-conc. of $n \times 0.1$ mol. of oxy-acid solution without boric acid, and b the (H^+)-conc. of the same solution, but with 0.1 mol. of boric acid, then, if the variation in the conc. of the undissociated acids is neglected, the following equations hold:

$$K_1 = \frac{(H^+) \times (Z^-)}{(HZ)} = \frac{a^2}{n \times 0.1} = \frac{b \times p}{n \times 0.1}$$

$$K_2 = \frac{(H^+) \times (BZ_2^-)}{(HB) \times (HZ)^2} = \frac{b \times q}{0.1 \times (n \times 0.1)_2}$$

p and q being resp. the (Z^-) and the (BZ_2^-) concentrations of the boric oxy-acid mixture.

Hence:

$$p = \frac{n \times 0.1\ K_1}{b},\ q = \frac{n^2 \times 10^{-3}K_2}{b},\ \text{and } n \times 0.1\ K_1 = a^2$$

$$\text{Now } p + q = b = \frac{a^2}{b} + \frac{n^2 \times 10^{-3}K_2}{b}$$

Hence $\dfrac{b^2 - a^2}{n^2} = c$ must be constant for different values of n

Lactic acid.

Conc. oxy. acid	H^+ conc. without boric acid	H^+ conc. with 0.1 mol of boric acid	$c \times 10^4$
0.1	6.07×10^{-3}	8.36×10^{-3}	0.33
0.2	9.06	17.1	0.52
0.3	11.5	21.7	0.37
0.4	13.5	27.6	0.36
0.5	14.6	35.1	0.40
0.6	15.8	38.0	0.33
0.7	17.1	41.2	0.29

For the mono- and the tri-complex acid, the values of resp. $\frac{b^2 - a^2}{n}$ and $\frac{b^2 - a^2}{n^3}$ would have to be constant, which is, of course not the case in the above observations, where n varies from 1-7.

A similar result, though not so beautiful, is also yielded by the glycollic acid measured by Rimbach and Ley.

II. For the determination of the dissociation constants of the acid complexes of boric acid and α-oxy acids, the pH-curve was determined for the titration of 10 cc 0.1 mol. of oxy acid with 1.0 cc 1.0 mol. KBO_2-solution. Assuming the 1-2 complex acid to constitute the last stage of the tendency to complexity of boric acid, we have, therefore, here four acids side by side, with the following dissociation constants:

$$K_2 = \frac{[H^+] \times [BZ_2^-]}{[HB] \times [HZ]^2} \qquad K_1 = \frac{[H^+] \times [BZ^-]}{[HB] \times [HZ]}$$

$$K_3 = \frac{[H^+] \times [Z^-]}{[HZ]} \qquad K_4 = \frac{[H^+] \times [B^-]}{[HB]}$$

Further, when b mol. of KBO_2 are added:

initial conc. of oxy acid $a = 2[BZ_2^-] + [BZ^-] + [Z^-] + [HZ]$.

all the negative ions $b + [H^+] = [BZ_2^-] + [BZ^-] + [Z^-] + [B^-]$.

all the boric acid $b = [BZ_2^-] + [BZ^-] + [HB] + [B^-]$.

The whole titration curve lying in an acid region, we may neglect the (B^-) conc. with respect to (HB), so that remains:

$$K_2 \times [HZ]^2 \times [HB] = [H^+] \times [BZ_2^-]$$
$$K_1 \times [HZ] \times [HB] = [H^+] \times [BZ^-]$$
$$K_3 \times [HZ] = [H^+] \times [Z^-]$$
$$a = 2[BZ_2^-] + [BZ^-] + [Z^-] + [HZ]$$
$$b + [H^+] = [BZ_2^-] + [BZ^-] + [Z^-]$$
$$b = [BZ_2^-] + [BZ^-] + [HB]$$

For a pretty well equal electrolyte concentration, K_3 may be measured by means of a simple potentiometric titration of the oxy-acid with alkali, so for a definite point of the titration curve K_3, a, b, (H^+) are known; unknown are: K_2, K_1, (BZ_2^-), (BZ^-), (Z^-), (HZ), and (HB).

Hence there are 6 equations, and 7 unknowns.

By the application of a neglection, K_2 can be calculated for a portion of the titration curve, in consequence of which 6 equations and 6 unknowns remain for the general case.

After elimination of the unknown quantities, two equations remain in the end from which the (HZ) cannot be eliminated any more

$$2)\ldots.K_2K_3[HZ]^3 - K_2[H^+]^2[HZ]^2 + [H^+]^2[HZ] - [H^+]^2\{a - b - [H^+]\} = 0$$

The value of (HZ) to be approximated from this is filled in, in the following equation, from which K_1 can be calculated

$$3)\ldots.K_1 = \frac{[H^+]}{[HZ]} \times \frac{[H^+]\{2b - a + 2[H^+] + [HZ]\} - K_3[HZ]}{K_3[HZ] - [H^+]^2}$$

We now proceed to the computation of K_2:
By division of K_2 by K_1, follows, compare: 1)

$$\frac{[BZ_2^-]}{[BZ^-]} = \frac{K_2}{K_1} \times [HZ]$$

If K_2/K_1 has a value of $\pm 10^3$ or $> 10^3$, as has appeared to be true for the polyols, and as afterwards will appear to be true here too, (BZ^-) may be neglected with respect to (BZ_2^-) over the portion of the titration curve where $(HZ) > 0.02$ mol. as the quantity of (BZ^-) is then less than 5% of the quantity of (BZ_2^-).

These values may be neglected over the part of the titration curve from 0.10-0.40 cc KBO_2.

Hence we get for the calculation of K_2:

$K_2 \times [HB] \times [HZ]^2 = [H^+] \times [BZ_2^-]$

$K_3 \times [HZ] = [H^+] \times [Z^-]$

$a = [HZ] + [Z^-] + 2[BZ_2^-]$ (initial conc. of the oxy-acid)

$b = [HB] + [BZ_2^-]$ (total boric acid)

$b + [H^+] = [Z^-] + [BZ_2^-]$ (all negative ions)

From these 5 equations (BZ_2^-) (Z^-), (HB), (HZ) may be eliminated after which we get:

$$4)\ldots.K_2 = \frac{\{K_3 + [H^+]\}\{b + [H^+]\} - K_3a}{K_3(a - 2b) - [H^+]\{K_3 + [H^+]\}} \times \frac{\{[H^+] - K_3\}^2}{[H^+]\{a - 2b - 2[H^+]\}^2}$$

Recapitulating: with formula 4) K_2 can be calculated over the first part of the titration curve (0.10-0.40 cc KBO_2), with formulae 2) and 3) K_1 can be calculated over the remaining part, where the appearance of BZ^- ions is very perceptible. The pH-curves are measured for α-oxy-iso-butyric acid, cyclo-pentane-α-oxy-carbonic acid, cyclo-hexane-α-oxy-carbonic acid.

Determination of K_3 at an electrolyte concentration varying between 0.025-0.075 mol. by potentiometric titration of 10 cc 0.1 mol. of oxy-acid with 1.0 cc 1.0 N. potassium hydroxide.

	cc's KOH	pH	K_3
α-oxy-iso-butyric acid	0.254	3.387	1.4×10^{-4}
	0.525	3.894	1.4
	0.790	4.438	1.4
cyclo-pentane-α-oxy-carbonic-acid	0.267	3.562	1.0×10^{-4}
	0.532	4.066	1.0
	0.792	4.581	1.0
cyclo-hexane-α-oxy-carbonic-acid	0.226	3.514	0.90×10^{-4}
	0.537	4.104	0.91
	0.690	4.383	0.92

Now follow the different points of the determined pH curves for the titration of oxy-acid with KBO_2 with the values calculated for K_2 and K_1.

A typical phenomenon, which has not yet been accounted for, was that the adjustments over the second parts of the titration curves required a good deal of time.

α-oxy-iso-butyric acid

cc's KBO_2	pH	K_2	K_1
0.147	2.664	2.3	
0.194	2.758	2.3	
0.240	2.869	2.2	
0.288	2.991	2.2	
0.336	3.119	2.4	
0.384	3.282	2.4	
0.532	3.934		3.1×10^{-3}
0.582	4.225		3.1
0.630	4.502		3.3
0.731	5.038		3.2
0.783	5.290		3.3
0.836	5.523		3.6

cyclo-pentane-α-oxy carbonic acid

cc's KBO_2	pH	K_2	K_1
0.100	2.641	3.2	
0.144	2.724	2.7	
0.192	2.812	2.8	
0.239	2.901	3.3	
0.285	3.032	3.2	
0.331	3.154	3.2	
0.337	3.312	3.2	
0.616	4.644		3.8×10^{-3}
0.663	4.943		3.6
0.712	5.199		3.4
0.762	5.434		3.9
0.808	5.659		3.7
0.854	5.842		4.2

cyclohexane-α-oxy-carbonic acid

cc's KBO_2	pH	K_2	K_1
0.150	2.713	3.9	
0.197	2.795	4.0	
0.246	2.895	4.1	
0.293	3.018	4.0	
0.343	3.166	4.3	
0.390	3.349	3.7	
0.530	4.178		2.3×10^{-3}
0.577	4.596		1.9
0.626	4.962		2.1
0.675	5.291		2.2
0.725	5.544		2.3
0.776	5.807		2.4
0.825	6.045		2.4

The result is that it appears from the fact that K_2 and K_1 have been found to be constant for these 3 α.oxy acids, that the suppositions on which formulae 2), 3) and 4) are based, are correct.

In consequence of the fact that K_1, K_2 and K_3 are known, it should now be possible to calculate the quantities of different components accurately for every point of the titration curve, but this cannot be done exactly as K_1, K_2 and K_3 are no pure ionisation-constants, but ion-activity-constants, constants measured in a solution with a considerable electrolyte content.

In order to obtain a good idea of the concentrations of the different components during the titration, these have been calculated for an imaginary acid with $K_1 = 3 \times 10^{-3}$, $K_2 = 3$, $K_3 = 10^{-4}$, and represented in a graph.

It appears clearly that with the ratio alkali: boric acid: oxy acid = 1 : 1 : 2 (A) the BZ_2-ions, and that on the contrary with alkali: boric acid: oxy acid = 1 : 1 : 1 (B) the BZ^- and the Z^- -ions play the most important part.

It is evident that with different concentrations, and especially with other acids with other constants, the graphs will present an entirely different aspect.

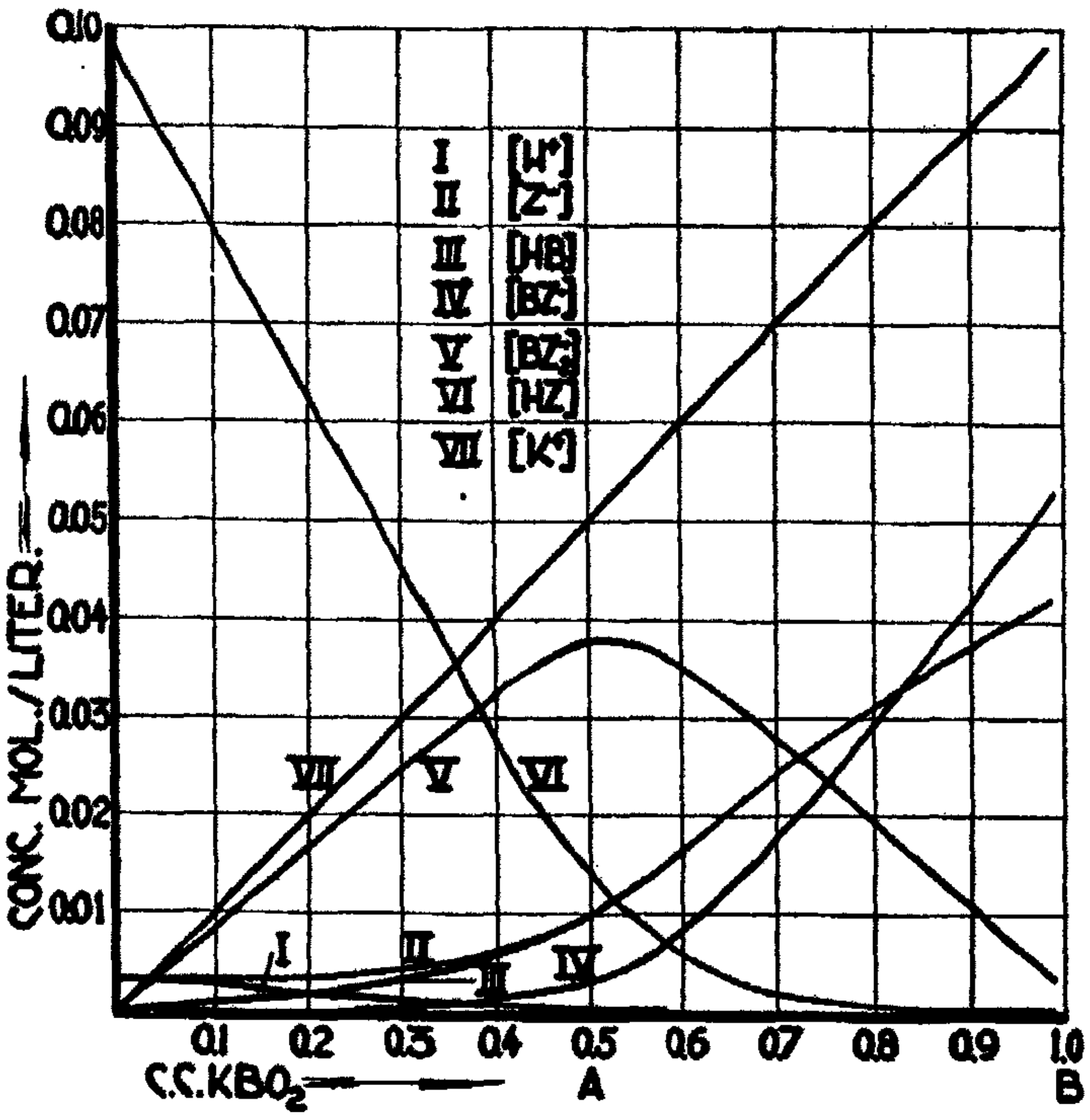


FIG. 1

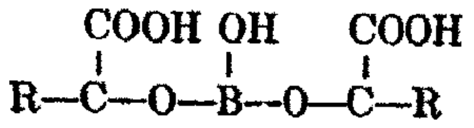
Conclusions

1. The measurements and computations mentioned in Rec. **49,** 711 and in this article have established that the greatest number of molecules of favourable diol or α-oxy acid that one molecule of boric acid in 0.1 mol solution can bind, is *two* for the cases investigated.

2. In three α-oxy acids the presence of the acid consisting of 1 mol. of boric acid and 1 mol. of oxy acid was shown. Also for polyalcohols (fructose, mannitol) the presence of the acid consisting of 1 mol. of boric acid and 1 mol. of diol is found. These investigations will be published later on.

3. The appearance of the two complex acids depends on the dissociation constants K_2 and K_1, and also on the concentration of the free oxy acid.

4. The ring structure proposed by Böeseken, which had already been convincingly proved by the separation of the optically active isomers of boric acid-α-oxy acid compounds,[13,2,3,4,6] has been fully confirmed also by these measurements. How could acids as Bancroft and Davis[1] propose



$$R-\overset{\displaystyle COOH}{\underset{}{C}}-O-\overset{\displaystyle OH}{B}-O-\overset{\displaystyle COOH}{C}-R$$

be monobasic?

5. The existence of such feebly acid complex compounds is plausible for all other (not α-hydroxy-or orthohydroxy) acids.[9]

6. The appearance of tetraboric acid in concentrated solutions[10] and the fact that mannitol possesses still another set of favourable OH-groups, render a study of the concentrated boric acid-mannitol solutions very difficult, which quite accounts for the absence of an "indication of a solid compound in the phase study of aqueous solutions of mannitol and boric acid."

7. It has been explained why Meulenhoff and others, working with solutions in which alkali: boric acid: oxy acid = 1 : 1 : 2, separated the di-complexes[14], whereas Kolthoff[15] demonstrated the presence of the mono-complex in his measurements of the solubility of silver salicylate in boric acid, in which he worked with alkali: boric acid = 1 : 1, the possibility exists, however, that in salicylic acid the ratio K_2/K_1 is entirely different from that in the saturate α-oxy acids examined.

8. The above results leave no room for the assumption that "these phenomena are solubility phenomena," but prove on the contrary that "the increased acidity must be due to the formation of compounds."

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[13] Böeseken: Proc. Akad. Wet. Amsterdam, **27**, 174.

[14] Meulenhoff: Doctor thesis, Delft, p. 61 (1924).

[15] Rec. Trav. chim., **45**, 607 (1925).

13 - 1

A REFRACTOMETER FOR REACTIVE LIQUIDS

BY WALTER CULE DAVIES AND WILLIAM J. JONES

The determination of the refractive indices of some liquids is rendered difficult by their reactive and corrosive nature. For instance, certain organo-metallic compounds are so quickly decomposed by oxidation on exposure to the air, and most acid halides are so rapidly hydrolysed by the atmospheric moisture, that the measurement of their indices by means of ordinary refractometers, such as the Abbe and the Pulfrich, in which contact with the air is involved, is out of the question. Even if special, air-tight, cells are used with such instruments, troubles are encountered where such liquids as the chlorides of phosphorus and arsenic are placed in contact with the optical glass, which they and their products of decomposition rapidly pit and corrode. For these reasons, where reactive liquids have to be dealt with, a refractometer with an air-tight cell of readily replaceable optical parts is desirable, and such an instrument, based on the principle of the spectrometer with liquid-filled prism, is illustrated in Fig. 1.

The prism, P, is of glass, through which a cylindrical hollow has been bored parallel to the base. The hollow is closed by a thin plane glass front and a back, plane, glass covered, mirror. These parts are kept in position by means of rubber bands, or in certain cases it may be preferable to cement the plates to the prism with Canada balsam. Communication to the hollow is afforded by two tubes carrying taps which are ground into the base and top of the prism, respectively. The assembled empty prism is placed on the prism table, where it is filled, and is held in position by means of the spring clip, C.

The angle of the prism and parts is determined by the use of a standard liquid. This determination was found to be necessary; although the prism used in the present work had itself been accurately cut to 30°, owing to adjustments of the plates, involving the use of bands or of Canada balsam, the composite prism did not actually function with exactly that angle. The standard benzene used for this purpose had the following refractive indices: $n_F^{20°}$ 1.51171, $n_D^{20°}$ 1.49989, $n_C^{20°}$ 1.49527. To take the readings, the source is placed so that the light falls on the rhomb on the left-hand side of the eyepiece. The zero position, in which the ray is reflected back from the front plate along its original path, is obtained by narrowing the slit, controlled by the milled head, S, and bringing the image of the slit into coincidence with the intersection of the cross wires. The prism with its table is then rotated by means of the arm, A, until the refracted image of the slit is brought into coincidence with the intersection of the cross wires. The refractive index is given by the ratio of the sine of the angle of rotation to that of the angle of the prism, and, the value of the index being known for the standard liquid, benzene, the angle of pos.

Fig. 1054

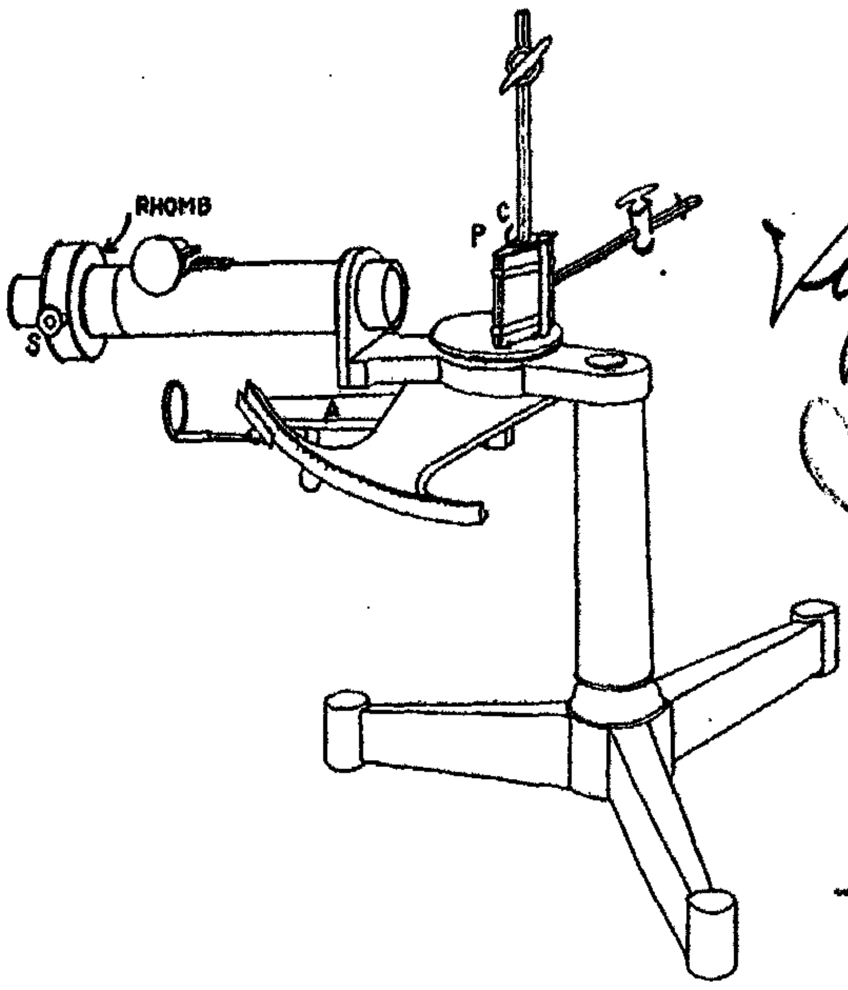

Fig. 1

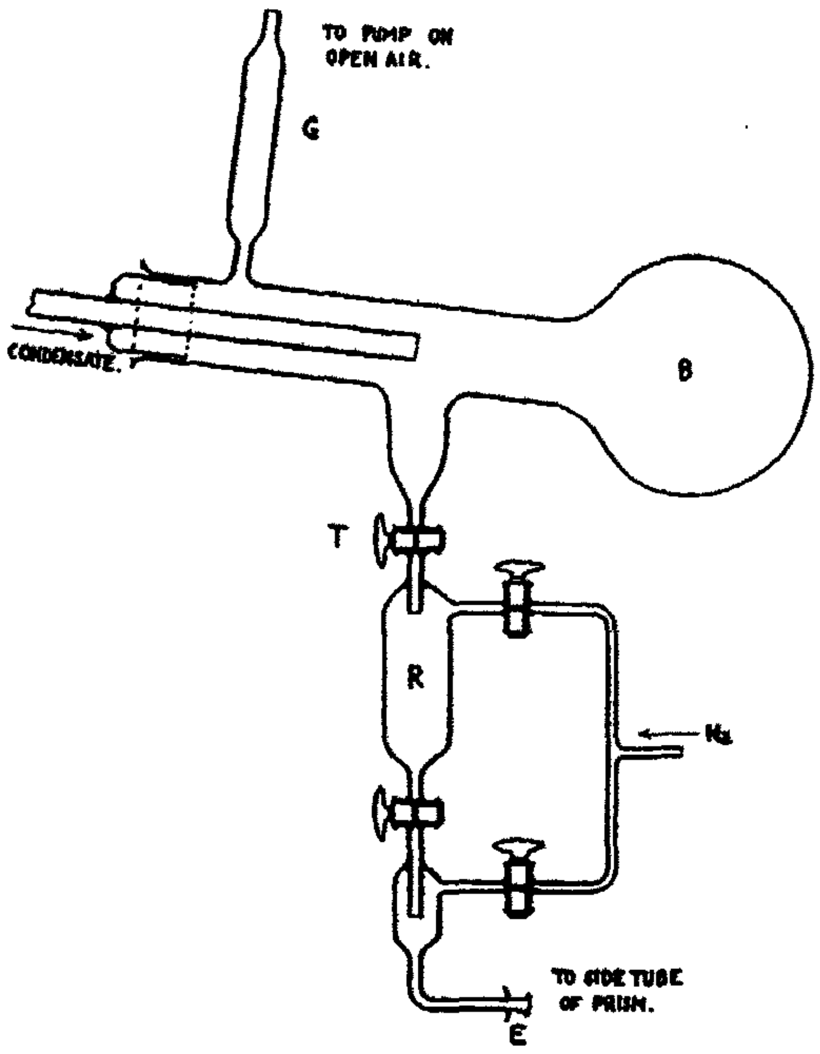

Fig. 2

the prism and parts is found. For instance, the angle of the prism and parts thus determined in one of the present settings was 30° 2′. The benzene is then removed, without disturbing the plates, from the prism, which is thoroughly dried by a rapid stream of air.

The liquid under investigation, already purified, is now distilled in an all-glass apparatus, and is condensed and collected in the two-way receiver, shown in Fig. 2, with guard tube, G. Air is swept out of the apparatus by the admission of an indifferent gas, and, if necessary, the apparatus is then evacuated. Half of the liquid is collected in the bulb receiver, B, and then the receiver, R, originally horizontal, is turned into the vertical position shown in the figure, and the collection of a specimen is effected in R. The tap, T, is then closed, and the receiver, R, is attached by its ground end, E, to the corresponding ground end of the horizontal tube of the prism, which is now swept out with the inert gas, a guard tube having been affixed to the vertical tube on the top of the prism. The liquid is now allowed to flow into the prism. It is an easy matter to maintain the temperature at the standard, *viz.*, 20°C. As an example we may quote the following measurements of the refractive index of acetyl chloride: $n_F^{20°}$ 1.39335, $n_D^{20°}$ 1.38708, $n_C^{20°}$ 1.38548.

Investigation of the refractivities of highly reactive liquids such as acid chlorides by means of this instrument is now in progress.

In conclusion we have to thank Messrs. Bellingham and Stanley, London, for their help and advice in the construction of the instrument.

Tatem Laboratories,
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October 28, 1930.

THE THERMAL DECOMPOSITION OF DIAZOMETHANE

BY E. W. R. STEACIE

According to v. Pechmann[1] diazomethane decomposes thermally to give ethylene and nitrogen as indicated by the equation

$$CH_2N_2 = N_2 + \tfrac{1}{2}C_2H_4;$$

and if the vapour is heated above 200°C it may explode violently.

Staudinger and Kupfer,[2] however, claim to have used the vapour of diazomethane at 400-500°C in the synthesis of ketene.

An attempt was made by the writer to investigate the slow decomposition of the substance at temperatures below that at which it explodes. This attempt was abandoned after a number of serious explosions, but a few of the results which were obtained may be of interest and are given in the present communication.

Preparation of Diazomethane

Diazomethane was prepared by treating an amyl ether solution of nitroso methyl urethane with a 70 per cent aqueous solution of potassium hydroxide, and refluxing the mixture.[3] The gas evolved was condensed in a bulb immersed in a carbon dioxide-acetone mixture. The liquid thus obtained was fractionally distilled and was stored as a liquid in a bulb at −80°C.

The Products of the Thermal Decomposition

Experiments on the thermal decomposition were carried out by letting small quantities of the vapour into a bulb contained in an electric furnace at temperatures from 140° to 220°C. The progress of the decomposition was followed by pressure measurements made with a McLeod gauge.

In the slow decomposition the products were ethylene and nitrogen as indicated by the equation

$$CH_2N_2 = N_2 + \tfrac{1}{2}C_2H_4.$$

This would correspond to an increase in pressure of 50 per cent when the reaction reached completion. Some of the observed increases in pressure under various conditions of temperature and initial pressure were 50, 54, 51, 48, and 54 per cent. The products of the reaction were analysed in a number of cases, and two typical analyses follow.

217°C. Initial pressure 5.2 cms.

$N_2 = 68.8\%$, $C_2H_4 = 28.8\%$

saturated hydrocarbons (as CH_4) $= 2.4\%$.

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[1] Ber., 31, 2643 (1898).

[2] Ber., 45, 508 (1912).

[3] v. Pechmann: Ber., 28, 855 (1895).

187°C. Initial pressure 10.9 cms.

N_2 = 67.2%, C_2H_4 = 32.0%, CH_4 = 0.8%.

These are in satisfactory agreement with the calculated composition from the above equation, viz. N_2 = 66.6%, C_2H_4 = 33.3%.

In the explosive decomposition a large amount of carbon and tarry material was deposited, the gaseous products being mainly nitrogen, together with various hydrocarbons and some hydrogen. This is to be expected since, at the high temperature of the explosion wave, ethylene would be largely decomposed.[1]

The Explosive Decomposition

The explosion limits of the reaction were determined approximately. At 217°C an explosion occurred if the pressure of the diazomethane was above 10 cms. At 187°C the limiting pressure was about 18 cms. Any accurate determination of these limits was impossible since, as will be discussed later, the explosive nature of the substance is very susceptible to traces of organic matter. The explosion limit was definitely lowered, however, by the presence of an inert gas as is usual with an explosion of the chain type. Thus a mixture having partial pressures of 8 cms. of diazomethane and 30 cms. of nitrogen exploded violently at 187°C.

It was found that explosions also occurred at low temperatures due to traces of organic matter such as carbon or tarry material deposited in a previous explosion. In one case a bulb containing about one gram of liquid diazomethane was connected to a small evacuated bulb which was at room temperature. When the pressure of the vapour in the small bulb reached about 5 m.m. an explosion occurred which detonated the supply of liquid at −80°C. A number of serious explosions occurred in this way and, as it was not found possible to control the behaviour of the substance even at −80°C, the work was abandoned.

The Slow Decomposition

Only a few experiments were performed on the slow decomposition. The results of these are listed below:

Slow Decomposition in Quartz Bulb

Temperature °C.	Initial Pressure, mms.	Time in seconds for a 10% increase in pressure, i.e. for 20% completion.
217	52	11
217	45	12
187	109	120
187	54	231
162	155	358
162	87	760
162	45	1435
135	202	9400
135	91	20600
135	45	38000

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[1] Hurd: "Pyrolysis of Carbon Compounds," 56 (1929).

The reaction is apparently bimolecular since the time required for a given fraction of the reactant to decompose is approximately proportional to the reciprocal of the initial concentration.

The addition of powdered quartz to the reaction vessel had no appreciable effect on the rate of decomposition. The reaction therefore is homogeneous.

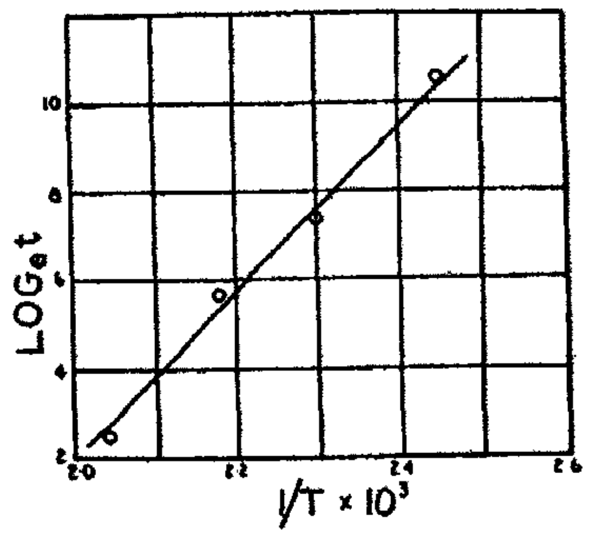

Fig. 1

The Temperature Coefficient

In Fig. 1 the logarithm of the time to 20% completion is plotted against the reciprocal of the absolute temperature, for an initial pressure of 45 mm. The points fall satisfactorily on a straight line as required by the Arrhenius equation. The heat of activation calculated from the slope of the line is 36000 calories per gram molecule.

It should be emphasized that owing to the small number of experiments reported these results are to be regarded as merely semi-quantitative.

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A NOTE ON SOME PROPERTIES OF BENZALDEHYDE

BY JAMES R. POUND

It is of course well known that benzaldehyde oxidises rapidly in the air and that finally crystals of benzoic acid separate. Many conditions of this action have been studied recently,—see, for example, abstracts of papers by O. M. Reiff and by M. Brunner (1927); and we have also observed that oxidation occurs chiefly at the free surface of the liquid and on the surface of the containing vessel above the liquid, and also that solutions containing appreciable benzoic acid oxidise less readily than the pure benzaldehyde. We have determined some properties of benzaldehyde and simultaneously the benzoic acid content of the samples.

Commercial benzaldehyde was dried over calcium chloride, with which it possibly forms an unstable compound, and was then distilled in a stream of carbon dioxide; the B. P. (corr.) was 179°-181°; and the product contained some benzoic acid. Some of the distillate was washed with bicarbonate of soda solution, dried over calcium chloride, and filtered off through a filter-plate. Some of the solutions with benzoic acid were made up synthetically and others obtained by oxidation from the original benzaldehyde. The percentage of benzoic acid was determined by titration by carbonate-free caustic soda, using phenol-phthalein as indicator, in alcoholic or aqueous solution. The densities and viscosities at 30° and the refractive index at 20° were found in the usual manner. Typical results are given in the table in C.G.S units.

The density-concentration curve is linear and indicates that $D^{30°}_{4°}$ for the pure benzaldehyde is 1.0365. The densities of solutions containing x% weight of benzoic acid are,—

$$D^{30°}_{4°} = 1.0365 + 0.00125.x,$$
$$\text{and } D^{14°}_{4°} = 1.0567 + 0.00113.x$$

The viscosity-concentration is slightly convex to the concentration-axis and indicates that $\eta^{30°}$ for the pure benzaldehyde is 0.01296.

The refractive index of benzaldehyde varies little as benzoic acid is dissolved in it; probably $\eta^{20°}_{D}$ for pure benzaldehyde is 1.5460, decreases linearly with increasing concentration of benzoic acid, and the $\eta^{20°}_{D}$ for the solution containing 14% acid is 1.5456; however our refractometer only gives n within ±0.0001.

At 7° the solution of benzaldehyde saturated with benzoic acid contains 12.85% acid, and at 13° such contains 14.0% acid.

TABLE I

Properties of Solutions of Benzoic Acid in Benzaldehyde

%wt. Benzoic acid	$D^{30°}_{4°}$	$\eta^{30°}$	$n^{20°}_{D}$
0.23*	1.0371	.01309	1.5460
5.80*	1.04375	.01449	—
1.10	1.0379	.01316	1.5457
8.60	1.0470	.01512	—
13.0	1.0528	.01642	1.5459
14.01	1.05385	.01674	—

Note * These samples were from benzaldehyde after $NaHCO_3$ treatment.

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NEW BOOKS

Diatomaceous Earth. *By Robert Calvert. 23 × 16 cm; pp. 251. New York: Chemical Catalog Company, 1930. Price: $5.00.* In the preface, p. 9, the author says: "The present uses as well as the future possibilities of diatomaceous earth are attributable to its unique properties. Diatomaceous earth consists of the fossil remains of an order of unicellular plants called *Diatomaceae*. The individual particles of the earth are so small that forty million of a given species may be contained in one cubic inch. Yet the microscope shows each one of the millions to be delicately fashioned into a highly ornate structure, with numerous channels, perforations, and nodules, all combining to give an extensive surface area. The composition is nearly pure silica and, consequently, is infusible at a red heat."

The subject is presented under the headings: introduction; present status of the industry; occurrence of diatomaceous earth; mining and preparation of diatomaceous earth for the market; physical properties of diatomaceous earth; filtration medium of diatomaceous earth; filtration of sugar solutions; miscellaneous filtrations with diatomaceous earth; diatomaceous earth in the petroleum industry; action of alkalies upon the diatomaceous earth; diatomaceous earth as an admix in Portland cement and plaster; diatomaceous brick; miscellaneous insulating compositions containing diatomaceous earth; thermal conductance and loss of heat through furnace walls; diatomaceous earth as absorbent; miscellaneous uses of diatomaceous earth.

Fullers' earth must be distinguished from diatomaceous earth, p. 15. "The two earths are different in origin, composition, density, uses, and properties. Yet they are often confused in the general thought. Fullers' earth is of mineral, diatomaceous earth, of vegetable origin. Fullers' earth is a clayey substance, diatomaceous earth nearly pure silica. The one has an unctuous, greasy feel, the other is chalky. In compact form, fullers' earth weighs more than 100 pounds to the cubic foot, diatomaceous earth, 15 to 40. Fullers' earth has sufficient adsorptive power to be useful as a decolorant of oils; diatomaceous earth, unless specially treated, has little adsorptive power and functions in filtrations largely mechanically, as a straining agent, to remove insoluble suspended matter."

"Some diatoms live in fresh, some in salt water. Some lie at anchor. Others of the so-called plankton type float freely. Some appear under the microscope as almost naked skeletons while others show a pronounced gelatinous covering. Nearly all varieties are alike in secreting silica and accumulating a droplet of oil. . . . On the decay of the diatoms, the oil and the silica remain. Occasionally the conditions of growth, wind, or current favor the settling of the silica into great deposits that are only slightly contaminated. A similar concentration of diatom oil, either the primary oil or oil formed by decomposition of the vegetable matter of the diatom, is responsible for much of our petroleum. Certainly such vegetable growth is sufficient in quantity to produce enormous pools of oil, by suitable chemical decomposition. Card and Dun describe a deposit of mud no less than four hundred miles long by one hundred and twenty miles broad, found at a depth of between two hundred and four hundred feet, on the flanks of Victoria Land in 70° south latitude. This deposit is composed of diatom ooze, its thickness is unknown. In the Antarctic Regions the sea is often thick with *Diatomaceae* which also tinge it and the ice a dull yellow. Instances are on record of shallow estuarine harbours being choked by their rapid accumulation," p. 18.

"The present importance of diatomaceous earth is due largely to the widespread use of the powder for filtering raw cane sugar solutions and as an addition to concrete and of diatomaceous brick for thermal insulation. These represent the major uses of diatomaceous earth," p. 25.

"Approximately 2000 tons of diatomite are mined annually at Carlin, Nevada, over three-quarters of which are for insulation purposes, as it is claimed that the best grade material will stand an exceptionally high temperature without shrinkage. A good insulation brick is made using magnesium chloride as a binder. It does not make a good cane-sugar filter medium as the diatoms are too small, but the coarsest is used for beet sugar and molasses, also for clarifying dirty oils from crank-cases, etc. It makes an excellent silver polish and is also used in finger-nail polishes and tooth pastes, as well as for fillers, etc," p. 49.

According to Patty and Glover, "the overburden is removed and the thus exposed diatomaceous earth is quarried by hand, stacked outdoors to dry, milled by impact pulverizers, and conveyed by blowers through a pipe line over a series of hoppers into which the powder settles according to the size of the particle. The very fine dust which does not settle, even in the last hopper, is separated from the air stream by filtration through cloth in a so-called "bag-house." The powders thus obtained are packed in burlap sacks and sold according to grade. . . The product which settles in the single dust chamber or in any of the four hoppers is of satisfactory grade for the regular grade for the regular commercial uses. The fine dust which separates in the cyclone or in the cloth bags is exceedingly fine, free from grit, and much desired by the manufacturers of various polishes, particularly those for lacquered automobiles," pp. 69, 81.

"An excellent absorbent, diatomite is a poor adsorbent. It does not adsorb vapors or gases readily. Neither does it decolorize, to an important degree, liquids filtered through it. That it does adsorb in certain instances is true. For example, an alkaline, alcoholic solution of phenolphthalein, if poured into diatomaceous earth, loses its bright pink color at once and becomes colorless. Also, powdered diatomaceous earth in filtering raw sugar probably retains much colloidal matter and raises the purity of the raw sugar," p. 93.

"Finally, a removal of bacteria and enzymes is sometimes effected by filtration through powdered diatomaceous earth. Brewers of "near-beer" arrest the fermentation, when the alcoholic content approaches that allowed by law, by adding diatomaceous earth to the brew and filtering. Calvert and Knight have found that sugar syrups filtered through diatomaceous earth and then kept in fermentation tubes do not develop gas as quickly as unfiltered syrup. Owen, in very careful tests, has found such filtration removes 99 per cent of the bacteria," p. 100.

"Originally, varnish was 'cleared' by the simple process of settling out the undissolved gums and other solids. Centrifuging was more convenient but did not accomplish an absolute, positive clarification of the varnish. Some of the suspended gums and other solids are so finely divided and so light in weight as to defy every attempt at removal by centrifugal force. Therefore, it was but natural that filtration with pressure filters should persist for the clarification of the higher grades of goods, especially in the larger companies with reputations for the appearance and durability of their product. The absolute certainty of clear goods from the filter-press offsets, in a large measure, the objections accompanying the added labor, floor space, and handling of 'excess varnish.' At the same time, it was recognized that these objections are serious ones, and in many of the smaller varnish factories centrifuges were adopted and were accepted as an answer to the whole problem of clearing varnish.

"Recent developments have changed entirely the position which filter-presses hiterto have held in varnish manufacture. These improvements are, namely, the development for and the application to the varnish industry of the filter-aid Super-Cel which has materially changed the aspect of varnish filtration. Varnish makers are said to be able, through the use of Super-Cel, to accomplish tasks which previously were considered impossible. Ease of filtration, high capacity and more nearly continuous operation of filter-presses are the advantages claimed for the use of Super-Cel, together with greater clarity of product," p. 139.

"Of all the alkalies, lime has perhaps the most interesting effect upon diatomaceous earth. Lime gives a quick change in appearance and a product of interesting though unexplored possibilities. Diatomaceous earth, shaken with water and allowed to stand, settles slowly. With the usual grade of earth, the supernatant liquor will be turbid after even a day of subsidence. But, if lime is added to the suspension and the mixture boiled, coagulation occurs immediately. Now, on even brief settling, the supernatant liquor becomes quite clear. As the boiling is continued for an hour or more, the lime in solution apparently combines with the surface silica of the particles of diatomaceous earth, with attendant enormous swelling.

"The properties of the lime-treated earth are quite different from those of the original earth. A 10-gram sample of diatomaceous earth that settles in distilled water to a volume of 33 cc. has been found, after boiling for three hours with 50 per cent of its weight of lime in aqueous suspension, to occupy a volume of 375 cc. The increase in volume of settled material is over 1,000 per cent. Furthermore, Calvert finds the lime-treated diatomaceous earth to filter water at 4,600 per cent of the rate for the untreated earth. Also, the swollen product after being baked can adsorb vapors of volatile liquids, whereas the original earth has practically no adsorptive capacity.

"The product, when dried at ordinary temperature, is slightly whiter and smoother to the feel than the original diatomaceous earth. Also, the dry lime-treated material weighs only 5 pounds to the cubic foot, as compared to 7 or 8 for the untreated earth packed in the same manner," p. 156.

"Admixture of powdered diatomaceous earth with plaster produces a notable increase in spreading power. Admixture of the earth with Portland cement causes such conspicuous improvements in the quality as to justify the belief that the use in concrete may soon constitute the largest single demand for diatomaceous earth. Already this use is very important," p. 160.

"The firing of diatomaceous brick, in the usual manner, above 1900°F. converts a part of the silica (which comprises more than 90 per cent of the earth) into cristobalite, a highly objectionable, crystalline form. Cristobalite undergoes an abrupt change in volume at certain transition temperatures, as it passes from one crystal form to another. One such change amounts to approximately 1 per cent in length and occurs when the cristobalite undergoes a temperature change of only a few degrees at the critical point. If the cristobalite is cooled through this critical range, the change of 1 per cent in length is one of contraction. If it is warmed, the change is an expansion of a like amount. This, perhaps, explains why insulating bricks that have been improperly made will often spall when only a match flame is applied to the corner of the brick.

"To avoid the formation of cristobalite and consequent spalling, Coss fires his brick in the presence of an agent that favors, it is said, the formation of tridymite instead of cristobalite. Thus, he fires in the kiln to 2500°F. or higher without producing a spalling brick. He seems to obtain a large proportion of the desired tridymite, which, unlike cristobalite, has no transition temperatures at which it undergoes such sudden change of volume as to crack the brick.

"The agent which is used to cause the transformation of amorphous silica of the natural earth into tridymite of this brick is usually 1 to 3 per cent of lime. As a binder, there is used 2 to 7 per cent of a refractory of clay-like composition, such as feldspar. A grog of calcined material, for example, 12 per cent, and a small amount of plastic clay may also be used, p. 185.

"The user of diatomaceous insulation is interested more in the thermal conductivity and the amount of heat that will be saved by the use of the insulation than in the methods of manufacturing it. He is interested, for example, in such results as those obtained from the insulation of 90-ton annealing furnaces in a large malleable iron works. The insulation of walls, arches, and doors with a 4-1/2-inch course of Nonpareil insulating brick decreased the fuel oil consumption, for each ton of product, to 40 gallons as compared to 60 gallons in the older type of uninsulated furnaces. On a total production of 60 tons a day, the fuel saving is 1,200 gallons a day. At 3 cents a gallon this saving amounts to more than $10,000 a year," p. 200.

"The solidifying of alcohol by diatomaceous earth is an interesting illustration of the high degree of porosity of the earth, the amount which may be absorbed being very large. Thus, 100 cc. of the wet paste can be made to contain 86.4 cc. alcohol without being so fluid as to allow leakage of the alcohol from the paste when the container is inverted, either while cold or while the alcohol is burning and the composition is, therefore, warm. To make such a solidified alcohol one mixes, for example, 30 grams of diatomaceous earth, of the quality known as Filter-Cel, with 86.4 cc. alcohol. Although the diatomaceous earth when dry, is very bulky, the actual net volume of the 30 grams of silica composing the skeletons is 30 divided by 2.2 (the approximate specific gravity of such silica) or only 13.6 cc.

"Alcohol thus absorbed in diatomaceous earth is being marketed in Germany, it is said, under the name 'Lithosprit.' In the United States, solidified alcohol or 'canned heat' is now preferably made by allowing a warm solution of soap in alcohol to set to a gel on cooling or by the precipitation of pyroxylin in a dilute alcoholic solution," p. 221.

"Silica *per se* is a poor catalyst as compared with the oxides of iron or aluminum or with many other oxides. Yet the very large extent of surface in diatomaceous earth, its condition of neutrality, insolubility, and inertness under most conditions, its low density, and slow rate of settling from solutions make diatomaceous earth an excellent supporting agent for catalysts," p. 235.

The photomicrographs are good. The reviewer was especially interested in Fig. 2 of diatoms from New Zealand. *Wilder D. Bancroft*

Tables annuelles de constants et données numériques de chimie. (*Annual Tables of Constants and Numerical Data, Chemical, Physical, Biological and Technological*). *Edited by Ch. Marie. Published by the International Committee appointed by the Seventh Congress of Applied Chemistry. Vol. VII, Parts 1* and *2, 1925-1926. 28 × 23 cm; pp. Part 1, xxxv + 946, Part 2, xv + 950. New York: McGraw-Hill Book Company, 1930. Price: $25.00.* The new volumes of tables give a very valuable survey of the numerical data discovered in the years 1925-26. As was the case for the earlier volumes, the tables are divided into more than fifty sections, each written by specialists who are well known in their respective fields. Two new sections have been introduced into Part 2 on Explosives and Explosions in Gaseous Mixtures and two old sections, those on Photography and Geophysics, have been omitted. The specialists in charge of the last two sections prefer that these subjects be dealt with once in every two volumes.

Since there is a large amount of explanatory description given with some of the tables, the various chapters partake somewhat of the nature of monographs. The descriptive matter makes the tables more valuable in that it will not be found so necessary to refer from them to the original literature. When this is necessary, as in the case of details of preparation of new compounds, the reader is aided by being given the number of the page on which the new substance is described.

One feature of the tables which increases their value to the searcher through the literature is the bibliography of papers whose contents cannot readily be expressed in tabular form. It is of interest to note to what extent the attention of the scientific world is being directed to the study of spectra. More than 450 pages are devoted to data on emission and absorption spectra, out of a total of 1896 pages. The chapters on dielectric constants and on X-ray analysis of crystals are also very largely augmented.

The Secretary of the International Committee, Dr. Marie, announces that Volume VIII for the years 1927-28 is already in the press and should appear very shortly. After the publication of this volume, it is proposed to commence a yearly publication of the annual tables. The International Committee is to be congratulated on the manner in which they have overtaken the arrears of publication. *W. E. Garner*

Jahrbuch des Forschungs-Instituts der Allgemeinen Elektrizitäts-Gesellschaft. *Vol. I, 1928-1929. 30 × 22 cm; pp. 240. Berlin: Julius Springer, 1930.* The scope of the research work of the laboratories of those great corporations whose interests depend on applications of pure scientific knowledge is year by year growing wider, and their outlook more philosophic. It *pays*, in every good sense of that much-abused word, to take the long view. And so we find engineering companies fostering research on surface-forces in liquids, and telephone research laboratories enlisting the aid of physicists, physiologists and psychologists. Now we welcome the first volume of the Yearbook of the A. E. G. The range covered by the papers is remarkable, and to attempt to consider it in any detail within the limits of a brief review is an impossible task. Briefly, the volume is made up of some thirty-five papers grouped together under seven headings—Akustik, Elektrotechnik, Elektronenphysik, Atomphysik, Atomchemie, Stoff-physik and Elektro-optik. Subjects so diverse as sound-films, contact potentials, the application of electron-waves to the analysis of crystal structure, the frequency curves of membranes, and the electrical conductivity of molten silicon—to name but one or two titles—are discussed both experimentally and mathematically, and the volume closes, appropriately enough with an essay under the heading "Sollen die technisch-physikalischen Forschungslaboratorien der Industrie rein wissenschaftliche Forschung betreiben?"

The volume is well-produced and bound, and the illustrations, whether line drawings or photographic reproductions, are excellent of their kind. *A. Ferguson*

Solvents. *By Thos. H. Durrans. 22 × 14 cm; pp. xv × 144. New York: D. Van Nostrand Company, 1930. Price: $5.00.* In the preface, p. vii, the author says: "Both the number of organic solvents which are available to industry and the extent to which they are used have increased greatly during the recent years, and there is in consequence a need for a scientific exposition of the technical application of solvents, more particularly in connection with the cellulose-lacquer industry....

"The first part of this book takes the form of a more or less connected series of chapters dealing with the fundamentals in a broad and simple manner. The second part is of a more utilitarian nature and deals comprehensively with individual solvents, mainly with the view of facilitating the intelligent use of these solvents in the cellulose-lacquer industry."

The chapters in the first part are entitled: introduction; solvent action; solvent power; plasticising solvents; solvent balance; viscosity; vapour pressure; imflammability; toxicity. In the second part of the chapters are: introduction; hydrocarbons; alcohols; ketones; esters; glycols; cyclohexane derivatives; chloro-compounds; furfurals; plasticising solvents.

It should be noted that the solutions which the author discusses are practically exclusively colloidal solutions. "It is well known that certain varieties of cellulose nitrate are soluble in a mixture of alcohol and ether, although not soluble in either liquid separately. Neither of these liquids contains any group, such as carbonyl, which usually imparts solvent properties, as, for instance, does acetone or amyl acetate," p. 1.

"If to a solution of cellulose nitrate a miscible non-solvent be gradually added, a dilution is ultimately reached, at which the cellulose nitrate begins to be thrown out of solution either as precipitate or as gel. The solution is said to 'tolerate' the addition of this definite proportion of the diluent under the conditions of temperature and cellulose-nitrate content obtaining. It is common to regard tolerances or dilution ratios as a measure of the solvent power of a solvent," p. 5.

"Plasticisers are solvents which are practically non-volatile; they may be liquids or solids, the latter being known as 'solid-solvents.' The term 'solid-solvent' arose from the use of the solid, camphor, which is a ketone and, like many other ketones, dissolves cellulose nitrate. If a solution of a cellulose ester be allowed to evaporate so as to leave a film, a certain but diminishing quantity of the solvent remains in the film according to the conditions obtaining. This small quantity of solvent imparts to the films a degree of softness or plasticity depending on the solvent and the quantity of it which is present," p. 9.

"The terms 'plasticiser' and 'softener' are not quite happy ones, for what is really desired is not a soft or plastic film but a stable, highly elastic, non-shrinking film with a hard non-scratchable surface. A soft film is one which is susceptible to deformation of its surface; a plastic one retains such deformation; an elastic film returns quickly to its original form," p. 10.

"Platicisiers have a pronounced effect on 'secondary flow,' a loose term applied to the very slow smoothing effect which takes place shortly before the film sets and no longer is capable of flowing. The gloss of a film is largely governed by this secondary flow and it is for this reason that high-boiling solvents tend to produce glossy films, the slow rate at which the solvent evaporates allowing time for microscopic irregularities of the surface to disappear," p. 11.

"For many years it was not possible to make satisfactory factory lacquers with the cellulose nitrates then available, since those nitrates gave solutions of excessively high viscosity when prepared in a state sufficiently concentrated to ensure films of the desired thickness and strength. Many, more or less successful, attempts were made to reduce this viscosity by employing various solvents, but this generally resulted in introducing other undesirable characteristics. It was not until the introduction of the low-viscosity cellulose nitrates, such as the well-known 'half-second cotton,' took place, that the widespread use of such lacquers became possible; even now it is common practice to 'load' the lacquer with resins for the purpose, among others, of giving 'body' to a film without of necessity producing unduly viscous solutions.

"The viscosity of a lacquer may be adjusted in several ways; thus mixtures of different cellulose nitrates may be employed, these being available in grades giving a wide range of viscosity, or the viscosity may be varied by suitable choice of solvent or solvent mixture. Viscosity and vapour pressure are apparently to a considerable extent concomitant properties, the greater the vapour pressure of a solvent the lower the viscosity of its solutions," p. 18.

"The lowering of temperature of a solvent evaporating in free air causes the air in its immediate neighbourhood to fall in temperature, and if the humidity of this air be sufficiently great a temperature below that of the dew-point may be reached and water will be deposited. If the solvent contain a substance insoluble in water, for instance, cellulose nitrate or resin, this deposition of water may cause their precipitation with the consequent formation of a white opaque film on the surface of the solution; this effect is known as 'chilling.' If the solvent is one able to dissolve water to a considerable extent, such as ethyl lactate, diacetone alcohol or ethyl alcohol, this chilling effect may be delayed, since the water may be dispersed in a greater depth of the solution. If, on the other hand, water is completely insoluble in the solvent no chilling can occur, since the water will merely deposit on the surface and not penetrate at all," p. 30.

"It is safe to say that the vapours of all volatile substances are toxic or at least narcotic, if they be inhaled in a sufficiently concentrated state for a sufficient length of time. With some the effect is merely that of suffocation caused by the deprivation of oxygen, others cause anesthesia, whilst a third class includes those definitely poisonous by reason of some physiological action, causing functional derangement of the metabolism. The three classes are not closely defined but merge one into the other and vary with the individual. The majority of lacquer solvents belong to the earlier classes, the term 'solvents' being taken to include the diluents. . . .

"The poisonous effects of most solvents is not cumulative, and their vapours can be inhaled without any apparent effect, provided that they are present in a sufficiently diluted state; prolonged inhalation of such dilute vapours has been known to give immunity to the poisoning by concentrations normally lethal. It has been found, for instance, that workmen constantly employed in the manufacture of ether cannot be anaesthetised in the normal manner by this substance. It should, however, be realised that the continual inhalation of quite small quantities of solvent vapours cannot but have a deleterious effect on the general health, although the effect may not be sufficiently pronounced to be apparent; generally speaking the risk is not greater than that obtaining in other industries, but the importance of adequate ventilation is to be emphasised.

"With some solvents, however, the effect is cumulative, notably with methyl alcohol, tetrachloroethane, tetrachloroethylene and carbon disulphide, although some persons are insensitive to the action of the last-named. Prolonged exposure to benzene vapour has also been found to be highly dangerous, especially to persons of advanced age. Turpentine vapour is poisonous to some, and it would appear that the poisonous action of lead-pigmented paints may have been wrongly ascribed in some instances to the lead pigment; 4 to 6 mg. of turpentine per litre of air can produce symptoms of poisoning; 16 mg. per litre killed a cat within one hour.

"Of the various classes of solvents employed, the chloro-compounds are undoubtedly the most poisonous, and they are potent anaesthetics. Carbon tetrachloride and tetrachloroethylene are definitely poisonous, causing enlargement of the liver. This disease, when produced by the action of the latter solvent, is notifiable in England. In Germany, the use of tetrachloroethylene is forbidden. Tetrachloroethane is also said to be highly poisonous, but trichloroethylene is relatively harmless, whilst di-chloroethylene causes dermatitis," p. 40.

"In many cases it is not desirable or expedient that a chemically-pure substance should be used for lacquers. In some instances the presence of 'impurities' considerably enhances the desirable properties of a solvent. On the other hand, the cost of removing certain impurities is out of proportion to the advantages to be gained," p. 45.

The second part contains chiefly data concerning the different substances used as solvents, plasticisers, etc.

Wilder D. Bancroft

Application of Interferometry. *By W. Ewart Williams. 19 × 13 cm; pp. iv. + 104. London: Methuen and Co., Ltd., 1930. Price: 2 shillings, 6 pence.* This small monograph, written for advanced students, contains a clear and correct presentation of the fundamental principles of interferometry. The different methods of obtaining interference effects are divided into such in which the interfering beams start out from a primary line or point light-source or from a similar secondary source, such as a narrow slit ("division of wave-front") and such in which a broad beam is divided by a partially reflecting surface and later is re-united ("division of amplitude").

For the physical chemist, instruments in the former category are particularly important (the Rayleigh interferometer and the designs worked out by Haber and Löwe are of this type). The methods for size measurement of microscopic and ultramicroscopic objects, worked out by Gehrcke, O. v. Baeyer and Gerhardt, employ the same principle, and are analogous to the method developed by Michelson for the determination of the angular diameter of the stars.

The Jamin and Mach instruments, belonging to the second category are also of interest to the physical chemist, applicable as they are to the investigation of reaction rates in gaseous systems.

Finally, the various interferometers for the examination of the fine structure of spectral lines (Fabry-Perot; Lummer-Gehrcke) are of importance to the modern spectroscopist.

The manifold possibilities offered by interferometry for purely physical measurements of length and of thickness, form the main theme of the present small volume, and it should be a real stimulus for physical chemists to see set out so clearly the close relations which exist between their own interferometric experiments and the most precise measurements of modern physics.

Fritz Weigert

German for Chemists. *By Louis de Vries. 23 × 16 cm; pp. vi + 178. Easton: The Chemical Publishing Co., 1929. Price: $3.00.* In the preface the author says: "This text contains material taken from the works of well-known Chemists, such as Emil Fischer, Wilhelm Ostwald and others. The different chapters embrace many phases of chemistry. including Organic, Inorganic, Analytical, Biophysical, Physiological and Nutritional, Soil, Plant, and Enzyme Chemistry. The reader, prepared for the use of students who wish to acquire a reading knowledge of German, gives in addition to practice in reading the language, an introduction to German chemical literature."

The selections are well made and the reviewer confesses both to pleasure and profit from reading the book. In the vocabulary verbs with separable prefixes have a hyphen between verb and prefix. That simple little detail will make life a good deal easier for the student.

There are several misprints which should be corrected in future editions: Vergroszerung, p. v; kapilla, p. 17; Gesets, p. 25; Kekule, p. 43 and elsewhere; versichieden, Wurtz, p. 45; umstandilch, p. 66; Herterozyklus, p. 76; nebeneiander, p. 77; Zukkerarten, p. 103; geblidet, p. 104. These are obvious misprints but they might bother the beginner. The author has Inhalt in the vocabulary and Jnhalt in the text, p. 8. The reviewer thinks that Deutsche chemische Gesellschaft, p. v, should not be written with three capitals.

Wilder D. Bancroft

THE HEAT CAPACITY AND FREE ENERGY OF FORMATION OF ETHANE GAS*

BY VICTOR R. THAYER WITH GEBHARD STEGEMAN

A number of thermodynamic calculations have been made by Francis[1] and Smith[2] from which the optimum conditions for certain reactions may be predicted. Both writers admit that some of their results are reduced to the status of estimates, due to inadequate and uncertain specific heat data. This investigation involves the redetermination of the specific heat of ethane gas for reasons which are indicated.

Dixon, Campbell, and Parker[3] measured the velocity of sound in various gases, including ethane, and used the data to evaluate the respective specific heats. Their results for ethane, recalculated by Partington and Shilling[4] are as follows:

Temperature	Cp.
10°C.	11.015
50°C.	11.610
100°C.	12.637

The following direct measurements of Cp for ethane are reported by Scheel and Heuse:[5]

Temperature	Cp.
−82°C.	10.43
−35°C.	11.04
+15°C.	12.40

The divergence between the two sets of data is apparent in Fig. 1. The value of Cp at 15°C., obtained by interpolation of Dixon, Campbell, and Parker's results, is 11.09. The difference between this and the value of 12.40 obtained by Scheel and Heuse, amounts to approximately 11 percent.

Although the results of Dixon and his co-workers at high temperatures have been criticized[6] because his assumptions regarding the effect of the inclosing tube on the velocity of sound are now believed to be incorrect, his

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* Contribution No. 203 from the Department of Chemistry, University of Pittsburgh.

[1] A. W. Francis: Ind. Eng. Chem., 20, 277 (1928).

[2] D. F. Smith: Ind. Eng. Chem., 19, 801 (1927).

[3] Dixon, Campbell and Parker: Proc. Roy. Soc., 100A, 1 (1921).

[4] Partington and Shilling: "Specific Heats of Gases," (1924).

[5] K. Scheel, and W. Heuse: Ann. Physik, (4) 37, 79 (1912); 40, 473 (1913).

[6] Eastman: J. Am. Chem. Soc., 50, 727 (1928).

data[7] at room temperature, except in the case of ethane, are in fairly close agreement with those of Scheel and Heuse. The values in the following table indicate this:

Gas	Cp Dixon	Cp Scheel and Heuse	Temp.
C_2H_4	10.33	10.22	18°C.
CO_2	8.84	8.88	20°C.
N_2	6.92	6.98	20°C.

The 11 percent variation in the case of ethane can therefore hardly be attributed to an error of method.

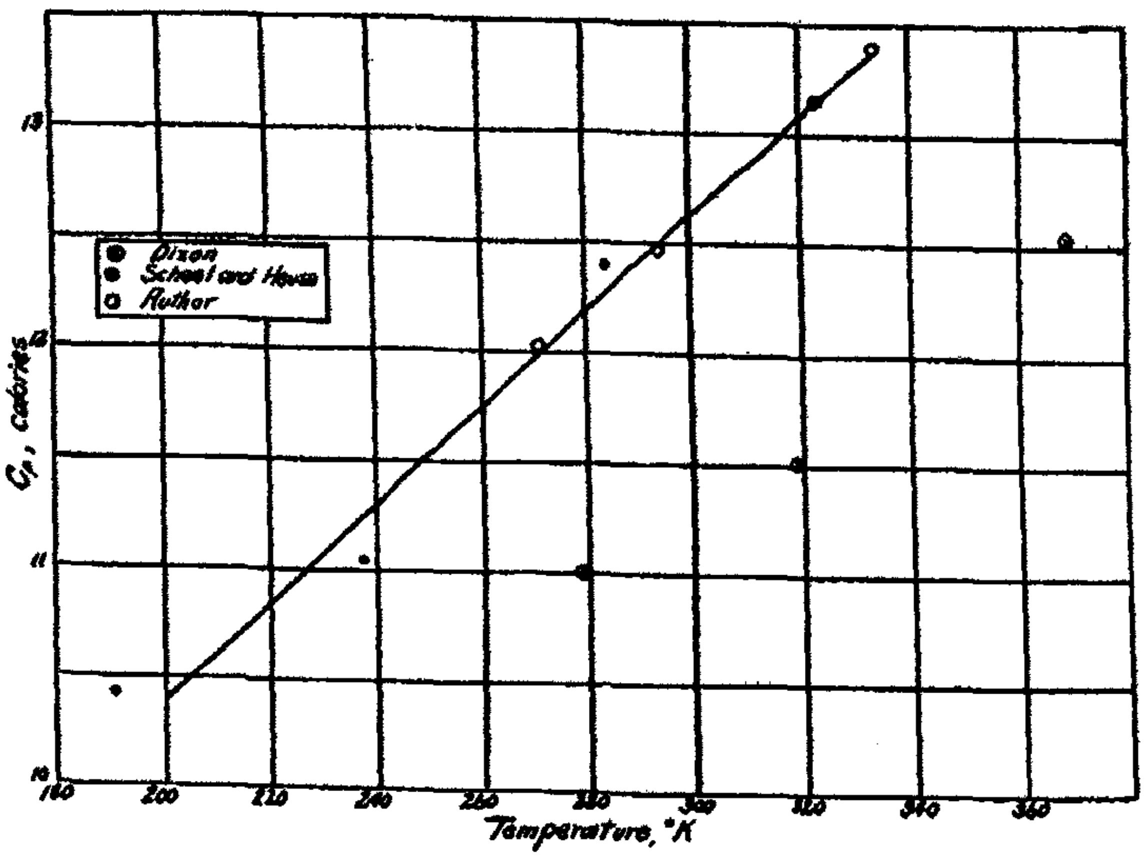

FIG. 1

Preparation of Ethane. Ethane was prepared by the method of Murray[8] modified by suggestions of Loomis and Walters.[9] Briefly, the procedure was as follows: electrolysis of a 60 percent solution of potassium acetate with platinum electrodes, removal of CO from the anode gases by pipettes of the Orsat type, passage of the gas in turn through fuming sulfuric acid, 98 percent sulfuric acid, potassium hydroxide, and phosphorous pentoxide; condensation to a solid; and fractional distillation. Two samples, the second of which received two additional distillations, showed identical specific heats within the limits of experimental error.

Calorimeter. The design of the constant flow calorimeter follows that of Scheel and Heuse.[10] Its detail is shown in Fig. 2 with the path of the gas

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[7] Partington and Shilling: op. cit., 190-199.

[8] Murray: J. Chem. Soc., 61, 10 (1892).

[9] Loomis and Walters: J. Am. Chem. Soc., 48, 1052 (1926).

[10] K. Scheel, and W. Heuse: Ann. Physik, (4) 37, 79 (1912).

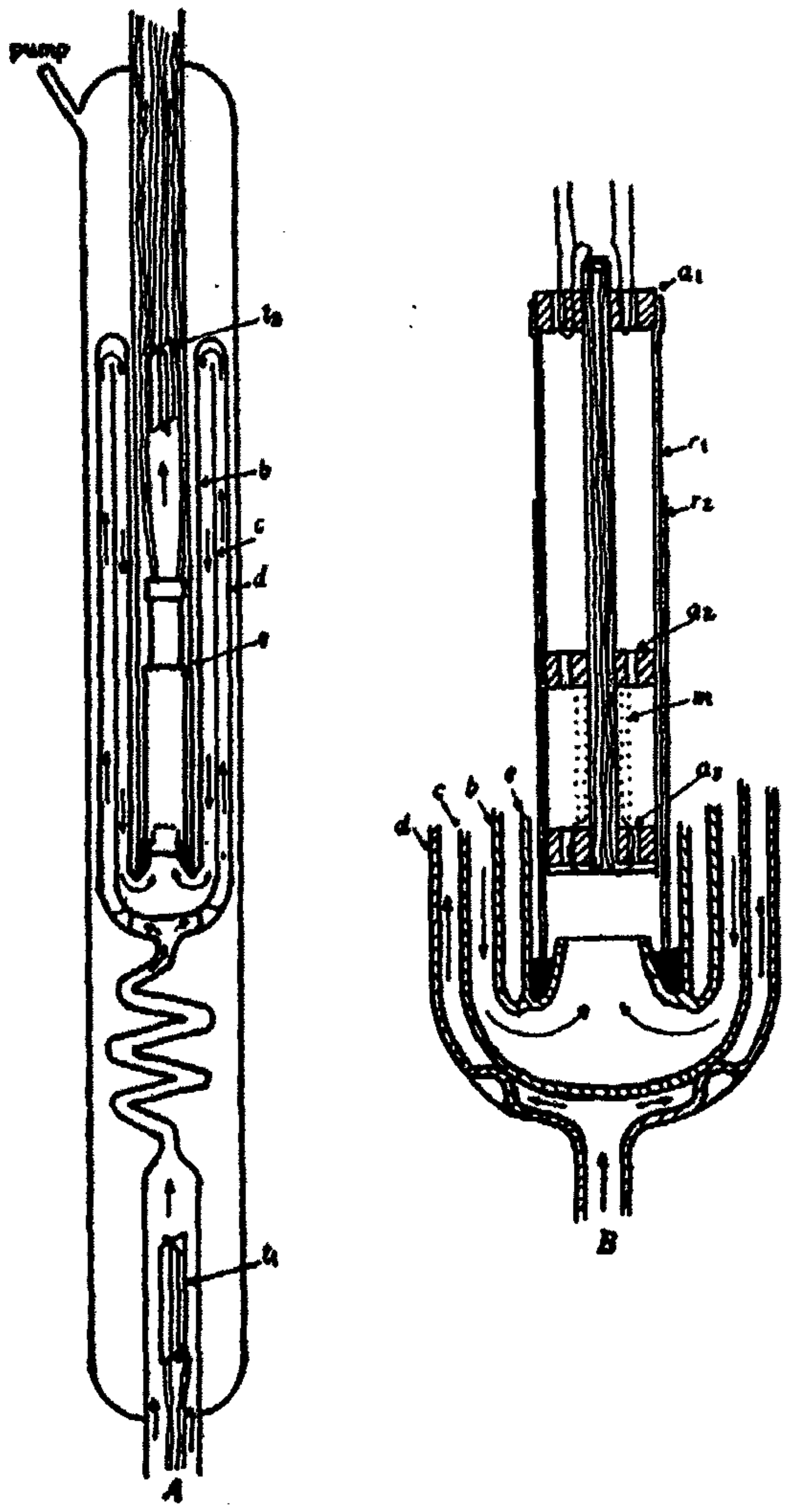

Fig. 2

stream indicated. The relation among the observed specific heat, the true specific heat, and the radiation loss is given by the following equation:

$$C_p = \frac{E}{M\Delta T}\left[1 - \frac{K}{M^2}\right]$$

where

C_p = true specific heat in Watt-seconds per gram,
E = energy input in Watts,
M = grams of gas flowing per second,
ΔT = temperature rise in the gas stream
K = heat loss constant for the calorimeter.

This equation may be considered a straight line in which $E/M\Delta T$ and $E/M^3\Delta T$ are variables, and Cp and K are constants. The constants are evaluated by making a number of observations with different values of M, adjusting E each time so as to keep T approximately constant, and obtaining the equation of the straight line by the method of least squares. The value of K so obtained may then be used to reduce individual observations. The constant for the calorimeter was found to have the same magnitude (0.000046) with either air or ethane.

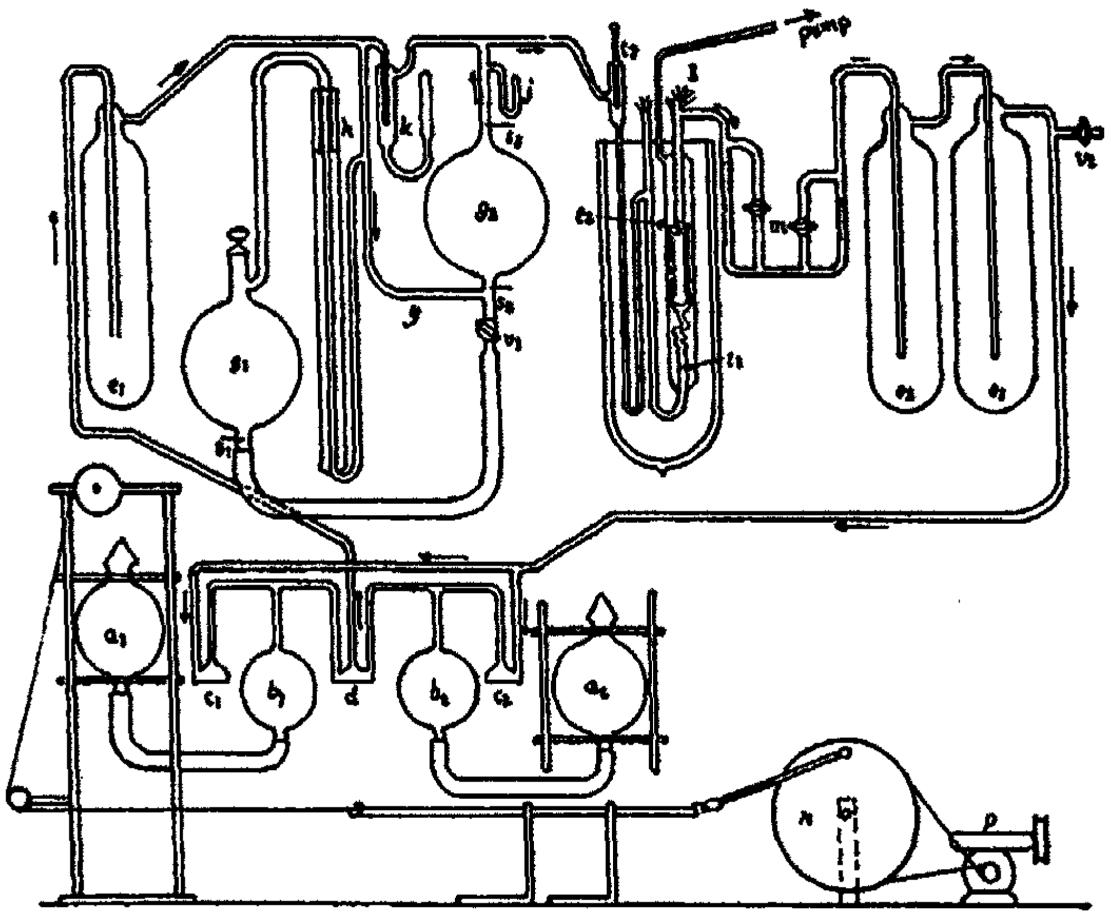

FIG. 3

Platinum resistance thermometers, constructed and calibrated according to specifications of the Bureau of Standards[11] are designated t_1 and t_2 in the detailed drawing of the calorimeter (Fig. 2).

The heating element, shown in detail in Diagram B, Fig. 2, consisted of about 150 centimeters of No. 36 double silk insulated manganin wire wound on a small bore glass tube. A roll of copper gauze was slipped over the coil and inside the brass tube r_1, the whole being held in place by perforated disks a_2 and a_3 of hard rubber. Tube r_1 above disk a_2 was packed with copper gauze and was closed at the top by disk a_1.

The gas circulating system is shown in Fig. 3. The arrangement consists of four units; the circulating pump $a_1a_2b_1b_2c_1c_2d$; the calorimeter 1; the flow meter g_1g_2hkj; flow adjusting devices which are large bulbs $e_1e_2e_3$, used to smooth the flow; and the by-pass capillaries, m, used to vary the resistance.

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[11] H. C. Dickinson, and E. F. Mueller: Bureau of Standards Sci. Paper No. 200.

The direction of flow is indicated. Continuous reciprocation of the bulbs a_1 and a_2 operates the pump.

The flow meter was operated without interrupting the constant passage of the gas stream as follows:

The gas was circulated to the calorimeter by way of the bulb g_2. When it was desired to measure the rate of flow, the valve V_1 was opened, and the bulb g_1 which was full of mercury raised at such a rate that the pressure in the bulb g_2 which was indicated on the manometer j, remained at the usual level. The flow of mercury from g_1 to g_2 blocked the normal path of the gas, which was then diverted to the space being vacated in g_1 by way of the movable seal h.

Timing the flow of mercury between the wires S_1 and S_2 measured the number of seconds normally required for the gas volume contained between the wires, to flow through the calorimeter. The pressure of the gas was measured on the manometer j, and its temperature by the thermometer t_3. Its density and in turn the mass of the gas flowing per second could thus be calculated. When the bulb g_1 was lowered, so that it refilled with mercury, the gas contained in it and also that approaching from the pump was forced out across the by-pass k, a part entering g_2 and the rest proceeding at nearly normal rate to the calorimeter.

As bulb g_1 was emptying of gas, the total resistance to flow in the system was increased slightly, due to the introduction of the by-pass k. The rate of flow was therefore slightly lowered, and the temperature of the gas stream above the heater slightly raised. It was therefore necessary to take a final reading of the temperature increase in the gas stream before flow measurements were begun, or to allow 30 minutes after the latter measurements were completed for equilibrium to be reestablished in the calorimeter.

All the required potential measurements were made with the use of a White Double Potentiometer.

As a test of the reliability of the apparatus and the method, the specific heat of dry carbon dioxide free air was determined at room temperature.

Four of the more recent investigations of the heat capacity of air are listed.

Scheel and Heuse[12]	continuous flow	6.965
Gruneisen and Merkle[13]	velocity of sound	6.936
Hebb[14]	velocity of sound	6.952
Shields[15]	adiabatic expansion	6.947

The value obtained in this investigation as a result of thirteen determinations, at varying rates was 6.495 cals. per mol. Three typical determinations of the thirteen are listed in Table I below.

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[12] Scheel and Heuse: Ann. Physik, (4) **37**, 79 (1912).

[13] Gruneisen and Merkle: Ann. Physik, (4) **72**, 193 (1923).

[14] Hebb: Trans. Roy. Soc. Canada, **13**, (3), 101 (1919).

[15] Shields: Phys. Rev., (2) **10**, 525 (1927).

TABLE I

Temp. °C.	M g/sec.	E Watts	ΔT °C.	$\frac{E}{M\Delta T}$	Specific Heat in Watt Seconds per gram
22.40	.02041	0.1009	4.351	1.136	1.011
22.40	.01956	0.0992	4.460	1.138	1.001
22.40	.02668	0.1249	4.324	1.082	1.012

$K = 0.000046$

The condensed results for ethane are listed in Table II.

TABLE II

Temp. °C.	Specific Heat in Watt Seconds per Gram	Specific Heat in Cals. per Mol
2.20	1.675	12.03
24.50	1.736	12.47
54.50	1.833	13.17
64.40	1.865	13.40

Free Energy of Ethane. The free energy of formation of ethane was calculated by the usual formula:

$$\Delta F = \Delta H_0 - \Delta\Gamma_0 T \ln T - 1/2\, \Delta\Gamma_1 T^2 - \ldots\ldots\ldots\ldots + IT$$

The coefficients of T are defined by the following equations:

$$\text{Heat of Reaction} = \Delta H = \Delta H_0 + \Delta\Gamma_0 T + 1/2\, \Delta\Gamma_1 T^2 + \ldots\ldots \text{etc.}$$

$$\Delta Cp = \Delta\Gamma_0 + \Delta\Gamma_1 T + \ldots\ldots\ldots\ldots\ldots \text{etc.}$$

$$Cp = \Gamma_0 + \Gamma_1 T \quad + \ldots\ldots\ldots\ldots\ldots \text{etc.}$$

ΔCp is obtained by summing the equations for the heat capacities of the substances involved, considering reactants positive and resultants negative.

According to the data of this investigation, the heat capacity of ethane is represented by the equation:

$$Cp = 5.981 + 0.2193\, T.$$

Francis[1] gives the following values for carbon and hydrogen:

Carbon: $Cp = 1.1 + 0.004\, T,$

Hydrogen: $Cp = 6.65 + 0.0007\, T.$

Also, Francis gives $\Delta H_{298} = -23{,}075.$

Accordingly:

$$\Delta Cp = -16.17 + .012\, T$$

$$\Delta H = \Delta H_0 - 16.17\, T + .006\, T^2$$

$$-23{,}075 = \Delta H_0 - 16.17\,(298) + .006\,(298)^2$$

$$\Delta H_0 = 18{,}789.$$

For ethane, therefore:

$$\Delta F = 18{,}789 + 16.17\ T\ln T - .006T^2 + IT.$$

Smith[2] estimates by the third law of thermodynamics applied to fugacity data that $\Delta F_{298} = -10{,}700$. Using this figure to evaluate I, the equation for the free energy then becomes:

$$\Delta F = -18{,}789 + 16{,}17\ T\ln T - .006T^2 - 63.9T.$$

Francis who used the data of Dixon, Campbell, and Parker (See Fig. 3), gives the following equation for the free energy of ethane:

$$\Delta F = -18{,}789 + 15.18\ T\ln T - .004T^2 - 62.8T$$

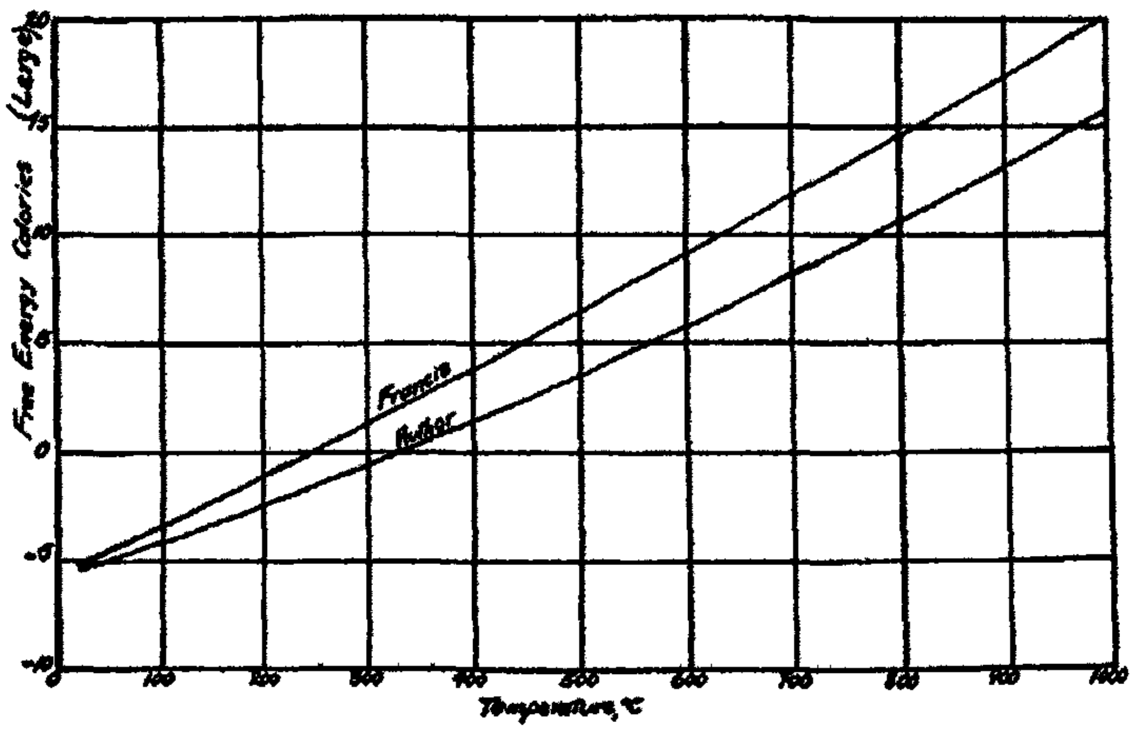

FIG. 4

The latter two equations are represented graphically in Fig. 4.

The precision attained in the measurment of the values reported by the writers was such that the results are believed to be accurate within one percent.

The writers wish to acknowledge the criticism and aid given by Dr. A. G. Loomis and Dr. R. Wiebe of the United States Bureau of Mines, and to express their appreciation to Mr. G. St. J. Perrot, the Director of the Bureau, for the use of facilities which made this investigation possible.

Summary

The heat capacity of ethane gas has been measured at various temperatures and the values obtained, together with those of other investigators are shown graphically in Fig. 1.

The free energy of ethane gas has been recalculated using the specific heat data obtained in this investigation in place of the results of Dixon, Campbell, and Parker, which have been used in previous calculations reported in the literature. The values for the free energy together with those calculated by Francis appear in Fig. 4.

FURTHER STUDIES IN PERIODIC PRECIPITATION

BY FRANCIS E. LLOYD AND VLADIMIR MORAVEK

During our studies leading to the publication of a previous paper (1928) the authors were impressed by the wide variety of behavior and the static forms of precipitate resulting from interaction of reagents in fluids and gels to such an extent that it was determined to make as extensive a survey as possible of all systems in which periodic precipitation might occur. We believe it necessary before a comprehensive generalization can be formulated to make a broad survey and to acquaint ourselves with all possible behaviors and their results; and as such results cannot be adequately described verbally, we adopted the method of record by careful photography and cinematography. Indeed the complexity of the subject is so great that nothing short of visual experience can make the variations of behavior comprehensible and especially since many authors have not made adequate records of their experiments—few of the photographs published show clearly what they are intended to show and are often very poor and unconvincing—and because most if not all papers hitherto published advance theories based on one or a few experiments with a single system only. Their authors have frequently lacked perspective to be gained only by a wide survey.

I. The Effect of Spatial Relations.

We have found that many experiments done, as is usually the case with test tubes show no periodicity for hours or days, or even not at all, whereas the same experiments done in capillary tubes show periodicity within the first few minutes of experimentation. This is in many cases due to the enhanced if also microscopic visibility due to the smallness of the masses of precipitate. Nevertheless, we have already found other effects due to the small extent of the space in which the reactions proceeded (1928) and we therefore tried to determine more exactly to what such effect might be ascribed.

Two such effects have been noticed, viz. (1) that on the rate of diffusion and (2) that resulting from adsorption on the walls, when adsorption occurs.

a. In the system NH_4OH diffusing into $MgCl_2$-gelatin we found that in the lowest concentrations no periodicity could be observed in test tubes, while in capillary tubes, well-marked, widely separated, periodic massive bands occurred. (Figs.[1] 1, 3). This is due to the slowing up of diffusion rate in the capillary tubes, which measured .5 to 1 mm. in diameter. Under these conditions the OH-ions being negatively adsorbed by the glass wall move forward in the middle of the column and the Mg-ions move radially to meet the OH-ions. The precipitate therefore takes that form of a spindle, more especially the smaller the tube and therefore the greater the curvature. In

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[1] All "figs." refer to figures in the plates. Text figures are so designated.

the inverse system $MgCl_2$ diffusing into NH_4OH—gelatin (Figs. 2, 4), marked irregularities also occur in both test tubes and capillary tubes, but here because the Mg-ions are positively adsorbed the bands usually fill the lumen, but are of irregular form, the negative adsorbability of OH playing a minor rôle, and, in the test tubes especially, the questionably periodic masses of precipitate are very irregular, due to local impermeability of the initial precipitate plug, and are attached strongly to the glass wall, being adsorbed thereto. In this system also the differences as between test tubes and capillary tubes are very marked; in the former usually no periodicity is observable, while in the latter it is well marked. When we repeated the above experiment, we obtained in one concentration, curiously enough, a very regular distinct band. (Fig 2a, Plate IX). This does not invalidate the general truth of our conclusions. (Figs. 1-4).

b. Also in the system 20% NH_4OH into 2N $CoCl_2$ in 10% Difco gelatin in tubes 1, 3, 10 and 50 mm. in diameter, we found that in the narrower tubes the white precipitate was more extensive and colored bands wider and the whole diffusion column shorter than in the widest tube. In the latter there was little or no white precipitate, while in the capillary tubes the spaces between the bands were filled with it and a broad band of white precipitate was produced in advance of the last blue colored band. The tubes of intermediate diameters showed intergradations of behavior. (Fig. 8).

c. Effect of convection currents. In large tubes, because of convection currents and gravitational effects, it is impossible to obtain evidence of periodicity in fluid media. When, however, we enclosed $Pb(NO_3)_2$ diffusing into KI (or the inverse) in a very narrow space between a slide and cover glass, well marked bands of crystalline PbI_2 were obtained. (Fig. 7). The same result was obtained in .5N $Pb(NO_3)_2$ into .5N NaCl. (Fig. 110).

d. In the system .2N $Pb(NO_3)_2$ diffusing into .1N-.0125N $K_2Cr_2O_7$ in gelatin in capillary tubes 3 mm. wide it was not possible to observe periodicity except in microscopic sections. In a very thin layer of gelatin formed by the pressure of a large bubble beautiful bands were developed. In this instance the resulting forms afforded a charming spectacle (Fig. 9).

e. The trichomes of plants afford minute capillary spaces of tubular form and in such we have obtained clear and visible periodicity with the system NH_4HS into $Na_3Co(NO_2)_6$. Moreover, the precipitate occurs within the cellulose wall itself, not in the lumen except toward the end of the trichome. This can be due to the washing out of the free reagent, since the preparations were repeatedly treated with cold distilled water before adding NH_4HS (Lloyd, 1925) (Figs. 5, 6, 10). In tubes of much greater calibre periodicity occurs or at least becomes visible only after a relatively long time. (Lloyd and Moravek, 1928).

f. To be mentioned here is the example set forth by us in 1928, that in the same system as in (e) above only *rings* of precipitate are to be obtained in minute capillary tubes, whereas in larger tubes rings and discs or saturn structure are formed.

From the foregoing it will be seen that clean-cut periodicity may be procured in large spaces, but obscurely or not at all in small ones and, vice versa, periodicity may occur in small spaces and not at all in large ones. Such behaviors are indeed secondary in nature demanding special explanation, for it is clear that in many systems the tendency to periodicity is always and indubitably present but may be obscured by the special conditions present. The importance of this from a biological point of view can hardly be overestimated since many interactions must occur in restricted spaces, often of irregular shape.

The now familiar case of the "Fromman striations" on the treatment of medullated nerve fibers with silver nitrate "is the result of the operation of physical processes which in capillary spaces produce the Boehm (or Liesegang) phenomenon." (A.B. Macallum, 1906).

II. Nature of the Medium.

It has often been thought that the nature of the medium determines in a primary sense the incidence of periodicity. This, however, is not true, as many experiments in the literature, as well as our own, prove. As Doyle and Ryan correctly observe, an explanation of the phenomenon which attributes a fundamental rôle to a gel as a medium cannot be correct. We may regard this aspect of the case as a closed issue.

We cannot therefore agree with Bradford that "the nature of the gel is of fundamental importance," but rather take the position that the effect of the gel in each case must be explained and that also the rôle of the gel is a purely secondary matter. Concerning the theory of Dhar (1922) and his associates, we have to say that it assumes the presence of a gel or other *peptizing substance.* The secondary influence of the gel medium has been discussed and demonstrated experimentally very successfully by Wo. Ostwald (1926) *contra* Chatterji, Dhar and Dogadkin.

We think that McGuigan and Brough (1923/4) are mistaken when they declare that "no new chemical process is involved in the formation of rings," and when further they attach a dominant value to the dampering effect of the medium. Dampering effect there is, but it plays a secondary rôle, and it would be difficult according to their views to explain why a periodical system should occur in water and not in gelatin. See also Rouppert, whose paper contains pertinent citations (1926). Rouppert cites the important fact that periodicity can be obtained with gases only if water vapor be present, as observed by Chapin and Holmes (1918), E. Karrer (1921) and Fischer and McLaughlin (1922).

We have made use of gaseous, fluid, gelatinous and solid media. The most obvious and indeed the most important practical character of gaseous and fluid media is their instability and the consequent instability of the whole system. On the other hand, a gel supplies a framework which can stabilize the system and thus prevent mass movements which obscure or obliterate the results. This can be regarded as obvious, but it cannot be stated as a corollary that the higher the viscosity of the medium the more certain periodicity is to occur. Our experiment shown in Fig. 35 illustrates this point and will be referred to beyond under concentration of gels. Periodicity depends rather upon the amount of material (which can be expressed as dry weight) present and not at all on the viscosity of the medium.

This conclusion makes it possible to understand more clearly the comparative behavior of a particular reaction system in different gels. We have worked with gelatin, agar and starch. It is well known that agar preserves its inhomogeneity and substantial character in spite of heating at boiling temperatures, and starch still more so. We may now consider the effect of the various media used, viz. gaseous, fluid, solid and gel.

Gas:—R. B. Peet (1925) in Young's laboratory experimented with HCl and NH_3. He experienced much difficulty which we avoided by the use of capillary tubes in which the air respectively gas column is relatively stable. Without much difficulty we obtained rhythmic precipitation which settled on the glass wall. It has been observed that such periodicity demands the presence of water vapor for its realization (Rouppert, 1926) and we regard this fact important from our point of view. Since the salt formed is readily soluble and since the water vapor present puts the salt into solution soon after formation, the periodicity is quickly lost. We, however, observed its occurrence under the microscope, and were able to preserve the deposit sometimes by quickly drawing oil up into the tube. (Fig. 11).

When this system is inverted (NH_3 into HCl) the formation of periodic rings on the surface of the tube was easily observable microscopically. These were, however, quickly obliterated by extension of crystallization, so that the evidence of periodicity was quickly lost. (Fig. 12).

Any theory which attempts to account for periodic precipitation and fails to explain the above systems is inadequate. In order to do so in accordance with our views we must assume the presence of water vapor which, as we have seen, must be present if periodicity is to occur. The water vapor present, we believe, makes a temporary compound which can react with the penetrating gas. In forming the initial precipitate (the plug) water will be set free, which is now available for further reaction. Since the internal gas is highly soluble in water, the water set free moves toward the higher concentration of gas, i.e. further into the tube until a concentrated solution is formed at some distance away from the first formed crystals. The concentrated layer must now diffuse backwards to some point where it will react with the indiffusing external reagent, and a second ring will then be formed.

Fluid (Water):—It is practically less difficult, if still not easy, to obtain periodic precipitation in a fluid medium. The difficulty is overcome by employing capillary spaces. We repeated Hedges' experiments of allowing concentrated HCl to diffuse in 30% NaCl in capillary tubes. Single crystals were formed periodically and these were large enough to block, but incompletely, the mouth of the tube. Here at the moment of crystallization water is set free and it must diffuse in both directions, diluting the reagents. The space of too low concentration of the interacting reagent for crystallization must be crossed before another position of high concentration is reached by the entering reagent (Fig. 13a-c).

In the immediately foregoing experiments we do not have to consider any reaction product. Such cases are examples of periodic crystallization, the factors which prevent continuous crystallization being water and changes in temperature due to release or uptake of heat of crystallization, complicated by the formation of various crystalline modifications. In those experiments which follow a reaction product does have to be considered.

In the systems $Pb(NO_3)_2$ diffusing into KI and into NaCl in water in capillary spaces we obtained similar results, the former yielding periodic bands of crystals (Fig. 7), the latter of droplets of metastable compound which later became transformed into crystals. Notboom (1923) used this method and obtained the same results.

A most striking result was obtained with Na_2CO_3 diffusing into $AgNO_3$ in water in capillary tubes. At first the mouth of the tube was blocked by precipitate. Thereafter marked rings of metastable product attached to the glass wall appeared. In the course of three days the reaction was completed throughout the tube and we found then that, although the insoluble precipitate occurred scattered everywhere, there was a periodic accumulation of crystals in irregular bands throughout the length of the tubes (Fig. 14a-c).

In the system 1N $BaCl_2$ diffusing into 1N H_2SO_4 in capillary tubes 0.5 millimeters in diameter, rings of large crystals are formed with fewer small crystals in the interspaces. Doyle and Ryan observe that barium sulphate and silver chloride can be obtained as periodic precipitates only "with great difficulty," being very slightly soluble. Nevertheless, we have been able to do so in water. W. M. Fischer (1925) used water with a little gelatin and erythrosine admixed, and thought these to be necessary. (Figs. 16, 17, 15). Morse and Pierce (1903) got bands of silver chromate in capillary tubes in water, allowing silver nitrate to diffuse into potassium chromate.

Gels (*Gelatin, Agar and Starch*):—In the system .2N $Pb(NO_3)_2$ diffusing into .1N KI in starch and the same in agar in capillary tubes we obtained very clear cut periodicity of a yellow salt (PbI_2), but no such periodicity was obtained when gelatin was used. In the starch (Fig. 22) there was a strong tendency toward irregularity, spirals and other abnormalities appearing, or even a discontinuous band of granules representing the continuous bands elsewhere. Also here, since the salt was strongly absorbed on the glass wall the ring-and-disc structure was pronounced. In the course of time the yellow salt, which has here a metallic lustre, is dissolved or is hydrolyzed, or otherwise changed, and a product is set free—probably I_2—which produced a purple coloration in the starch medium, the color being deepest where the yellow salt had occurred.

When potato-starch is used instead of the much finer grained corn-starch, no continuous bands are formed. In their place we find a periodicity in the form of discontinuous zones of crystals. These appear even at the very beginning of diffusion. It is also interesting to note that the release of I_2 is much more rapid, so that the yellow salt quickly disappears and the starch becomes colored.

In agar beautifully regular and clean cut ring-and-disc bands or spirals occurred in harmonic periodic array, which were dissolved in the entering reagent as the higher concentrations advanced into the tubes. (Figs. 18, 19).

Hatschek (1921) and doubtless others (Dogadkin) observed the formation of spirals following the addition of acetic acid to the entering reagent. We have, however, repeatedly found that spiral structures are likely to occur in at least one in a dozen tubes under the same circumstances, and we have particularly observed that a small bubble attached to the surface of the medium, locally preventing diffusion at a small point, will induce the irregularity of the first precipitation membrane or surface of the precipitation which will by repetition give rise to a spiral (Figs. 19, 22).

In gelatin at first a yellow, continuous column was formed (Fig. 21). This disappeared as the concentration of the entering reagent increased and the presence of a vitreous, probably organic, precipitate of a colorless salt in the form of globuloids was apparent. As the precipitation advanced, rings appeared independently in the yellow precipitate, which became more and more visible as the yellow precipitate disappeared. These were insoluble in the entering reagent and were composed of an apparently vitreous mass with a cloudy milky-white interior (Fig. 21a). We must here point out that the medium cannot be a simple mechanical framework in these and possibly other cases and we have always to consider the possibility of the gelatin, at least, entering into the reaction in some way both here and in regard to other systems in gelatin. Indeed recent work done by one of us strongly supports this idea, but the limitations of this account prevents us from exposing our further evidence here.

The system $AgNO_3$ diffusing into $K_2Cr_2O_7$ with gelatin, with agar and with starch. (Figs. 20, 25, 26). In these cases there is no evidence that there is other than mechanical action of the medium. Periodicity occurs in all three, but more clearly cut and regular in gelatin and least so in agar. In starch there appears to be no evident protective action so that a precipitate of coarse, dark red crystals appears, the coarser the further away from the mouth of the tube. Here also the periodicity may be absent or may appear in quite clear-cut and evident fashion for a short distance only. Periodicity is most likely in these cases to occur at low concentrations of the entering reagent.

In gelatin and agar, two salts, red and yellow (Ag_2CrO_4) and a complex between this and $K_2Cr_2O_7$ respectively, always appear. In the gelatin both are sharply periodic; in agar only the red is periodic. As the concentration of the entering reagent increases the yellow rings become red and this indicates that the complex is split and that the products proceed in the direction of Ag_2CrO_4.

In agar the yellow salt does not as readily pass into the red salt, the protective action of agar being less than that of gelatin, so that in the former large crystalline masses build up vague red bands of irregular cloudy form without sharp edges as viewed laterally (Fig. 25).

The system $HgCl_2$ diffusing into KI in starch, in agar and in gelatin (Figs. 27-30). In starch, large red crystals were first formed in a broad band laid down with an evident but not strikingly obvious periodicity followed by a broad band of large, feathery, yellow crystals shot through with long, acicular red crystals with no evident periodicity, these in turn followed by fine red crystals in which a well marked fine periodicity occurred, more evident at greater length. The starch here formed a mere mechanical medium and had only slight or no protective action (Figs. 27, 28).

In agar a more pronounced but still low protective action occurred. Fine red crystals were first formed, but later yellow, in which a fine-grained but definite periodicity occurred (Fig. 29).

In gelatin a chemical action on the medium occurs. This shrinks transversely, leaving the glass wall as the concentration of the entering reagent increases; diffusion is much retarded and periodicity does not occur, or is, at any rate, extremely vague (Fig. 30).

The system $Pb(NO_3)_2$ diffusing into K_2CrO_4 in starch, in agar and in gelatin. All three afforded a very well defined periodicity. Here these media accidently so to speak, have no chemical action and have nearly the same mechanical action toward the precipitate (Figs. 31, 32, 33, 51, 52, 57).

When the foregoing systems are inverted, no evidence of any periodicity at any concentration is obtained in agar or gelatin, while in starch a very sharply defined regular periodicity occurs (Fig. 24, 112, 113).

It is evident that this system is very complicated, since periodicity appears in one direction of diffusion and not in the other. It is noteworthy that starch is here the one medium which affords periodicity for K_2CrO_4 when diffusing into $Pb(NO_3)_2$. It may be a question of diffusion.

When the conditions are the same except that dichromate is substituted for chromate, periodicity is obtained in all three media but is better developed in agar than in starch and still better in gelatin. We shall endeavor to offer an explanation of the above in the discussion beyond (Figs. 23, 34, 80).

The system 20% NH_4OH into 2N $CoCl_2$ in gelatin, for which the gelatin was liquified at a low temperature (50 deg.C) at concentrations of 5, 7 and 15% of gelatin. In no case was periodicity observed. At the lowest concentration (5%) of gelatin, a broad band of white precipitate precedes the blue precipitate. In 7% the white band is not so pronounced and is only slightly apparent in 15% (Fig. 35).

If the 25% gelatin is liquefied and used at once for making up the internal complex, bands do not appear as quickly as when the gelatin is kept for 30 seconds at 100 deg. C. If, on the other hand, exposure to this temperature is sustained for two hours the result becomes complicated by the production of white precipitate and the periodicity of the blue salt is quite irregular (Fig. 36).

It is evident here that gelatin is changed by the treatments indicated and that the resulting changes are reflected in the character of the periodicity.

In the same system the importance of the concentrations of gelatin is brought out by an experiment in which it varied in concentration from 15% to 3% in eight steps. In all concentrations the diffusion is constant until periodicity appears, which happens earliest in the highest concentrations when the bands formed hinder the diffusion rate (Fig. 37).

In agar (.5 to 2.5%) the same relation holds.

Solid Media:—Various observers have obtained periodicity in solid media of divers sorts. We tried gypsum with the system .2N $AgNO_3$ diffusing into .05N $K_2Cr_2O_7$ in a capillary tube. The progressive reaction was made apparent by the appearance of small dark red crystals of Ag_2CrO_4. There was evident periodicity, lacking however obvious harmonic arrangement.

Summary and Theory

In our previous paper we argued that every reaction can proceed periodically. We now hold that it can be obtained in every kind of medium if the necessary conditions of space and concentration are supplied. The exceptions are to be found in those cases in which a reagent has reacted with the medium or in which the gel fails to act as a protective colloid for the precipitate. Even then periodicity may occur occasionally.

The medium can act chemically or be purely passive in this regard and so act merely mechanically.

Viscosity plays a very minor rôle in influencing diffusion.

In higher concentrations of the medium, however, more periodicity occurs than in the lower.

III. Effect of Surface.

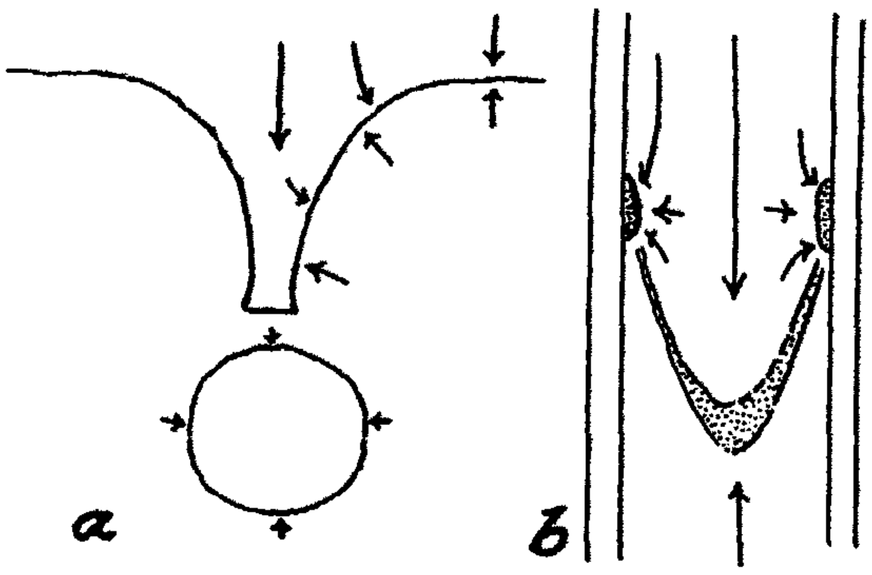
a. The surface of the tube, etc., enclosing the system.

We have already indicated in our previous publication the rôle played by the surfaces of the enclosing vessel. The principle is further illustrated by the following additional observations.

The system Na_2CO_3 diffusing into $AgNO_3$ in capillary tubes. In this reaction coarse crystals are formed which attach themselves on minute irregularities on the inner surface of the tube. These are minute areas of high curvature caused during the blowing of the glass tube, as shown by the fact that the crystals are attached in parallel lines running lengthwise inside the tube. As long as the saturation of the salts resulting from the reaction is too low, scattered crystals only occur. When the saturation is sufficiently high, a ring of separate lines of crowded crystals is formed, the whole picture showing periodicity. In this case the reaction product is very strongly positively adsorbed on the glass wall. If this were not the case the precipitate would be distributed as a diffuse, vague cloud of particles in the corresponding zones (Fig. 14a-c).

The system K_2CrO_4 diffusing into $AgNO_3$. In this case we give one in which the concentration of the reaction product is too low to supply sufficient material to form a complete band. Since here the precipitate is very strongly adsorbed on the glass wall, it attaches itself to the minutest irregularities in periodic fashion. Since the irregularities of the same order of magnitude occur in a particular line, the clumps of precipitate are to be found along this line, of two or more. If the precipitate is not positively adsorbed it will be found scattered throughout the whole medium and no periodicity might then be observed (Figs. 38, 39).

In the case in which oversaturation occurred, as in the system 2% $K_2Cr_2O_7$ diffusing into .5N $AgNO_3$ in gelatin, the reaction product, being strongly positively adsorbed on the glass wall, is deposited in a dense ring which so far depletes the corresponding transverse zone that a reaction of oversaturation is reached only in advance more or less of the already deposited ring. Thus is formed a disc corresponding to the ring (Text Fig. 1b.) This is the "saturn structure," so called by Popp. We must accordingly always find the disc to be laid down somewhat later than the corresponding ring and this, more easily in the greater depths of the tube, can be seen to occur, the ring being formed some time before the disc. The time interval increases the deeper in the tube we go. Between the rings the precipitate is formed more slowly, due to the low saturation as the entering reagent advances and it is deposited on the glass wall. If in sufficient amount it may entirely obscure the periodicity (Figs. 40, 41, 44-46, 77).



TEXT FIGS. 1a AND 1b

Since adsorption will play a greater rôle in small tubes, it becomes less important in large tubes in which the surface therefore will play a minor rôle. The deposit of precipitate will go at once to the disc and the ring is not formed appreciably earlier.

In order to explain the ring-and-disc structure Dogadkin has postulated a curved surface (meniscus) of the medium where the external reagent enters. In order to assure this structure, the meniscus must be concave. This view is quite without foundation, as we have been able to obtain the ring-and-disc structure when the meniscus in question was curved in the opposite sense. It is, furthermore, absent when the precipitate formed is negatively adsorbed on the glass wall.

We tried to determine if the kinds of material would have any effect, using the system 20% NH_4OH diffusing into 2N $CoCl_2 6H_2O$ in 10% gelatin in tubes 10 millimeters in diameter of the following materials: silica, soft glass, hard Jena glass, chemical glass tubes lined with caoutchouc, collodium, cacao butter, paraffin and lecithin. In all, the rates of diffusion and the number of rings were the same (Fig. 47).

Summary: The surface plays an important rôle in capillary tubes, but a less important or even negligible rôle in tubes of larger diameter. Accordingly we may obtain periodicity in the former, but not in the latter. The relative importance will depend on the nature of the precipitate or on the degree of adsorption.

Wulff (1929) had investigated the deposition figures of iodine *in vacuo* and found the first deposition always in places where there are minute curvatures, scratches and tension lines on the glass surface. We have observed the same and have offered evidence in many of our illustrations. Such minute irregularities as Wulff speaks of can account for many appearances in the case of substances adsorbed on the glass wall unexplained otherwise.

b. Surfaces in the medium, inhomogeneity.

The following interesting behavior took place in the system .25N $AgNO_3$ diffusing into .25N NaCl in gelatin in test tubes. The preparation which was observed during two months, yielded at first a very fine periodicity observable only through the microscope and later broad bands with no interspaces appreciable to the eye, so that the bands could not be distinguished until the preparation was exposed to the light, when a differential blackening, due to difference in densities, occurred. The preparation had been kept in the dark. During the period, fungus hyphae developed in the column of gelatin beyond the precipitate and when these were overtaken by the reacting salt a microscopically coarse crystalline precipitate was deposited (AgCl), which, being negatively adsorbed on the glass wall, was scattered throughout the medium. It was, however, positively adsorbed on the fungus hyphae so that the form of the fungus was made evident by the crystals attached to it. (Fig. 48).

Appearances in the system $AgNO_3$ diffusing into $K_2Cr_2O_7$ in gelatin when the experiment is carried out in the classical fashion of Liesegang, i.e. when a drop of the entering reagent is placed on a field of $K_2Cr_2O_7$—gelatin in a glass plate (preferably a Petri dish so that it may be protected from evaporation the more easily). Under these conditions three sets of rings (here well enough so called) are produced, not two only as usually supposed. First a set of fine colorless rings (regarded as phosphates by us). These are produced with great regularity and uniformity until at some distance from the center of diffusion they lose all regularity and periodicity is quite lost. On the colloidal suspension forming the precipitate of these rings, a second dark red silver chromate set is formed by adsorption but the regularity of these is disturbed by the loss of regularity of the primary rings and more or less by the presence of various foreign bodies (minute fibers, particles, etc., etc.) in the gelatin. The rings of the third set are brown and ribbon-like, occurring only at the *gelatin-air interface* and while obviously related to the second set, to some extent are independent. Such rings do not occur at the gelatin-glass interface and are evidently circumstanced by the presence of the gelatin-air interface, *which does not occur in tubes.* If a sheet of thin glass is placed on the gelatin so that the radially extending diffusion must pass partly under the glass, this system of rings is formed only at the gelatin-air interface up to the edge of the glass cover, beneath which it is not to be found, though there is some scattered granular material adsorbed at the gelatin-glass interface, due especially to dirt, etc. on the glass. It becomes apparent that we are here dealing with the saturn structure which occurs only as above described, viz. when a gelatin-air interface is available.

The ribbon-shaped ring can occur, if the layer of gelatin is thin, without any accompaniment of precipitate inside the gelatin, just as the ring alone may occur in a test tube beyond the rings-and-discs.

In our previous paper we have referred to similar conditions procured experimentally.

Fungi, of course, grow readily on some media. In .2N Na_2HPO_4 diffusing into .5 to .006N $CaCl_2$ in test tubes, the preparations of which were observed during the period of a month, there occurred an abundance of fungus colonies which grew in spherical form. Since in this case the reaction product was negatively adsorbed on the fungus, the dense spherical colonies merely formed barriers which hindered the diffusion of the reagents, more or less, according to the position of the colony with regard to the band being formed. The forms of the precipitate were therefore determined by the new directions of diffusion, affording curious funnel- or dome-shaped irregularities in the disc of the ring-and-disc, which latter as a whole is referable to the positive adsorption on the glass wall (Figs. 42, 43, also text Fig. 1a).

With the system $Pb(NO_3)_2$ diffusing into K_2CrO_4 (.5N into .1 to .0031N) in agar in capillary tubes we obtained quite unusual and at present inexplicable results. For the most part the resulting periodicity consisted in fine regular bands of very fine precipitate not adsorbed on the glass wall. In one tube of the highest concentration of entering reagent two periodic systems became visible (a) a relatively coarse band, each band preceded by an interspace relatively free from precipitate and (b) fine banding locally confined to small columns of the medium, being absent elsewhere. In a transverse section we found that there was a very irregular distribution of precipitate, rather obviously connected with a considerable inhomogeneity in the material of the medium. A section from another tube in which the fine bands were uniform and spanned the whole lumen of the tube, showed a quite different picture, only very minute irregularities appearing (Figs. 49, 50, 51, 52).

It is much more likely that starch should produce such irregularities if prepared so that the grains are incompletely hydrated, when nuclei poor in water will occur suspended in a colloidal mass of more highly hydrated starch. Systems especially in which there is a delicate equilibrium between periodicity and non-periodicity are easily upset in starch while in agar and gelatin they afford very regular pictures. This is especially well shown in the system $Pb(NO_3)_2$ diffusing into KI in corn starch paste (Figs. 19, 22).

When potato-starch (Fig. 22, three right hand tubes), with its much larger grains, is used, while periodicity is produced, especially in finer capillaries (.2-4. mm. diameter) the precipitate consists wholly of coarse crystals and there occur no continuous bands such as we see in the five left hand tubes of Fig. 22.

By introducing certain adjuvants to the medium we have changed the surface tension of the minute components (micellae, granules) of the medium and we have sought to determine the effect that such additions would have on the periodicity of the system when substances which lower the surface tension were introduced. The following substances were used and the corresponding surface tensions at the air-water interface as determined by means of a de Nouy tensiometer are given as follow:

1%	Sodium oleate	surface tension	37.3
.1%	do.		41.1
	Capryl alcohol saturated solution		55.5
.1	do. do.		56.9
.3	Cholesterol by the Moravek method		42.2
.03	do. do.		47.8
.003	do. do.		not measured.

These were added to $CoCl_2$ in 10% gelatin. In sodium oleate and cholesterol the banding was identical with that in distilled water, the control. In capryl alcohol in both solutions there was a considerable departure from the control in the great prominence of white precipitate with few and diffuse blue rings. We must assume a chemical interaction in the case of the capryl alcohol, for it is clear that the changes in surface tension had no effect (Fig. 53).

Macro-inhomogeneities, as in starch and agar (especially when prepared by partial hydration), affect the behavior of the reagents and of the precipitate in any system.

IV. Final Form of the Precipitate.

Crystalline precipitate. The precipitate occurs in the form of crystals (micro and macro) in water and in media which do not act protectively and which therefore behave, aside from purely mechanical support, as if not present; e.g. 2% $CaCl_2$ diffusing into 2% $(COONH_4)_2$ in gelatin in capillary tubes. Here no trace of periodicity was visible. The crystals were small placques, single or aggregated into small spherocrystalline groups. In the inverse of this system we obtained at first small crystals which became larger the further in the tube where the diffusion was slower. A very slight indication of periodicity was evident in one or two tubes e.g. the right hand tube, Fig. 55. (Figs. 54, 55, 72).

The precipitate may be at first diffuse and suddenly pass into a periodic condition if the entering reagent is hindered from rapid diffusion as e.g. by a bubble (Fig. 57). Whereas in the system $K_2Cr_2O_7$ diffusing into $AgNO_3$ in starch (.5N into .1 to .0031N) we observed all intergraduation between periodicity and nonperiodicity (Fig. 56).

In the system $Pb(NO_3)_2$ into NaCl in gelatin (.5N to .25 into .5 to .25N) we obtained periodic bands of spheroidal crystals which very slowly developed from the already laid down colloidal precipitate (Figs. 58, 59).

It is evident that periodicity is not at all conditioned by the colloidal state of the precipitate as we obtained well defined periodicity in many experiments in which the salts formed are hardly to be obtained in colloidal form, as in the case of $BaSO_4$ in water (Figs. 15, 17).

Colloidal precipitations: growth forms. In the systems $K_2Cr_2O_7$ diffusing into $AgNO_3$ in starch (.5N into .1 to .0031N) we obtained the reaction product in the form of semi-permeable cells, more or less in periodic grouping. We recognized these as Traube membranes, which grew in size after breaking out and producing various curious and fantastic shapes (comma, comet and other). We removed some of them, mounting them for microscopic examination in the entering reagent, when on crushing we could observe the formation of new membranes and the growth of older ones (Figs. 60–64). Similar, very uniform, comet-shaped membranes were obtained in 50% $AgNO_3$ diffusing into .5N $K_2Cr_2O_7$ in gelatin in a glass plate. The thinness of the gelatin was here a factor (Fig. 60, inset). *Sharp banding.* The reaction product according to rate of diffusion and of concentration yielded different forms of colloidal precipitate in the two main types of diffuse and sharp (Figs. 65, 67, 68). These appeared, e.g. in the systems $(NH_4)_2HOP_4$ diffusing into $CaCl_2$ in gelatin (.2N into .1 to .006N) and NH_4OH diffusing into $MgCl_2$ in gelatin, as also in some other systems. Popp (1925) obtained bands in the system ammonia and magnesium chloride in both directions, whereas we obtained bands usually only when the ammonia was the entering reagent. Once, however, we got the same result as Popp when 0.5 sat. soln. MgCl diffused into 1N NH_4OH in gelatin. (Fig. 2a, Plate IX) This does not, however, militate against our view. We used various concentrations of gelatin and our results were the same as hers, so far as they go.

In 4% $Pb(NO_3)_2$ into 4% KI in gelatin we obtained a yellow colloidal cloudy periodic precipitate which was changed on the increase of concentration of the entering reagent to white granules which grew into spheroidal crystals grouped periodically (Fig. 66). There is difficulty in the interpretation of Pb and Ag reactions in gelatin. As is well known, Pb $(NO_3)_2$ with gelatin alone afford a periodic precipitate negatively adsorbed on the glass wall. If tubes are thus set up as control, similar tubes with KI give, in addition, a cloudy colloidal yellow precipitate with a sharply banded white periodic precipitate within the yellow.

We have already pointed out that when the precipitate is colloidal and positively adsorbed on the glass wall (or other suitable interface) the ring-and-disc structure always appears. Whether it is well defined and regular or ill defined and irregular or otherwise depends on secondary conditions, especially on diffusion rates. Bradford's observations (1919) on the adsorption of a cloudy or colored precipitate in the region of the band accords with ours but does not militate against our theory.

Periodicity is evidently independent of all possible states in which the reaction product may occur. The problem of periodicity then is to be solved quite in disregard of these conditions, contrary to some theories which have been advanced.

Influence of one precipitate on a second. Phosphates in the gelatin. System $AgNO_3$ diffusing into Na_2HPO_4 and inverse (Figs. 71, 73, 86). When we experimented with these we found in all cases two systems of rings, one of fine bands in advance and, adsorbed on these, a second dark appearing precipitate. We attribute these fine rings tentatively to phosphates in the gelatin, chlorine being absent. They are developed most abundantly and uniformly in the lower concentrations of the internal reagent. In the higher concentrations the fine rings were more poorly developed and coarse spheroidal masses showing weak or no periodicity took their place. In certain intermediate concentrations we obtained intergrading conditions, in which the coarse precipitate was adsorbed on the finer.

In experiments in which $AgNO_3$ is allowed to diffuse into gelatin without additional reagent a fine periodic precipitation is obtained and this, when other reagents are added, forms a groundwork for the additional precipitate to be adsorbed upon. Stansfield (1917) also observed a microscopical periodicity in the system silver nitrate diffusing into K-chromate. In the plug it had the same periodicity as the chromate. This groundwork again seems to be due to phosphates in the gelatin. When NaCl is added to the gelatin a different and much finer periodic precipitation is obtained with readiness recognizably different from phosphate rings which are more soluble in the entering reagent than the chloride. Liesegang examined the behavior of silver nitrate diffusing into potassium chromate-gelatin and the inverse, observing the fine white bands which he attributed to chlorides, which, however, he stated as not being necessary to the formation of the chromate bands and as not present when the chromate diffuses into the gelatin.

Nor are they present when the medium is prepared by adding $AgNO_3$ to the gelatin, followed by $K_2Cr_2O_7$, (and therefor containing the reaction product, but neither free chlorides or phosphates). The excess $K_2Cr_2O_7$ reacts with the entering $AgNO_3$ periodically, but no fine banding is seen (Fig. 71a).

Lagergren (1899) observed negative adsorption of NaCl and Bradford on the addition of this to $K_2Cr_2O_7$-gelatin obtained only diffuse cloudiness with $AgNO_3$, whereas we have found clear cut periodicity.

We agree to some extent with Bradford that there is something either already present in the gelatin (impurities, he calls them) or, as we have already suggested, which appears in the course of the reaction periodically as fine bands facilitating the periodicity of the chromates of Ag and Pb, but which assuredly is not a *sine qua non*. If mineral impurities are present we argue that they are phosphates since we obtain similar periodicity when Ag or Pb diffuses into gelatin containing phosphate (Figs. 70, 71, 74, 75). On the other hand we admit that the fine bands may be due to a reaction of Ag or Pb with the gelatin itself.

When $Pb(NO_3)_2$ diffuses into gelatin alone a mixed cloudy and coarse periodic precipitation is formed, the latter composed of spheroids of pearly appearance. When K_2CrO_4 is added to the gelatin the chromates, being weakly developed at low concentrations of the internal reagent, form insufficient surface for the adsorption of the phosphates and these are then present as scattered globulites. In the higher concentrations of chromates the very numerous bands present allow the full adsorption of the phosphates, which are then periodically deposited thereon (Fig. 33).

It should be added as confirmatory of the foregoing statements that we never obtained the precipitation of phosphates in agar alone or in starch alone. Also we obtained with the system $Pb(NO_3)_2$ diffusing into K_2CrO_4 in agar the same fine bands, which we attribute to chromates, as we did in the above mentioned experiment in which such bands serve as a groundwork for the emplacement of the coarser phosphate precipitation (Fig. 57).

Summary: There can be at least two sets of periodic precipitation in a single system. When one is adsorbed positively on the other the appearances are complicated and are different according to the concentrations of the reaction products.

V. *Influence of Concentrations.*

(a) *Silver chromates.* System K_2CrO_4 diffusing into $AgNO_3$ in 6% gelatin (.5N into .1 to .0031N). In the highest concentrations complete rings with discs are formed in sets of 2 to 4. The earlier formed rings have their accompanying discs, the later have no discs; the material being entirely used in forming the rings. This results from the reduced rate of diffusion and concentration allowing time for all the reaction precipitate to be adsorbed on the glass wall, at least for the most part. Whenever the disc fails to be formed in addition to the ring on the glass wall there are always scattered granules of precipitate in the interspaces due to the presence of local adsorption centers. In the lowest concentration of internal reagent in which any precipitation occurred (.0125N) the whole of the reaction precipitate is adsorbed on the glass wall. Either entire rings are formed or, as is usually the case, only clumps of precipitate, attached to irregularities on the glass wall, form rough and irregular rings. In extreme cases when the tube is too large the precipitate will be entirely on the glass wall and may show no periodicity at all. At medium concentrations the ring-and-disc structure is marked and generally regular, showing, however, minor irregularities of structure (incomplete rings, gaps in the discs, etc.). Most important, however, is the fact that the discs are always bowl-shaped with the convex surface inwards (directed away from the mouth of the tube). This is to be explained by changes in the concentration of the reagent due to its rich and very rapid accumulation on the glass wall (Fig. 77).

In the inverse of the above system, viz. in $AgNO_3$ diffusing into K_2CrO_4 in gelatin there is laid down a set of phosphate bands (in the inverse system the phosphates are already precipitated by mixing with $AgNO_3$) upon which and upon the glass wall the chromate reaction precipitate is strongly adsorbed. As Davis (1922) correctly suggests, the opaque bands (which we call phosphate bands) extend from the beginning of the precipitation column and do not delay their appearance to some time after the process begins, in the case of silver nitrate diffusing into chromate-gelatin. In the highest concentration periodicity of chromates is not established for some time. In this and in medium concentrations rings and discs are first formed giving place more or less quickly according to concentration to rings alone and finally to granules scattered more or less periodically.

As Stansfield (1917) observed, however, the banding in silver chromate extends much further into the plug, as a fine microscopic structure, than is detectable by the eye. In the lowest concentration the periodicity of the chromate became cloudy and vague but regular and quite evident, the small amount of chromate being adsorbed on a large number of phosphate bands (Fig. 76).

Stansfield (1917) studied silver nitrate diffusing into K-chromate and the inverse, finding little difference, as had also Liesegang.

In the same chemical system but with agar instead of gelatin, the phosphate bands being absent, the chromate alone is precipitated periodically as *minute colloidal spheroids with much precipitate in the interspaces.* The bands are broadest in the higher concentrations and are scarcely present at all in the lowest (Fig. 78). When we repeated the experiment with a poured agar plate (instead of tubes) we could observe a colorless but non-periodic zone preceding the red precipitate, which occurs first as a cloudy precipitate roughly, but evidently periodic, which quickly becomes irregular. This irregularity is owing to the quick formation of centers of low vapor tension, that is, adsorption centers, which grow at the expense of neighboring smaller centers. It is adsorption of the salt on such centers which discomposes the disposition of the precipitate in regular periodic fashion. The presence of a fiber disturbing the periodicity in Fig. 103a exemplifies this. Lastly, when starch is substituted for agar somewhat coarser crystals are obtained, coarsest in the highest concentrations with no trace of periodicity (Fig. 76b). When, however, we invert this system (K_2CrO_4 into $AgNO_3$ in starch) similar crystals are formed but a good periodicity is obtained, very sharply defined in the higher concentrations but absent from the lowest. The rate of diffusion is as usual more rapid in the lowest concentrations of internal reagent (Fig. 56).

System $AgNO_3$ into $K_2Cr_2O_7$ in gelatin. The diffusion rate is highest in the lowest concentration of internal reagent, as Stansfield observed (1917). Very regular phosphate periodicity occurs in all concentrations equally. The chromate is laid down periodically and is adsorbed on the phosphate bands. Each band of chromate is compound of one to several phosphate bands carrying the chromate according to the distance from the mouth of the tube. Irregularities of chromate deposition are not referable to deposition between the phosphate bands, but to irregular and scattered deposition on the regular phosphate bands, which themselves become irregular at length and this increases the confusion. It is important to note that here the chromate is negatively adsorbed on the glass wall. We have already pointed out that it is positively adsorbed at the gelatin-air interface (Figs. 74, 79).

Liesegang (1914) has thought of the possibility that there are two modifications of silver chromate of which one makes the diffuse precipitate and the other the rings and that the one has no "*Keimwirkung*" on the other. We have thought the same, but we do not find any need for bringing the factor of *Keimwirkung* into account.

In starch and agar there are, of course, no phosphate rings and while periodicity of the chromates is evident it is not at all so sharply defined and although more evident in some concentrations it may be vague or scracely observable in others (Fig. 26).

System $AgNO_3$ diffusing into $K_2Cr_2O_7$ in starch, the inverse of the immediately foregoing. No phosphate bands are present and no periodicity of the chromate occurs in the highest and lowest concentrations. In the medium concentrations well developed periodicity of coarse granular precipitate of growing Traube membranes occurs (Fig. 82).

(b) *Lead chromates.* System $Pb(NO_3)_2$ diffusing into K_2CrO_4 in gelatin. Here the phosphates do not afford bands but merely white sphero-crystals. The lead chromates are not adsorbed on the phosphates and therefore effect a regular independent periodicity. The phosphates, on the contrary, are adsorbed on the chromates and in higher concentrations form irregular clumps attached to the chromate bands, smaller and smaller as the concentration of chromate is lower (Fig. 33).

System $Pb(NO_3)_2$ diffusing $K_2Cr_2O_7$ in gelatin. A deep lemon yellow crystalline precipitate always occurs, coarser in the higher and finer in the lower concentrations of internal reagent. Immediately within the first few minutes of diffusion periodicity becomes evident; regular narrow bands with interspaces filled with more scattered crystals, the more regular and numerous in the lower concentrations. The periodicity soon fades away and the precipitate then becomes continuous (Figs. 34, 80).

In the course of a week a second periodicity makes its appearance, this time of a few broad bands more lightly colored, or more numerous narrower bands, so that always there occurs two periodicities, the one early the other late. We may perhaps attribute the latter to the presence of sulphates, the S_2 being derived from the gelatin, as we found to occur previously (1928) (Fig. 80).

Systems $Pb(NO_3)_2$ diffusing into K_2CrO_4 in agar and the reverse. In the former a very fine and regular periodicity occurred in all except the lowest concentration. In the latter there was no periodicity at all, beyond a very fine microscopic periodicity in two of the tubes (.05N and .025N) (Figs. 49, 50, 51, 52, 112, 113).

In the same systems with starch as medium. A fine periodicity of the same general character as in agar occurred in both. In K_2CrO_4 diffusing into

$Pb(NO_3)_2$ the reaction product appears to be negatively adsorbed on the glass wall but in its inverse positively (Figs. 24, 31).

(c) *Phosphates.* a. System Na_3PO_4 diffusing into $CaCl_2$ in gelatin. Near the open end of the tubes there is an appearance of periodicity. The rings are of cloudy precipitate but are irregular and somewhat vague. From the very (open) end of the tubes crystal masses are present and show a gradual gradient in dimensions until they reach a critical size, after which periodicity disappears.

Periodicity appears only in the highest concentration used, probably because the triphosphate is too alkaline and is neutralized partly because of the acidity of the 1N solution $CaCl_2$ (Fig. 81).

b. Na_2PO_2 diffusing into $CaCl_2$. In all concentrations white phosphate bands strongly adsorbed on the glass wall are formed. In the higher concentrations the interspaces are filled with metastable crystals which evaporate and give up their material to the rings and discs (Figs. 83, 84).

c. $NH_4H_2PO_4$ diffusing into $CaCl_2$ in gelatin. In the highest concentrations coarse spheroidal crystals are first formed without periodicity, after which periodic rings strongly adsorbed on the glass wall appear. Each ring and disc is formed at the inner limit of a periodic group of crystals. In a lower concentration (.05N) only crystals appeared without periodicity and no precipitate at all occurred in still lower concentrations (Fig. 85).

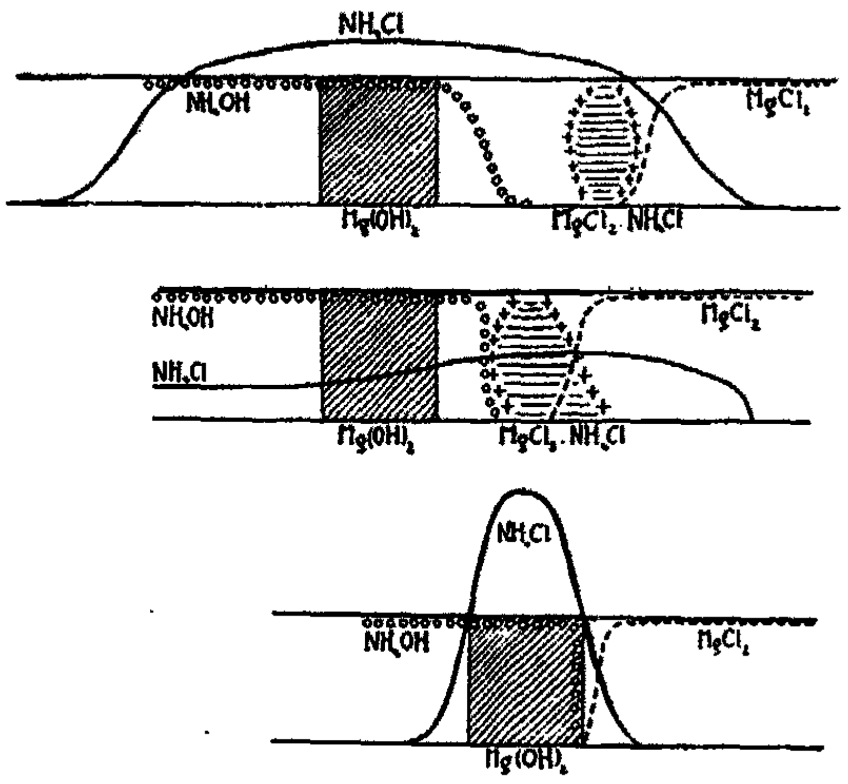
d. $(NH_4)_2HPO_4$ diffusing into $CaCl_2$ in gelatin. Spheroidal crystals appeared without periodicity in the upper three concentrations, more in the highest concentration. At the same time rings of colloidal precipitate were formed, strongly adsorbed on the glass wall, and these grew at the expense of the crystals. In the lower concentrations only colloidal precipitate forming ring-and-disc structure were formed. The rings were broader and denser toward the depth of the tube. The discs (Fig. 69) were curiously irregular (Figs. 67-69).

e. .1N $AgNO_3$ diffusing into .1 to .0035N Na_2HPO_4 in gelatin. In the lower concentrations there occurs the same fine periodic precipitation which occurs in every case in which $AgNO_3$ diffuses into gelatin, viz. fine phosphate bands. With increasing concentration the fine bands are reduced in number till in the highest none appear. A second precipitate is also present in the higher concentrations in the form of coarse spheroidal masses which decrease in size with the decrease of concentration (.0031N and lower) and in which there is no periodicity until the particles become of colloidal dimensions when they are adsorbed upon the fine bands in a sharp periodicity which, however, becomes vague and cloudy, if still evident, in the lowest concentration (Figs. 71, 86).

The failure to produce bands in the higher concentrations appears to depend on the formation of a difficulty permeable plug at the mouth of the tube, which naturally lowers the diffusion rate. In consequence also the coarse precipitate noves forward in the higher concentrations only very slowly. We must assume both kinds of precipitate to be modifications of the same salt.

The inverse system Na_2HPO_4 into $AgNO_3$ in gelatin. Periodicity was observed only in the four higher concentrations. The precipitate is colloidal and very strongly adsorbed on the glass wall and a long initial plug in the three higher concentrations (.2 to .05N) has no periodicity. In the highest concentration the bands were broad, regular but vaguely delimited, more irregular in .1N while in .05 it became a lobulated strand. In .025N the periodicity was fairly regular and the precipitate very fine. We note again the adsorption on the glass wall of the reaction product in one case but not in its inverse. With time a secondary change overtook the primary precipitate and spheroids were formed at the open ends of the tubes, showing little if any periodicity (Fig. 73).

System .5N ammonium oxalate into .1 to .0031N $CaCl_2$ and the inverse. In both a crystalline precipitate occcurred without any periodicity. In the former the crystals are large and become feathery progressively toward the depth of the tube. In the latter the precipitate was extremely fine, nearly colloidal. In both the size of the particles diminished with concentration. In the case of an insoluble precipitate being at once formed, periodicity appeared with great difficulty, if at all (Figs. 54, 55).



TEXT FIG. 2

Experiments in test tubes. System NH_4OH diffusing into $MgCl_2$ in gelatin. Here the diffusion was more rapid in the high concentration of the interval reagent than in the lower, contrary to our other experiments (Figs. 1, 3).

Hedges (1928) showed that the outward diffusion of ammonium chloride is not essential to the production of periodic structure in the system ammonia-magnesium hydroxide-gelatin. The outward diffusion of the reaction product can in any event be outward only from the place of highest concentration and must be inwards also from this point. We believe that this inward diffusion leads to the formation of a complex with the reagent already present, which in turn diffuses outwardly (text Fig. 2).

The theory of Bechhold as cited by Hedges postulates three diffusion waves, those of the two reacting substances and that of the soluble product. Our view also demands three—that of the entering reagent, the reaction product and the complex which arises when the concentration of the inwardly diffusing reaction product becomes high enough to form this complex with the internal reagent. This complex will now have an independent diffusion carrying it back to meet the entering reagent at a new point to which by this time the entering reagent has traveled. A new lot of reaction product is then formed and behaves similarly.

Fricke and Suwelack (1926) point out that E. Weitz (1924) has shown that Mg-salts in a concentrated solution of ammonia containing ammonium chloride, amine complexes are formed, and they used this to explain the formation of Mg-hydroxide rings, which are less soluble in the higher concentrations of ammonia. They say that this is an exceptional case in the formation of rings, but we take the view that every periodic phenomenon must be preceded by the formation of a complex salt.

System $MgCl_2$ diffusing into NH_4OH see p. 1530, 1543.

System NH_4OH diffusing into 2N, 1.5N, 1N and .5N $CoCl_2$ in 20% gelatin. The rate of diffusion of the entering reagent is slowest where the concentration of the interacting reagent is highest and vice versa. Where diffusion is slowest periodicity is earliest to appear. In the lower concentrations the precipitate is dissolved by the entering reagent and more rings are formed in the higher concentrations than in the lower (Fig. 91).

The same system but altering the concentration of the entering reagent, viz. NH_4OH 10, 15, 20 and 25% into 2N $CoCl_2$ in gelatin. The higher concentrations of the entering reagent diffuse more rapidly than the lower and the periodicity is more developed in the higher than in the lower (Fig. 90). The same system with agar instead of gelatin. The diffusion rates are the same as for gelatin. The periodicity in the lower concentrations begins closer to the mouth of the tube and the bands are more diffuse and broader than in the higher (Fig. 89).

Summary. At higher concentrations of the internal reagent there is a tendency for a plug to be formed at or near the mouth of the tube and the entering reagent is also used up more rapidly, reducing the rate of speed at which it reaches the depths of the tube. In the majority of cases therefore, the slowest diffusion is in the tubes of highest concentration of the internal reagent but the reverse may be true where the plug is permeable to the entering reagent as, e.g., NH_4OH diffusing into $CoCl_2$.

VI. *Influence of Temperature.*

The system 20% NH_3 diffusing into 2N $CoCl_2$ in gelatin at 24, 15, 7 and 3 deg. C. At the higher temperatures the march of the entering reagent is most rapid and the periodicity appears earliest and the rings are narrower and more numerous. At the lowest temperature no bands at all were formed. The solution of the plug took place most rapidly at the highest temperature. The first suggestion which occurred to us was that these differences are due to differences in viscosity of the medium due to difference in temperature, but we already have shown that a difference in viscosity of the gel has no effect on the diffusion rate. We must therefore explain the difference observed as due to the effect of temperature on the reaction velocity. The reaction velocity of some reactions is high at high temperature and low at low temperature, while in others the reverse is true. The absence of periodicity at the lower temperature may be accounted for as follows. At these temperatures (3 deg. C) reactions take place which do not take place at the higher temperatures, and the resulting products may prevent the periodic precipitation of the $Co(OH)_2$ for at these low temperatures large pink crystals of $(Co(NH_3)_6)Cl_2$ are developed in the upper portion of the tubes (Fig. 92).

VII. *Influence of Light.*

It is well known in the case of photochemical reactions exposure to light at periodic intervals will induce a pseudo-periodicity. There are, however, cases in which the periodicity occurs in the dark. Exposure to light can however induce the onset of periodicity or cause some disturbance in periodicity already established. Such an example is found in the system .25N $HgCl_2$ diffusing into .1N to .003N KI in gelatin. On exposing a tube of internal reagent of such concentration in which no evident periodicity had occurred to the illumination used for photography, banding was at once induced and continued afterward in the dark. In other concentrations (.1N) fine banding had already occurred but on exposure to light there was an evident disturbance of the process in the incidence of broader bands (Fig. 97).

In the system .5N $Pb(NO_3)_2$ diffusing into .1 to .0031N K_2CrO_4 in agar we found that in tubes in which no periodicity was visible (concentrations .0125N and .0062N) exposure to light while we were making a photograph induced periodicity. In some cases it continued after that. Hatchek (1921) also observed that the periodic precipitation of lead chromate is affected by light.

Such variations in banding as observed by Dunin and Schemjakin (1926), to which they appear to have attached considerable importance, can easily occur, as Dogadkin (1928) showed, as the result of external influence, and as we also have found. Their illustration itself shows at once that there was but a single system of red bands and the disturbance in these may have been due wholly to disturbance in the phosphate rings, as we regard them. We have observed such irregularities to occur in this and other systems.

We see, therefore, that in cases in which the equilibrium is easily disturbed, exposure to light can induce true periodicity, or can disturb periodicity already established.

VIII. *Influence of Foreign Ions:*

Influence of the reaction product. The system 20% NH_4OH diffusing into 2N $CoCl_2$ in gelatin plus 2N, 1.5, .5, .25, .1, .05N NH_4Cl, and control. We observed the following:

a. In the two lowest concentrations and in the control the periodicity was normal but disturbances were more and more apparent as the concentration of the reaction product increased. These disturbances were initiated in the final by the accumulation of crystals of (Co(NH$_3$)$_5$)Cl$_2$ near the surface, greatest in the highest concentration.

b. The increasingly greater amount of dissolution of the Co(OH)$_2$ at the top of the column and

c. The increasingly greater accumulation of white colloidal precipitate and

d. Less, and in the two highest concentrations, no periodicity.

During the progress of the precipitation however, even in the highest concentrations, there were first laid down (a) a clear zone with crystals, (b) a dark reddish colored zone with no precipitate, and (c) a zone of periodicity alternating blue and white. All these zones grew in depth and by the same token advanced down the tube, the periodicity being lost in a broad white zone.

In high concentrations of NH$_4$Cl the reagents react in the direction not of Co(OH)$_2$ but of (Co(NH$_3$)$_6$)Cl$_2$. For the high concentrations of NH$_4$Cl other salts may be substituted. If the diffusion rate of NH$_4$Cl is delayed, as can occur in fine capillary tubes, the (Co(NH$_3$)$_6$)Cl$_2$ accumulates and the formation of the blue salt can be obviated entirely. The high concentration of NH$_4$OH works against formation of the (Co(HN$_3$)$_6$)Cl$_2$ and under such conditions merely blue Co(OH)$_2$ is laid down (Figs. 93, 94).

If we reverse the foregoing experiment and add NH$_4$Cl to NH$_4$OH which then is allowed to diffuse in to 2N CoCl$_2$ in gelatin we get the same result and we see that the NH$_4$Cl diffuses readily (Fig. 95).

The idea of the influence of the reaction product on the solubility of the precipitate, thus preventing precipitation until a sufficiently high concentration has been reached, when a new band is formed (in the case of silver nitrate and ammonium chromate), was formulated by Bechhold in 1905 and has been repeated without any theoretical addition by Wo. Ostwald (1925) for the system ammonia diffusing into magnesium chloride.

Our theory postulates the diffusion of the reaction product away from the precipitate to form a complex with the internal reagent, allowing time for the inward diffusion of the entering reagent to meet the complex as it diffuses backward. The two theories are similar in emphasizing the importance of the reaction product but the function of the reaction product is different in them. Bechhold's it merely increases the solubility of the precipitate; in our view it must first unite with the internal reagent to form a complex which then moves backward toward the mouth of the tube to meet the entering reagent which itself has already moved inward some distance beyond the last-formed band.

Influence of various salts (cations). The following chlorides were substituted for NH$_4$Cl in the preceding experiment, viz. Li, Na, K, Rb, Cs, Ca, Sr and Ba, each in two concentrations, 1N, and .1N, in the gelatin. These salts in low concentrations had no influence. In the higher concentrations the diffusion rate is nearly the same in all. The clear zone is widest in Li >K > Rb > Na >Ca >Ca and was absent from Sr and Ba. The crystals are very prominent in Li, few in Na and are absent from the others. The white precipitate is more abundant in Li >Ca >Na >Cs >Rb >Sr >K >Ba. The blue rings are more abundant in Na >Rb >Cs and absent from the others (Fig. 96). The cations which are most similar in their chemical properties to NH_3 act most like it in the system with which we worked.

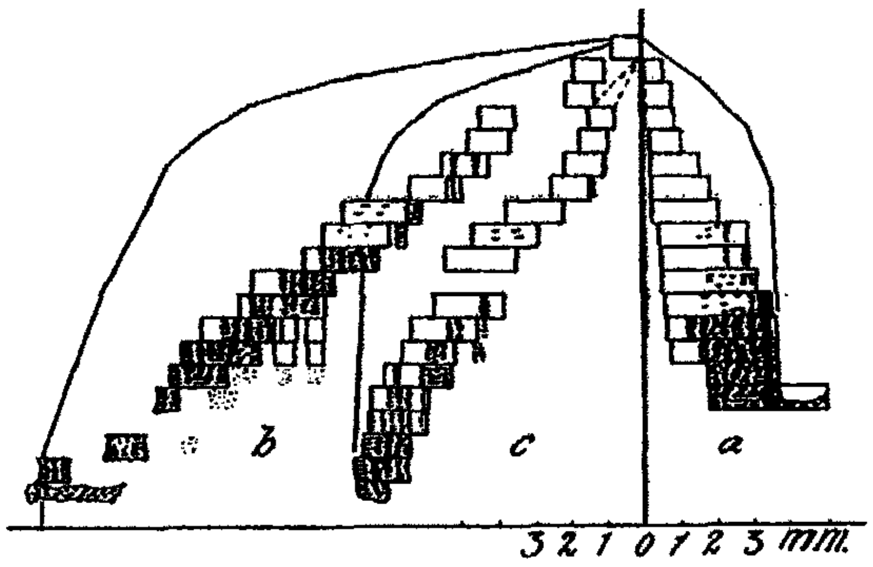
Influence of anions. When $Co(NO_3)_2.6H_2O$ and $CoSO_4.7H_2O$ were added to the gelatin no periodicity was observed. In the higher concentrations of $Co(NO_3)_2$ (2N and 1.5N) the dark red plug is dissolved for some distance from the surface of the gelatin.

Experiments in U-tubes. Recalling Pringsheim's experiments with U-tubes, we have also done a considerable number of similar experiments in order to enable us to see what might be contributed to the solution of the problem of periodicity by means of them. Pringsheim has already found that the precipitate first laid down may move, that is, be dissoved and then recrystallize, and that the column of precipitate may grow first in one direction and later in the other. He observed also the occurrence of periodicity. Our experiments were of value to us in that they enabled us to determine the variety of salts which may occur from the interaction of the two chemical factors in a given system when the one or the other is superabundant. For illustration we may describe the special case of $HgCl_2$ and KI in agar. Experiment: In one arm of a U-tube a saturated solution of $HgCl_2$ and in the other a .25N Ki were put. The tube was made simply by drawing out a tube and bending the wider ends at right angles to the narrow part which was then filled with the medium, agar. The point of meeting of the two reagents was marked on the tube. Here at first a diffuse red precipitate occurred, which persisted for some time but finally disappeared. A new zone of precipitate was soon formed, this time of the yellow salt laid down on the KI side of the primary red zone. The progress of precipitation was observed for 12 days during which (a) a compact column of finely periodic yellow crystals moved slowly forward toward the KI side. This showed also (a) a sort of secondary periodicity consisting in the occurrence of very narrow transverse zones entirely free of precipitate and (b) the laying down of red crystals in the form of rings, paired or grouped, and adsorbed on the glass wall. With time these became more numerous as the column of crystals grew in the direction of the KI. The former periodicity must be regarded as that of crystallization merely, the latter, the red precipitate occurring more and more on the KI, must be due to the periodic higher concentration of this salt. This red salt is strongly adsorbed on the glass wall and occurs as a transverse band only at the end of the column when it ceases to advance.

More complete observations were made with starch as a medium in three U-tubes with the following concentrations:

$HgCl_2$		KI
a. saturated solution 0.04	→	0.25N
b. 1/2 do. do.	←	1N
c. 1/4 do. do.	←	0.25N

The arrow indicates the direction of the movement of the crystalline column. In (a) above a permanent narrow zone of fine red crystals was first laid down (text Fig. 3). This was followed by a column of yellow crystals, which showed fine periodicity. For three days only yellow crystals were formed; on the fourth day the red appeared adsorbed on the glass wall in two zones (rings). This red crystallization then spread backward and forward while the yellow disappeared. The red salt became now so abundant as to salt out the medium. (a, text Fig. 3), (b) and (c). The columns moved toward the Hg. The case (b) (text Fig. 3): At the point of meeting only fine yellow crystals were formed. On the second day two narrow rings of red crystals appeared. Subsequently the red crystals became more extensive and the yellow disappeared until on the eleventh day a dense plug of red precipitate was formed and this became irregular in form due to its slight and irregular permeability. It acted as Traube membrane. The history of (c) was similar, but the column did not move so far in the same time. The initial precipitate was, however, of mixed red and yellow crystals.



TEXT FIG. 3

$HgCl_2$ and KI diffusing into each other. The blank rectangles indicate yellow salt. The appearance of red salt is indicated by short transverse lines. Dissolution of these by stippling. The curves are constructed on an x-y coördinate; but the advance and changes in the columns of precipitate are represented in true but irregular sequence as regards time. A zone blackened by exposure to light is indicated in (a).

Conclusion. Both precipitates are soluble in excess of KI and are laid down only at suitable concentrations. Pringsheim believed that in U-tube experiments the movement of the precipitate always is toward the hypotonic member of the system. This is Pringsheim's rule. In our experiments we found this not to hold in the case of $HgCl_2$ and KI. The movement of the column of crystals in (a) is opposite to that of the osmotic pressure, in (b) and (c), in the same direction and proportional to the difference in concentrations. This movement is not due to non-permeability, since the crystalline zones formed initially and afterwards are freely permeable. Only at the end of the process does an impermeable plug of red salt appear. This always arises from degrading yellow salt and is blackened in strong light but not in the longer wave lengths, viz. to the end of the green. Whether the column move toward the KI or to the $HgCl_2$ side the older part of the column is dissolved and since the salt is not soluble in $HgCl_2$ we must suppose that KCl, the other reaction product, is responsible for the dissolution of the rear end of the column. During the reaction $K_2HgI_2Cl_2$ is formed, which diffuses in both directions. On the KI side the complex is split, yielding HgI_2, and on the $HgCl_2$ side it remains in solution. This we regard as important to account for the movement of the precipitate and for the presence of spaces between bands expressing periodicity (Figs. 98, 99 and text Fig. 3).

X. *Diffusion, and the Head of the Diffusion Column.*

The most satisfactory theory assuming one-way diffusion is that of W. M. Fischer (1925) who followed the theory of W. Ostwald, adding the conception of an induction period which is needed for the separation of one ring from another. He says (p. 326), "Massgebend für die Entstehung der Schichten ist eine bestimmte Diffusionsgeschwindigkeit und zwar eine solche, dass sich die Induktionsperioden der Fällungen ausbilden können. Ist die Diffusionsgeschwindigkeit zu gross, so wird der ausfallende Stoff bei Uebersättigungen gefällt wo keine Unstetigkeit der Ausfällung vorhanden ist, und wir erhalten eine kontinuierliche Fällung."

Our observations support the idea, inasmuch as when diffusion takes place very quickly no rings are formed. Fischer says that the reaction period of barium sulphate is not sufficiently great in water solutions and that he has obtained rings of barium sulphate in such cases in which he introduced some gelatin and dyes, which substances are supposed to lengthen the induction period. We have, however, produced the rings in pure water solutions.

Theory. We see no essential difference between the theories of W. Ostwald and W. M. Fischer. That of the latter has the advantage of greater clearness by virtue of the introduction of the term "induction period," but unfortunately the idea is difficult of experimental proof. The two theories stand or fall together.

Doyle and Ryan have investigated this matter, giving data which correspond to our own, and properly conclude that "Any theory of periodic precipitation which postulates the formation of the precipitates at the head of the diffusion column cannot offer a correct explanation of the phenomenon." Jablczynski's (1926) statement descriptive of the fact is to the effect that though the bands occur behind the head of the diffusion column there is a roughly approximately constant relation between the advance of the reagent and the formation of the bands, in a particular case. The theories which assume that the periodic precipitation takes place at the head of the diffusion column may be at once thrown out of court.

In his conclusion Fricke (1923) says that the diffusion follows the Fick diffusion equation, with which we agree, but we must add that Jablczynski has arrived at quite exact mathematical expressions of the whole phenomenon. In 1903, however, Morse and Pierce had found that diffusion in capillary tubes during periodic precipitation follows Fick's law.

In the case of 10% NH_4OH into 5% $Co(NO_3)_2$ in gelatin, we were able to see that the head of the diffusion column of the entering reaction is some distance in advance of the last periodic band of precipitate. This was due to the alteration of the index of refraction of the gelatin as the NHOH penetrated and caused swelling, so that with suitable illumination we were able to photograph the plane separating the swollen and unswollen gelatin (Figs. 87, 88). It is clear that a reaction must take place in the medium beyond the position of the last ring or, in other words, the position of the band is not the position of the primary reaction. That this is the case is attested by the change in color or other appearance of the medium between the last ring and the end of the diffusion column. It is clear also that the reaction product is free to diffuse both backward and forward.

The head of the diffusion column is to be seen also in the system $AgNO_3$ diffusing into Na_2CO_3 in gelatin. (Fig. 100).

In the system .5N, .5N .25N Pb $(NO_3)_2$ diffusing into .5N, 0.5N into .25N and .25N into .25 N NaCl we observed that at higher concentrations a strong cloud of colloidal precipitate formed behind the head of the diffusion. As a periodic precipitate in the form of pearly spherical globoids appeared the cloudy precipitate disappeared, partly by diffusion forward but chiefly by diffusion backward against the primary diffusion current to contribute to the formation of the crystals (Figs. 101, 102).

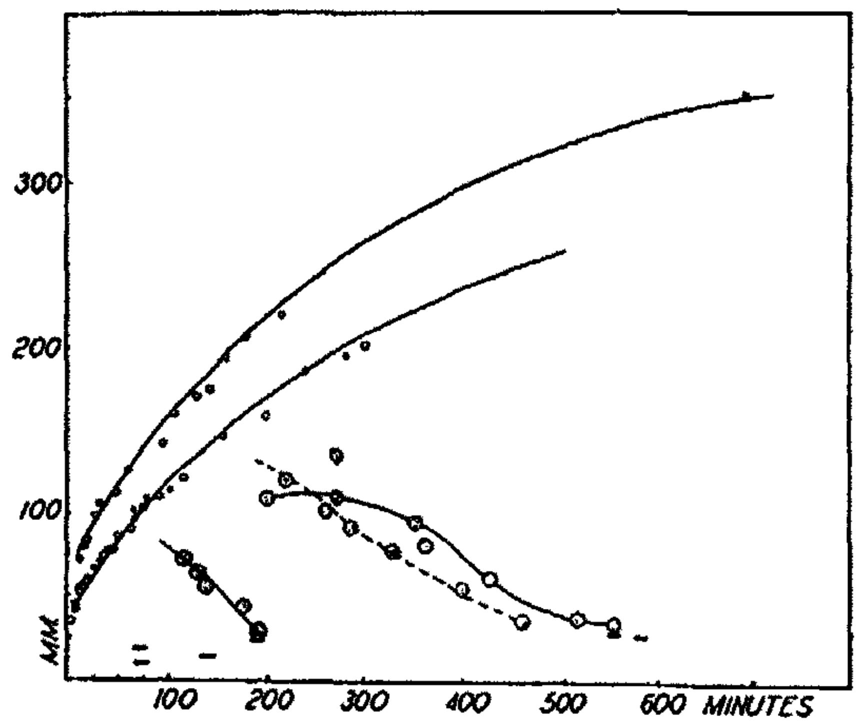
It should be noticed that there was sufficient cloudy precipitate to form only one globoid in one of the cases which we have used for illustration (Fig. 101 d).

In the system .5N $Pb(NO_3)_2$ diffusing into .05N to .0031N NaCl in gelatin again the reaction product appears as a white cloud in advance of the periodic system precipitate. This cloud is itself periodic and gives rise to a periodic grouping of crystalline globoids toward which the cloudy precipitate moves forward, but chiefly backward (Figs. 105, 106).

An excellent example of the backward diffusion of the reaction product was seen in the system .2N Na_2HPO_4 into .5 to 0.16N $CaCl_2$ in test tubes in which the internal reagent was invaded by fungi. These formed small spherical colonies which interfered with the direction of diffusion in such a way that the disc was deformed (Figs. 42, 43, 45). It would be impossible to explain these curious forms except on the assumption of a backward diffusing substance, in this case $NaCl.CaCl_2$.

The system 2% $Pb(NO_3)_2$ diffusing into 4% KI in 6% gelatin supplies us with the best illustration we know of to demonstrate the backward diffusion of the reaction product. For this reason we made a motion picture record on standard size film, the pictures being spaced four minutes apart. In this case, the like of which rarely occurs, the reaction product occurs in an exceedingly fine colloidal cloud in which, due to the smallness of the particles, there is no hindrance to diffusion (Figs. 114-115).

The final form of the periodic precipitate is a banding of white precipitate which is oxyiodide of lead, but the primary reaction product which is formed far in advance is the yellow oxide PbI_2. When we plot the course of advance of the yellow cloud from data obtained by measuring the photographic images, we obtain a curve, the shape of which is that of a diffusion curve. (Text fig. 4). For two cases we obtained quite the same values. In both curves, however, there occur certain deviations which indicate that the diffusion occurs periodically and these deviations are to be found at the time when we observe the impact of the curve of the backward diffusing cloud.



TEXT FIG. 4

Plotted from measurements of a motion picture, a few frames of which are shown in Figs. 114, 115. Large stippled circles represent the clouds of backward-moving complex. Short horizontal lines represent periodic bands. Upper two curves, the advancing heads of two columns.

Under observation we can see the formation of a brilliant cloud at the forward end of the diffusion column which at length begins to move backward to the outer end of the column and there disappears, but *at precisely this time a band of precipitate is formed.* We have plotted the movement of two such clouds in the accompanying diagram and in spite of obvious difficulties of measurement there is no doubt of the general correctness of the data. We observe that the first cloud moved more quickly than the second, but both were observed to end in the formation of the ring. It is evident that if the whole story were similarly plotted we should have a cloud for each band formed, but that each earlier cloud would be represented by a steeper curve than that of the next following.

If the white periodic precipitate is laid down in this way we must believe that the yellow precipitate is laid down in similar fashion. We must further infer that the yellow product here is $KI.PbI_2$ which diffuses backward against the higher concentration of the entering reagent. At the point where both will be sufficiently concentrated a colloidal precipitate will occur. The above mentioned relations are represented diagrammatically in text Fig. 5.

XI. Adsorption.

In the system 1.25 N $AgNO_3$ diffusing into .1 to .0062N $K_2Cr_2O_7$ in gelatin the following takes place. First, there is a periodic precipitation of Ag-phosphate in fine white bands. On this a red silver chromate (a basic complex) is strongly adsorbed periodically. If the process is followed microscopically the gradual darkening of the particles constituting the Ag-phosphate bands can be easily and surely followed. In the interspaces there will be a lower concentration of the entering reagent and here the yellow salt appears so that in time the white phosphate rings not already darkened become yellow since adsorption here occurs also.

The periodicity of the Ag-salt appears to be exactly parallel to that of the phosphate, or harmonic with it, since the identity of the Ag bands (at first sets of discrete rings) with the phosphate bands is at first quite evident. As the precipitation column lengthens, however, and the phosphate bands separate, and become irregular, or may even fail to form, the Ag bands then become displaced or vague, consisting of clouds or scattered granules, a condition typical of this system in agar. We must infer, therefore, that the apparent harmonical relation is due to the very strong adsorption of the Ag salt on the phosphate. The phosphate salt is in its turn adsorbed on the glass wall and the earliest deposition of the red salt is always where the phosphate is strongly adsorbed on the glass wall and hence we may obtain groups of red rings (Figs. 74, 75, 76a, 79, 103, 104).

Experiments with chromates are very difficult to explain chemically because the salts are complex and not well understood. We know merely that the yellow salt is the chromate and that the red salts are different intermediate stages between the complexes of the basic salt of the metal and the chromate. These complexes will have different electrical charges and different surface properties and therefore we cannot be surprised if we find different adsorption relations among these salts. And, as we have already found that the periodicity is induced largely by the adsorption relations among these salts, we have met with different periodicities in the same system with different kinds of chromates since their adsorption relations are different.

Concerning the system silver dichromate-gelatin, Hedges raises the question as to the nature of the "pale yellow fringe," this according to Friend being silver chromate and Reinhard sodium chloride. But Hedges got the same results even after the supposed chlorides had been precipitated by the addition of silver nitrate and further that the addition of a drop of silver nitrate to the yellow fringe induced an independent ring system. He regards the first product of the reaction to be silver dichromate which is afterwards coagulated into rings in excess of the indiffusing silver nitrate. But we have shown that clear cut rings occur by adsorption of the reaction product on rings already present, viz. phosphate rings (Morse and Pierce, 1903). We have also learned that the silver chloride banding has a different periodicity from that of the supposed silver chromate system, even in the presence of sodium chloride. The silver dichromate appears to be negatively adsorbed on silver chloride but positively adsorbed on phosphate. We would also say that the yellow fringe contains chromate and a complex of chromate and KNO_3.

Here we quote P. B. Ganguly (1927) as pertinent. It is well known that the charge on a colloid particle can be traced in many cases to the presence of adsorbed ions. In certain cases by the introduction of suitable ions the sign of the charge can be changed at will. Lottermoser obtained silver halide solutions which were positively or negatively charged according as an excess of silver salts or of halide salts was used. Thus the sign of the charge was directly dependent on the nature of the common ion which was present in excess and was capable of being adsorbed by the precipitate.

XII. Recrystallization and Chemical Transformations.

In the system $K_2Cr_2O_7$ diffusing into $AgNO_3$ in gelatin we have observed that the character of the salt formed depends on the concentration of the entering reagent. At first when the concentration of the entering reagent is low and the Ag salt is excess, only a red salt is formed, and as the concentration of the K salt increases with further diffusion the red salt disappears and recrystallizes as a yellow salt at some distance away, the red salt evaporating and condensing as yellow and partly recrystallizing *in situ*. Thus is given rise to a very complicated pattern (Figs. 107, 108). In the inverse case ($AgNO_3$ into $K_2Cr_2O_7$ in gelatin) at the mouth of the tube the salt formed is red, the yellow salts appearing further in the tube where the concentration of K salts is higher; and in the gelatin, since the yellow salt is adsorbed on the phosphate it is sharply periodic.

But if agar is used as a medium (Ag diffusing into K) the yellow salt is not sharply if at all periodic, while the red salt is periodic, sometimes regularly, sometimes irregularly. Since the red salt is adsorbed on the yellow and since the nuclei formed are irregular in size, there is a transformation of the red salt from a finely colloidal to a coarsely crystalline condition (Fig. 109). Inverted, (viz. K diffusing into Ag in agar) the advancing zone is marked by disappearance of the darkish brown color in the medium (reduction of silver) indicating the head of the diffusion column. Near to the point of entrance there appears a dark membranous colloidal precipitate in rounded or irregular (comet-shaped) masses with vague, if any, periodicity accompanied in higher concentrations by beautiful red crystals. The advance of high concentration of the entering reagent is accompanied by chemical change of the dark red to a pale (white?) precipitate, also with vague periodicity. At low concentrations of the internal reagent, the time factor becomes such that the red salt is wholly adsorbed on the glass wall (very like Figs. 60, 61).

When starch is the medium (K diffusing into Ag), coarse dark red irregular crystalline masses with metallic lustre appear. These are semi-permeable (Traube) membranes which grow into curious forms (see above). As the entering reagent increases in concentration the dark red salt disappears and is in part recrystallized *in situ*, producing pseudomorphs of the original precipitate, and in part is sublimated and deposited elsewhere (Figs. 60-64).

The inverse (Ag diffusing into K) appears to be negative, the red salt appearing at once, and no change occurs.

In $Pb(NO_3)_2$ into $K_2Cr_2O_7$ in gelatin we find the same general conditions resulting as in the case of the Ag corresponding system, since these chromates make quite analogous chemical complexes. Here no phosphate rings occur and the chromates are positively adsorbed on the glass wall. Since we get two systems of periodicity, one near the mouth of the tube and the other deeply removed therefrom, we must infer that we are dealing with two different chromates. In the case of higher concentrations two different sets of bands are laid down simultaneously (Fig. 111 a and b).

In the system $HgCl_2$ into KI in gelatin, the precipitate is laid down as fine red crystals which give way deeper in the tube to yellow where the KI is in excess. In both gelatin and starch there are always two modifications of the salt, yellow and red, and these may be laid down periodically. The red precipitate occurs where the Hg concentration is higher (Figs. 27, 28, 29).

In the system $Pb(NO_3)_2$ into KI in gelatin the primary precipitate occurs as a yellow salt in a finely dispersed colloidal state. As the concentration of $Pb(NO_3)_2$ increases, the yellow salt PbI_2 is changed into a basic lead iodide. We have already described the process above.

At low concentrations of KI only white bands are formed, i.e., when $Pb(NO_3)_2$ is in high excess. If the concentrations are nearly the same or if KI is in excess, the yellow precipitate is laid down to be changed to white as the concentration of the $Pb(NO_3)_2$ increases (Figs. 114, 115).

In the systems $(NH_4)_2HPO_4$ into $CaCl_2$ and Na_2HPO_4 into $CaCl_2$ at high concentrations of the internal reagent, at first crystalline spheroids are formed with little if any periodicity. At the same time white rings and discs appear. With time the crystals disappear and are recrystallized as material added to the rings. In low concentrations only rings and discs appear and no crystals. (Figs. 67, 68, 83, 84).

When $Pb(NO_3)_2$ diffuses into NaCl in water a fine colloidal precipitate is first formed which quickly condenses by evaporation and recrystallization into relatively large crystals (Fig. 110). In gelatin crystals appear only in the form of spheroids.

XIII. Density of the Initial Precipitate (plug) and its Permeability.

According to Bradford the interaction of an aqueous reagent on a gel containing a suitable solute will create a solid boundary surface between them and thus initiate periodicity. This however is only a special case and we have found that when the initial precipitate is discontinuous it is equally possible to obtain periodic precipitation.

It is generally to be observed in almost all, if not all, systems that the higher the concentration of the interacting reagent the slower the diffusion of the entering reagent and the slower therefore the growth of the precipitation column. The slower the diffusion also the closer together are the periodic bands and the more regular the form of the precipitate laid down. (Fig. 74 *etc.*).

XIV. Absence of Periodicity, Apparent and Real.

We have already committed ourselves to the view that the problem of periodicity involves also the problem of non-periodicity. Not seldom in the literature authors express the opinion that one medium or another is not "good" for the production of periodic precipitation. We have in the same breath to explain the absence as well as the presence of periodicity. That purer gels are less suitable for the production of rings because of the absence of salts, as suggested by Doyle and Ryan (1929), is well known, but we have shown that the difference can be explained by adsorption.

Fischer and McLaughlin (1922) say that periodic precipitation is possible only in those cases where a semi-permeable membrane is formed, which later becomes permeable. We have found that it can occur without such a membrane, as in the cases where only widely separated crystals constitute the initial precipitation and where only rings on the glass wall are formed accompanied or not by discs, which in any event only partially block the path. The same can be said of the theory of Traube and Takehara (1924). The non-appearance of periodicity or the inappreciable character of it may not actually correspond to the objective fact.

We have seen many cases where a very slight amount of periodicity, quite evident to the eye, might lead to the conviction that everywhere else periodicity is present but inappreciable to the senses. And also in the same concentrations of reagents and under precisely similar, or even identical, conditions periodicity occurs in one tube and not in another, or in one part of a tube and not in another. (Fig. 20). We are therefore led to predicate non-periodicity as the logical continuum of periodicity. We believe we are right in regarding certain cases as non-periodic.

Case. $Ag(NO_3)_2$ into $K_2Cr_2O_7$ in starch. In six tubes coarse crystalline precipitate occurred non-periodically, except in a region in one of them where the crystals were smaller, where distinct banding occurred (Fig. 20).

Case. 2% $CaCl_2$ into ammonium oxalate and inverse. In the former a uniformly distributed precipitate of plaque-shaped crystals without periodicity (Figs. 72, 54, 55).

Apparent absence of periodicity may, on microscopic examination, turn out not to be objectively non-periodic (Stansfield, 1917). Case. $Pb(NO_3)_2$ diffusing into $K_2Cr_2O_7$ in gelatin in tubes 3 millimeteres in diameter revealed no periodicity to the eye, even with a strong lens. On examining with a microscope a section from the surface at the open end of the tube we found a sharply defined very fine periodicity (Fig. 112). Much the same was seen in $HgCl_2$ into KI in agar. In gelatin no periodicity was observed (Figs. 29, 30). Case. $K_2Cr_2O_7$ into $Pb(NO_3)_2$ in agar in capillary tubes. No concentration showed any visible periodicity. Nevertheless when we examined all the tubes microscopically we found a very fine periodic banding in two concentrations (.05N and .025N) (Fig. 113).

We are convinced that many observers who have failed to find periodicity have done so because they have merely failed to see it. Case. $Pb(NO_3)_2$ into

$K_2Cr_2O_7$ in agar. At concentrations .5N into .0062N. One tube of a set of six tubes was accidentally plugged by an air bubble which effectively lowered the diffusion rate of the entering reagent. For a short space beyond the bubble the precipitation was uniform but at a certain point it changed abruptly into a distinctly periodic condition. In all the other tubes periodicity did not begin for a long time later (Fig. 57). In such cases we have critical conditions in which a slight difference of any factors which influence periodicity in one way or another many hinder or effect it.

XV. Inversion of the Reaction.

Cases (a) $CaCl_2$ diffusing into ammonium oxalate and (b) its inverse. In case (a) we obtained a very fine colloidal precipitate, but no periodicity in either case. (Figs. 116, 117).

Cases (a) NH_4OH diffusing into $MgCl_2$ in gelatin and (b) its inverse. In one case (a) we obtained periodicity, in the other (b) little or no periodicity,[1] in test tubes. In capillary tubes we obtained periodicity in both cases—another proof that at critical points slight differences may determine the incidence of periodicity (Figs. 1-4).

Cases (a) $AgNO_3$ diffusing into K_2CrO_4 in gelatin and (b) its inverse. Periodicity occurred in both cases but in one case (b) there were no phosphate rings and the precipitate was very strongly adsorbed on the glass wall, while in case (a) phosphate rings occurred and the Ag-chromate was adsorbed on the Ag-phosphate precipitate, never on the glass wall. We therefore see that in the two cases the properties of the medium are different (Figs. 76a, 77). We have observed similar differences in many cases. If we change the salt in the gelatin we may get a medium with opposite (electrolyte) properties with respect to the precipitate.

Bradford states his belief that the occurrence or non-occurrence of bands of the same substance in different gels is due to the influence of the reaction medium on the dispersity of the precipitate. But we think it is due to the adsorption relations between the precipitate and the gel or the glass wall.

Fricke (1923) very pertinently remarks that the various factors of adsorption, coagulation of electrolytes, influence of solubility of the precipitate, etc. regarded as fundamental by other authors, are not so, but on the contrary are not essential—"wesentlich." The gel as a medium has, according to him, the chief rôle of furnishing a steady diffusion current and prevents convection streams.

Discussion

In the large majority of cases which have been studied periodicity occurs. In exceptional cases it does not occur. We shall endeavor first to formulate a theory to account for periodicity.

In the practice of inorganic chemistry the reactions which are allowed to take place do so in a pure medium, pure water for the most part, a medium which is continuous and presents no complications, such as surface phe-

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[1] As pointed out above, in a repeat of these experiments we obtained a clear cut band in one concentration. (Fig. 2a Plate IX.)

nomena. Biological reactions and those in which we meet with periodicity are quite different systems. First, they take place under circumstances where there are great mixtures of substances. Second, these take place in a medium which has viscosity and high concentrations and where the diffusion of reagents and reaction products proceeds very slowly as compared with that in a watery or gaseous medium. Third, they take place on microstructures, in capillary spaces characterized by the presence of many interfaces where physical forces complicate the chemical reactions. From these three considerations we get divergencies in the solubility of the precipitates e.g., we obtain crystalline modifications which we never get in a watery medium at corresponding concentrations of the precipitate. Further, we get different dimensions of crystals ranging from the finest colloidal suspension to the coarsest crystalline or spherocrystalline product. And still again, the time factor is sufficiently long for reactions to take place for which normally there is insufficient time.

We must also take account of the fact that surfaces in capillary spaces, e.g. in fine capillary tubes, between sheets of glass, etc., can act so strongly by way of adsorption that the intermolecular forces are more or less overcome or nullified. In those cases where a soluble reaction product remains in the vicinity of the place of reaction such a high concentration may occur that in many cases complex salts are formed.

We would suppose that every biological reaction should be periodic, since in the great majority of cases in our experiment we procured periodicity; but we must not overlook the important fact that the systems in which we obtain periodicity are such in which diffusion streams move along a single path in a single direction or the reverse, whereas in biological materials the diffusion currents may, and probably do, move in all directions, or at least in many, certainly very rarely in one direction alone. We admit that it is quite thinkable that the conditions for unidirectional diffusion may be supplied in some cases, as suggested, for example, by the transverse striping in some elongate plant leaves. Even the stripes of the zebra, a favorite example, might conceivably result from unidirectional diffusion of pigment or pigment-forming substance in the ectoderm of the blastodisc but, on the other hand, nobody yet knows that this is the case. Again, we can obtain periodical precipitation in plant structures (Lloyd and Moravek, Rouppert) but no one can say when transverse markings are met with, either in leaves or trichomes, etc., in nature that they are actually produced in this way. It is our opinion quite idle to cite the annual rings of trees, in the roots, etc. of plants (Beta, etc.) and many other oft-quoted examples, and we dismiss such loose analogies at once from consideration. The much argued case of agate may be in better case.

In a system in which a periodic precipitate may occur, a first membrane must be laid down. In this membrane two kinds of ions are precipitated and at the same moment there must be close to the membrane a very high concentration of the reaction product, which now diffuses in both directions. (It at the same time increases the osmotic value of the medium, and this may therefore swell.) That part of the reaction product which diffuses toward the internal reagent causes, when the concentration becomes high enough, the formation of a complex salt.

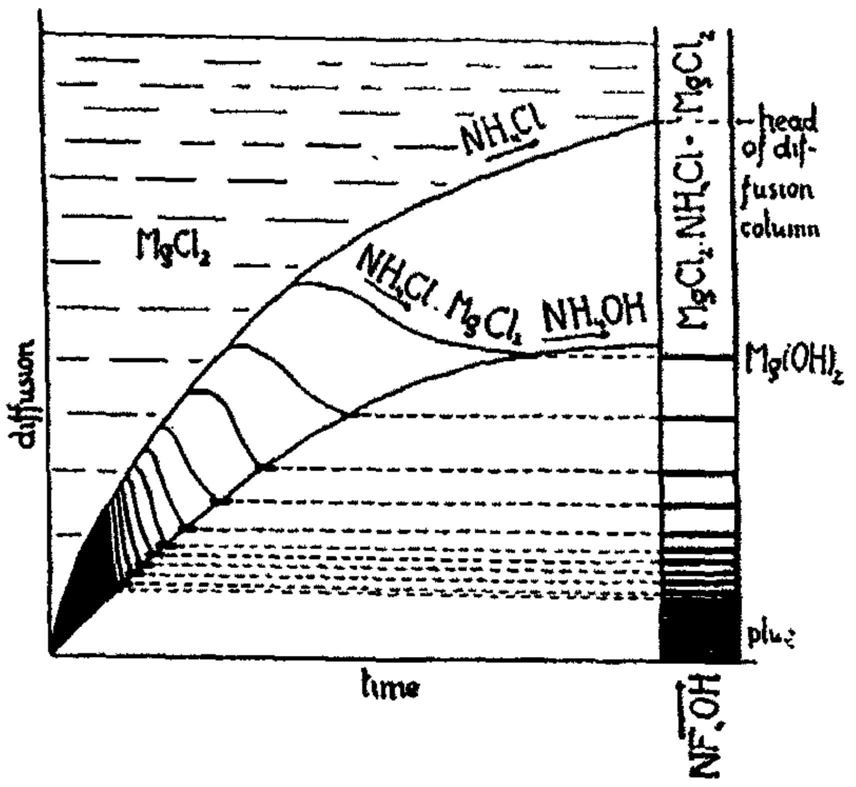
The space in the diffusion column expressed as the difference between the curves of the diffusion head and ring formation carefully worked out by Jablczynski (1926) for a number of systems is the space in which the complex which we postulate is formed and in which it diffuses toward and to meet the entering reagent. (text Fig. 2).

It will be apparent that various factors, essentially of secondary importance (adsorption, concentration and nature of medium, nature of reacting salts, viscosity, influence of foreign ions, etc.), may in special cases play so large a part that the essential factor, the backward diffusion of the complex, may be obscured and therefore we meet with theories which appear to explain special cases but which fail when they are applied to the entire known series of cases. Such complexes are frequent and well known in the field of inorganic chemistry, but sometimes are not known and we must suppose that the medium (respectively the surfaces) permit such to occur. When there has been reached a sufficiently high concentration of the reaction product for the formation of such a complex with the internal reagent to be achieved, the latter (the internal reagent) will diffuse toward it from both directions. Having once formed, the complex itself will begin to diffuse in both directions. In the meantime the ion of the entering salt which forms the insoluble precipitate diffuses through the initial membrane or plug, but meets with none or, at any rate, a much reduced number of ions of the internal reagent with which it reacts and therefore must move some distance before it meets that part of the complex which is diffusing backwards. It reacts also with more or less of the internal reagent on its way and in this matter also arises more or less precipitate in the interspace, which is rarely quite free from such.

When the complex and the primary reacting entering ion meet, oversaturation will then occur and precipitation will begin. If in the special case of tubes, etc. the product is adsorbed on the glass wall, a sharp ring will be formed, followed by a disc which is always somewhat further in the tube than its corresponding ring. The saturn structure is thus accounted for. If the product is not adsorbed on the glass wall a more or less diffuse band occurs. Irregularities consisting of interruptions in bands on the glass wall, producing sometimes spirals, sometimes other irregularities, are all caused by chance interruptions in diffusion. We know positively that a small bubble can cause the appearance of spirals in place of circular bands.

Each time this occurs the reacting ions of the internal reagent will be diluted more and more and the external reagent must then diffuse further and further in order to meet concentrations suitable for precipitation and hence the bands will be formed at increasing distances. The complex may be colorless or colored, or it may be an invisible or a visible colloidal cloud. In the case of $Pb(NO_3)_2$ diffusing into KI in gelatin we have an example of the last. It is evident that the above process demands suitable relative concentrations of both of the entering ions. If the difference of concentration is too small the two ions will move through the plug or initial membrane at approximately equal rates and a continuous precipitate will be formed. If there is a large difference of concentration of the entering ions periodic precipitation will occur. Such a difference occurs when one ion is used up in the reaction, setting the other free. The difference in concentration of the entering ions will be greater the lower the concentration of the entering reagent and the sooner will periodicity occur. (Text Fig. 5).

We have been led to formulate the foregoing theory from our actual observation of cases in which a movement backward of precipitate to form a ring-and-disc could be observed and such backward movement we regard as an incontrovertible fact. Precisely what complexes will occur in any particular case is of secondary importance. (Figs. 114, 115, text Fig. 4).



TEXT FIG. 5

Diagrammatic scheme to show the backward diffusion of a complex formed near the head of the diffusion column to form a band of precipitate where the entering reagent is met with.

We are equally of the opinion that in some cases no periodicity occurs. The following conditions are possible:

1. The initial precipitate is permeable to the ion which does not enter into the reaction. If, however, the ion does not react with the internal reagent to form a complex the equilibrium is not disturbed, no backward diffusing substance is formed and no periodicity occurs.

2. The initial precipitate is permeable to both ions, but if these are in too high concentration the ratio of the ions of the entering reagent will be only slightly disturbed for some time dependent on the concentration and the precipitate will be continuous.

3. The initial precipitate, that is the membrane first formed, is not at all, or only very slightly, permeable for the entering ion which does not enter into the reaction. If the former, only a membrane will be formed; if the latter, a column of precipitate is built up without periodicity.

Note: The work reported in this paper was done by the authors jointly in the Botanical Laboratory of McGill University, Montreal, and, in part, in co-operation at Masaryk University, Brno, C.S.R. During the period the junior author was Research Associate of the Department of Botany, McGill University. The senior author spent six weeks in the summer of 1930 at Masaryk University. The expense was partly met by a grant from the Cooper Fund, Medical Faculty, McGill University, for which grateful acknowledgment is here made.

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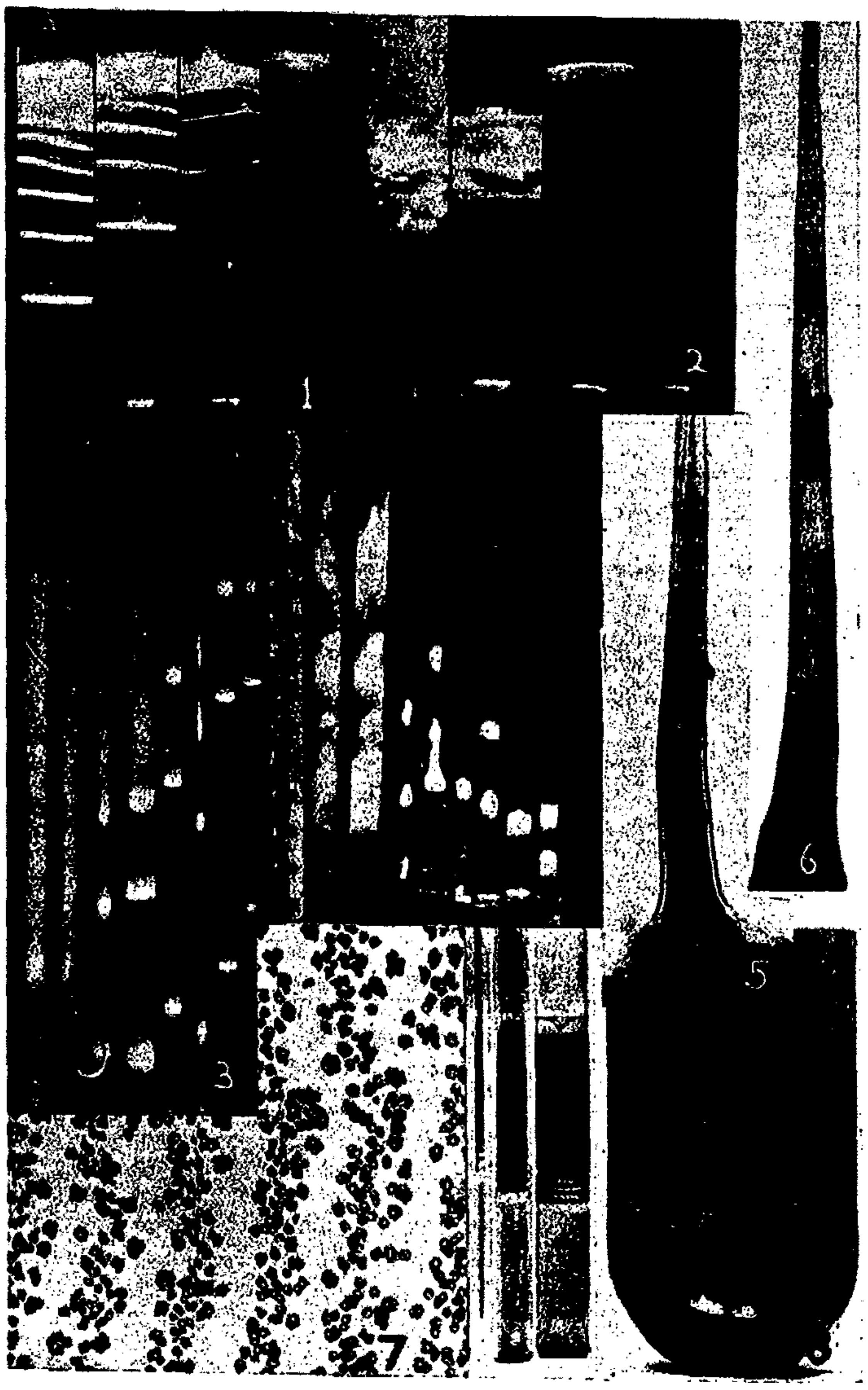


PLATE I

References to the text are given in brackets

1. 12N, (on the left) 6N, 3N and 1.5N NH_4OH diffusing into 1N $MgCl_2$ + 8% gelatin in test tubes. (p. 1512, 1530, 1543)
2. Saturated solution .5, (on the left) .25 and .125 $MgCl_2$ diffusing into 1N NH_4OH in 8% gelatin in test tubes. (p. 1513, 1543)
2a. See plate IX. .5 saturated solution MgCl diffusing into 1N NH_4OH in gelatin. A perfect zone formed. (p. 1513, 1524)
3. Same as (1) above, but in capillary tubes. Entrance to tubes above; highest concentration on the left. (p. 1512, 1530, 1543)
4. Same as (2) above, but in capillary tubes. Entrance to tubes below; highest concentration on the left. (p. 1513, 1543)
5. Trichome of *Begonia* sp. Ammonium sulphide diffusing into cobalt-sodium hexanitrite. (p. 1513)
6. Trichome of *Laportea canadensis* similarly treated. (p. 1513)
7. 4% KI diffusing into 1% $Pb(NO_3)_2$ in a capillary space between glass plates. (p. 1513, 1516)
8. Effect of difference in diameter of the glass tubes, viz. 1, 3, 10 and 50 millimeters. 20% NH_3 diffusing into 2N $CoCl_2$ in 10% gelatin. (p. 1513)

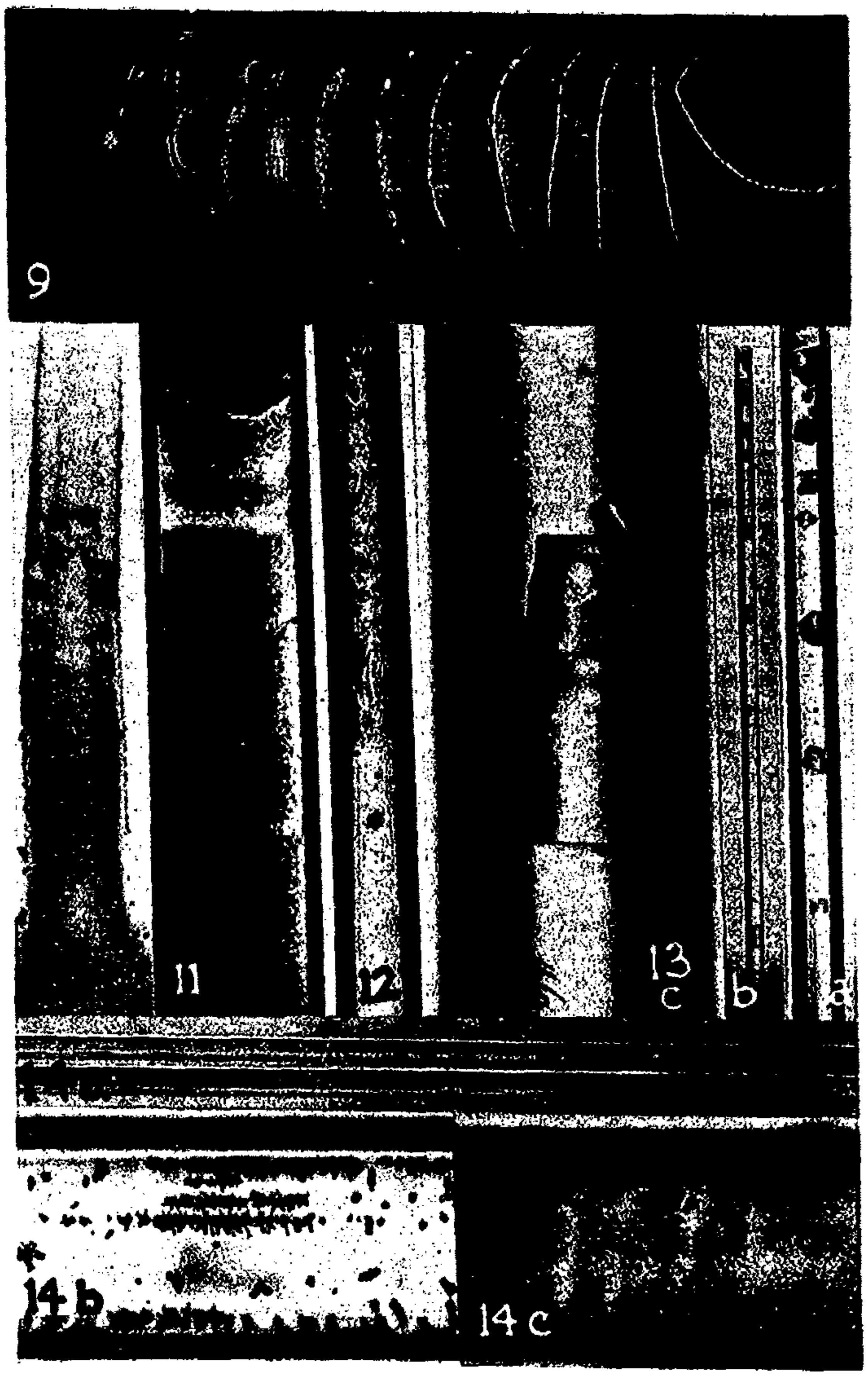


PLATE II

9. .2N $Pb(NO_3)_2$ diffusing into .1N $K_2Cr_2O_7$ in a very thin capillary space. (p. 1513)
10. Trichome of *Begonia* sp. as in fig. 5. (p. 1513)
11. HCl (gas) diffusing into NH_4OH (gas) in capillary tube. (p. 1515)
12. NH_4OH (gas) diffusing into HCl (gas) in capillary tube. (p. 1515)
13. HCl (concentrated) diffusing into 30% NaCl in capillary tube. (a) earlier, (b) later, (c) a single crystal. Tube .17 millimeter in diameter. (p. 1516)
14. Na_2CO_3 diffusing into .25N $AgNO_3$ in H_2O; capillary tube .2 mm. in diameter. (a) final condition, (b) detail of (a), (c) early rings. (p. 1516, 1519)

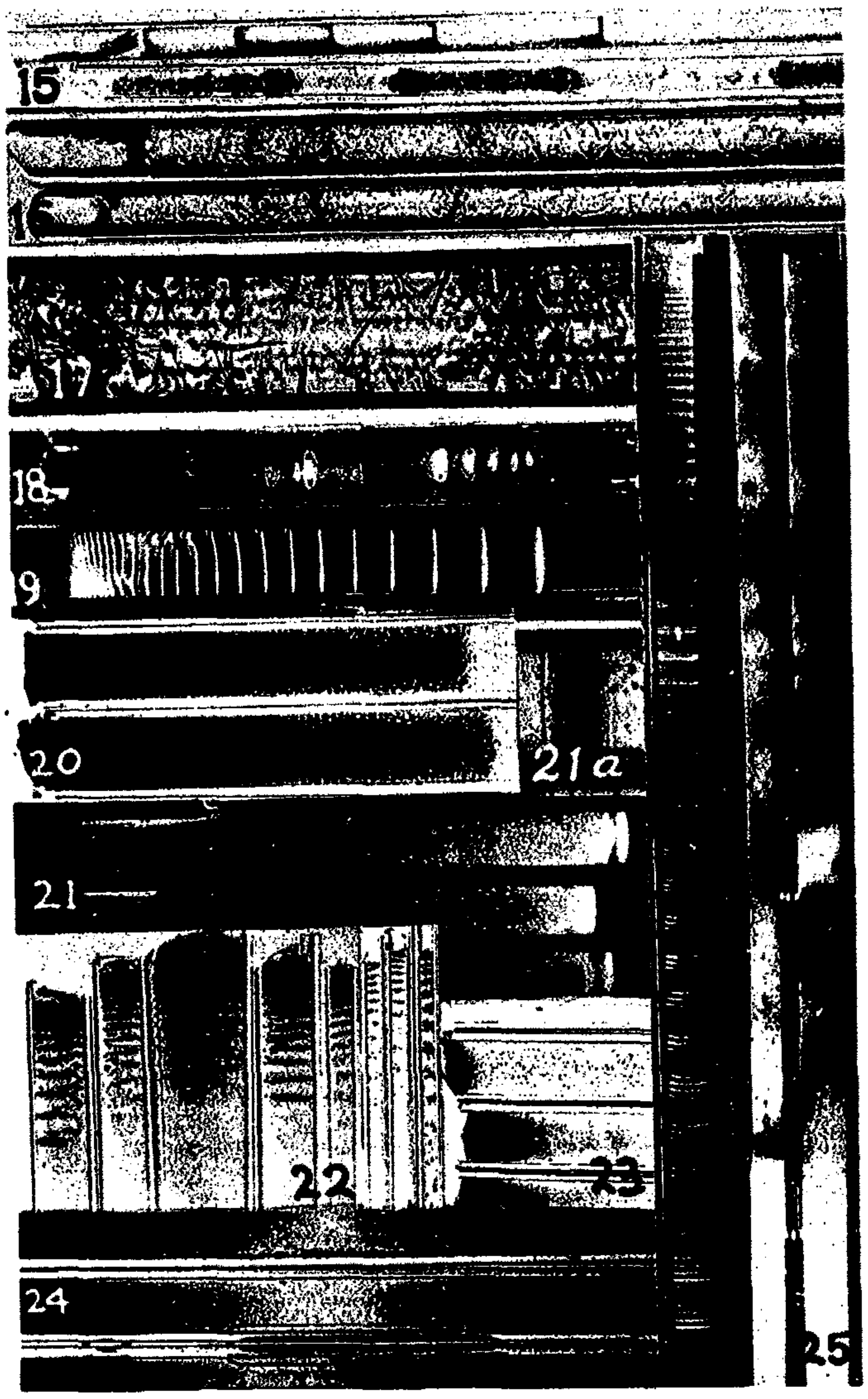


Plate III

15. 1N NaCl diffusing into .1N $AgNO_3$ in capillary tube .3 millimeter in diameter. (p. 1516, 1524)
16. 1N $BaCl_2$ diffusing into 1N K_2SO_4 in capillary tubes .3 millimeter in diameter. (p. 1516)
17. Detail of fig. 16, showing two zones. (p. 1516, 1524)
18. .25N $Pb(NO_3)_2$ diffusing into .1N KI in starch. (p. 1517)
19. The same as fig. 18, but in agar. (p. 1517, 1523)
20. $AgNO_3$ diffusing into $K_2Cr_2O_7$ in starch. (p. 1517, 1542)
21. The same as in figs. 18 and 22, but in gelatin. Column yellow, discs white. (p. 1517)
21a. The same. A single band showing the white colloidal precipitate imbedded in a vitreous mass. (p. 1517)
22. The same as fig. 18. The five left hand tubes, corn starch paste; the three right, potato starch. (p. 1516-7, 1523)
23. .5N $Pb(NO_3)_2$ diffusing into .0062 $K_2Cr_2O_7$, in starch (above) and agar. (p. 1518)
24. .5N K_2CrO_4 diffusing into .1N – .025N $Pb(NO_3)_2$ in starch. (p. 1518, 1529)
25. .5N $AgNO_3$ diffusing into 2% $K_2Cr_2O_7$ in gelatin (right) and agar. The dark precipitate is red, the light pale yellow. (p. 1517, 1518).

PLATE IV

26. $AgNO_3$ diffusing into .1N-.0031N $K_2Cr_2O_7$ in agar (nos. 1-11 from bottom) and in starch (nos. 2-12). The lowest three tubes were photographed by reflected light, the others by transmitted light. (p. 1517, 1528)

27. .1 saturated solution $HgCl_2$ diffusing into .1N KI in starch. (p. 1518, 1541)

28. The same tube, later. The pale band across the middle of the tube is an accidental reflection. (p. 1518, 1541).

29. .25 $HgCl_2$ diffusing into .1N KI in agar. (p. 1518, 1541-2)

30. The same as fig. 29, but in gelatin. (p. 1518, 1542)

31. .5N $Pb(NO_3)_2$ diffusing into .05-.025N K_2CrO_4 in starch. (p. 1518, 1529)

32. The same as fig. 31, but in agar. (See also figs. 51, 52, 57). (p. 1518)

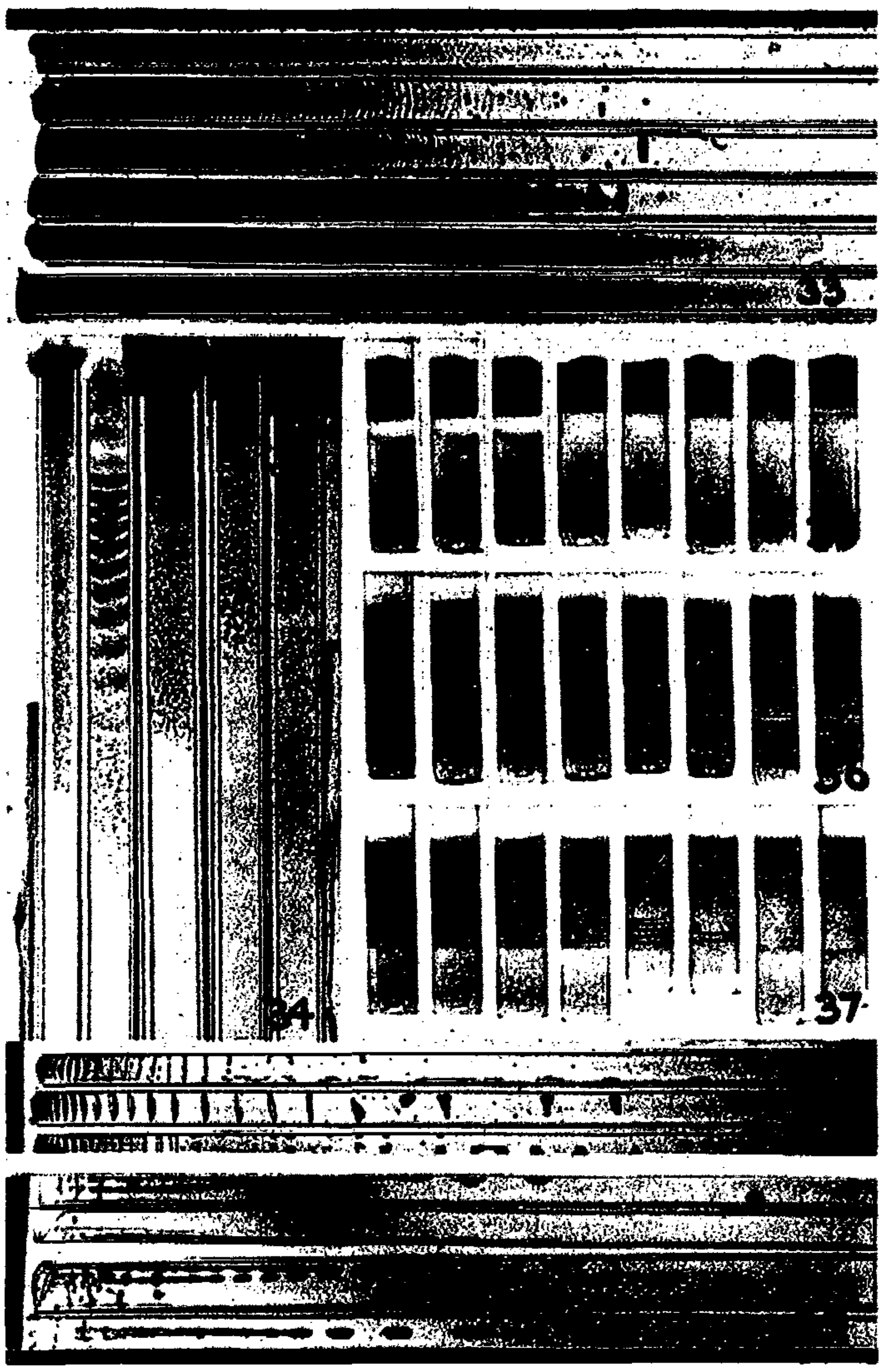


PLATE V

33. .5N $Pb(NO_3)_2$ diffusing into .1N-.0031N K_2CrO_4 in gelatin. The highest concentration below. (p. 1518, 1526, 1528)

34. .25N $Pb(NO_3)_2$ diffusing into .1-.006N $K_2Cr_2O_7$ in gelatin. The highest concentration to the right. (p. 1518, 1528)

35. 20% NH_4OH diffusing into 2N $CoCl_2$ in 5% gelatin (tubes 1-3 from the left), in 7% gelatin (tubes 4 and 5) and in 15% gelatin (tubes 6-8). Gelatin dissolved at 50°C. After nine days. (p. 1515, 1518)

36. As in fig. 35 but the gelatin (10%) was heated variously: tubes 1 and 2 (from the left) heated in water bath till dissolved; tubes 3 and 4 as above, but kept at 80°C. for 30 seconds; tubes 5 and 6 kept at 100°C. for 30 seconds; tubes 7 and 8 kept at 100°C. for two hours. Photo after 16 days. (p. 1518)

37. As in fig. 35, but in various concentrations of gelatin:

Tube no. 1 (from the left)	15%	gelatin
2	12%	"
3	11%	"
4	10%	"
5	9%	"
6	7%	"
7	5%	"
8	3%	"

(p. 1519)

38. .5N K_2CrO_4 diffusing into .025N $AgNO_3$ in gelatin. (p. 1520)

39. The same as fig. 38, but .0125N $AgNO_3$. (p. 1520)

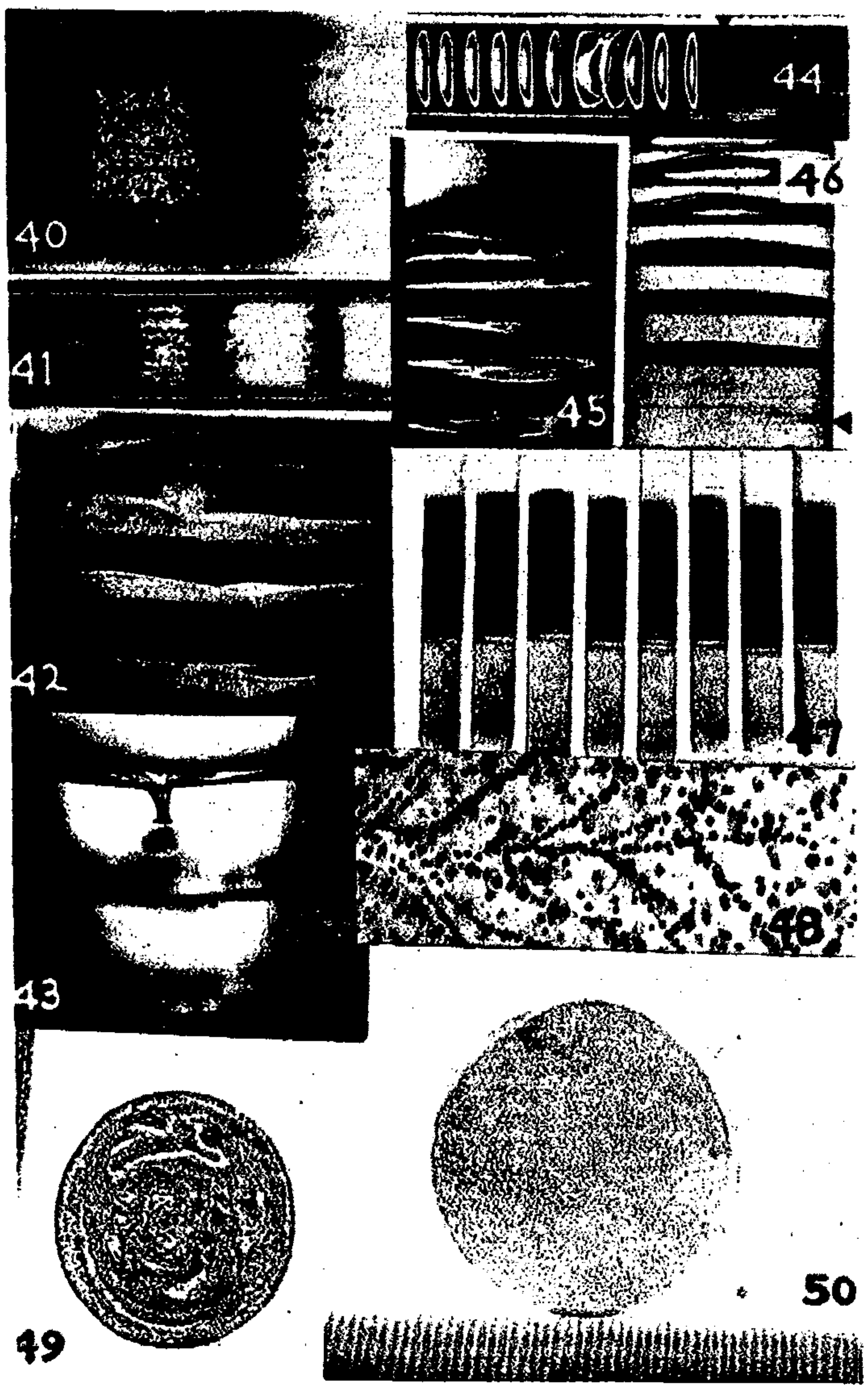


PLATE VI

40. 2% $K_2Cr_2O_7$ diffusing into .25N $AgNO_3$ in gelatin. (p. 1520)
41. The same, at a later stage, to show the disc. (p. 1520)
42. .2N Na_2HPO_4 diffusing into .0062N $CaCl_2$ in gelatin. Reflected light. (p. 1522, 1537)
43. The same. Detail, transmitted light. (p. 1522, 1537)
44. NH_4OH diffusing into $CoCl_2$. "Saturn structure." The ring is formed on the glass wall earlier than the disc (indicated by the black triangle) (p. 1520)
45. The same as fig. 42, to show rings on glass wall without discs being formed. (p. 1520, 1537)
46. NH_4OH diffusing into $CoCl_2$. "Saturn structure." The ring on the glass wall is nearer the mouth of the tube than the disc. A new ring is being formed, as in fig. 44. (p. 1520)
47. 20% NH_4OH diffusing into 2N $CoCl_2 .6 H_2O$ in 10% gelatin. Tube no. 1 (left) silica; no. 2, soft glass; no. 3, hard Jena glass; no. 4, tube lined with caoutchouc; no. 5, lined with collodium; no. 6, lined with coco butter; no. 7, with paraffin; no. 8, with lecithin. (p. 1521)
48. .25N $AgNO_3$ diffusing into .25N NaCl in gelatin. (p. 1521)
49. .5N $Pb(NO_3)_2$ diffusing into .1N K_2CrO_4 in agar. Transverse section, detail of fig. 51 and 52. (p. 1522, 1528)
50. The same as fig. 49, from a tube in which the periodicity was regular, as seen at the bottom of the figure (p. 1522, 1528)

PLATE VII

51. .5N $Pb(NO_3)_2$ diffusing into .1N K_2CrO_4 in agar. (p. 1518, 1522, 1528)

52. The same as fig. 51. Detail—a portion of fig. 51 sectioned and more highly magnified. (p. 1518, 1522, 1528)

53. NH_4OH diffusing into $CoCl_2$ in gelatin mixed with
    (a) distilled water (tube no. 1 on the extreme left)
    (b) 1% sodium oleate
    (c) 0.1% sodium oleate (tube 3); saturated solution capryl alcohol (tube 4): .1 saturated solution capryl alcohol (tube 5); 0.3% cholesterol (tube 6); 0.03% cholesterol (tube 7); 0.003% cholesterol (tube 8). (p. 1523)

54. 2% ammonium oxalate diffusing into 2% $CaCl_2$ in gelatin. (p. 1523, 1530, 1542)

55. The same, at lower magnification. (p. 1525, 1530, 1542)

56. .5N K_2CrO_4 diffusing into .1N-.0062N $AgNO_3$ in starch. The highest concentration below. (p. 1527)

57. .5N $Pb(NO_3)_2$ diffusing into .0062N K_2CrO_4 in agar. Diffusion hindered by a bubble (the black mass at the left). (p. 1518, 1526, 1543)

58. 1N $Pb(NO_3)_2$ diffusing into 1N NaCl in gelatin. (p. 1524)

59. The same. Detail, between crossed Nicols. (p. 1524)

PLATE VIII

60. .5N $K_2Cr_2O_7$ diffusing into 0.1N $AgNO_3$ in starch. 1.5 hours diffusion. (p. 1524, 1540) Inset: 50% $AgNO_3$ diffusing into 2% $K_2Cr_2O_7$ in agar. See fig. 103a and b. (p. 1524)

61. .5N $K_2Cr_2O_7$ diffusing into 0.1N $AgNO_3$ in starch, later. (p. 1524, 1540)

62. The same, detail. (p. 1524)

63. The same, later, when chemical alteration is overtaking the dark red precipitation membranes. (p. 1524, 1540)

64. .5N $K_2Cr_2O_7$ diffusing into .0125N $AgNO_3$ in starch, showing vague but evident periodicity. (p. 1524, 1540)

65. NH_4OH diffusing into $MgCl_2$ in gelatin. Compare with fig. 3. (p. 1524)

66. 4% $Pb(NO_3)_2$ diffusing into 4% KI in gelatin. (p. 1524)

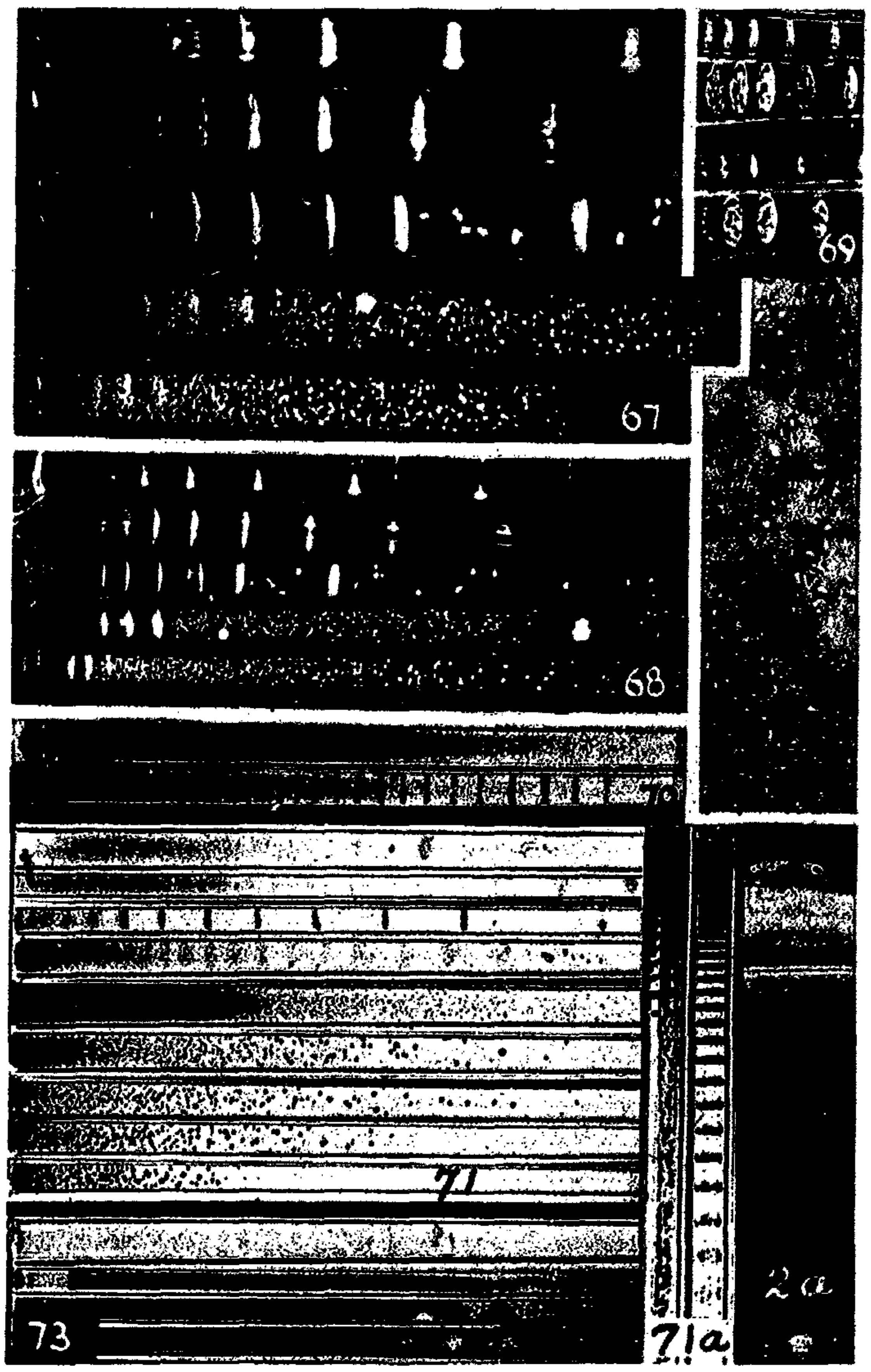


PLATE IX

67. $.2N(NH_4)_2HPO_4$ diffusing into .1N-.0062N $CaCl_2$. High concentrations below. (p. 1524, 1529, 1541)
68. The same, later. (p. 1529, 1541)
69. The same, oblique view of zones. (p. 1529)
70. Lower tube: .1N $AgNO_3$ diffusing into .0031 $K_2Cr_2O_7$ + .0031 NaCl in gelatin. (p. 1526)
Upper tube: .1N $AgNO_3$ diffusing into .0031 NaCl in gelatin (p. 1526)
71. .1N $AgNO_3$ diffusing into .1N-.00035N (9 concentrations) Na_2HPO_4 in gelatin. See fig. 86. (p. 1525-6, 1529)
71a. $AgNO_3$ diffusing into $K_2Cr_2O_7$ in gelatin previously treated with $AgNO_3$ and $K_2Cr_2O_7$, the latter finally in sufficient excess. (p. 1525)
72. 2% $CaCl_2$ diffusing into 2% ammonium oxalate in gelatin. (p. 1523, 1542)
73. .1N Na_2HPO_4 diffusing into .2N-.025N $AgNO_3$ in gelatin. (p. 1515, 1530)
2a. See plate I.

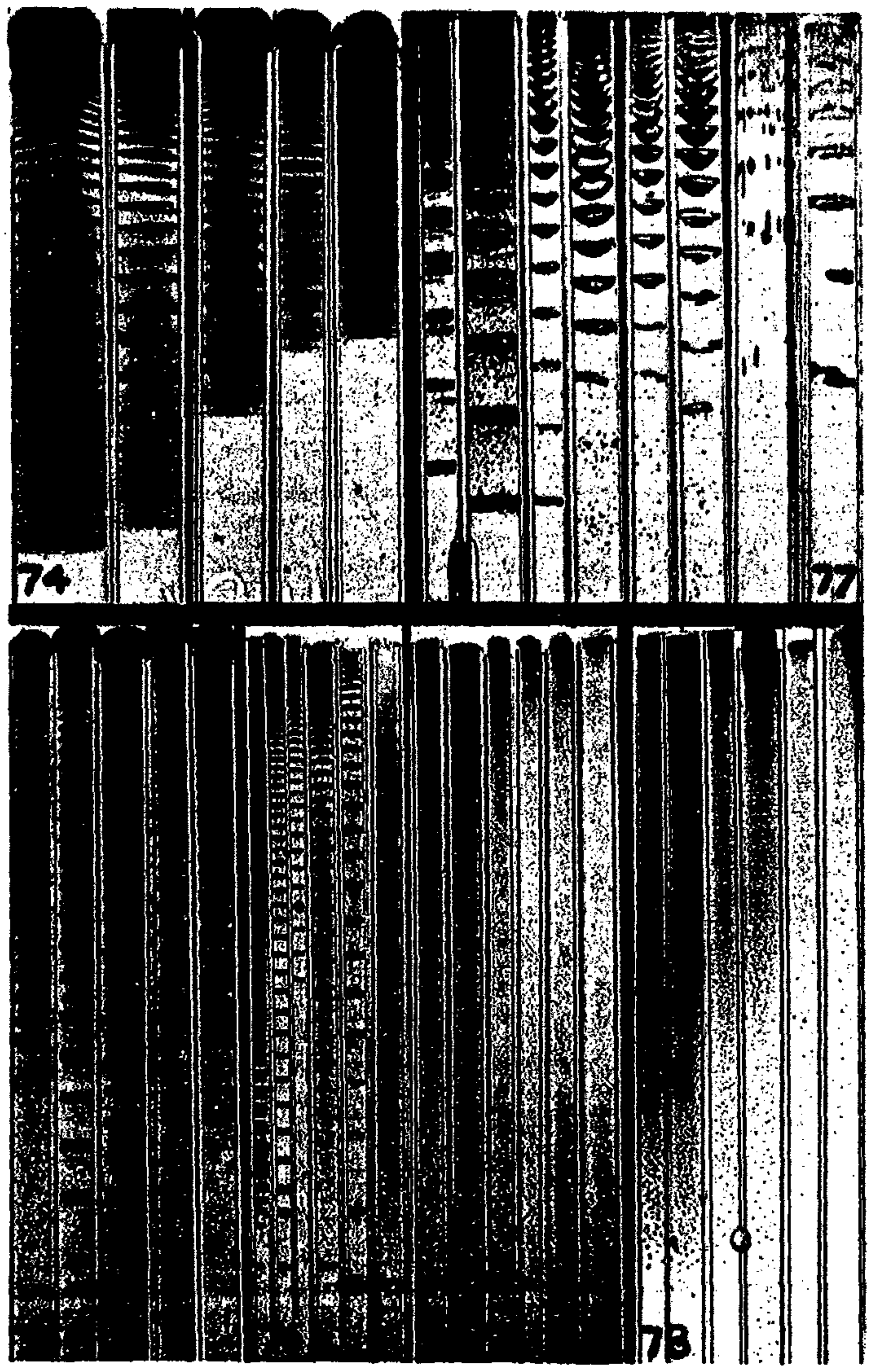


Plate X

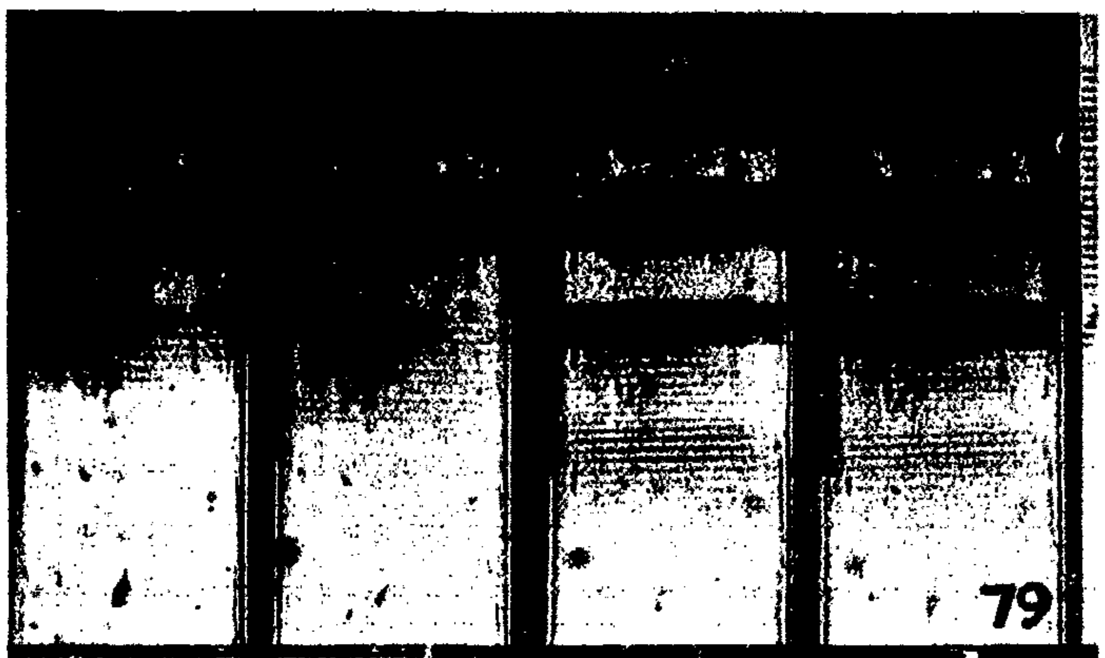
74. 1.25 N $AgNO_3$ diffusing into 0.1 N-.0062 N $K_2Cr_2O_7$ in gelatin. Dark bands are red adsorbed on fine white bands. Highest concentrations on the right. (p. 1520, 1528, 1539, 1541)

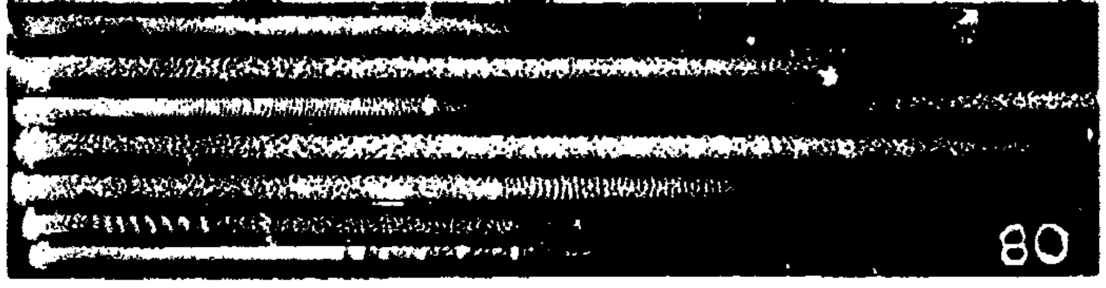
75. The same, later. (p. 1526, 1539)

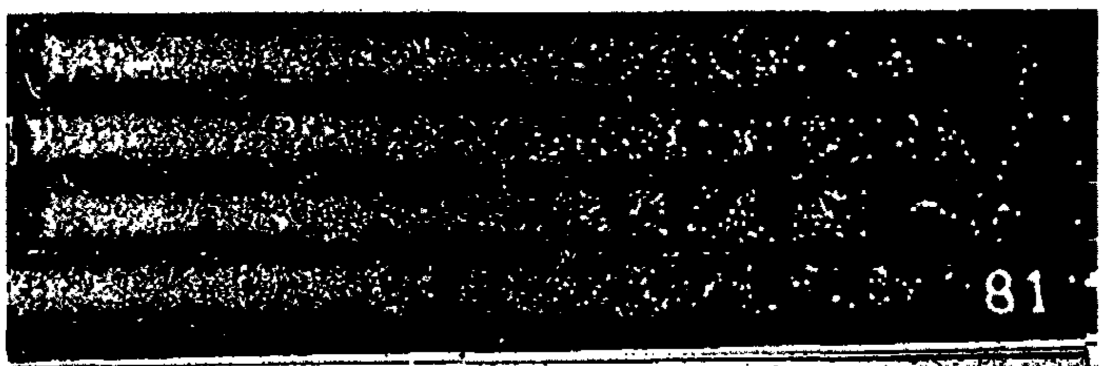
76a. .5N $AgNO_3$ diffusing into .1N-.0031N K_2CrO_4 in gelatin.
b. .5N $AgNO_3$ diffusing into .1N-.0031N K_2CrO_4 in starch.
The highest concentrations are on the left. (p. 1527, 1539, 1543)

77. .5N K_2CrO_4 diffusing into .1N-.0125N $AgNO_3$ in gelatin. High concentration on left. (p. 1520, 1526, 1543)

78. .5N $AgNO_3$ diffusing into K_2CrO_4 in agar. High concentration on the left. (p. 1527)







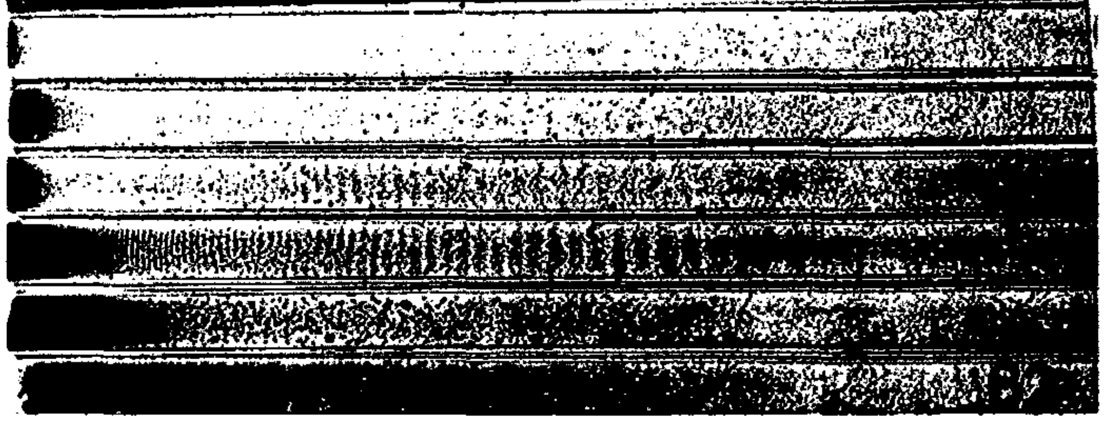


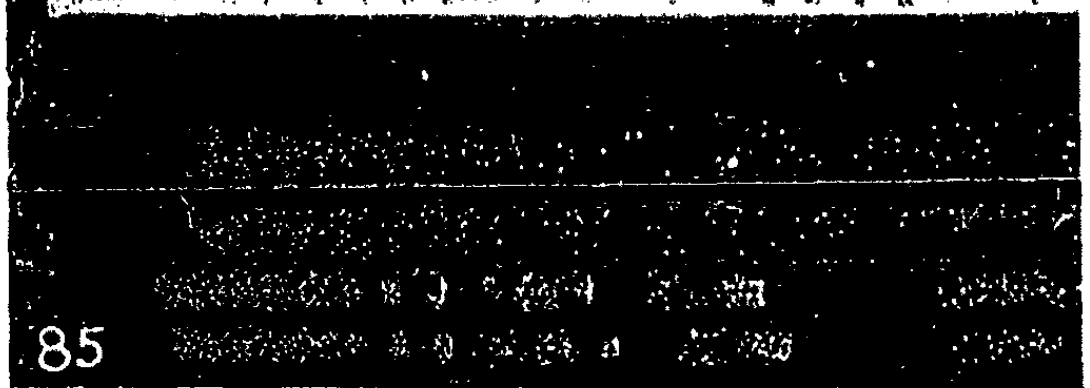
PLATE XI

79. .5N $AgNO_3$ diffusing into 2% $K_2Cr_2O_7$ in gelatin. Four stages of the same tube. (p. 1528, 1539)

80. .25N $Pb(NO_3)_2$ diffusing into .1N-.006N $K_2Cr_2O_7$ in gelatin. Upper two tubes .1N; second two tubes .05N; third, fourth and fifth .025N, .0125N and .0062N, respectively. (p. 1518, 1528)

81. .2N Na_3PO_4 diffusing into .1N $CaCl_2$ in gelatin. (p. 1529)

82. .5N $AgNO_3$ diffusing into .1N-.0031N $K_2Cr_2O_7$ in starch. (p. 1528)



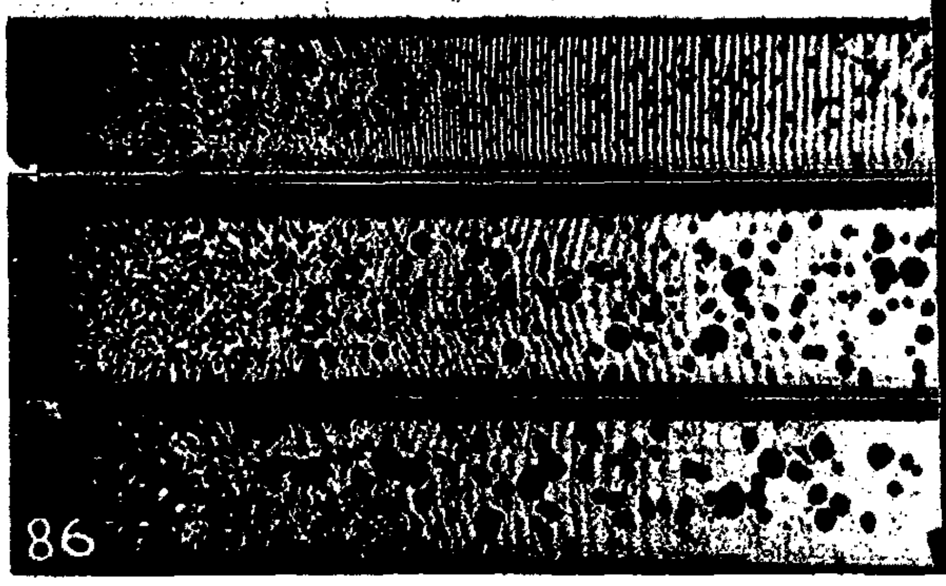


PLATE XII

83. .2N Na_2HPO_4 diffusing into .05N-.0031 N $CaCl_2$ in gelatin. High concentration below. (p. 1529, 1541)

84. The same, later. High concentration below. (p. 1529, 1541)

85. .5N $NH_4H_2PO_4$ diffusing into .1N-.0031 N $CaCl_2$ in gelatin. High concentration below. (p. 1529)

86. .1N $AgNO_3$ diffusing into .1N-.025N Na_2HPO_4 in gelatin. Three concentrations, the highest below. See fig. 71 (p. 1525, 1529)

87. .1 saturated solution NH_4OH diffusing into .5% $Co(NO_3)_2$ in gelatin. The dark line marked by the white triangle is the head of the diffusion column. (p. 1537)

88. The same, later. The head of diffusion column marked by white triangle. (p. 1537)

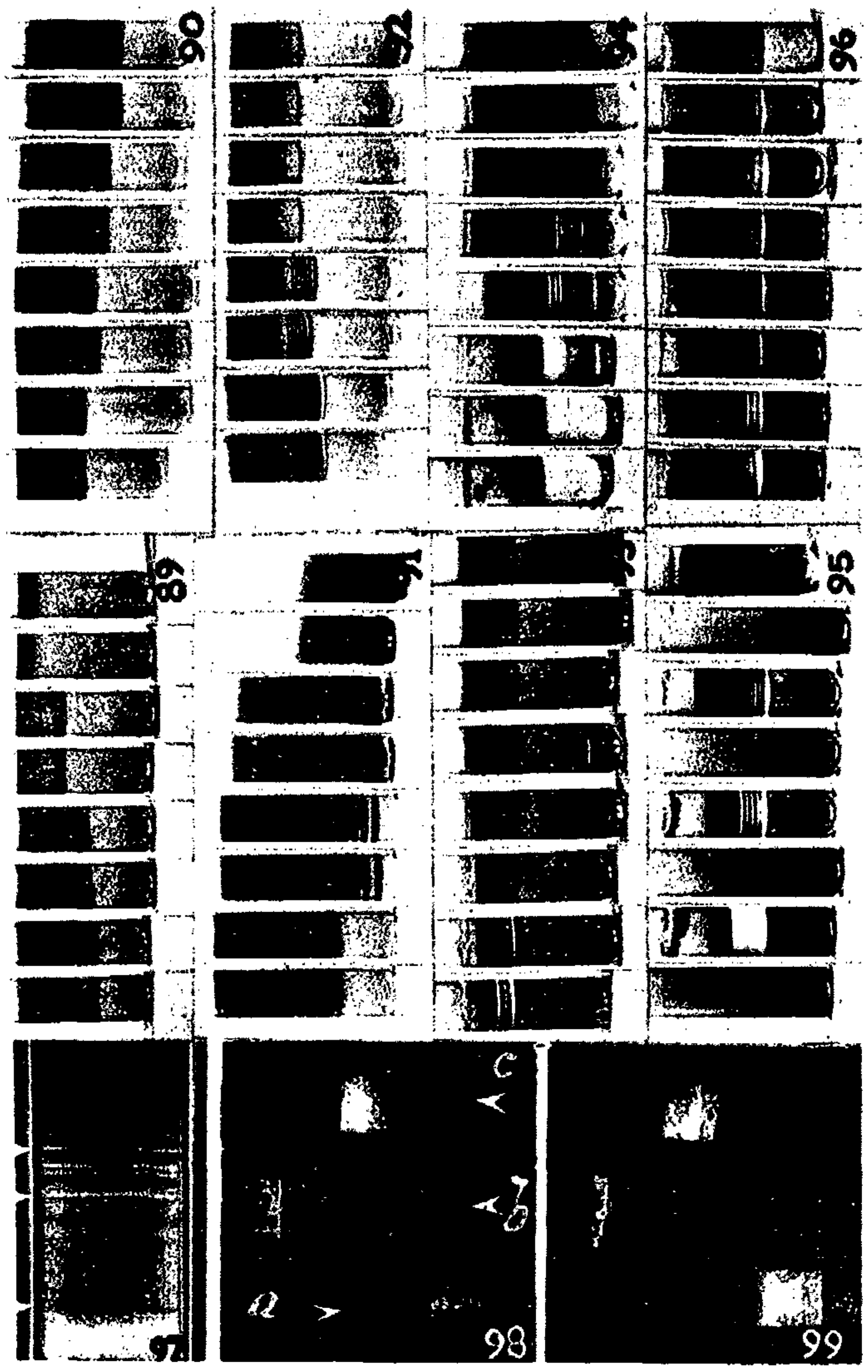


PLATE XIII

PLATE XIII

89. 25%, 20%, 10% and 5% NH_4OH diffusing into 2N $CoCl_2.6H_2O$ in 2.5% agar. Highest concentration to the left, 2 tubes for each concentration. (p. 1531)

90. 10%, 15%, 20% and 25% NH_4OH diffusing into 2N $CoCl_2$ in 10% gelatin. Lowest concentration to the left, two tubes for each concentration. (p. 1531)

91. 20% NH_4OH diffusing into 2N, 1.5N, 1N and 0.5N $CoCl_2$ in gelatin. Highest concentration to the left, two tubes for each concentration. (p. 1531)

92. 20% NH_4OH diffusing into 2N $CoCl_2$ in gelatin. Tubes 1 and 2 (to the left) kept at 24° C; 3 and 4 at 15-17° C; 5 and 6 at 7° C; 7 and 8 at 3° C. (p. 1532)

93. 20% NH_4OH diffusing into 2N $CoCl_2$ in 10% gelatin to which had been introduced 2N, 1.5N, 1N, 0.5N, 0.25N, 0.1N, 0.05N NH_4Cl and control to the eight tubes respectively, reading from left to right. (p. 1533)

94. The same, after 10 days. (p. 1533)

95. Tube no. 1, 4N NH_4Cl (extreme left hand tube)
2 “ “ plus 20% NH_4OH
3 2N “
4 “ “ “ “ “
5 1N “
6 “ “ “ “ “
7 .2N “
8 “ “ “ “ “
diffusing into 2N $CoCl_2$ in 10% gelatin. (p. 1533)

96. 20% NH_4OH diffusing into 2N $CoCl_2$ in 10% gelatin, to which was added the following chlorides in IN concentration: Tube no. 1 (left hand), Li; no. 2, Na; no. 3, K; no. 4, Rb; no. 5, Cs; no. 6, Ca; no. 7, Sr; no. 8, Ba. (p. 1534)

97. .25N $HgCl_2$ diffusing into .025N KI in gelatin in darkness, but exposed to light for 39 minutes at 16.25 o'clock (uppermost triangle), and for 37 minutes at 19.35 o'clock (lowermost triangle); middle triangle indicates 17.04 o'clock. (p. 1532)

98. HgCl and KI diffusing into each other, $HgCl_2$, from the left, KI from the right, in the following concentrations:
   a. (top tube) saturated solution $HgCl_2$ and .25N KI
   b. (middle tube) .5 saturated solution $HgCl_2$ and 1N KI
   c. (bottom tube) .25 saturated solution $HgCl_2$ and .25N KI.

   The points indicate the direction of the movement of the column of precipitate. (p. 1534-6)

99. The same, later. (See diagram in the text.) (p. 1534-6)

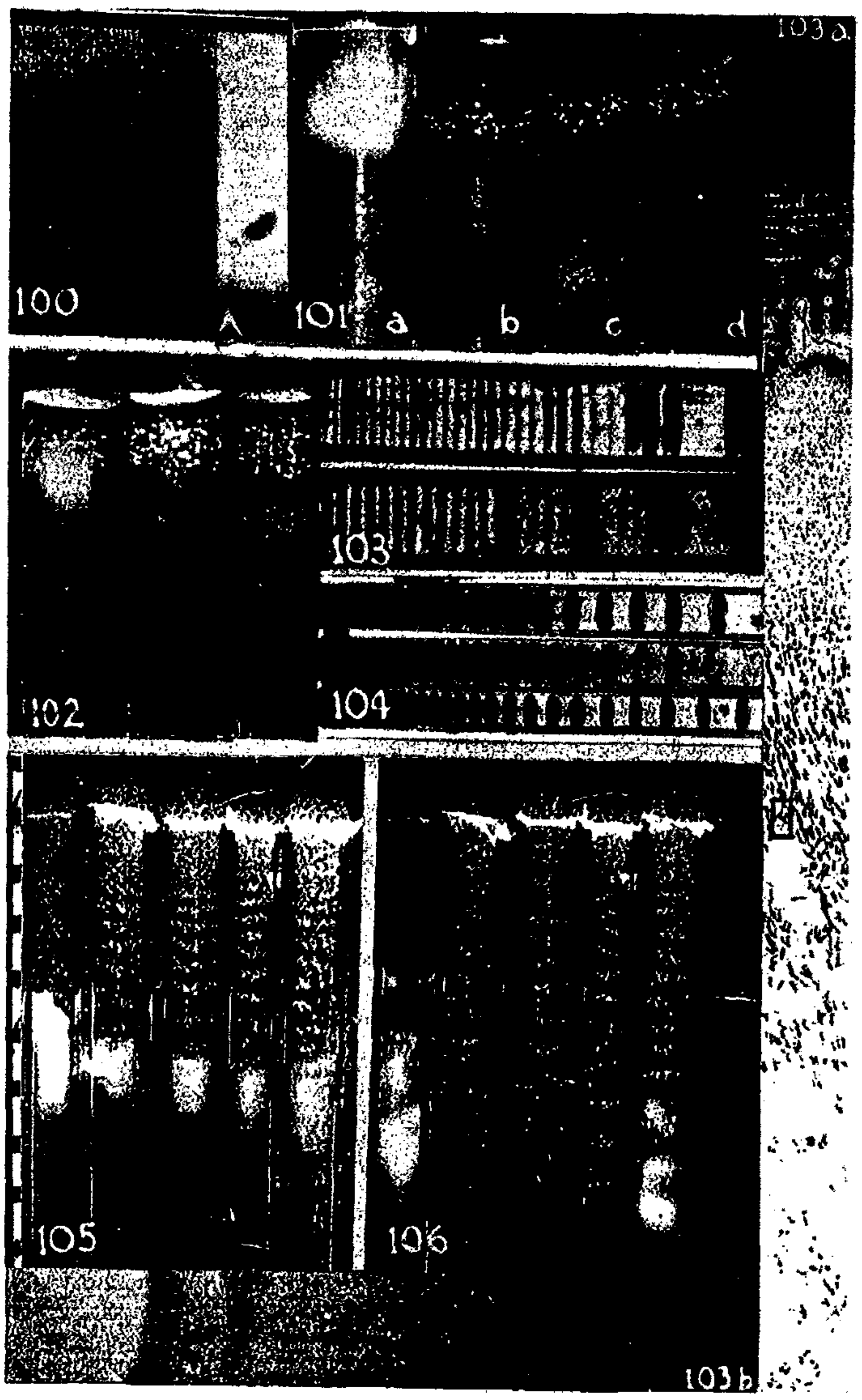


PLATE XIV

100. .25N $AgNO_3$ diffusing into .05N Na_2CO_3 in gelatin. Head of diffusion column at arrow point. (p. 1537)

101. .25N $Pb(NO_3)_2$ diffusing into .25N NaCl in gelatin. In tube d, the single crystalloid arose 34 days from the beginning of the experiment and 20 days later than tube c. Tubes a and b, earlier stages of a parallel series. (p. 1537)

102. The same, but another series. (p. 1537)

103. $AgNO_3$ diffusing into $K_2Cr_2O_7$ in gelatin. (p. 1539)

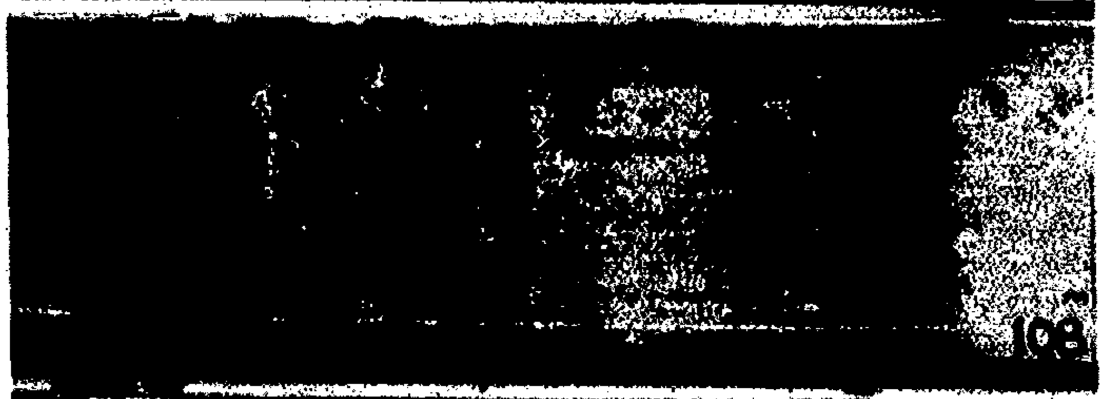
103a. The same, but agar. Poured plate. (p. 1527)

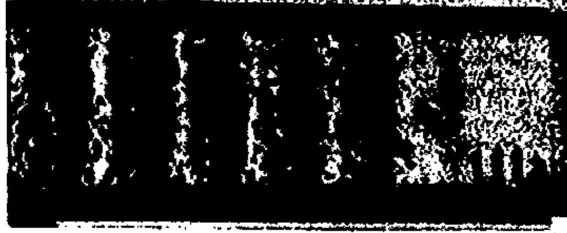
103b. The same, an earlier stage of diffusion, showing the colorless zone. See fig. 60, inset (p. 1555)

104. 1.25 $AgNO_3$ diffusing into 0.1N-.025N $K_2Cr_2O_7$ in gelatin, photographed obliquely. (p. 1539)

105. .5N $Pb(NO_3)_2$ diffusing into .05N-.003N NaCl in gelatin. High concentration on the left. (p. 1537)

106. The same, later.





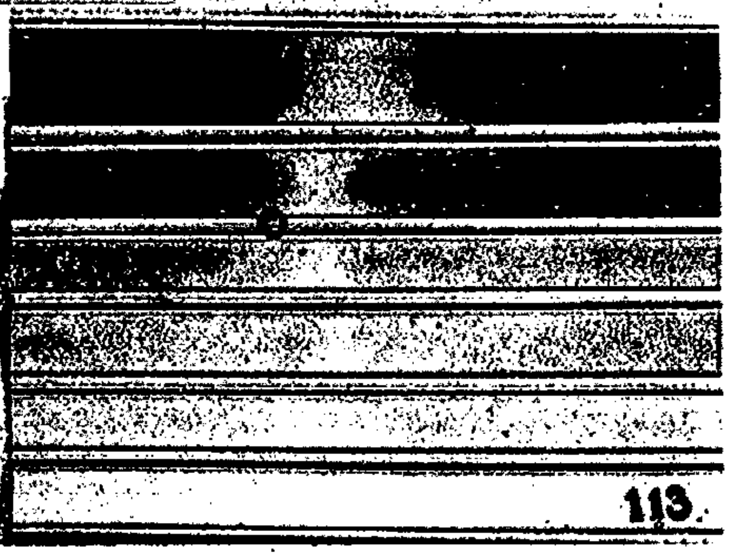


PLATE XV

107. 2% $K_2Cr_2O_7$ diffusing into .5 $AgNO_3$ in gelatin. Red salts disappearing and yellow taking their place The *last dark band on the right* only is red; the rest yellow. (p. 1540)

108. The same system: adsorption of red salts on the glass wall. The last dark band on the right is red; the rest yellow. (p. 1540)

109. .5N $AgNO_3$ diffusing into 2% $K_2Cr_2O_7$ in 10% (bottom tube), 5%, 2.5%, 1.25% and .62% agar. (p. 1540)

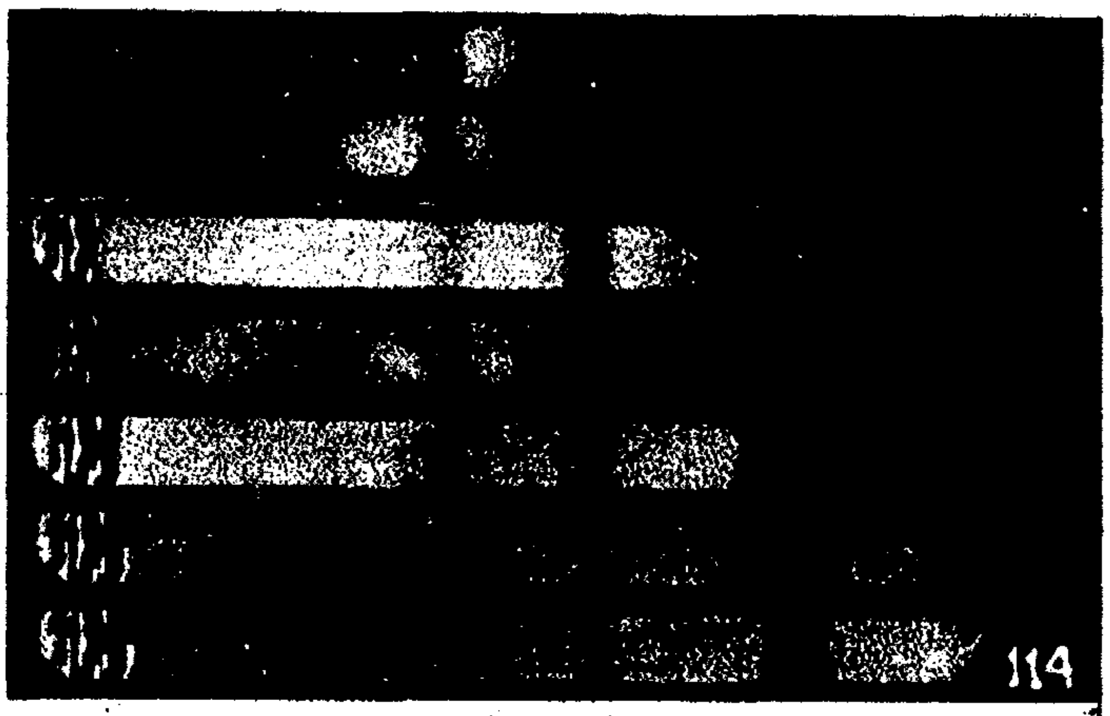
110. .5N $Pb(NO_3)_2$ diffusing into .5N NaCl in water in capillary space. (p. 1513, 1541)

111a. 2% $Pb(NO_3)_2$ diffusing into $K_2Cr_2O_7$ in gelatin. (p. 1541)

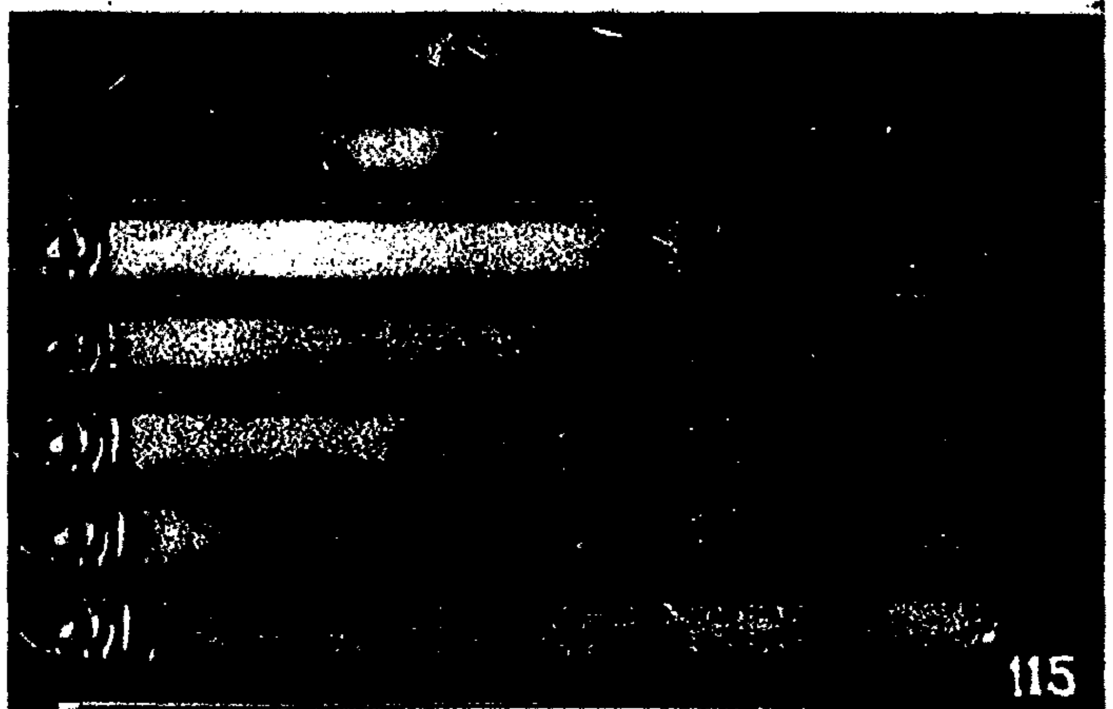
111b. The same, earlier stage. (p. 1541)

112. .5N $K_2Cr_2O_7$ diffusing into .05N $Pb(NO_3)_2$ in agar. (see figure 113). (p. 1518, 1528, 1542)

113. The same, the internal reagent in six concentrations: .112-.003N, the highest concentration above. (see figure 112). (p. 1518, 1528, 1542)



114



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116

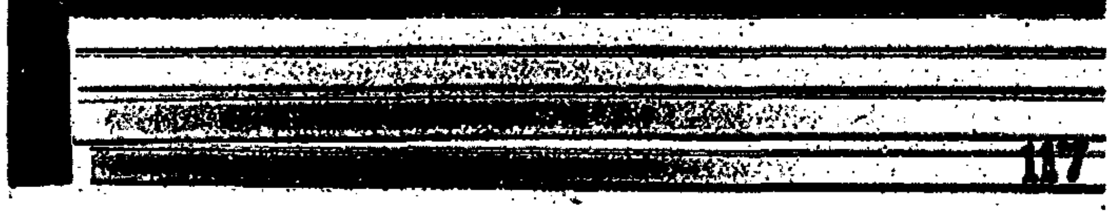

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PLATE XVI

114. Selected "frames" from motion picture, viz. exposures numbers 45, 66, 80, 103, 125, 154 and 166, reading from top. 2% $Pb(NO_3)_2$ diffusing into 4% KI in 6% gelatin. (p. 1537, 1541, 1546)

115. Another tube of the same series. The sharp bands are white; the diffuse cloudy ppt. yellow. (p. 1537, 1541, 1546)

116. .5N Ammonium oxalate diffusing into .1N-.025N $CaCl_2$ in gelatin. (p. 1543)

117. .5N $CaCl_2$ diffusing into 0.1N-.0125N Ammonium oxalate in gelatin. (p. 1543)

PHYSICO-CHEMICAL STUDIES ON PROTEINS

V. A Comparative Study of the Peptization of the Protein Complex in Various Seeds and Grains*

BY ERNEST V. STAKER AND ROSS AIKEN GORTNER

Historical

That certain proteins were soluble in saline solutions was first shown by Denis[1] in 1859. This observation was later confirmed by Hoppe-Seyler.[2] Denis observed that when sodium chloride extracts were made of both animal and vegetable tissue, certain proteinaceous substances were dissolved. While this discovery opened to chemists an entirely new means for isolating and purifying these proteins, its real significance was not appreciated until several years later.

In 1862 Ritthausen began his work on the vegetable proteins. For a number of years he devoted himself to the separation and purification of proteins and to their ultimate analysis. Ritthausen also became interested in that protein fraction which was extracted from seeds by weak alkaline solutions. As a result of these and other investigations, it became evident that the proteins in seeds existed in many diverse forms.

Weyl,[3] using the method of Denis, examined a large number of seeds and found that they all contained protein soluble in solutions of sodium chloride. Using his experiments as a basis, he divided the "globulin" thus extracted into two groups, the "vitellins," soluble in saturated solutions of sodium chloride, and the "myosins," insoluble in such solutions. Soon afterward, Vines[4] investigated the action of salt solutions on the aleurone grains in different seeds.

About this same time Weyl, who had been examining the data of others, made a severe criticism of Ritthausen's work. He maintained that the preparations which Ritthausen had obtained by extracting seeds with dilute alkali were altered products and that they did not represent the original constituents of the seed. Ritthausen soon afterward, however, showed that many of his preparations were largely or wholly soluble in saline solutions, and had for the most part retained unaltered their original solubility; also that the products obtained by direct extraction of seeds with neutral salt solutions agreed in many cases entirely with those he had previously described. Regardless of his assertion Ritthausen thought it best to apply the method of Denis to a number of seeds, especially those which he had previously studied, and he was able to show that most of the seed proteins were globulins The experience of others has since substantiated this conclusion.

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It is difficult to understand why Ritthausen's preparations extracted from the seed by dilute alkali, and which he claimed to be of "highest purity" should later have been completely soluble in neutral saline solutions. If his samples had contained glutelins which are "insoluble" in salt solution but "soluble" in dilute alkali, they should not have become soluble in neutral salt solutions. One must conclude that either his proteins were almost wholly "globulins" and albumins and that no appreciable quantities of glutelins were present, or if originally present they had undergone partial hydrolytic cleavage into simpler fractions.

Thomas B. Osborne was the next investigator of importance in the field of the vegetable proteins. For more than twenty years he was primarily engaged in separating, classifying, and studying the protein constituents of seeds. His work included an extensive investigation not only of cereal grains but also of a large number of other kinds of seeds. Because of this fact the further historical review is divided into sections.

The Cereals

Barley.—As far as the authors are aware the salt- or water-soluble fractions of barley have been studied but little. Osborne[5] made the first preliminary survey. He observed that the seeds contained proteins which were soluble in water, in 10% sodium chloride, and in alcohol.

Osborne's conclusions from his investigation of the barley proteins were that "the barley contained 1.83% of nitrogen and if it be assumed that this all belonged to proteid matter with 17% of nitrogen, the flour would contain 10.75% proteids. The barley accordingly contained about 4.5% insoluble proteid, 4% of 'hordein' soluble in dilute alcohol, 0.3% albumin and 1.95% of globulin and proteose." If the albumin plus the globulin-proteose fraction is expressed in terms of the percentage of the total proteins, it is found that the total salt-soluble fraction amounts to 20.93% of the total protein. It will be noted also that the globulin fraction is 6.5 times that of the albumin fraction.

The only other paper since Osborne's studies on the salt-soluble proteins of barley, bearing directly on the subject, is that of Bishop[6] who recently reported some investigations on the composition and quantitative estimation of the barley proteins. His methods for the isolation of the globulin and albumin fractions are distinctly different from those employed by Osborne. Bishop extracted the seed meal with 5% potassium sulfate solution. The albumins in this extract were estimated by buffering the solution to pH 4.6 with an acetate-acetic acid buffer, and then coagulating the albumins at 82°C. The coagulum was filtered off and its nitrogen content determined. Total protein on the potassium sulfate extract was estimated by precipitation with trichloracetic acid and a subsequent nitrogen determination on the precipitate. The difference between the total protein nitrogen and the albumin nitrogen was assigned to "globulin" nitrogen.

Bishop found that approximately 34% of the total nitrogen in the seed was extracted when treated with 5% potassium sulfate solution. This is approximately 13% greater than was found by Osborne, although Osborne made his extractions with 10% sodium chloride, using very different experimental conditions. Sodium chloride usually, however, extracts a greater percentage of the total protein than does potassium sulfate when equal concentrations of the salts are used. The non-protein nitrogen reported by Bishop (11.5-16.3% of the total nitrogen of the seed) is unusually high for sound grain, so much so as to cast serious doubt on the validity of his albumin and globulin values. Bishop found the globulin fraction to be much less than the albumin fraction, although Osborne reported that there was 6.5 times as much globulin as albumin in barley. We believe that this discrepancy lies not in the difference in chemical composition of the samples used by these investigators, but in the different methods which they employed.

Oats.—Norton[7] as early as 1848 recognized three proteins in the oat kernel, 0.5-2.17% of an albumin, 15.76-17.72% of "casein" (or avenine), and 1.33-2.47% of gluten.

Von Bibra[8] claimed the protein constituents to be an albumin (1.24%) precipitated by boiling the cold water extract of ground oats, casein (0.15-0.17%) the product separating from the hot alcoholic extract on cooling, plant gelatin (3.00-3.25%) the substance soluble both in hot and cold alcohol, and nitrogenous substances insoluble in water and alcohol 11.38-14.85%.

Osborne[9] was the first to extract oats with water and with 10% sodium chloride solutions. He observed that such extracts had a strong acid reaction and that upon neutralization a precipitate formed which he called acid albumin After making several analyses of the water extract of oats he concluded that they contained (1) an acid albumin, (2) one or more globulins, and (3) a proteose which remained in solution after dialysis of the ammonium sulfate precipitate. The relative amounts of each of these stated either in terms of the weight of sample extracted or in percentage of the total nitrogen present, were not given.

In connection with his study of the oat kernel, Osborne's attention was called to the denaturizing effect of water. This was admirably demonstrated in the following experiment:

Osborne added 6 liters of water to 5 lbs. of "ground" oats. The mixture was allowed to stand over night when the supernatant liquid was decanted. Another 6 liters of water were added to the residual meal and the extraction repeated. The combined extracts were then saturated with ammonium sulfate, the precipitate separated from the remaining liquid, and suspended in water. This suspension was dialyzed in running water for 14 days. After filtering, the residue was extracted with a 10% sodium chloride solution, the solution again filtered and dialyzed. No precipitate of globulin formed, showing that all of the protein in the 10% sodium chloride solution was soluble in water. Osborne concluded that no globulin had been extracted from the substance which separated on dialysis of the aqueous extract, the globulin having been converted into an insoluble form. Osborne observed that such transformations were always the result of the use of water or salt solutions as contrasted with the use of alcohol, alkali, or heat: three agents known to suspend or destroy enzyme action. He therefore suggested that the reason for the apparent anomaly referred to above was that the water had permitted enzyme action to proceed.

From numerous and varied experiments on the oat proteins, Osborne finally concluded that the primary constituents were: (1) an alcohol-soluble protein amounting to 1.25% of the total protein of the oat kernel, (2) a globulin amounting to 1.5%, and (3) an alkali-soluble protein which made up the remainder with the exception of extremely small amounts of proteose and acid-albumin.

Wheat.—Most of the very early work on wheat has little bearing on the present problem and will therefore not be reviewed. We again turn to Osborne[10] for much of our knowledge regarding the proteins of wheat.

Osborne has made a rather detailed study of the globulin and albumin fractions from the embryo and endosperm portions of the kernel. By extracting 3000 grams of germ meal with 9 liters of water and heating the filtrate to 65°C., he obtained 279 grams of albumin or 9.3% of the oil-free germ meal. In another experiment germ meal was extracted with water, the solution adjusted to neutrality by the addition of alkali, and dilute calcium chloride solution was added as long as a precipitate formed. The clear filtrate when heated to 65° gave rise to a coagulum, which, when dried, amounted to approximately 3.4% of the oil-free germ meal. It will be noted that this figure is only about one-third of the value given in the former experiment. The difference in yields was probably due to varying experimental conditions.

An estimation of the globulin fraction in the above experiment gave a value of 9.17% or 2.67 times as much as the albumin. In another determination where the quantity of globulin in the embryo was estimated by extracting 200 grams of the meal with 2000 cc. of 3% sodium chloride, a value of 5.05% of globulin was obtained. Still other studies indicated that 9.5% of the embryo was leucosin (albumin), 4.84% globulin, and 3.03% proteose.

Like differences are to be noted in the albumin fraction extracted from wheat flour. In one experiment flour was extracted with 10% sodium chloride, the solution filtered and the filtrate saturated with ammonium sulfate. The supernatant liquid was filtered and heated at 60-65° for 1 hour. The resulting coagulum upon washing and drying formed 0.064% of the original meal. In another experiment exactly like the preceding, except that dialysis was employed to precipitate the globulin and the albumin in the filtrate was coagulated at 90° instead of 60°, Osborne obtained a yield of 0.16% albumin. Osborne further determined the globulin: albumin ratio in the meal obtained from the entire kernel of winter and spring wheats. The meals were extracted with 10% sodium chloride solution, the extracts dialyzed to separate the globulins and the albumin in the residual solution coagulated by heat. Spring wheat was found to contain 0.624% globulin and 0.391% albumin, giving a globulin: albumin ratio of 1.60. Similar figures for winter wheat were 0.625% globulin and 0.359% albumin with a ratio of 1.74.

Considering the differences which might have resulted from using two different classes of wheat, the results check very closely. But it must be emphasized that exactly the same method of procedure was used in each instance. This undoubtedly explains the very close agreement of the protein analyses of the two wheats.

Ladd[11] proposed a method for the determination of albumin and globulin in wheat and other cereals. Two hundred and fifty cc. of 1% sodium chloride solution was added to each 5 grams of flour. Total nitrogen was determined on a portion of the filtrate. To a like portion phosphotungstic acid was added, thus precipitating the true proteins and any organic nitrogen bases which may have been present in the extract. Nitrogen was then run on the filtrate, giving the "non-protein" nitrogen present in the extract. The albumin and globulin are then approximated by subtracting the non-protein nitrogen from the total nitrogen. This method assumes that only albumins and globulins are precipitated by phosphotungstic acid, whereas we know that other nitrogenous compounds including ammonia are precipitated.

Jones and Gersdorff[12] isolated and analyzed the globulin and albumin of bran. An extraction with water was first made at 1-2°C., using 20 cc. per gram of bran. This was continued until nothing more was removed. The combined extracts were dialyzed 12-14 days and the precipitated globulin removed. Further treatment of the filtrate with carbon dioxide eliminated the last traces of globulin. The filtrate was then boiled until coagulation of the albumin was complete. The residue from the water extraction was exhaustively extracted with 4% sodium chloride. The joint extracts were acidified with acetic acid and boiled until there was no further separation of globulin coagulum.

The percentage of the proteins isolated, expressed in terms of the total proteins in the bran, were: albumin, 16.64%; globulin, 13.62% with a globulin: albumin ratio of 0.83.

Bailey and Blish[13] made a study of the proteins extracted by diluted salt solutions from wheat flour. They estimate that only 48.3% of the protein nitrogen extracted by 1 per cent sodium chloride solution is referable to albumin and globulin, whereas 83.1% of the protein nitrogen extracted by 10% sodium chloride solution and 85.7% of the protein nitrogen extracted by 5% potassium sulfate solution are derived from albumin and globulin.

They believe that the extract of a patent flour when 1% sodium chloride is used as the solvent contains a large proportion of gliadin amounting to more than half of the total protein extracted. The extracts when 10% sodium chloride or 5% potassium sulfate solutions was used contained only 15% of the protein as gliadin. It was their conclusion therefore that 5% potassium sulfate solution should be used for the determination of the non-gluten proteins.

Hoffman and Gortner[14] have recently reported the results of some investigations in isolating the different proteins of wheat flour. The globulin fraction prepared by extracting flour with 5% potassium sulfate, and dialyzing the extract free of sulfate, was found to be practically insoluble in either 5% potassium sulfate or 10% sodium chloride solutions. It was soluble, however, in 0.2% sodium hydroxide. This product was designated as "globulin A." Since they thought that they might not have been dealing with a globulin in this experiment, another preparation was attempted using 10% sodium chloride solution. This was called "globulin B." This product was found to be nearly all soluble in 10% sodium chloride solution. They point out the possibility that the dialysis of the final preparation may have been carried too far, thus causing a protein→protean transformation.

The filtrates after the globulins had been removed, were concentrated in vacuo and the albumins isolated by exactly the same procedure. The filtrate from "globulin A" yielded 21 grams of albumin and that from "globulin B" approximately 1 gram. Thus 5% potassium sulfate extraction gave a globulin: albumin ratio of 0.28, whereas 10% sodium chloride extraction gave a ratio of 3.0. The difference in these ratios must lie in the methods followed, since the same flour was used in both cases. In discussing these differences the authors add: "Certain experiences in making the separations reported in this paper, together with subsequent experience to be reported later, make us strongly doubt whether or not any apreciable amount of a true globulin exists in patent wheat flour. We are certain that if a globulin is present it is in extremely small amounts. We are equally certain that no appreciable amount of proteose was present in the sample of flour which we examined."

Corn.—To Gorham[1f] must be given the credit for our first reference to the proteins of corn. From evaporating a clear alcoholic extract of corn, he obtained a yellow wax-like substance to which he gave the name "zein." He described zein as resembling gluten but differing from it in not containing any nitrogen, the nitrogen content being overlooked in his methods of analysis. Other early contributions were the observations of Ritthausen[16] concerning "maize fibrin," a substance soluble in alcohol, and the bare statement made by Th. Weyl[3] that "powdered seeds of maize yield to a 10% solution of sodium chloride a globulin-like substance which, after purification by repeated precipitation with water and resolution in 10% sodium chloride, coagulates at 75°."

Nothing further was done until Osborne[17,18] took up the question. He used as usual 10% sodium chloride for securing the saline extract. Osborne concluded that the maize kernel in addition to other proteins, contained three globulins, which together form 24.67% of the total nitrogen in the meal. It was his observation also that "through the long-continued action of strong solutions of salt, as ammonium sulfate, the myosin-like globulin, and the globulin with a still lower content of nitrogen, are changed into insoluble modifications, soluble, however, in 0.5% sodium carbonate solution from which they are precipitated by neutralization apparently as albuminates." This is evidence again of the denaturing action of water and salt solutions. Osborne also reached the conclusion that no true albumin existed in the maize kernel. This was a rather striking conclusion since he had found an albumin to be present in all the seeds previously examined.

Legumes

Beans (*Phaseolus* sp.).—Ritthausen[19] made water extracts of the white bean (*Phaseolus vulgaris*) as early as 1883. In the following year he made extractions with 2% sodium chloride. These were cleared by subsidence and the residues, when dry, were reported as forming 13.2 and 11.45%, respectively, of the meal.

Osborne[20] extracted samples of kidney bean meal with 10% sodium chloride and concluded that it contained about 15% phaseolin, 2% phaselin, and 20.6% alkali-soluble protein. The first two were classified as globulins.

No further studies on beans were made until 1897 when Osborne[21] again turned his attention to the *Phaseolus* species. This time it was the small, red bean (*Phaseolus radiatus*) commonly grown in Japan. From 2 kg. of the ground seed treated with 8 liters of 10% sodium chloride solution he obtained 92.23 grams of globulin or 4.6% of the total weight of the meal. The percentage of nitrogen in the bean meal was not recorded.

Jones *et al*[22] investigated the proteins of the lima bean (*Phaseolus lunatus*). A 3% sodium chloride solution, at room temperature, extracted 72.32% of the total protein in the meal or 15.31% of the bean meal. They also noted that the soluble salts occurring naturally in the seeds were sufficient to dissolve 15.13% of protein when the meal was extracted with distilled water in the proportion of 2.5 cc. of water per gram of meal. This was practically as much as was extracted by the 3% sodium chloride solution. By fractional precipitation with ammonium sulfate they secured two globulins, α and β, which formed 2.74 and 1.58% of the total protein, respectively. An albumin, amounting to 1.75 per cent of the meal or 8.26% of the total protein, was obtained by coagulating by heat the residues of a distilled water extract of the meal after all of the globulins had been removed. This percentage of albumin is considerably higher than that obtained from the other beans which have been studied.

The proteins of the Mung bean (*Phaseolus aureus* Roxburgh) have been investigated by Johns and Waterman.[23] This bean they found to contain 21.74% protein of which about 87.5% was extracted by a 5% sodium chloride solution. Experiments with aqueous sodium chloride in different concentrations indicated a 5% solution as the most effective extractant; it dissolved 19.0% of protein from the finely ground seed. This extract yielded two globulins (designated α and β) by fractional precipitation with ammonium sulfate and subsequent purification. These fractions were equal to 0.35 and 5.75%, respectively, of the dry meal extracted. Only traces of an albumin were found in the meal.

Peas, Lentil, Horse Bean, Vetch.—In the early literature legumin was commonly referred to as a substance extracted from seeds by caustic alkalies, and more or less altered by the action of the solvent. After Ritthausen had repeated a number of his experiments, he concluded that his former preparations were a mixture of two proteins, one soluble in salt solutions after dissolving in dilute potassium hydroxide and precipitated with acid, and the other originally soluble in salt solution but rendered insoluble in that fluid by treatment with alkalies. This latter substance Ritthausen called "legumin."

Osborne and Campbell[24] pointed out that legumin forms the chief protein constituent of the pea, lentil, horse bean, and vetch. Vetch contained approximately 10% of this protein. These seeds also contain a globulin called vicilin which is associated with legumin but difficult to separate from it. Osborne and Campbell found that when seeds containing legumin were extracted with water, the following percentages of that protein in terms of weight of the seed were dissolved: pea 4%, vetch 2.5%, lentil 10%, and horse bean 16%. Legumelin, an albumin, was found in all legumes studied with the exception of *Phaseolus vulgaris*. The pea contained 2%, vetch 1.5%, and horse bean 1.25%.

In another experiment,[24] where a large quantity of peas was extracted with 10% sodium chloride solution, a ratio of 1 part albumin to 3.42 parts of globulin was obtained. Unfortunately in many of his papers Osborne does not report the yields of his proteins. He was primarily interested in the nature of the proteins and in their analysis in contrast to the exact amount of the protein in the original biological material.

In their studies on the legume proteins Osborne and Harris[25] were able to show, "that from the pea, *Pisum sativum*, horse bean, *Vicia faba*, lentil, *Ervum lens*, and vetch, *Vicia sativa*, preparations of the globulin can be obtained which agree strictly in properties and composition with one another but are distinctly different from those obtained from seeds of the genus *Phaseolus* and other kinds of legumes."

In connection with his studies on the pea Osborne[26] made some 10% sodium chloride extractions of finely ground vetch. A globulin equivalent to 5.2% of the original meal was isolated. In another experiment, where water was used as the extracting agent the globulin equaled only 1.04% of the original meal.

Peanuts.—Until recently Ritthausen[27] was the only individual who had published any experimental work on the proteins of the peanut (*Arachis hypogea*). In 1880 this author extracted oil-free peanut meal with solutions of sodium chloride, potassium, calcium, and barium hydroxides. From the 10% sodium chloride extract he obtained 27% of globulin by saturating the diluted extract with carbon dioxide, or simply by diluting the extract with a large volume of water. Apparently the same globulin was obtained by acidifying the alkaline extracts with acetic or sulfuric acids. Ritthausen found no evidence of the presence of more than one globulin in the peanut.

The peanut meal used by Ritthausen had been dried over sulfuric acid in a desiccator and contained 10.18% of nitrogen or 56% of protein, using 5.5 as the nitrogen factor.

Lechnikov[28] found the total nitrogen in the peanut to be 9.1% of which 8.74% occurred as "albuminous substance," including albumin, gluten, and globulin.

Johns and Jones[29] extracted air-dried oil-free peanut meal containing 42% of protein (N × 5.5) with a 10% sodium chloride solution and found that about 32% of protein, based on the weight of the meal used, was dissolved at room temperature. When the temperature was raised to 40-50°C., the yield was not increased. Only a very small quantity of albumin was obtained.

Miscellaneous Seeds

Flax-seed.—Osborne[30] found that the proteins of ground flax seed which had been freed from oil by extraction with benzine or ether were largely soluble both in water and solutions of sodium chloride. He reported that flax seed contains a globulin precipitated by dialysis; a protein resembling both globulin and albumin precipitable by long-continued heating at 100°C., as well as by sodium chloride in the presence of acid; a proteose and peptone fraction, and a protein not extracted by sodium chloride but soluble in dilute alkali. Osborne states that "all attempts to determine the amounts of these substances failed because of change, while in solution, into non-proteid bodies. It was further found that the relative amount of the various proteids was very variable; it is almost certain that the more soluble forms were largely, if not wholly, derived from the globulin in consequence of alteration during extraction and separation." In one instance water extracted from 100 grams of meal, protein material equal to 10.5% of the weight of the meal. Forty grams of material, using a saturated sodium chloride solution as solvent, gave a yield of 3.7 grams of protein equal to 9.25% of the weight of the original meal.

Sunflower.—Prior to the work of Osborne, the only published observations on the proteins of the sunflower seed were made by Ritthausen[27] and by Vines.[31] By extracting with very dilute alkali, Ritthausen obtained from the finely ground oil-free meal 44.71% of protein. By treating with sodium chloride solution, diluting the extract with 5 volumes of water and passing carbon dioxide through the solution, the yield was 25.3%. He observed that a considerable part of the protein of the sunflower seed was insoluble in salt solutions but soluble in dilute alkali.

Osborne[32] extracted the oil-free sunflower meal with 10% sodium chloride solution and precipitated the protein by dilution, dialysis, or by saturating the solution with sodium chloride. He obtained 7.4% of a globulin, "edestin," and concluded that this was the principal protein of the seed.

Other seeds.—The salt- and water-soluble fractions of a number of other seeds have been studied. Johns and Chernoff[33] reported that distilled water at room temperature extracted 2.5% of protein from buckwheat flour, while 5 or 10% sodium chloride solutions extracted 4.5%. A 5% solution of magnesium sulfate extracted 3.8% of protein.

Jones *et al*[34] state that distilled water, 2% sodium chloride solution, and a 10% sodium chloride solution, extracted 15.0, 18.5, and 18.0% of protein, respectively, from the jack bean (*Canavalia ensiformis*). Johns and Finks[35] found that a globulin, obtained by extracting cocoanut meal with 10% sodium chloride solution, comprised 10% of the weight of the meal. Davies[36] observed that 25% of the total protein of the rape seed (*Brassica napus*) is extractable using a 10% sodium chloride solution. Other studies of this nature include those of Johns and Gersdorff[37] who studied the proteins of the cohune nut (*Attalea cohune*), that of Cajori[38] on proteins of the pecan nut, Jones[39] on proteins of the cantaloupe seed, and that by Takahashi[40] on the proteins of adzuki bean.

Proteins and the Lyotropic Series

The existence of the Hofmeister or lyotropic series of ions has been noted by Jaeger,[41] Frumkin,[42] Freundlich,[43] and others, under conditions where lyophilic or organic colloids were absent. Loeb[44] argued against such a series, at least in so far as protein behavior was concerned. However, Bancroft questioned the line of reasoning used by Loeb, and McBain stated: "The effects of the Hofmeister or lyotrope (Freundlich) series of ions are too striking to be ignored. They have been observed with too many types of colloids in connection with too many systems not even containing colloids to be attributed to systematic experimental error."

Gortner, Hoffman, and Sinclair[45] were the first to emphasize the effect of salt solutions of various concentrations on the differential solubility or peptization of proteins. Twelve samples of wheat flour were studied, including flours milled from the most important commercial classes of wheats. At almost constant hydrogen ion concentrations (pH 5.0 to 6.0) a marked lyotropic effect was observed. It is evident that the hydrogen ion concentration *per se* could not have been playing the major role, and that such peptization differences as they observed must be attributed to some other factor.

Considering the percentage of total protein peptized by the potassium halides, they found a very definite lyotropic effect of the order KF < KCl < KBr < KI. Considering those salts which had potassium as the cation, they found for N/2 concentrations a series F < SO_4 < Cl < tartrate < CrO_4 < Br; for N/1 concentrations F < SO_4 < Cl < tartrate < Br < I; and for 2 N concentrations F < Cl < Br. The same relative order held for all the salts studied.

These authors further point out that the results as obtained were not due to hydrolysis since there was no increase in free $-NH_2$ and $-COOH$ groups. The phenomenon must therefore have been purely a colloidal one involving differential and more or less specific peptization behavior.

In conclusion they remark that "there is a lyotropic series of ionic effects in an aqueous system of protein and salts, and that these effects are due to properties of the anion and the cation of the salt and are observable and measurable even at a constant hydrogen-ion concentration."

Pascoe, Gortner, and Sherwood[46] made extracts of various flour streams, using 0.5N solutions of KBr, KCl, KF, and $MgSO_4$. The grades of flour ranged from first break to bran and shorts duster. The data as presented substantiated in all respects the findings of Gortner, Hoffman, and Sinclair. Without a single reversal the ionic effect was F < Cl < Br.

Although the flours used differed not only among themselves in chemical composition and physical properties, but from normal wheat flours as well, the same distinct lyotropic effect as encountered by Gortner *et al* was manifest throughout.

Very few pure proteins have been studied in relation to their solubility in solutions of different salts. Osborne and Harris[47] were the first to make such a study. They investigated the action of salts on the globulin edestin obtained from hemp-seed. This protein had been very carefully prepared in a pure crystalline state and was wholly insoluble in water.

Two grams of the air-dried preparation were suspended in a glass-stoppered bottle by adding a known quantity of a molar salt solution and sufficient water to make the final volume 20 cc. The mixture was then agitated at 20° for an unstated length of time and the undissolved globulin allowed to settle. Ten cc. of the clear solution was drawn out with a pipette, its nitrogen content determined, and from this the amount of dissolved edestin calculated. By using successively larger quantities of the molar salt solution and correspondingly less water, a series of determinations was made. The amount of edestin, in every case, was in decided excess of that dissolved, so that presumably as nearly complete saturation of the solution as was possible, under the conditions of the experiment, was attained.

The chlorides of the monovalent bases sodium, potassium, and caesium were found to have very nearly the same solvent power. The divalent bases, barium, strontium, calcium, and magnesium, dissolved approximately twice as much edestin as the monovalent chlorides. The solubility in general was observed to be independent of the nature of the base, but proportional to the number of chlorine atoms. Lithium chloride proved to be the only exception, its solvent power being much less than that of the other monovalent chlorides.

The effect of sulfates on the solubility of the globulin was very similar to that of the corresponding chlorides of the divalent bases. A half-molar solution of sodium sulfate dissolved edestin freely while a full-molar solution dissolved scarcely any. With potassium sulfate the same effect was noticed, but owing to its limited solubility precipitation of the protein did not take place. The curve for lithium sulfate followed those of potassium and sodium sulfate until the latter began to fall. With lithium sulfate, however, the amount of dissolved edestin remained practically constant with increasing concentration of the salt solution, and no evidence of diminishing solubility appeared. Magnesium sulfate, though commonly considered to precipitate globulins, when added in sufficient amount, followed the same course as that taken by the chlorides of the divalent bases.

Solutions of sodium and potassium iodide each had the same solvent effect, which was much greater than that of solutions of the bromides of the same molecular concentration, and slightly greater than that of the chlorides of the divalent bases. Sodium and potassium bromide had nearly the same solvent power, which was considerably higher than that of corresponding solutions of the chlorides. The bromides of barium and calcium also had practically the same solvent power. In this case, however, it was only a little greater than that of the bromides of the monovalent bases, and was distinctly less than that of the chlorides of the divalent bases or of the sulfates. Lithium bromide, like lithium chloride, had less solvent power than the corresponding solutions of sodium and potassium bromide, but the same solvent power as solutions of sodium chloride of the same molecular concentration.

Osborne and Harris point out the similarity between the solubility of edestin in solutions of salts of strong bases with strong acids and that of the solubility of certain insoluble inorganic salts in solutions of other salts due to the formation of complex salts in solution. They, therefore, thought it reasonable to assume that soluble addition products of the globulin and salt were also formed, a suggestion which had previously been made by Pauli.

In commenting further[48] on the problem of the solubility of proteins in salt solution, Osborne says: "Attention is called to these observations in the hope that someone may extend these investigations to other proteins with a view to developing better methods for extracting proteins from seeds than those now employed which depend almost entirely on the use of sodium chloride."

The above remarks were given little thought for a number of years. At least no well-planned experiments were undertaken in that direction. Just recently Sinclair,[49] realizing that much knowledge might be gained by following Osborne's suggestions, made a study of the solubility (peptizability) of pure gliadin in solutions of neutral salts.

Sinclair showed that normal solutions of various neutral salts peptized various amounts of gliadin. A normal KI solution peptized larger quantities of protein than did a normal solution of KBr, while the latter possessed a greater peptizing capacity than did a N KCl solution. When gliadin was treated successively with N KI solution, there remained some protein that was not capable of being peptized with N KI solution. However, if this non-peptizable protein was purified by repeated precipitations from alcohol in the same manner as the gliadin had been originally prepared the protein was then capable of being further peptized by N KI solution. The insoluble residue remaining after gliadin had been peptized the first time was repurified from salts by dialysis followed by solution in dilute alcohol and reprecipitation by absolute alcohol and ether. Following such repurification, it was indistinguishable from the original gliadin as judged by its repeptization by KI solution, analysis, etc.

Experimental

The Problem.—A review of the literature has disclosed the following points: (1) No systematic study has ever been made of the peptization of the proteins of seeds except those found in wheat flour and the protein, edestin (hemp seed); (2) There is a lack of quantitative data on the percentage of the total nitrogen extracted from seeds by water and by salt solutions; (3) The proportion of globulin to albumin in seeds has not been sufficiently studied; (4) Where such ratios have been computed using the data of other investigators, and considering the same kind of seed, a great variation has been noted. The investigation of the above problems, in so far as time would permit, formed the basis for the experiments reported in the following pages.

The Materials.—The seeds used were so chosen as to represent a number of the botanical families. In addition, they were selected so as to have them differ as widely as possible in their physical and chemical characteristics. They varied from 1.859 to 8.330 in percentage total nitrogen; from 1.850 to 70.72% in ether extract; and from 1.69 to 8.45% in ash content.

The plants from which the seed was obtained are listed below, grouped in accordance with the family represented.

Cereals	
Barley	*Hordeum vulgare*
Oats	*Avena sativa*
Triticum species	
Alaska	*Triticum turgidum*
Einkorn	*Triticum monococcum*
Emmer	*Triticum dicoccum*
Club	*Triticum compactum*
Durum	*Triticum durum*
Marquis and Quality	*Triticum vulgare*
Polish	*Triticum polonicum*
Spelt	*Triticum spelta*
Leguminosae	
Common alfalfa	*Medicago sativa*
Navy bean	*Phaseolus vulgaris*
Alsike clover	*Trifolium hybridum*
Andes Pea	*Pisum sativum*
Peanut	*Arachis hypogea*
Vetch	*Vicia angustifolia*
Cruciferae	
Mustard sp.	
Radish	*Raphanus sativus*
Rape	*Brassica napus*
Miscellaneous	
Yellow dent corn	*Zea mays*
White Ural millet	*Panicum miliaceum*
Sweet sorghum	*Andropogon saccharatus*
Teosinte	*Euchlaena Mexicana*
Brazil nuts	*Bertholletia excelsa*
Red Wing flax	*Linum usitatissimum*
Hemp	*Cannabis sativa*
Russian sunflower	*Helianthus annus*

Brazil nuts, radish, and vetch seeds were purchased on the open market. Those of hemp, teosinte, peanut, and vetch, were available at our own laboratories. The Alaska, White Polish, and Little Club varieties of the cereal grains were obtained through the courtesy of Dr. J. L. St. John, of the Washington State Agricultural Experiment Station. The remainder of the seeds or grains were furnished by the Department of Agronomy, University of Minnesota.

The seeds used had not been processed in any way and were in their natural state when secured. The seeds were bright in color and fully matured.

All samples before grinding were cleaned of dirt and other foreign material. As an extra precaution, and to make sure that the seed was all of one kind and type, the samples were "hand-picked."

In experiments involving the peptization of a plant material the necessity of standardizing the particle size is obvious. A survey of the literature showed that only one study had been made of the relation of particle size to the percentage of salt-soluble nitrogen. Bishop[6] observed that barley flour ground to pass a 1 mm. sieve yielded 25.6% of its nitrogen as "salt-soluble," when ground to pass a 1/2 mm. sieve this was increased to 31.2%, and when this material was reground in a "coffee mill" 36.2% of the nitrogen was extracted by the salt solution.

In our experiments it was thought best wherever possible to grind the samples sufficiently fine that they would all pass through a 100-mesh sieve. After grinding, the samples were thoroughly mixed so that uniform aliquots could be obtained. All samples were then stored at 0°C., until used.

A number of the seeds contained so much fat or oil as to make the fine grinding and sieving of the raw seed impracticable. Such seeds were first ground to a fineness commensurate with their oil content and then extracted in a large Soxhlet extractor with petroleum ether. After extraction and drying at room temperature, it was very easy to grind the material to the specified particle size.

The seed meals were analyzed for moisture, ash, and total protein. For the moisture determination 2-gram samples were dried at 100° to constant weight in the vacuum oven. Ash was determined on 5-gram samples, using the A.O.A.C. method. Total nitrogen was determined on 1-gram samples by the usual Kjeldahl-Gunning procedure.

The Methods.—(a) *Peptization of the Seed Proteins.*—The method used was essentially the same as that followed by Gortner *et al.*[15] Six grams of seed meal were weighed into a heavy-walled 100 cc. centrifuge tube and 50 cc. of the salt solution was added. The tube was then shaken in a mechanical shaker for exactly 30 minutes. Following the shaking, the meal was packed tightly in the bottom of the tube by whirling in a centrifuge, centrifuging being continued until the supernatant liquid was clear. This clear liquid was then carefully decanted into a Kjeldahl flask. After loosening the residue in the tube by means of a stirring rod, a fresh 50 cc. of salt solution was added, and a second extraction made in exactly the same manner as the first. The contents of the tube were again centrifuged and the clear supernatant liquid decanted into the same Kjeldahl flask. A third extraction was made in a similar manner. The nitrogen dissolved by the three successive salt extractions was then determined on the combined extracts by the usual Kjeldahl-Gunning method. Duplicate extractions were made in all instances. In case the usual limit of error for a Kjeldahl determination was exceeded, the extractions were repeated on fresh samples of meal until satisfactory analytical agreement was obtained. Half-gram samples were employed for the legumes and 1-gram samples for corn, in that section of the work where a comparison was made between the percentage of the total nitrogen peptized in unextracted meal and that in ether-extracted meal.

(b) *Extraction and Separation of the Albumin and Globulin Fractions.*—Ten-gram samples of the various meals were weighed into 250 cc. wide-mouth bottles and 200 cc. of distilled water was added. A single extraction of the meal was then made by shaking the bottle in the mechanical shaker for 2 hours and centrifuging as usual. Total nitrogen was then determined in duplicate on 25 cc. aliquots of the clear supernatant liquid. A 100 cc. portion of the supernatant liquid was placed in a cellophane dialyzing tube, and dialyzed against repeated changes of distilled water for 60 hours (room temperature) using toluene as a preservative. Upon completion of the dialysis, the contents and washing of the casing were poured into a beaker and the resulting mixture filtered. The filtrate and washings from the precipitate were caught in a 250 cc. volumetric flask, the solution made up to volume and total nitrogen determined in duplicate on aliquots.

Only in the case of flax was it necessary to use the centrifuge instead of a filter to separate the globulin from the albumin liquid. The water extract of the flax meal contained so much gummy material as to make filtering impossible.

The meal residue remaining from the original water extract was treated twice more with 200 cc. portions of distilled water. As usual the bottles were shaken two hours for each extraction and then centrifuged. These extracts were discarded. It was assumed that such a procedure would remove the remainder of the albumin contained in the sample and that whatever protein might be dissolved by further treatment with salt solutions would be globulins. Accordingly, the meal residues remaining after three water extractions were subsequently treated with M/2 KCl solution. In order to make the results strictly comparable to those where salt extractions had been made on 6-gram samples, 85 cc. of the salt solution was added to each sample. Three separate extractions of 30 minutes each were made and the extracts decanted into the same Kjeldahl flask and a total nitrogen determination was made.

The residues from the KCl extraction were re-extracted using 0.5 M KBr solution. Here again three extractions were made, the residues being treated each time with 85 cc. of the salt solution. These data form a part of that recorded in Table VI.

We have already noted in the historical review that different globulin : albumin ratios are frequently obtained where two different methods are employed

TABLE I

The Percentage of Total Nitrogen peptized from Seed Meals by Various M/2 Salt Solutions
Six-gram Samples used

Classification	Seed used	Moisture	Ash	Total Nitrogen	Total Nitrogen Peptized by*** KF	K_2SO_4	KCl	KBr	KI
		%	%	%	%	%	%	%	%
Cereals	Barley	7.80	3.13	2.634	24.50	27.77	28.51	31.84	33.33
	Oats	6.58	4.25	1.859	25.35	30.42	34.78	46.49	55.30
	Tr. Species (Av.)	9.67	2.09	2.76	24.86	26.24	30.98	40.16	55.01
	T. Vulgare (Av.)	10.04	1.90	2.288	29.79	31.61	36.88	46.14	57.02
Legumes	Common alfalfa*	8.08	3.81	6.044	49.68	65.05	59.08	66.74	73.69
	Navy beans*	12.66	3.96	3.768	82.41	83.26	85.45	84.29	90.61
	Alsike clover*	8.03	3.94	6.037	53.83	64.13	56.34	63.72	76.22
	Andes field pea*	10.46	3.51	4.215	85.23	83.93	84.05	88.33	95.18
	Peanut	8.89	4.37	8.242	65.99	89.19	86.09	89.51	93.19
	Vetch	8.72	2.84	5.266	70.66	73.08	71.49	74.48	77.96
Cruciferae	Mustard Sp.**	6.98	4.75	4.889	57.56	59.41	60.05	59.66	58.19
	Radish	7.31	4.31	5.774	72.36	73.11	74.74	76.57	77.43
	Rape	8.19	4.47	4.322	67.71	70.78	72.73	74.59	74.61
Miscellaneous	Yellow dent corn	8.48	1.81	1.98	19.39	19.72	19.72	21.38	22.01
	White ural millet	8.35	4.02	2.187	9.79	11.87	11.91	12.55	12.54
	Sweet sorghum	9.18	2.29	1.978	8.24	7.91	7.93	7.96	8.03
	Teosinte	6.01	2.69	1.880	6.22	6.42	6.39	7.05	7.69
	Brazil nut	8.81	5.96	5.323	81.58	82.46	82.13	82.97	83.19
	Red Wing flax	8.23	4.86	5.050	53.53	65.26	57.64	63.51	60.94
	Hemp	8.02	8.37	5.716	24.65	46.39	30.32	57.42	70.58
	Russian sunflower	7.07	3.24	2.849	41.18	49.44	56.00	58.67	64.90

* 0.5 grams samples.

** The values recorded for mustard are probably not representative of any single species, since the seed was undoubtedly a mixture of various mustard species.

*** The peanut, mustard, radish, rape, corn, flax, sunflower, and Brazil nut meals were extracted with petroleum ether prior to peptization of the meal by salt solutions.

TABLE II

Comparison of the Percentages of the Total Nitrogen in Extracts of Various Seed Meals
Ten-Gram Samples Used*

Classification	Seed used	Nitrogen Water Extract A	Nitrogen remaining in Solution following Dialysis of Water Extract B	Nitrogen peptized by M/2 KCl following Water Extractions C	Globulin extracted by Water A−B=D	Total Globulin C+D=E	Total Albumin + Globulin B+E=F	Peptized by KCl (no water extraction) G	Globulin denatured G−F=H	Globulin/Albumin D/B=I
		%	%	%	%	%	%	%	%	
Cereals	Barley	15.12	3.74	7.05	11.38	18.43	22.17	28.51	6.33	3.04
	Oats	16.77	1.73	6.62	15.04	21.66	23.39	34.78	11.38	8.69
				9.12**		24.16**	25.89**	46.48**	20.59**	
	Tr. species (Av.)	20.01	4.41	9.40	15.60	25.00	29.41	30.98	1.57	3.53
Leguminosae	Alfalfa	41.80	3.29	8.52	38.51	47.03	50.32	59.08***	8.76	11.70
	Navy beans	73.15	14.11	9.29	59.04	68.33	82.44	85.45	3.01	4.18
	Alsike clover	25.16	3.42	14.05	21.74	35.79	39.21	56.34***	17.13	6.36
	Andes field pea	78.87	10.86	10.09	68.01	78.10	88.96	84.05	−4.91	6.26
	Wild vetch	25.48	4.02	35.62	21.46	57.08	61.10	71.49	10.38	5.34
	Peanut	66.69	5.36	4.57	61.33	65.90	71.26	86.09	14.83	11.44
Cruciferae	Radish	49.67	8.46	21.58	41.21	62.79	71.25	74.74	3.49	4.87
	Rape	47.80	12.37	19.55	35.43	54.98	67.35	72.73	5.38	2.86
Miscellaneous	Yellow dent corn	12.59	3.34	7.17	9.25	16.42	19.76	19.72	−0.04	2.77
	White Ural millet	5.94	1.43	3.70	4.51	8.21	9.64	11.91	2.27	3.15
	Sorghum	8.29	0.83	0.42	7.46	7.88	8.71	7.93	−0.78	8.99
	Teosinte	4.98	0.83	0.92	4.15	5.07	5.90	6.39	0.49	5.00
	Brazil nut	35.33	8.40	37.94	26.93	64.87	73.27	82.13	8.86	3.21
	Red Wing flax	64.07	15.64	10.38	48.43	58.81	74.45	57.64	−16.81	3.10
	Hemp	13.63	1.31	9.51	12.32	21.83	23.14	30.32	7.18	9.40
	Russian sunflower	37.65	12.74	10.21	24.91	35.12	47.86	56.00	8.14	1.95

* The technic of extraction employed in this table differs from that employed in the case of Table I, in that in the present table a 10-gram sample was given a single extraction with 200 cc. of water (or salt solution) during a two-hour period.

** KBr extraction.

*** 0.5 gram samples used.

TABLE III

The Percentage of the Total Nitrogen Peptized from Various Wheat Meals by Distilled Water and by M/2 Salt Solutions

Wheat Variety	Moisture	Ash	Total Nitrogen	Total Nitrogen Peptized by					
				H_2O	KF	K_2SO_4	KCl	KBr	KI
	%	%	%	%	%	%	%	%	%
Alaska	9.73	1.96	2.729	19.58	21.86	23.74	28.29	38.07	54.80
Einkorn	9.37	2.22	2.891	17.89	22.39	23.27	27.67	36.28	56.42
Emmer	9.32	2.25	2.477	21.28	21.08	22.65	28.33	38.73	52.99
Little Club	10.57	2.25	2.99	19.72	25.97	27.10	30.61	38.76	53.55
Marquis	10.50	1.69	2.464	23.16	26.84	28.63	33.24	42.57	54.40
Mindum	10.47	2.25	3.017	21.58	24.93	26.01	30.91	41.18	58.09
Polish	8.34	1.81	3.64	18.34	21.97	23.20	27.39	36.42	55.53
Quality	9.58	2.11	2.112	26.72	32.74	34.59	40.53	49.72	59.65
Spelt	9.18	2.28	2.509	23.26	25.94	26.93	31.83	39.75	49.63
Average	9.67	2.09	2.76	21.28	24.86	26.24	30.98	40.16	55.01

in isolating the albumin and globulin fractions of a seed. To ascertain whether or not the same ratio of globulin to albumin would be found using a salt solution as was found in the distilled water experiments, the extractions were repeated on 10 grams of the seed meal of corn, millet, sorghum, and teosinte, extracting with 200 cc. of 0.5 M KCl solution. The method followed in the separation of the albumin and globulin fractions was exactly the same as that described above. Dialysis was continued until there was no further test for chloride in the dialysate. The data are shown in Table VII.

All data contained in the tables were computed on the moisture-free basis. Wherever extractions were made, the nitrogen thus dissolved was expressed in terms of percentage of the total nitrogen of the meal. In case the oil or fat had been removed previous to peptization this percentage was again added to the total dry matter and the results computed on that basis.

The Data.—The data are contained in Tables I to XI and in Figs. 1 and 2. The graphs, as diagrammed, are not mathematically correct, since there is only one variant. However, it is felt that for the purpose intended, they represent the data much better than would a graph of the "block" type.

TABLE IV

Relative Differences in the Percentage of the Total Nitrogen of Wheat Sorts which is peptized by Various Salts*

Wheat Variety	Difference between the Percentage of the Total Nitrogen Peptized by				
	K_2SO_4 and KF	KCl and K_2SO_4	KBr and KCl	KI and KBr	KI and KF
Alaska	1.88	4.55	9.78	16.73	32.94
Einkorn	0.88	4.40	8.61	20.14	34.03
Emmer	1.57	5.68	10.40	14.26	31.91
Little Club	1.13	3.51	8.15	14.79	27.58
Marquis	1.79	4.61	9.33	11.83	27.56
Mindum	1.08	4.90	10.27	16.91	33.16
Polish	1.23	4.19	9.03	19.11	33.56
Quality	1.85	5.94	9.19	9.93	26.91
Spelt	0.99	4.90	7.92	9.88	23.69
Average	1.38	4.74	9.18	14.85	30.15

* The first salt named in the column peptized the largest amount of nitrogen.

TABLE V

A Comparison of the Various Nitrogen Fractions expressed as per cent of the Total Nitrogen and the Albumin:Globulin Ratio obtained from the Extracts of Wheat Meals

Wheat Variety	Total Nitrogen peptized by:			Globulins extracted by Water	Total Globulin	Total Albumin + Globulin	Extraction originally by M/2 KCl (No water Extraction)	Globulin denatured by dialysis and which then appears in the Glutelin	Globulin/Albumin
	Water* (Albumins + Some Globulin in Soln.)	Water Following Dialysis (Albumins in Soln.)	M/2 KCl Following Water Extractions (Globulin)						
	A	B	C	A−B=D	C+D=E	B+E=F	G	H	D/B
	%	%	%	%	%	%	%	%	
Alaska	19.18	4.70	8.71	14.48	23.19	27.89	28.29	0.40	3.08
Einkorn	16.67	2.77	10.91	13.90	24.81	27.58	27.67	0.09	5.02
Emmer	20.39	5.00	8.29	15.39	23.68	28.68	28.33	−0.35	3.08
Little Club	18.94	4.01	10.05	14.93	24.98	28.99	30.61	1.62	3.72
Marquis	21.21	7.04	8.08	14.17	22.25	29.29	33.24	3.95	2.01
Mindum	19.34	5.94	8.57	13.40	21.97	27.91	30.91	3.00	2.26
Polish	17.47	3.74	8.54	13.73	22.27	26.01	27.39	1.38	3.67
Quality	24.94	3.78	13.01	21.16	34.17	37.95	40.53	2.58	5.60
Spelt	21.92	2.69	8.42	19.23	27.65	30.34	31.83	1.49	7.15
Average	20.01	4.41	9.40	15.60	25.00	29.41	30.98	1.57	3.53

*The values in this column differ somewhat from values in the similar column of Table III, because a different technic was employed. In Table III the data represent the extractions of six-gram samples with three successive treatments of 50 cc. of water, each treatment with water being for 30 minutes. In the present table a *single* extraction with 200 cc. of water during a two-hour period was employed.

TABLE VI

The Percentage of the Total Nitrogen peptized from the Same Charge of Seed Meal using Successive Extractions with Different Reagents

Seed used	Total Nitrogen peptized by				Ratios		
	Distilled Water* A	M/2 KCl following Water Extract† B	M/2 KBr following Extraction by M/2 KCl‡ C	Total extracted A + B + C	A/B	B/C	A/C
	%	%	%	%			
Barley	15.12	7.05	3.38	25.55	2.14	2.09	4.47
Alsike clover	25.16	14.05	2.79	42.00	1.79	5.04	9.02
Red Wing flax	64.07	10.38	4.50	78.95	6.17	2.31	14.24
Hemp	13.63	9.51	3.86	27.00	1.43	2.46	3.53
Oats (sample 1)	16.77	6.62	5.25	28.64	2.53	1.26	3.19
Oats (sample 2)	16.81	9.12**	2.58***	28.51	1.84	3.53	6.52
Wild vetch	25.48	35.62	6.88	67.98	0.71	5.18	3.70

* Ten-gram samples submitted to single extractions, using 200 cc. of water for a two-hour extraction period.

** KBr

*** KCl

† Residue from water extraction peptized with three successive portions of 85 cc. 0.5 M KCl, each treatment being for a period of 30 minutes.

‡ Residue from KCl extraction peptized with three successive portions of 85 cc. 0.5 M KBr, each treatment being for a period of 30 minutes.

TABLE VII

Comparison between the Globulin/Albumin Ratios when Extractions were made with 0.5 M KCl and Distilled Water, respectively

Seed Used	Fraction of Total Nitrogen peptized by M/2 KCl* A %	Nitrogen Remaining in Solution Following Dialysis of KCl Extract B %	Globulins A-B %	Ratios $\frac{\text{Globulin}}{\text{Albumin}}$ from KCl Extracts	Ratios $\frac{\text{Globulin}}{\text{Albumin}}$ from Water Extracts (Table II)
Yellow dent corn	20.10	4.17	15.93	3.82	2.77
White Ural millet	11.57	1.96	9.61	4.90	3.15
Sweet sorghum	7.79	1.24	6.55	5.28	8.99
Teosinte	7.13	2.08	5.05	2.43	5.00

* The values in Column A differ from those in Table I and Column G, Table II, because of a somewhat different technic employed in the extraction. In Tables I and II, the data represent the extractions of six-gram samples with three successive treatments of 50 cc. of M/2 KCl, each treatment with M/2 KCl being for 30 minutes. In the present table a single extraction of 10 grams of the meal with 200 cc. of M/2 KCl during a two-hour period was employed.

TABLE VIII

Comparison of the Ratio of the Total Nitrogen peptized by M/2 KCl and M/2 KI, respectively, and the Percentage of the Total Protein appearing in the Globulin Fraction

Classification	Seed used	Ratio of KCl/KI	Total Globulin %
Cereals	Barley	0.855	18.43
	Oats	0.628	21.66
	Wheat (av.)	0.563	25.00
Leguminosae	Alfalfa	0.801	47.03
	Navy beans	0.943	68.33
	Alsike clover	0.739	35.79
	Andes pea	0.883	78.10
	Hairy vetch	0.917	57.08
	Peanut	0.923	65.90
Cruciferae	Radish	0.965	62.79
	Rape	0.974	54.98
Miscellaneous	Corn	0.895	16.42
	Millet	0.949	8.21
	Sorghum	0.987	7.88
	Teosinte	0.830	5.07
	Brazil nut	0.987	64.87
	Flax	0.945	58.81
	Hemp	0.429	21.83
	Sunflower	0.862	35.12

Table X

The Percentages of the Total Nitrogen peptized by M/2 Salt Solutions from Whole Seed Meals and from Seed Meals which had been exhaustively extracted with Ether

Seed Meal Used	Nature of Sample	Ether Extract removed	Percentage of Total Nitrogen peptized by:				
			KF	K_2SO_4	KCl	KBr	KI
		%	%	%	%	%	%
Navy beans	Whole meal	—	82.41	83.26	85.45	84.29	90.61
Navy beans	Extracted meal	1.85	86.71	88.97	87.94	88.48	93.10
Navy beans	Difference*	—	+4.30	+5.71	+2.49	+3.79	+2.49
Alsike clover	Whole meal	—	53.82	64.12	56.34	63.72	76.22
Alsike clover	Extracted meal	9.48	55.09	70.04	63.89	70.83	76.61
Alsike clover	Difference	—	+1.27	+5.92	+7.55	+7.11	+0.39
Andes field pea	Whole meal	—	85.22	83.94	84.05	88.34	95.18
Andes field pea	Extracted meal	1.45	85.59	91.22	89.33	90.15	95.13
Andes field pea	Difference	—	+0.37	+7.28	+5.28	+1.81	−0.05
Yellow dent corn	Whole meal**	—	15.84	16.69	16.92	18.48	19.96
Yellow dent corn	Extracted meal	4.30	19.16	19.29	19.24	20.13	21.47
Yellow dent corn	Difference	—	+3.32	+3.40	+2.32	+1.65	+1.51
Alfalfa	Whole meal	—	49.68	65.05	59.08	66.74	73.69
Alfalfa	Extracted meal	11.72	49.95	65.48	56.57	61.37	69.34
Alfalfa	Difference	—	+0.27	+0.43	−2.51	−4.37	−4.35
Hemp	Whole Meal	—	24.65	46.39	30.32	57.42	70.58
Hemp	Extracted meal***	0.61	26.17	64.44	41.54	63.69	71.55
Hemp	Difference	—	+1.52	+18.05	+11.22	+6.27	+0.97

* A + sign indicates that a greater peptization of the proteins occurs in the ether-extracted meal.

** These values for corn differ from those reported in Table I probably because of the fact that the meal used in the extractions reported in Table I had been extracted with petroleum ether.

*** The "whole meal" was from a larger lot originally prepared in our laboratories for other purposes. It had been washed in gasoline to remove the greater proportion of the oil so as to prevent rancidity.

TABLE IX

Comparison of the Ratio of the Total Nitrogen peptized by M/2 KCl and M/2 KI, respectively, and the Percentage of the Total Protein appearing in the "Globulin" Fraction

Wheat	Ratio of KCl/KI	Total Globulin %
Alaska	0.516	23.19
Einkorn	0.490	24.81
Emmer	0.534	23.68
Little Club	0.571	24.98
Marquis	0.611	22.25
Mindum	0.532	21.97
Polish	0.493	22.27
Quality	0.679	34.17
Spelt	0.641	27.65

Discussion

Peptization of the Proteins of Barley and Oats.—The first part of Table I shows the percentage of the total nitrogen peptized for the grains, barley and oats. The same data are illustrated graphically in Fig. 2. A very definite lyotropic effect of the order KF < K_2SO_4 < KCl < KBr < KI is noted, the same order being followed by both grains. In every case, however, a greater percentage of the total nitrogen of oats is peptized than is the case with barley. It will be further noted that a M/2 solution of KF peptizes almost the same percentage of the total nitrogen of both cereals. However, as we proceed from the salt which peptizes the smallest amount (KF) to that peptizing the largest (KI), the difference between the same salts becomes increasingly greater. Thus the difference between the fluorides is 0.85%; between the sulfates 2.65%; the chlorides 6.27%; the bromides 14.65%; and the iodides 21.97%. The peptization range of barley is from 24.50% (KF) to 33.33% (KI), a difference of only 8.83%. When the same comparison is made with oats it is found to be from 25.35% (KF) to 55.30% (KI), a difference of almost 30%.

A glance at the graph illustrating these relationships shows that almost a straight line can be drawn for oats when the halogen salts are considered. Such a line cannot be drawn for barley, as all the points are best connected with a curved line. It will also be observed that the behavior of the proteins of oats toward salt solutions resembles that of the proteins of wheat. In fact if the curve for oats is compared with that for the average of the *Tr. vulgare* group of wheats, a very similar relationship is seen.

The question at once arises as to why the proteins of these cereals react so differently. It is evident that since the proteins from these grains were subjected to exactly the same kind of treatment, the differences found must be attributed largely to the properties of the proteins themselves. Other factors could enter which might influence the total amounts peptized by the various salts, but it is difficult to see how these would account for the difference in behavior when one cereal is compared with another. Reference is made here especially to the fat content of the seeds, a point which will be considered later.

If the chromosome numbers of barley, oats, and wheat are compared in relation to the peptization curves for these cereals, another relationship may be seen. The cultivated varieties of barley have 7 chromosome pairs, those of oats 21 and the *vulgare* species of wheats 21. The curve (Fig. 2) showing the average peptization for all the types or varieties of wheats is observed to be about midway between that for the *vulgare* class and the curve for barley. The only exception to this is the upper part of the wheat-average curve. Reference to Fig. 1 will show that it is those wheats which have the lower number of chromosomes, either 7 or 14, that bend the wheat-average curve toward the curve for barley. One might conclude then, that as far as the data presented here are concerned, ease of peptization of the wheat proteins seems to be associated with a correspondingly larger number of chromosomes.

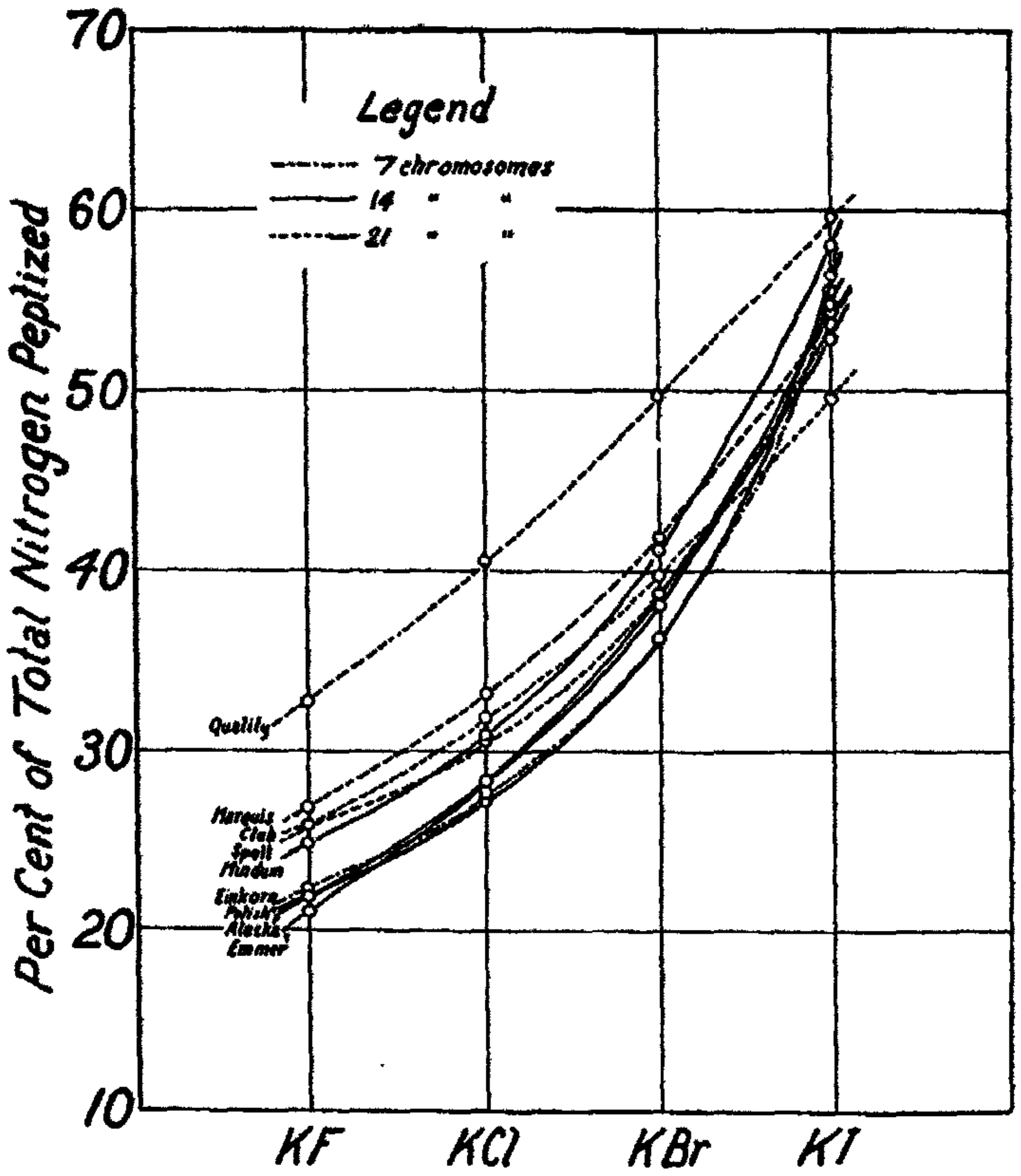

FIG. 1
Peptization of the Proteins of Various Triticum Species by 0.5 molar salt solutions.

The variation in the percentage of total nitrogen occurring in barley, oats, and wheat does not, apparently, account for the differences described above nor for the relative amounts of total nitrogen peptized. Oats contained the smallest amount of total nitrogen (1.859%) yet, with the exception of the *T. vulgare* group of wheats, a larger percentage of it was peptized than was true of either barley or the average for all of the *Triticum* species.

Peptization of the Proteins of Wheat.—In Table III and Fig. 1 are recorded the data obtained by peptizing the proteins of a number of wheats, most of which represent a distinct type. The fifth column of the table shows the percentage of the total nitrogen peptized by distilled water and was included for comparison with the amounts peptized by the various salts. Here again we have a marked lyotropic effect of the order $F < SO_4 < Cl < Br < I$. There is not a single reversal of this arrangement, although 10 different varieties of wheats were studied and 5 different salts employed.

If the peptization with one salt is compared with the peptization of another, proceeding from left to right across the table, it will be found that in a general way these differences are relative differences. These values have been recorded in Table IV. The differences as tabulated were obtained by subtracting the salt which peptized the least amount of nitrogen from the next one above it which peptized a larger amount. In Column 6 appear the figures found by subtracting the data for KF from that of KI. In this manner the differences are all positive. The last row of figures at the bottom of the table record the average differences between the various groups of salts. It is thus seen that there is less average difference between the peptization by K_2SO_4 and KF, than between KCl and K_2SO_4. The greatest variance is found, as one would expect, between KI and KF.

The data support the conclusion that considering all the wheats as a whole, their peptization behavior is very similar. Fig. 1 shows that while this statement is true generally, there are some differences. It will be seen that the grains divide themselves into three specific groups. The lower group includes White Polish, Emmer, Einkorn, and Alaska; the middle group comprises the varieties Spelt, Club, Durum, and Marquis, and the upper contains only one variety, Quality. This division, with the exception of Quality, is only true, however, with reference to the behavior of these grains toward the salts, KF and KCl. When the KBr level has been reached these differences have largely disappeared and nothing of this nature is observed when the peptization with KI is considered. In fact most of the lines have crossed one another.

It was thought that the division of the wheats into three groups might correspond to the classification of those grains which is sometimes made on the basis of their chromosome number. Sax[50] in confirmation of the studies of Sakamura[51] and Kihara[52] list the haploid numbers of the wheat group as follows:

Triticum monococcum	Einkorn group	7 chromosomes
T. dicoccum	Emmer group	14 chromosomes
T. durum		
T. turgidum		
T. polonicum		
T. spelta	Spelt group	21 chromosomes
T. vulgare		
T. compactum		

Reference to the graph will show that the grains are not thus divided on the basis of protein peptizability. It is to be noted, however, that three wheats of the Emmer group, *i.e., T. dicoccum, T. turgidum,* and *T. polonicum* are found in the lower division. Einkorn is also found there, whereas if a strict subdivision were maintained on the basis of the chromosome number, it should form a group by itself. *T. durum*, theoretically, should belong to the Emmer group. However, it shows the peptization behavior of the Spelt wheats.

With the exception of *T. durum*, the Spelt group corresponds to the classification made on the basis of chromosome number. It must be borne in mind that Quality is a soft wheat. Had a number of wheats of this nature been included in the study, the gap between Quality and the Spelt wheats might not have been so apparent.

The average results for the entire group or for the *T. vulgare* varieties are higher than those reported by Gortner, Hoffman, and Sinclair.[45] This might have been expected, since our results were based upon the peptization of the proteins from the kernel, while theirs included only the proteins from wheat flour. Our results are likewise higher than those reported by Pascoe, Gortner, and Sherwood[46] who extracted various flour streams with 0.5 M salt solutions. It is interesting to note, however, that as the values given by them for the lower grades of flour are approached there is in general an increase in the percentage of the total nitrogen peptized. However, these values are much lower than the average we have obtained from whole wheat meal, the same salt being considered.

Peptization of the Proteins of Legumes.—The results obtained from peptizing the seed meals of various legumes are shown in Table I and Fig. 2.

Again we have evidence of a lyotropic series, the order of the anions being as follows: alfalfa, peanuts, and vetch, $F < Cl < SO_4 < Br < I$; beans, $F < SO_4 < Cl < Br < I$; clover, $F < Cl < Br < SO_4 < I$; peas, $SO_4 < Cl < F < Br < I$. This order is not as consistent as was found for the cereal grains. The discrepancy, however, is largely due to the potassium sulfate, the position of which varies from seed to seed. If this salt is omitted, the halogen salts assume the same order as before: $KF < KCl < KBr < KI$. There is only one exception to this arrangement and that is in the case of the pea, where the order of the fluoride and chloride anions is reversed. Table I shows that KF peptized 85.23% of total nitrogen, while KCl peptized 84.05%. It was thought that the value for KF might have been too high, but four different subsequent determinations of this value gave results which checked within experimental error of that percentage.

A much larger percentage of the total nitrogen of the legumes is peptized than is the case with the cereal grains. In fact the lowest value for KF in the case of the legumes is almost as high as the KI value for any cereal. This may be partially accounted for by the large amount of total nitrogen found in the legumes as contrasted with the smaller amount contained in the cereals.

The peptization range, together with the resulting difference between the peptization by the salt having the lowest value and that having the highest, is shown in Table XI. In the case of the pea if the value for KF instead of K_2SO_4 is taken as the minimal per cent, the difference becomes 9.96% instead of 11.24%. In so far as these differences are concerned the legumes divide themselves into two groups; beans, peas, and vetch form one, while alfalfa, clover, and peanuts form the other group.

TABLE XI

Showing the Maximum, Minimum, and Difference in the Percentage of the Total Nitrogen of the Legume Seed Meal peptized by Salt Solutions

Seed used	Minimum	Maximum	Difference
	%	%	%
Alfalfa	49.68	73.69	24.01
Beans	82.41	90.61	8.20
Clover	53.82	76.22	22.40
Peanuts	65.98	93.19	27.21
Peas	83.94	95.18	11.24
Vetch	70.66	77.96	7.30

The relationships between the various legumes are illustrated more clearly in Fig. 2. The curves for the pea and bean are quite similar and occupy about the same position in the graph. Alfalfa and clover are likewise similarly placed, but the curve for alfalfa is practically the reverse of that for clover. Vetch occupies a midway position. So far as the shape of the curves are concerned, it will be noted that the curves for pea, bean, vetch, and clover bear a resemblance to one another. Alfalfa and peanut have curves which are practically the reverse of those just mentioned but which, when compared with one another, are found to be of the same general character.

Peptization of the Proteins of Cruciferae.—The *Cruciferae* studied included the mustard, radish, and rape seeds. The data appear in Table I and in Fig. 2.

As in the legumes these seeds are characterized by the ready peptization of a high percentage of the total nitrogen. The lyotropic order of anions is mustard, $F < I < SO_4 < Br < Cl$; radish and rape, $F < SO_4 < Cl < Br < I$.

Mustard shows a marked difference in lyotropic behavior when compared with the radish and rape seeds. KI, which normally peptized a larger percentage of the total nitrogen than either of the other salts, peptizes practically the same amount of total nitrogen as KF. The iodide ion does not always occupy a paramount position in the lyotropic series. Fischer,[63] for example, using a number of salts, found the order of acid radicals bringing about a diminution in the swelling of fibrin in any acid or alkali to be Cl < Br < NO_3 < CNS < I < acetate < SO_4 < phosphate < tartrate < citrate. The sulfate ion in this case had a greater effect than did the iodide ion.

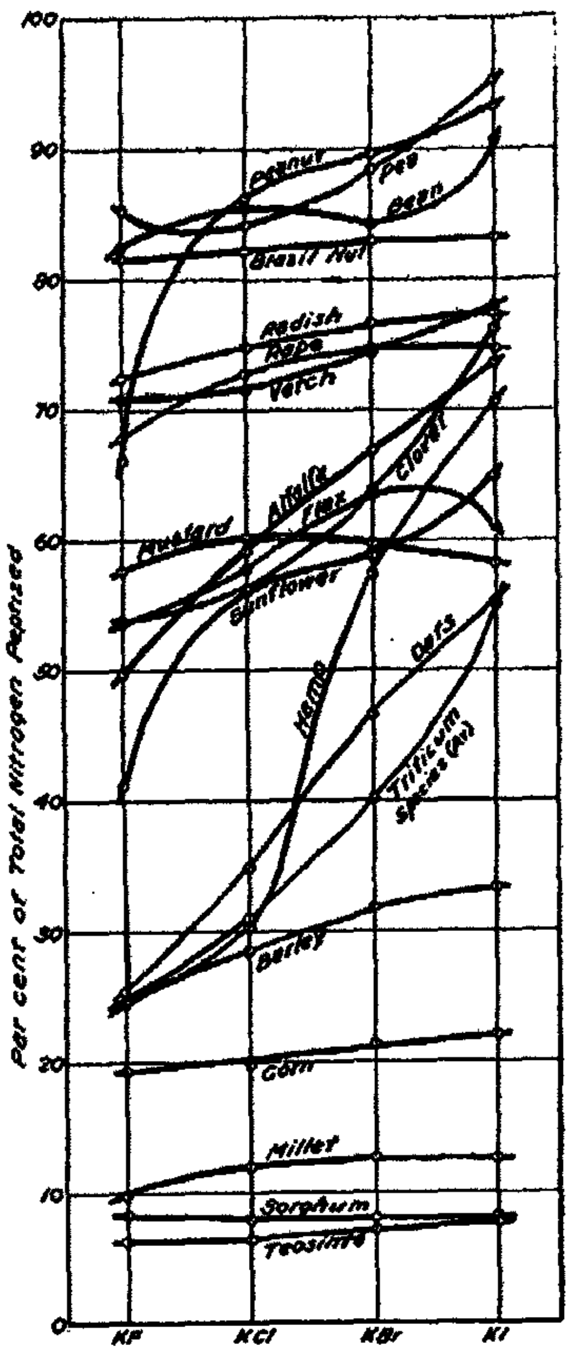

FIG. 2

A Composite Graph showing the Peptization of the Proteins of Various Seeds and Grains by 0.5 M. Salt Solutions

The peptization range of the *Cruciferae* is comparatively narrow, mustard ranging from 57.56 to 60.05% with a difference of only 2.49%; radish ranging from 72.36 to 77.43% with a difference of only 5.07%, and rape ranging from 67.71 to 74.61% with a difference of only 6.90%. The small differences in peptization behavior sharply distinguish the proteins of the *Cruciferae* from those of the other seeds thus far considered.

The curves for radish and rape are seen to be rather sharply differentiated from that of mustard, a much higher percentage of the total protein of the former seeds being peptized. The two curves are similar in nature which seems to indicate that the proteins of radish and rape have responded in an analogous manner to the action of the various salt solutions.

Peptization of the Proteins of Miscellaneous Seeds.—The seeds appearing under this title have been classified into two groups. The first four, yellow dent corn, white Ural millet, sweet sorghum, and teosinte, are in reality cereals and fall rather naturally into a group by themselves. Brazil nut, flax, hemp, and Russian sunflower make up the second group. The first four seeds will be designated collectively for the purpose of the present discussion as the "corn group."

(a) *The Corn Group.*—In many ways the "corn group" of seeds is the most interesting that has thus far been discussed. The entire group is characterized by having a very low percentage of peptizable protein. None of the other seeds or grains which have been studied in this laboratory even approach these low values. It is also noteworthy that the variation between the effect of the different salt solutions when a single seed variety is considered is in most cases of very small magnitude. It is obvious that in this group we are dealing with proteins having properties of an entirely different nature than was found, for example, in the case of the proteins of the other cereal grains.

If we list the anions in order of their lyotropic effect, the following series are found for the different members of the corn group: yellow dent corn and teosinte, $F < Cl < SO_4 < Br < I$; white Ural millet, $F < SO_4 < Cl < Br < I$; sweet sorghum, $SO_4 < Cl < Br < I < F$. *Actually*, however, these orders do not give the true picture, since the values for a number of the salts, considering a given seed variety, lie within experimental error of one another. Thus the percentages of the total protein of corn peptized are practically the same regardless of whether KF, K_2SO_4, or KCl solutions are employed. The lyotropic order accordingly would be more correctly indicated as F, SO_4, $Cl < Br < I$. In the case of millet, the salts, K_2SO_4 and KCl, have equal peptizing power, as have also KBr and KI; therefore, for this seed $F < SO_4$, $Cl < Br$, I. When the data for sorghum seed are considered, it is apparent that no lyotropic series exists. The same value is obtained in all cases, regardless of whether KF, K_2SO_4, KCl, KBr, or KI are used as the peptizing agent.

KF, K_2SO_4, and KCl peptize about the same percentage of the total nitrogen of teosinte, while KBr and KI peptize larger amounts; therefore, F, Cl, $SO_4 < Br < I$.

A graphical representation of the data for corn, millet, sorghum, and teosinte is included in Fig. 2. With the exception of millet, straight lines have been drawn connecting the points. The line for corn is separated from the other lines or curves, inasmuch as a higher percentage of its total nitrogen was peptized than was true of other members of the group. While teosinte and corn differ in the relative amounts of nitrogen peptized, yet it will be observed that the lines slope in the same direction. However, the angles which these lines make with the horizontal are not the same, the angle being greater in the case of corn.

(b) *The Proteins of Other Seeds.*—The peptization data for the second group of miscellaneous meals are also found in Table I and illustrated graphically in Fig. 2. The lyotropic series found for each of these seeds are Brazil nut and hemp, $F < Cl < SO_4 < Br < I$; flax, $F < Cl < I < Br < SO_4$; and sunflower, $F < SO_4 < Cl < Br < I$.

The percentage of the total protein peptized ranges from 81.58 to 83.19 with a difference of only 1.61% in the case of the Brazil nut; from 53.53 to 65.26 with a difference of 11.73% in the case of flax; from 41.18 to 64.90 with a difference of 23.72% in the case of sunflower, to 24.65 to 70.58 with a difference of 45.93% in the hemp seed meal.

The proteins of the Brazil nut are very easily peptized and resemble in this respect the proteins of the pea. With the exception of the position of the sulfate ion, the lyotropic series resembles that found for the cereal grains.

The peptization range, however, is much smaller, a difference of only 1.82% being found between KF and KI. Fig. 2 shows that a straight line can be drawn connecting all the points.

A very peculiar arrangement of the ions is found in the case of the flax-seed meal. While the fluoride solution peptizes the smallest quantity of protein, the sulfate instead of the iodide ion peptizes the largest amount. Perhaps the presence of gums or mucilages (typical lyophilic colloids) in the flax seed mask in some way the real lyotropic effect on the protein complex.

The data for hemp seed show that the sulfate solution peptizes approximately 16% more protein than does the chloride solution. However, the halogens follow the normal order. Hemp seed is especially interesting because of its great peptization range. KF only peptizes 24.65% of the total nitrogen, while KI extracts 70.56%. This difference of nearly 46% represents the greatest extreme of any of the seeds studied.

The sunflower seed has exactly the same lyotropic order of ions as was found for the cereals. The range in the percentage of total nitrogen peptized is also of the same order of magnitude as was found for oats and wheat.

The Albumin and "Globulin" Fractions of the Cereals.—Under the conditions of the experiment, water peptizes 15.12% of the total nitrogen of barley. Of this amount 3.74% is soluble in water and probably represents to a large extent the albumin fraction. The remainder, 11.38% may represent "globulins." Column (C) of Table II shows that following three water extractions, three extractions of the residue with 0.5 M KCl will dissolve an additional 7.05% of the total nitrogen. This added to the "globulin" presumably peptized by virtue of the salts originally present in the seed, gives a total of 18.43%. Thus, "globulins" amounting to 18.43% of the total nitrogen content were peptized by the combined effect of water and salt. To this we must add 3.74% to obtain the total amount of "globulin" and albumin peptized. The figures appearing in Column (G), Table II, were taken from the peptization experiments and show the percentage of total nitrogen peptized, using a KCl solution alone (no previous water extraction). Providing the protein was not denatured by water during extraction, the results given in Column (F) should be expected to check closely with those of Column (G). Column (H), which represents the difference between Columns (F) and (G) is a measure of the extent to which the protein was denatured by water previous to peptizing the meal residue with KCl. It is seen that 6.33% of the total protein of barley was denatured by water and was thus not peptizable by subsequent treatment with KCl solution.

While water extracts from oats but little more of the total nitrogen than it does from barley, nevertheless only 1.73% of the total nitrogen is water soluble as compared to 3.74% in barley. The apparent percentage of "globulin" is thereby increased. Two separate sets of figures appear for oats in Columns (C), (E), (F), (G), and (H). The top number in Column (C) shows the percentage of the total nitrogen peptized by an M/2 solution of KCl from the residue remaining after three extractions had previously been made with water. The lower figure indicates the percentage of the total nitrogen extracted by an M/2 solution of KBr following three water extractions. KBr, as would be expected, extracts a larger percentage of the total nitrogen than does KCl.

Osborne[9] found the proteins of oats to be rather easily denatured by dialysis. This conclusion is substantiated by Column (H), Table II. It is seen that 11.38% of the total nitrogen of oats was rendered non-peptizable by KCl and 20.59% by KBr, following a previous water extraction.

The data recorded in Table II for wheat (average) represent the average of all the results obtained from the various varieties and types of wheat, and were taken from Table V. It is included in Table II for purposes of comparison. The water-soluble fraction following dialysis is larger than for either oats or barley, although the per cent of "globulin" peptized is about the same as that for oats. Column (H) shows that the proteins of wheat are not so easily denatured by water as are those of barley or oats.

Table V contains the albumin-"globulin" data from a study made of a number of different types and varieties of wheats. The percentage of the total nitrogen peptized by water varies from 16.67% to 24.94%. The common wheats, Marquis and Quality, have 21.21 and 24.94%, respectively, of the total nitrogen which is peptized by water. Considerable variability is seen in the percentage of total water-soluble nitrogen. This ranges from Einkorn with 2.77% to Marquis with 7.04%. The "globulin" fraction remains fairly constant at 13 to 15% of the total nitrogen except for Spelt and Quality where values of 19.23% and 21.16% were found

The rather unusual behavior of Quality toward salt solutions is indicated in Fig. 1. The data of Table V show that it likewise ranks much higher in "albumin" and "globulin" nitrogen than any of the other cereals. This fact alone may account for the unique position occupied by this cereal in Table III and Fig. 1. However, in addition to Quality containing more albumin and "globulin," it is probable that its other proteins are more easily peptized by the salt solutions than is the case for the other wheats.

Column (H) of Table V is calculated in the same manner as the corresponding column in Table II and may be considered as an index of the degree to which the proteins of these cereals are denatured by water. It will be observed that the proteins of Alaska, Einkorn, and Emmer, are not easily denatured. Those of Little Club, White Polish, and Spelt are intermediate. The proteins of Mindum and the *T. vulgare* group, however, are more easily denatured, an average difference of about 3% being found between Columns (F) and (G).

The Albumin and "Globulin" Fractions of the Legumes.—The legumes (Table II) vary from 25.16 to 78.87% in the percentage of the total nitrogen extracted by water, the former figure representing Alsike clover and the latter Andes pea.

It is the opinion of most investigators that legume seeds contain large amounts of stored albumin. However, the term "albumin" seems to have had different interpretations placed upon it and has been rather loosely used. The generally accepted definition of an albumin is that of "a simple protein soluble in water and dilute salt solutions and coagulable by heat." Mann[54] however states that, "most of the vegetable albumins are globulins, *i.e.*, acid-albumins which are insoluble in pure water, but soluble in salt-solutions, and precipitable by dilution and acidification."

If we accept the present general opinion that albumins are proteins soluble in pure water, then our results as given in Column (B), Table II, do not substantiate the belief that legume seeds contain large amounts of albumin. It will be seen that navy beans contain only 14.11% of water-soluble nitrogen which is the largest amount found for any legume. Alfalfa seed contains only 3.29%.

Jones et al[22] isolated 1.75% of an albumin from the Lima bean. Only traces of an albumin were found by Johns and Waterman[23] in the Mung bean. Osborne and Campbell[24] found the legumin content of the pea to be 4%, lentil 10%, vetch 2.5%, and the horse bean 16% based on the weight of the meal used. On the other hand, Johns and Jones[20] found but a very small quantity of albumin in the peanut. These data indicate a considerable variation in the albumin content of legumes, just as we have shown in Table II. Osborne and Campbell found about twice as much legumin in the pea as in the vetch. Our figures show somewhat roughly the same relationship. In the case of peanut, however, we find 5.36% of the total nitrogen to be water-soluble, whereas Johns and Jones found but a very small quantity. A strict comparison, however, is hardly justified because of the difference in methods used and possibly differences in the samples employed for investigation, but it does indicate the need for further quantitative work on the proteins of the legumes.

Table II shows that the "globulin" fractions of the legumes differ considerably. The "globulins" extractable by water from Alsike clover meal amount to 21.74% of the total nitrogen, and from the pea meal to 68.01%. The total globulin content of these seeds as recorded in Column (E) gives clover 35.79% and peas 78.10%. In this respect alfalfa and clover resemble each other, whereas the bean and pea are grouped together at the other extreme.

Some very interesting relationships may be seen in Column (C). Peptization of the alfalfa meal residue with KCl solution following the water extractions peptizes only 8.52% of the total nitrogen. On the other hand, under the same conditions, 35.62% of the total nitrogen of the vetch seed is peptized. This amount is even greater than was peptized originally by water (25.48%). Water has a decided denaturing effect on the proteins of the legumes as may be seen by reference to Column (G), where a KCl solution peptized 71.48% of the total nitrogen, or over twice as much as was peptized by KCl following earlier water extractions.

That the legume "globulins" are denatured by water during dialysis is shown in Column (H). The proteins of the pea are less readily denatured than are those of the other leguminous seeds. The proteins of clover show the greatest denaturization effect.

It was found to be practically impossible to extract 6-gram samples of alfalfa and clover meals with 50 cc. of KCl solution. The presence of gums made it impossible to sediment the residual meal. Accordingly the percentages obtained by peptizing 0.5 gram portions of these meals have been inserted in the table in order that a comparative study might still be made in spite of the possibility that the difference in the size of the sample may have influenced to some extent the percentage peptized, and that the values appearing for alfalfa and clover in Columns (F) and (G) may not, for that reason, be strictly comparable with the figures for the other meals.

The Albumin and "Globulin" Fractions of the Cruciferae.—Only rape and radish seed meals were included in this phase of the problem. Water peptizes about the same percentage of the total nitrogen from both of these seed meals. They differ, however, in the percentage of the total nitrogen appearing as albumins. Column (B) shows that 8.46% of the total nitrogen of the radish seed peptized by water may be true albumin, whereas with rape the corresponding figure is 12.37%.

The Albumin and "Globulin" Fractions of the Corn Group.—These seeds form an isolated group of Table II when the various nitrogen fractions are considered. Only from 4.98 to 12.58% of the total nitrogen is extractable by water. These are the lowest values for any group of seeds studied. Of the four seeds, corn ranks highest in this respect and teosinte lowest. These seeds stand in Table II in almost the same relative order as they did when compared upon the basis of the percentage of their total nitrogen which was salt-soluble (Table I). Millet is an exception, however, and does not yield its nitrogen so readily to water as does sorghum seed.

Considerable difference between the four seeds is noticed when they are compared on the basis of the percentage of total nitrogen appearing in the albumin fraction. In this respect sorghum and teosinte have identical amounts (0.83%), with millet 1.43%, and corn 3.34%.

In percentage of total "globulin" the members of this group stand in exactly the same order as they did in Table I. It should be noted that the "globulin" content of corn is from twice to three times that of millet, sorghum, and teosinte, respectively. These seeds are also outstanding when their stability toward water is considered. The proteins of corn, sorghum, and teosinte are very stable, while the proteins of millet undergo some denaturation.

The Albumin and "Globulin" Fractions of Other Miscellaneous Seeds.—These seeds include the Brazil nut, flax, hemp, and Russian sunflower.

Brazil nut resembles vetch in that the salt extraction of the residue from the water extraction dissolved more nitrogen than was peptized by the water previous to treatment by KCl solution. Flax has 64.07% of the total nitrogen peptizable by water, of which 15.64% is albumin. Attention is called to Column (H), Table II, where a negative value of 16.81% is recorded. In the discussion of Table I we noted that the presence of gums in flax meal undoubtedly masked the lyotropic effect which might have been obtained had the gums not been present. The value of 57.64% which appear in Column (G) is, for that reason, probably too low. The figure given in Column (H), therefore, probably reflects in some manner the effect of the presence of gums upon the peptization behavior of the flax proteins.

The Effect of Different Reagents on the Total Nitrogen peptized, using the Same Charge of Sample.—Following the water and KCl peptization of a number of the samples listed in Table II, it was decided to re-extract the residues in the same manner, using 0.5 M KBr solution. No attempt was made to remove the small amount of KCl held by the moist residue before adding the KBr solution. The data are recorded in Table VI.

It will be seen that following the extractions by water and KCl, the addition of a 0.5 M KBr solution to the residue of barley peptized an additional 3.38% of the total nitrogen. The total amount extracted by water, KCl, and KBr was 25.55% of the total nitrogen. Column 6 shows that the water peptized 2.14 times as much of the total nitrogen of barley meal as did KCl following the water extraction. Column 7 indicates that KCl extracted 2.09 times as much nitrogen as did the subsequent extraction with KBr. Similarly 4.47 times as much nitrogen was extracted by water as was peptized by KBr following extraction by KCl.

An interesting relationship will be noted in the case of oats. Two samples of this meal were first extracted with water, 16.77% of the total nitrogen being peptized in the one case and 16.81% in the other. From this point on, the procedure was varied. Sample (1) was further extracted with KCl, followed by KBr. Sample (2) was further extracted with KBr followed by KCl. Column 5 shows that it makes little difference which salt directly follows the water extraction, since the total nitrogen extracted by water, KCl, and KBr totals about the same in either instance.

"Globulin"/Albumin Ratios from the Water Extracts.—The last columns of Tables II and V show the "globulin"/albumin ratios as obtained from all of the seeds studied. It will be observed that no two of the ratios are exactly alike. Even the cereal grains, which might have been expected to have had similar ratios, vary widely.

"Globulin"/Albumin Ratios from the Salt Extracts.—We have already suggested that the particular method employed in estimating the albumin and "globulin" fractions seemed to determine very largely the ratios found by other workers between these two proteins. In order to test this point further it was decided to make a number of salt extractions in exactly the same manner as was employed in the instance of the water extracts. The samples chosen for the study were corn, millet, sorghum, teosinte, and Brazil nuts. The results are shown in Table VII. Column 5 gives the ratios as computed from the salt extracts and Column 6 contains the ratios found from the water extracts. The disagreement between the two sets of values is most striking. Since exactly the same procedure was employed in both cases except that a different solvent was used, one must conclude that these differences are the result of employing two different methods. We feel justified, therefore, in concluding that our results substantiate what has been found by others, although never sufficiently emphasized, *i.e.* that the technic which is em-

ployed will determine to a large extent the ratio which one may expect to find between the globulin and albumin fractions of a seed. As to which method should be used of the many that might be considered, no data are at present available.

Does Elimination of the Ether-Extractable Material from a Seed Increase the Percentage of Peptizable Nitrogen?—This study included four legumes, beans, peas, alfalfa, and clover, together with hemp and corn. The percentage of ether extract ranged from 0.61% for the hemp meal which had previously been partially extracted with gasoline, to 11.72%. The data are shown in Table X.

It will be noted that with the exception of the alfalfa meal a greater percentage of the total nitrogen was peptized from the fat-free meal than from the whole seed meal. To explain the differences noted, one has only to assume that a part of the proteins of the seed are imbedded in or surrounded by a layer of fat or fat-like substances. Such an imbedding would act to prevent the ions of the salt from coming in contact with the proteins and thus exerting their maximum peptizing effect.

Protein Classification and the Lyotropic Series.—Gortner, Hoffman, and Sinclair[45] were the first to object to a system of protein classification based upon "solubility." Regarding the globulin fraction, they definitely raised the question of what salts should be used and what concentrations. As a result of their studies on twelve different wheat flours and solutions of twenty-two different inorganic salts, they state:* "We do not believe that any salt used, in any one of the concentrations, extracts a chemical entity which should be designated by the term 'globulin.' Our experiments would indicate that all of the various protein fractions (with the exception of the proteose) which have been considered fixed entities, and characteristic of wheat flours are, if we follow the prescribed routine procedure for protein isolation, capable of realization, but that, if the routine procedure is somewhat altered, fractions having different properties and characteristics are obtained." The recent work of Pascoe, Gortner, and Sherwood,[48] and Sinclair,[49] as well as the data reported in this paper have added confirmatory evidence to the findings of Gortner, Hoffman, and Sinclair.

Perhaps certain seeds or plant tissues may contain true chemical entities which can be designated as globulins. The peptization behavior of our Brazil nut meal indicates that a true globulin may be present in that seed and there are probabilities that the same may be true for radish, rape, and mustard seeds. It may be that only "crystalline" globulins are chemical entities and that the amorphous globulin preparations recorded in the literature are non-homogeneous fractions whose chemical and physical properties depend upon the technic employed in their isolation. However, the peptization behavior of the hemp seed meal certainly raises the question as to which salt solution isolates the chemical entity, "crystalline edestin;" which question can only be answered by further investigations.

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* It should perhaps be emphasized that their statement has particular reference to the proteins of the wheat endosperm.

Many years ago Ritthausen questioned the homogeneity of the albumin fraction as prepared from vegetable seeds. He suggested that the substance coagulated by boiling the aqueous extract of seed meals might belong to other groups of proteins which had to some extent been "dissolved" in the water. The protein literature to date renders questionable the existence in seeds of a true albumin with constant physical and chemical properties, such as characterize egg albumin. Therefore the preceding discussion of the varying albumin:globulin ratios with varying technic applies with equal force either to the "albumin" or the "globulin" fraction.

Only recently Blish and Sandstedt[55] have questioned the chemical individuality of the protein, glutenin, of wheat. They note that boiling 70% alcohol peptized glutenin and that six successive extractions of 20 grams of supposedly "pure" glutenin, each with one liter of boiling 70% alcohol peptized a total of 25.9% of the glutenin. Even after these six successive extractions more of the residue could be peptized by further extraction. However, the most striking feature of their work lies in the fact that *the composition (as expressed by a Van Slyke analysis) of the protein peptized varied from extract to extract* and also from the Van Slyke analysis of the original glutenin. They conclude: "It appears more than likely that 'glutenin,' as ordinarily prepared by the use of dilute alkali, is not a naturally occurring individual protein, but merely a 'fraction' derived through the action of the alkali, and varying somewhat in composition according to the strength of the alkali used, as well as with the time and temperature of extraction."

Glutenin has been regarded by workers in the field of the vegetable proteins as one of the most completely studied and characterized of the plant proteins. Osborne undoubtedly regarded it as a chemical entity so that in the light of the observations of Blish and Sandstedt, Osborne's[48] (p. 13) statement, "We can, therefore, for the present, treat as individual proteins only those products whose extensive fractionation has given no evidence that a mixture is being dealt with, and we must await new methods of study before any one of these proteins can be definitely accepted as a true chemical entity. Many, however, of the proteins with which we are at present familiar have shown such constancy of composition and properties that we feel justified in now considering them as substances of reasonably definite character," becomes doubly significant.

The above discussion has been directed primarily at the problems facing the worker in the field of the vegetable proteins. Whether or not they apply with equal force to the "proteins" isolated from animal fluids, cells, and tissues can only be answered by studies in which the animal fluids or tissues are peptized under a variety of conditions. However, the recent observations of Lustig[56] appear to be significant. Using non-standard technic Lustig isolates from blood serum three euglobulins, two pseudoglobulins, and three albumins! These preparations differed sharply from each other in both physical and chemical properties. If Lustig's fractions represent chemical entities, then the earlier preparations of the serum proteins were non-homogeneous. But there is no evidence that Lustig's preparations cannot be further fractionated by other technics. The whole question of protein individuality, protein classification, and protein isolation needs to be critically studied, and the workers in this field should divorce themselves from all preconceived notions as to what constitutes orthodox or non-orthodox technics.

Abderhalden[57] has drawn attention to the fact that the proteins as we work with them in the laboratory are not in the same physical state as they were originally in the cell. In fact the significant role they are called upon to play in vital phenomena depends upon their easy convertibility and sensitivity. He states that certain of the proteins in protoplasm undoubtedly have properties that are still unknown to us.

If Abderhalden is correct, then a number of the nitrogen-containing preparations which we term proteins may not in reality be distinct entities, but may be simply fractions of a large structure of which we know very little. From this viewpoint chemical reagents may, in many instances, merely bring about the peptization of a larger micelle into certain of its component parts, the properties and composition of which are determined by the reagent and technic which were used. Thus in the peptization of proteins by water, salt solutions, dilute alcohol, dilute alkali, etc., it may be that we are only fractionating a single primary substance and by changing to other reagents (*e.g.*, other salt solutions) another series of different fractions of this same primary substance may be obtained.

Summary

A study has been made of the peptizing effect of M/2 aqueous solutions of certain inorganic salts on the proteins of twenty-eight different seeds and grains. The investigation included barley, oats, and wheat, six different legumes, three *Cruciferae*, and other miscellaneous seeds. At least one variety of each of the eight principal types of wheats was investigated.

The data as presented seem to warrant the following conclusions:

1. A definite lyotropic or Hofmeister series of anions has been observed as influencing the peptization behavior of most of the seed protein complexes.

2. Barley, oats, and all of the varieties and types of wheats studied have the same lyotropic series, the anions arranging themselves in the order of increasing peptization effect of $F < SO_4 < Cl < Br < I$. Some variation is found in the case of the legume seeds. If the halogens alone are arranged, the order is essentially $F < Cl < Br < I$. The lyotropic order for the pea, however, is $SO_4 < Cl < F < Br < I$. Of the *Cruciferae*, radish and rape meals have the lyotropic order of anions of $F < SO_4 < Cl < Br < I$; mustard meal, $F < I < SO_4 < Br < Cl$.

3. The lyotropic effect in the case of corn, millet, sorghum, and teosinte meals is much less pronounced than that found for the other seeds. In fact no lyotropic order of anions could be demonstrated for sorghum seed.

4. Brazil nut meal and hemp meal had a lyotropic order of anions of $F < Cl < SO_4 < Br < I$; flax meal, $F < Cl < I < Br < SO_4$; and sunflower meal, $F < SO_4 < Cl < Br < I$.

5. The peptization behavior of the various groups of related seeds appears to be rather distinct and characteristic of each group.

6. Although the same methods were employed in each case, different globulin: albumin ratios were found where extractions were made with distilled water followed by 0.5 M KCl and those where only 0.5 M KCl was used.

7. A greater percentage of the total nitrogen was extracted from fat-free meals than from the whole grain meals.

In conclusion it is emphasized that protein "solubility" is in reality protein peptization, and that the technic which is employed may largely determine the yield and the properties of the protein complex which is isolated. The existence of true plant "albumins" as definitely characterized chemical entities is questioned. The available evidence indicates that many of the preparations which have hitherto been regarded as homogeneous and distinct plant proteins may in reality either be heterogeneous mixtures or else merely fragments of a larger and more complex protein micelle.

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THE COLLOID CHEMISTRY OF INSANITY. I*

BY WILDER D. BANCROFT AND G. HOLMES RICHTER**

It is only natural that a subject as interesting as insanity should have attracted the thoughts of men from the earliest times and invited speculations concerning its cause. In ancient times there was a difference of opinion even among the "wise men." Western civilizations regarded the afflicted person as one possessed of the devil and treated him accordingly. On the other hand, Eastern religions reasoned that the supreme being had prematurely removed the patient's soul as a special mark of favor. Neither of these explanations satisfy the intellect, nor are they acceptable to the medical science. However, the difference of opinion still exists.

Medical research was not slow to realize that physical causes were often at the base of the trouble. Indeed their studies of the subject showing the relation of diseases, growths, drugs, and in some cases the absence or underdevelopment of certain structures warranted the belief that all types of this affliction might be traced to some definite physical cause, i.e., some abnormal variation in the structures of the nervous system.

A Meyerson[1] expresses the idea thus: "When we speak about the causes of the major mental disorders, we must leave out of account the psychoanalytic and psychological points of view. Neither Freud, Jung, or Adler, to mention the great triumvirate who, like their Roman predecessors, once were in amity and now hopelessly divided, have dealt in sufficient measure with the insanities to give their points of view a validity. Nor is what they have contributed on these matters at all pragmatically recognized in the practical world which deals with the mentally sick. Nor is the psychological point of view, e.g., of Bernard Hart, that mental diseases are psychological situations which must be psychologically studied and treated, anything more than a philosophical pronunciamentio. When a patient has had his skull crushed in and develops a delirium (which is, of course, a mental disorder), neither psychiatrist nor surgeon is fundamentally psychological either in his understanding or his treatment of the case. Physical in its cause, they employ physical means."

It is indeed disappointing to admit that the above point of view has not withstood the criticisms, and that in a number of cases there have been found no definite physical variations in the nervous system that would justify that viewpoint. Meyerson again formulates this delicate situation thus: "The term 'organic' in medicine means that some organ is involved in its structure in a way which can be studied satisfactorily after death by the post-mortem

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** National Research Fellow in Chemistry.

[1] "The Psychology of Mental Disorders" (1927).

examination, or which can be tested out chemically or microscopically in life. This term is in contrast with the term 'functional' which implies that no study during life or after death reveals changes in structure, though very evidently there is something wrong with the working (i.e. function) of a part."

It is not the intention of this paper to discuss either point of view and its relative virtues but rather to indicate the application of colloid chemistry to this problem. To some workers this may appear audacious, that colloid chemists should claim that some of the phenomena are colloid in nature. We do not insist that colloid chemistry will explain all of the phenomena or serve as an extensive basis; but it is not improbable that, when medical knowledge is supplemented with colloid chemistry, the medical research worker, in addition to enjoying the fruits of both medical and chemical knowledge, will be freed of some of the present difficulties in regard to the "functional" disorders.

Colloid chemistry is still a very young science and indeed owes much to biological workers for its discovery and early development. Its close relationship to biology and medicine is shown in the universal regularity: that all living matter is colloidal in nature. The colloidal nature of the proteins, polysaccharides, fats, lipoids, enzymes, glycogen, etc., is the essence of their importance to the living cell. In fact everything in the cell is either colloidal in nature or can cause the colloids to undergo some change.

Despite this clear-cut case it is a perpetual source of surprise to some that medical workers do not attempt the study of colloid chemistry and apply it to their investigations. This peculiar state of affairs is understandable however if one considers the nature of some of their problems. A large number of pathological conditions can be easily demonstrated and studied by "fixing" and staining sections of the tissue and examining them with an ordinary microscope Let us take a specific example that concerns the nature of this paper, the histology of the nervous system. In order to examine this tissue in the regular way it is "fixed" usually in alcohol or formaldehyde containing various chemicals such as: bichloride of mercury, nitric acid, zinc chloride, ammonium molybdate, gold salts, acetic anhydride, picric acid, iodine, iron alum, osmic acid, silver nitrate, oxalic acid, or chromium salts.[1] The material is dehydrated, by passage through absolute alcohol, then embedded in paraffin. The material can now be cut easily into thin sections and stained by various dyes after removing the paraffin with xylene. This is the normal procedure for all material requiring microscopical examination. Colloid chemists will immediately note that the above reagents are, without exception, violent coagulating agents. The material that has been treated with such violent agents has nothing in common with a normal cell except the name.

The reason for this procedure lies in the fact that, when microscopes with bright-field condensers are used, naturally objects whose refractive index is close to that of the surrounding medium cannot be seen clearly unless they are stained. The normal protein colloids do not have any appreciable tendency to adsorb dyes and become stained as long as they are peptized. In order to

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[1] Lee: "The Microtomist's Vade-Mecum" (1928).

induce them to stain it is necessary to coagulate the material; hence the "fixing" agents are merely coagulating agents. The appearance of the finished preparation depends upon what fixing agent was used; naturally different types of coagulating agents produce different types of coagulation. It is interesting to note that when normal living cells are studied under the ultramicroscope they present an appearance radically different from that observed in the fixed and stained preparations.[1]

Still, this method can demonstrate bacteria in the tissues, the presence of abnormal growths, the absence of other structures, the extent of injury or degeneration, the differentiation of tissues, etc., so it has found a definite and valuable place in medicine. But it is indeed irrational to take the position that only knowledge gained through such methods is of any value to medicine, and that colloid chemistry is overstepping the bounds of propriety in pointing out that conclusions drawn from such studies are emphatically incomplete in relation to the living cell. For by their very nature they exclude the most characteristic properties of living material, namely the colloidal variations of the cell.

Insanity is a phenomenon exhibited by living beings and the fact that medicine has demonstrated only causative agents such as bacterial disease, presence of abnormal growths, the absence of other structures, and injury and degeneration causes no surprise to colloid chemists. It is a certainty that at least some types of mental disorders are due to the abormal variations of the colloids of the living nervous tissue. To what extent this may be generalized is not known at present but it cannot be excluded as a possible factor in any case not already explainable upon the basis of disease or organic disorders. Furthermore, since such variations are merely in degree of dispersion it will be impossible to observe these physical changes with modern histological methods because the basis of such technique depends upon complete coagulation before the material is ever examined.

Naturally, an interested worker would desire to know what would be the effects of a given variation in the degree of dispersion of the colloids of the nervous system, what variations are possible, and upon what evidence the conclusions have been based. The eminent pharmacologist, C. Binz,[2] and Claude Bernard[3] "the father of physiology" pointed out that the reversible coagulation of the sensory nerves and brain would account for all of the phenomena of narcosis. This theory soon fell into disrepute for two reasons: the assumptions regarding the process of coagulation were regarded as improbable and secondly their contemporaries were unable to fully comprehend the colloidal nature of the theory. Recently the assumptions were reinvestigated and found to be correct.[4] For the sake of clearness the reversible coagulation mentioned above does not mean the degree of coagulation observed in

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[1] G. Marinesco: Kolloid-Z., 11, 209 (1912); S. DeWitt Ludlum, Taft and Nugent: Archiv. Neurol. Psychiat., 23, 1121 (1930).

[2] Deutsche Klinik, Nr. 29, 277 (1860).

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eggs on boiling, or in milk on becoming acid, or in the clotting of blood. It is true that it is similar to these cases but it differs markedly in degree, the coagulation is very light: it cannot be seen with the naked eye and cannot be observed with an ordinary microscope. The flocculation can often be seen with the aid of an ultramicroscope and can be demonstrated in general by certain changes in the viscosity of the cell protoplasm.

By reversible coagulation is meant that the colloidal material returns to its normal state as soon as it is freed from the coagulating agent. This type of colloidal change in nervous tissue will inhibit its action and cause it to be in a state of narcosis. It is the "semi-coagulation" of Claude Bernard and can be brought about by certain drugs, suffocation, heat, cold, electrical currents, a physical blow, or even by the injection of water in some cases.[1] The first two agents are the most important from the biological point of view.

Various other explanations have been advanced to explain the action of drugs such as their distribution coefficients, surface tension, etc.; but the action of a drug does not depend so much on the physical properties of the substance as on the physical changes it initiates in the tissues. These changes are variations in the degree of dispersion of the colloids and this is the reason why intangible agencies as heat, cold, electricity, etc., can cause similar effects. The physical properties of a drug merely determine the distribution of the substance within the organism.

Suffocation can also bring about changes in the tissue colloids but in a roundabout fashion. Both aerobic and anaerobic oxidations not only serve as a source of energy to the cell but are very efficient detoxicating mechanisms. When asphyxiation is brought about, it allows the toxic products to accumulate to such a degree that they will cause the coagulation of the cell colloids. The following illustration may clarify the idea somewhat: most workers are familiar with the fact that a part of the lactic acid formed in certain tissues is converted back into glycogen and a part is oxidized to carbon dioxide and water. In the absence of oxygen the lactic acid accumulates to a marked extent. It is not so well known that lactic acid, or the lactates, can behave as narcotics. Nevertheless, it is an established fact.[2] The ability of lactic acid to coagulate bio-colloids is a familiar household experience in the souring of milk. One must bear in mind that there are a large number of substances that will accumulate and behave as in the above example, although the specific lactic acid example is used in the sense of an analogy rather than of an identity.

In connection with the phenomena of reversible coagulation it is interesting to note that the increasing instability of the colloids, before coagulation has taken place, is associated with the phenomena of stimulation. The stimulation is manifested in many forms depending upon the type of substrate which is affected, thus enzymes show greater activity, some cells show increased growth and activity, nerves an increased irritability, while in the brain tissue the stimulation is manifested by bizarre mental reactions as in

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[1] Bancroft and Richter: J. Phys. Chem., 35, 215 (1931).

[2] E. Mendel: Deutsch. med. Wochenschr., Nr. 17 April 29, (1875); Moskowski Wratschevni Westnik, 1876 No. 7.

drunkenness. Thus in passing into narcosis the tissue is first stimulated then narcotized; on recovery the passage back through the phase of stimulation is again noted. The increased activity of biological systems in their reactions and responses when the colloidal systems within them are approaching coagulation is quite important.

Another type of coagulation has been studied and its importance and application pointed out.[1] This type is the irreversible coagulation of the cell colloids. Whenever irreversible coagulation occurs within a cell the result is death, provided the coagulation is extensive. The reversibility depends to a large extent upon a time factor; as a rule the reversibility of the coagulation becomes increasingly difficult the longer it is allowed to stand. With disinfectants a dense, irreversible coagulation is produced and in a number of cases can be observed with the ultramicroscope. An antiseptic behaves towards bacteria as an anesthetic affects higher organisms. It inhibits the activity of the organism but does not kill unless the coagulation, due to the high concentration of the substance or the great length of time it is acting, becomes irreversible. The facts are briefly this: a coagulating agent first stimulates, inhibits, and then becomes lethal; the corresponding colloidal variations are: instability, reversible coagulation, and irreversible coagulation. If the substrate happens to be bacteria the order is the same: stimulation, antisepsis, and then disinfection. The phenomena and the colloid chemistry are the same on all simple substrates although the medical names vary. If we start with the assumption, that insanity is due to an abnormal state of dispersion of the brain colloids, we can have two types of insanity, one when the brain colloids are over-coagulated, and the other when the brain colloids are over-dispersed. The general changes on adding dispersing agents will be towards the left as given below, and towards the right on adding coagulating agents:

Death,	insanity,	normal,	insanity irritability,	sleep or anesthesia,	death.

Dispersion ⟷ Coagulation

Let us see what can be made of these facts and postulates in a few specific examples.

Alcohol is credited with some 8 or 10% of the mental disorders that lead to hospital incarceration. Alcohol is variously described as: an intoxicant, stimulant, narcotic, antiseptic, disinfectant, hypnotic, astringent, etc. Actually it is only a coagulating agent, which defines all of the above terms as soon as the substrate upon which it acts is given. If we confine our attention to its action on the brain, it is agreed that alcohol first stimulates and then depresses, the depression passing into sleep, anesthesia, or death depending upon the amount taken. If taken repeatedly in appreciable amounts it will cause some interesting disturbances. The stimulation of the visual faculties will bring about "the snakes," while stimulation of the auditory regions will bring about hallucinations of hearing, and stimulation of other regions of

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[1] Bancroft and Richter: J. Phys. Chem., 35, 511 (1931).

the brain will bring about general mental confusion. The combination of these effects in various degrees will mark the person as temporarily insane. These effects are due to the initial decrease in dispersion of the colloids of the nervous system and are entirely physical in nature. Since the initial phases of coagulation are easily reversible, it is not surprising to find that these cases recover in a short time. There is another type of reaction obtained after excessive and long-continued use of alcohol, marked by a demented state of long duration with pronounced disturbances of the intelligence, memory, and judgment. It is frequently associated with actual damage to the nervous system (Korsakoff's Disease). This slow or incomplete recovery with damage to the nerves is clearly a case of coagulation that is difficultly reversible.

The ability of alcohol to bring about alterations in the degree of dispersion of the colloids of the cell protoplasm is not hypothetical. Heilbrunn[1] has shown by means of his viscosity studies that this effect of alcohol is quite common. Marinesco,[2] using higher concentrations, was able to produce coagulations in the nerves of such density that he was able to photograph the colloidal change in the ultramicroscope. The mechanism of the coagulation with low concentrations of the material has been considered in another paper.[3]

Examples of damage to the nervous system, with the corresponding psychical changes, by means of known coagulating agents are very numerous. The action of lead on the nervous system is interesting. It is well known that lead salts can behave as coagulating agents towards bio-colloids. In fact their use in medicine as astringents and haemostatics depends upon this property. The effects of lead upon the brain are well known; it is found that there are but two phases of action.[4] In low concentrations or in the initial stage of poisoning, stimulation of the brain and of the optic nerves causes hallucinations of sight and mental disturbances which resemble those of delirium tremens. The second phase is exactly what one would expect of a coagulating agent. The stage of stimulation passes into depression, during which the early symptoms of paresis appear. In more advanced stages there is actual paralysis and damage to the nervous tissue. Lead is not alone in these effects; mercury, copper, and arsenic, which are coagulating agents, will cause disturbances of this type.[5]

Iodoform, an innocent coagulating agent, has a variety of actions that are understood best from a colloid point of view. The following quotation from "Useful Drugs" (1917) gives a good description of its effects. "Iodoform is a mild local analgesic, antiseptic, and stimulant. When adsorbed through the skin or from denuded surfaces, it produces intoxication which is not evident until after the lapse of some time. When swallowed, it is partially decomposed with the production of iodides which produce their ordinary effects. Part of the drug is adsorbed, however, in a form of combination not yet under-

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[1] "The Colloid Chemistry of Protoplasm" (1928).

[2] Kolloid-Z., **11**, 209 (1912).

[3] Bancroft and Richter: J. Phys. Chem., **35**, 215 (1931).

[4] J. F. Goodheart: J. Nervous and Mental Disease, 9, 435 (1882).

[5] Dana: "Textbook of Nervous Diseases" (1915).

stood, and produces symptoms that are different from those ordinarily caused by iodine. Iodoform is excreted slowly, iodine compounds appearing in the urine for several days after a single dose.

"The symptoms are restlessness, anesthesia, sometimes unconsciousness, occasional convulsions, hallucinations, and delusions of persecution, rapid pulse and elevated temperature; in many cases collapse, coma, and death may follow." Here is a case where local anesthetic, stimulant, intoxicant, hypnotic, antiseptic, and disinfectant are combined in one and the same substance. This action can be best explained on a colloid basis as outlined in the first part of this paper. The stimulation both locally and mentally being associated with the initial destabilization of the tissue colloids, which is later followed by reversible coagulation producing the anesthetic effect, hypnosis, or antiseptic action. Disinfection and death are due to the irreversible coagulation.

Schede[1] discusses a number of cases of insanity due to iodoform. He describes cases where the use of iodoform has been attended with marked psychical symptoms. One type noted among children was a marked dullness of special senses. In adults he has seen great mental confusion produced by the external use of iodoform. In one case there was loss of personal identity, general mental confusion, loud singing, and violence.

The substances mentioned above are in no manner exceptional. There are a host of other coagulating agents that cause identically the same thing, to name but a few: morphine, henbane, cocaine, hashish, atropine, hyoscyamine, hyoscine, carbon bisulphide, tea, coffee, tobacco, and the interesting case of a mechanical blow upon the head. When one is struck upon the head, the preliminary stage of stimulation is passed through so rapidly that the effect seems only to be anesthesia or death. On recovery from such mechanical anesthesia the stage of stimulation can be seen as symptoms similar to those of intoxication. The case for the mechanical coagulation of the colloids of nerves has been discussed in another paper.[2]

Indirect narcotics, such as carbon monoxide, have been known to produce insanity. A more interesting type is that produced by lowering the pressure of oxygen in a medium that is breathed by the subject. The exclusion of oxygen will lead to an asphyxiation narcosis; but, if the oxygen pressure is not decreased that far, an interesting series of mental reactions is observed. Such cases are important, because it is recognized that aviators in flying to high altitudes become temporarily incompetent.[3] There is a height for each aviator above which it is not safe for him to go. This is termed his "flying ceiling." The symptoms of the disturbance produced by tensions of oxygen lower than this value are mental confusion, leading to errors of performance: sometimes hallucinations of sight and hearing were found; in some men an uncontrollable desire to sing and whistle were manifested.

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[1] Centr. Chirurgie, Nr. 3 (1882).

[2] Bancroft and Richter: J. Phys. Chem., 35, 215 (1931).

[3] Sheep: The Flight Surgeon, Air Service Information Circular. July, 1921; Bagby: Psychopathology under low Oxygen Tension, ibid. May, 1920.

In conclusion, we may sum up the effects of both the direct and indirect coagulating agents by pointing out that when they are acting upon a given substrate, the increasing instability of the colloids followed by a reversible coagulation, which may later become irreversible, is associated with the stimulation, depression or narcosis, and actual damage observed in that tissue. The stimulation in particular is important because it is believed to be the source from which some of the mental phenomena of insanity originate.

The important point is that not just any degree of dispersion of the cell colloids will satisfy the needs of the cell. There must be some normal and definite state of dispersion of the nerve colloids and any alteration from this normal state will bring about the same type of mental disturbance as is observed in cases with organic disorders. There are at least two major alterations that are possible; first a decrease in dispersion (coagulation) and second, an increase in dispersion (peptization). It has been shown that those coagulating agents that have a preferential adsorption for the higher nervous centers and bring about the alteration of the colloids of that tissue to a lower state of dispersion will reproduce phenomena that are associated with certain types of insanity.

The alteration of the cell colloids in the opposite direction, towards an increase of dispersion, are also of an interesting character. Such an alteration can be accomplished by the preferential adsorption of an ion that will increase the potential difference between the colloid and the surrounding medium, or by the adsorption of another colloid, and thirdly by the adsorption of water. These are the three methods commonly employed in the laboratory to bring about peptization. If something were known of the chemistry of nerve cytoplasm it would be possible to discuss clearly the possibilities of peptization. Dana[1] gives the necessary data. The reaction of the tissue is alkaline, water is the dispersing medium, the important thing being that "the albuminous substances, called also proteins by Halliburton, have little or no phosphorus and make up the most of the cell-body or the cytoplasm." Peptizing salts for protein material in an alkaline medium have already received the attention of chemistry; from the Hofmeister series it is known that bromides, iodides, and thiocyanates will show this property in an alkaline medium.

Deliberate studies of the physiological or psychological effects of peptizing agents on the nervous system do not exist. However, since the bromides, iodides, and thiocyanates have been extensively used without realizing that they were potent peptizing agents, the literature on these substances will furnish the necessary data if properly interpreted. Before considering the data it is well to point out that, since the increasing instability of the nerve colloids are associated with stimulation, stabilization would be expected to bring about the opposite effect, at least up to a certain point. Also, it must not be overlooked that while the bromides, iodides, and thiocyanates are peptizing agents in an alkaline medium, they are just as potent coagulating agents in acid medium. This point will be emphasized later.

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[1] "Textbook of Nervous Diseases" (1915).

Krosz[1] gives a good description of the effects of the bromides and a summary of the earlier literature. The bromides lower the reflex irritability, this is noticeable in the throat where the base of the tongue, palate, and pharynx are involved, making swallowing difficult and a perceptible slowing of speech. Mentally there is a feeling of exhaustion and confusion combined with a dimness of vision and a slight deafness. The heart action is slowed. Albertoni[2] showed directly that the bromides lowered the irritability of the brain. He exposed the brains of dogs and by means of electrical stimulation found areas that when stimulated would produce convulsions in the animals. The animals were then fed upon bromides and the experiment repeated; it was found that in consequence of the bromide ion there was an enormous reduction in this irritability. Similar results were obtained by Bickels and Zbyszewski.[3] Although bromides are frequently referred to as hypnotics, they differ in that bromides produce restfulness through lowering of the reflex irritability, thus permitting a normal uninterrupted sleep to be realized. It is for this reason that they are so effective in combination with a true hypnotic such as chloral.

Peptization, unlike coagulation, is not very rapid; hence the administration of small amounts over long periods of time shows some effects that are different from those of a single dose. When administered over long periods of time there is no great tendency to sleep and the motor regions lose their irritability to such an extent that paralysis results and continued administration at this stage produces death.

The effect of the iodides have been studied by M. Sgalitzer.[4] The decrease in respiration frequency, lowering of the temperature, slowing of the pulse, etc., are similar to that produced by the bromides. In high concentrations there is the decreased irritability of the motor regions which will pass into paralysis. It was noted that narcosis was not produced by the iodides. Death is due to the paralysis of the breathing center. The ready decomposition of the iodides in the body with the liberation of iodine and the additional effect of iodine upon the thyroid complicate the pure peptizing action somewhat.

The literature on the action of the thiocyanates upon the nervous system is not very extensive. As to be expected, their effects are not unlike those of the bromides and iodides in lowering the irritability of the motor regions.[5] The ability of the thiocyanates to cause mental disturbance has been noted. J. F. Borg[6] describes the condition: "Toxic psychoses developed in four patients, with disorientation, hallucinations of sight and hearing, mania, confusion, and ideas of persecution, singly or in combination. They lasted only from five to seven days after the drug was stopped. They were all in patients to whom it had been necessary to give large doses to obtain a desirable reduc-

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[1] Archiv. exp. Path. Pharmakol., 6, 1 (1877).

[2] Archiv. exp. Path. Pharmakol., 15, 251 (1882).

[3] Neurol. Zentr.. 17, 1081; Zentr. Physiol., 34, 366.

[4] Archiv. intern. Pharmacodynamie, 18, 284.

[5] Münch. med. Wochenschr., 50, 153 (1903); Centr. ges. Ther., 22, 19 (1904); Med. Klinik, 8, 234 (1912); Wiener klin. Wochenschr., 25, 794 (1912).

[6] Minn. Med., 13, 281 (1930).

tion [of blood pressure]." The thiocyanates have been the least studied of all the peptizing agents, although it is probable that they will show this property to a greater degree than any other ion.

Throughout this series of bromides, iodides, and thiocyanates two interesting side effects are always noticeable, namely, irritation of the stomach and the skin. It will be recalled that in acid media these ions are strong coagulating agents. Naturally the coagulating effect in the stomach is due to the acidity of the gastric juices and will lead to the nausea and vomiting that are frequently observed. The effect on the skin is also intelligible if it is remembered that in most cases the perspiration is acid in reaction,[1] naturally the effect of coagulation would be irritation.

The conclusions that can be drawn from the study of the influence of coagulating and peptizing agents on the nervous centers are evident. A variation in the degree of dispersion of the colloids of such tissue from the normal state will bring forth abnormal mental reactions that are found to be not unlike the phenomena of insanity. Hence it is not improbable that in mental disorders not directly traceable to any organic disturbances, the cause may be due to some variation from the normal state of the brain colloids. Such a point of view is of great service because it can explain the effects of drugs on cases of insanity, give a simple classification of the types of disorders, and at the same time suggest substances that would alter favorably the course of the disorder.

A few specific examples will clarify this position somewhat. If a case of mental disorder could be found that was due to the over-peptization of the brain colloids such a state would be favorably altered by coagulating agents, provided enough of the drug were given to decrease the dispersion to the normal state. Such cases that respond to treatment by coagulating agents are known and the following experiments make it seem highly probable that the abnormally high dispersion of the brain colloids are responsible for the condition. In 1916 Loevenhart, Lorenz, Martin, and Malone[2] were conducting experiments on stimulating the respiratory center with sodium cyanide. A very interesting observation was made in the case of a patient with dementia praecox. This patient had been mute for several months, but following the injection of sodium cyanide there was a short period in which "the patient made a few coherent and relevant responses to simple questions." This peculiar property of sodium cyanide is not very marked and the substance is unsatisfactory. Later carbon dioxide was employed as a stimulant with very striking results.[3] The results of this significant piece of work are best given in the authors' own words: "The most favorable and striking reactions occurred in those patients who had been mute and mentally inaccessible for long period of time. In these cases, after a short period of respiratory stimulation, this inaccessibility disappeared and the catatonia passed off. A

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[1] Hammarsten: "Text Book of Physiological Chemistry."

[2] Archiv. Int. Med., 21, 109 (1918).

[3] Loevenhart, Lorenz, and Waters: J. Am. Med. Assoc., 92, 880 (1929).

number of patients have carried on conversation. A few mentioned depressive thoughts. One patient was markedly facetious, making responses typical of talkative hebephrenic dementia praecox. Another patient, the least reactive of those so far observed, showed only a disappearance of muscular tension and a voluntary looking about the room and at those standing near.

"A number of patients appeared frightened when the cerebral stimulation developed; they looked about apprehensively but became calm and at ease quite promptly when efforts were made to reassure them. In other words, they seemed to comprehend the situation correctly, and, following this almost immediately, they made coherent and relevant replies to questions. In one patient who had been mute for more than six years, the efforts at speech for about two minutes resulted in a jumble of unintelligible but speech-like sounds, after which the words became distinct and a successful conversation was held.

"The cerebral stimulation, as evidenced by free muscular movements, animated features, and ability to carry on conversation and to comply with requests has lasted from two to twenty-five minutes."

"During the period of cerebral stimulation, the inhalation of carbon dioxide and oxygen was stopped. If no more gaseous mixture is given, the patient gradually returns to his former condition. This return is as striking as is the development of increased psychic activity. Gradually the patient's attention can no longer be held; he ceases to respond to questions; muscular tensions redevelop, if previously present, and quite like the drawing of a curtain on psychic function, the patient returns to his former stuporous condition. In some cases, during the period of stimulated mental function, the patient responded quite like a talkative psychotic person, expressing many bizarre delusions and resembling in every way rather typical psychotic patients. In one notable case there was a prolonged period of from two to twelve minutes during which the patient maintained a comprehensive conversation without any evidence of psychosis; then quite suddenly the patient seemed to become frightened and began to express many delusions in a loud voice."

Since this manuscript was sent to the printer, there has appeared in the *New York Times* of March 29, an account of experiments by Dr. Karl Langenstrass on catatonic stupor at St. Elizabeth's Hospital in Washington. "Several years ago it had been observed that, by making the patient inhale a mixture of carbon dioxide and oxygen, it was possible to bring him back to consciousness for a period no longer than thirty minutes, during which he would behave in a normal manner. With this as a clue experiments were begun at St. Elizabeth's Hospital two years ago under the direction of Dr. Karl Langenstrass, who today described the results [at the annual clinical session of the American College of Physicians].

"Various ways of prolonging the period of recovery have been tried out. Beginning with a mixture of five percent carbon dioxide and ninety-five percent oxygen, the proportions were shifted gradually until it was found that a mixture of twenty-five percent carbon dioxide and the rest oxygen was the most advantageous. In addition to the inhalation treatment, Dr. Langenstrass told further that suggestion therapy, a mild form of hypnosis, was tried on the patient as soon as the gas mask was removed from his face after about half an hour of inhaling the mixture. Typhoid vaccine and coli fluid were also administered for the purpose of producing a rise in temperature.

"The net result, Dr. Langenstrass stated, is that one patient who had been in a mental stupor for over ten years has now been perfectly normal for the last two years. One woman is now supporting a drunken husband and three or four children. In all, three cases have been sent out into the world again functioning normally without any need of further treatment. The original treatment lasted for about a month."

Both sodium cyanide and carbon dioxide are known to be narcotic or coagulating agents, the carbon dioxide acting directly[1] while the sodium cyanide is an indirect narcotic.[2] It is to be noted that the reactions were observed before narcosis, or reversible coagulation was reached. It was also found that it was possible to narcotize a patient and observe the interesting phenomena after narcosis. W. F. Lorenz[3] describes the observations: "It was found that cases of catatonic stupor responded to this narcotic [sodium amytal] quite like a normal individual. That is, within 4 or 5 minutes, and before a total of 10 to 14 c.c. of the solution are injected they sink into deep sleep. The muscular rigidity disappears; the reflexes are abolished; breathing becomes slow and quite shallow; the systolic blood pressure falls 30 to 40 millimeters of mercury. After an hour the blood pressure returns to its former level; the patient can then be aroused and will respond to painful stimuli. Then follows a period of what appears to be normal sleep, the duration of which is largely determined by noises or other disturbing environmental influences.

"In the stuporous, catatonic cases we have seen prolonged periods of mental clearness following the state of deep narcosis. A brief account of one such case will serve to illustrate the striking change in mental condition, which is being presented. Case—T.W. (female); age 27; married and the mother of two children. She had been in a state of catatonic stupor for a period of four months when she was admitted to our service and sodium amytal administered. At this time the patient showed rather extreme muscular rigidity; active negativism; her limbs, head and body in a flexed position resembling the fetal posture. She had been tube-fed for over four months and voided involuntarily. Furthermore, she was in a state of extreme emaciation, weighing 66 pounds.

"This patient was given 1/2 gm. of sodium amytal dissolved in 10 c.c. of distilled water by intravenous route. Within 5 minutes she was in a state of deep narcosis. The muscular rigidity had disappeared; all reflexes, including the corneal, were absent. She continued in this state of deep narcosis for about an hour and then continued at a level of unconsciousness which could be influenced by slight painful stimuli. She remained in this condition

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[1] Heilbrunn: "The Colloid Chemistry of Protoplasm" (1928).

[2] Bancroft and Richter: J. Phys. Chem., 35, 215 (1931).

[3] Psychiatric Quarterly, 4, 95 (1930).

another three hours, or a total of 7 hours, after the time of the injection. She was then aroused by speech and she responded to conversation, asked for food and drink. She continued in this aroused mental state for a period of four hours, when no further efforts were made to keep her awake and she dropped into what appeared to be a natural sleep for a period of five hours, when the mutism, muscular rigidity, and active negativism slowly redeveloped."

Looney[1] studied the blood analysis of catatonic patients and found that there was an abnormally low amount of calcium present and an increase in creatine. He raised the calcium content slightly, but there was no change noted in the clinical condition of the patients. His investigation is being continued in the hope "that it will be possible to raise the calcium values up to about 15 mg. and keep it there for a period of at least a week so that definite conclusions may be drawn as to whether such a change results in any diminution of the muscle tension."

English[2] has employed an interesting coagulating agent, manganese chloride, in the treatment of nervous disorders. The following case is quoted from his study as indicative of the effects of treatment: "W.G.H.—18 years; single. Catatonic schizophrenia. Nutritive condition poor and inferior muscular development. Was defective as a student. Symptoms exhibited three weeks previous to admission. Dull, stupid state changing to one of impulsiveness and he became sleepless, stubborn and negativistic. He lay in bed markedly indifferent and refused food, and, if up, would stand for a considerable time even if placed in an uncomfortable position.

"He was given a course of manganese chloride and his weight, which was 88 pounds before treatment, increased to 146 pounds. There was also a marked change in his mental condition—he is now bright in manner, tidy in habits and thoroughly mischievous and over active." The original work should be consulted for other interesting cases.

Berger[3] has also had an interesting experience with the effect of coagulating drugs and catatonic stupor. He injected eleven patients with small amounts of cocaine hydrochloride and noted that the majority became suddenly active after the first injection. Like some of the above cases, the improvement did not last more than an hour or two. His observations lead him to regard the basis of catatonic stupor as a diminution of the processes of dissimilation and of the cortical functions generally. He does not regard the theory of psychic origin of catatonic stupor with favor.

Such striking responses as the above cases to known colloidal coagulating agents cannot help but impress one that the stuporous catatonic state is associated with an over-peptization of the colloids; and that the gradual decrease in dispersion produced by the narcotics must pass through the normal degree of dispersion before the other extreme of reversible coagulation is reached. Conversely, if the brain colloids of such cases are coagulated re-

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[1] Am. J. Psychiatry, 5, 213 (1925).

[2] Am. J. Psychiatry, 9, 569 (1929).

[3] Münch. med. Wochenschr., No. 15 (1921).

versibly and then allowed to pass slowly to the state of abnormally high dispersion, the system would again have to pass through the intermediate normal colloidal and mental state, as was found in the case that became normal anesthesia. The truth of this view is justified and strengthened in the fact that cases of mental disorders due to the opposite effect, i.e. decreased dispersion, can be materially relieved by peptizing agents. This statement will be made more convincing by illustration of facts.

Substances that so decrease the dispersion of the colloids of the central nervous system that it is in a state of stimulation can be antagonized by peptizing agents. Januschke[1] investigated a number of such cases. He was able to produce epileptoid convulsions in guinea pigs by means of camphor; running movements and clonic twitching of the muscles were marked. This condition would be maintained for several hours and in most cases would end with the death of the animal. Large doses of bromides would suppress these effects and even small doses would cause a marked diminution in intensity. Also the clonic contractions of the muscles of rabbits produced by cocaine, which are caused by the stimulation of the higher centers of the cerebrum, can be antagonized by bromides. The effects of picrotoxin can also be diminished by the bromides. He also found that the tonic reflex convulsions produced by strychnine could be abolished by means of the bromides. Since the bromides had no influence on physostigmine, which does not affect the cerebrum, he concluded that the primary effect of the bromide ion was on this and other centers of the spinal cord.

The effects of bromides on epilepsy afford a very interesting study. The actual cause, or causes, of epilepsy are not known, so it is a functional disorder; some of the external symptoms are produced by a host of toxic agents such as alcohol, lead, camphor, etc., and even by mechanical injury to the head. It does not seem improbable that in some cases a decrease in dispersion of the colloids is associated with the disorder. Dana[2] in speaking of the pathology says: "It is probable that in true epilepsy there is an instability of certain cell layers of the cortex cerebri and a tendency to degenerate". Degeneration from a colloidal viewpoint is nothing more than the coagulation and subsequent digestion of the involved structures, as it is impossible to digest peptized substrates. As already indicated, the phenomena of epilepsy are similar to those produced by stimulants, so it is no surprise to find that in many cases the phenomena can be antagonized by peptizing agents such as the bromides.

An unbiased account of the effects of bromides on epilepsy can be found in "Modern Medicine" by Osler and McCrae. They point out that "in view of the fact that the number of individual attacks is usually so speedily reduced by the exhibition of bromides, even to the entire suppression of them, the hope that the drug is a real curative agent in the disease has been and still is widely held. So great has been the reliance upon the bromides that real scientific therapy has actually been delayed by this erroneous empiricism.

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[1] Z. ges. exp. Med., 8, 17; Med. Klinik, 10, 389 (1913).

[2] Text Book of Nervous Diseases" (1915).

Until a few years ago the almost wholesale use of the drug made it possible for a public clinic to count the cases showing bromide poisoning as the rule rather than the exception. Happily the recognition that there is an acquired art in the use of bromides is removing this reproach.

"The whole plan of treatment including the bromides should be continued for years even though the attacks should cease. Some authorities regard the plan of successful routine a necessary plan of life henceforth; its long continuance after attacks have ceased (for several years at least) seems to upbuild and make for permanency of the restored normal psyche."

Wright[1] has recently studied the use of the bromides in functional disorders. He noted that the conditions which best respond to the bromide treatment were cases in which there was some degree of tension. Most of the cases in which the bromide treatment failed were found to occur in states of apathy.

If the disorders in epilepsy are due to an instability of the colloids with a tendency to decrease in dispersion, there should be two methods of relieving the symptoms. The first of which has already been discussed, i.e. peptizing effect of the bromides. It has already been indicated in the first part of this paper that a coagulating agent affects a normal tissue by first stimulating, then depressing the tissue. The depression passes slowly into sleep, narcosis, or death, depending upon the concentration of the drug and reversibility of the coagulation. If the tissue is in the stage of stimulation, as in epilepsy, then small amounts of narcotics will relieve the hypertension, because it will merely push it into the initial phases of the depression preceding narcosis. It is to this fact that the barbituric acid derivatives owe their popularity in the treatment of epilepsy.

The bromides have other interesting properties that would justify a more intensive investigation. In a recent paper we pointed out from theoretical reasons that peptizing agents might have a favorable effect in the treatment of drug addicts.[2] Since then our attention has been drawn to several interesting cases of this type.

MacLeod,[3] in 1897, treated a patient, suffering from migraine and a highly nervous state, with bromides. The patient was also a confirmed morphine addict. The course of the treatment was such that the patient was in a deep stupor for several days such as that produced by the bromides. Upon recovery from the effects of the bromide he noted: "To her own astonishment and that of the sisters (she had been in their charge previously) she had no desire for morphine from the time she entered the hospital, and I am glad to say it has not yet returned.

"This case was, so to speak, cured by mistake and is all the more interesting that the patient had no desire to be cured, as she had informed me on several occasions. Naturally desirous of being certain how far the bromidism con-

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[1] Am. J. Psychiatry, 5, 365 (1926).

[2] Bancroft and Richter: Proc. Nat. Acad. Sci., 16, 573 (1930).

[3] Brit. Med. J., 1897, 76.

tributed to the result, I determined to test the question by excluding other conditions."

His next case was that of a pilot on a boat who was a confirmed morphine habitué. The patient underwent a heroic treatment with the bromides and upon recovery was rejoiced over his deliverance from the craving for the morphine. An interesting side-light of this case was that he also lost the desire for liquor.

These are not isolated cases; the treatment was tried on several other drug habitués with favorable results in all except one case, which succumbed due to an error of the nurse in giving an overdose of the bromide.[1] Among these MacLeod says: "It is noteworthy that the loss of alcoholic craving in the second case was pointed out by the astonished patient himself."

Naturally, such interesting observations did not wait long before they were confirmed by other workers. Church[2] in America discussed the dangers of the treatment and apparently the whole matter was dropped. The unfavorable results were never due to lack of care, but more to the excessive doses of bromides. It should not be forgotten that it has never been shown that such large doses of bromides are necessary. As already mentioned, peptization is not rapid; hence the giving of bromides until toxic symptoms appear is dangerous, because the full toxic effect is somewhat delayed. The bromides should never be given to a patient with acidosis.

We do not wish to give the impression that drug addiction and its cure is all a purely colloidal problem. It is very important in treating addicts to hasten the elimination of the drugs from their system. In fact all the present-day treatments employ this as a preliminary measure; the next important thing is to restore the nerve colloids to their normal state, and this is best done only by colloidal means, such as peptization. The purging, education, hospital care, etc., of the patient are just as important but are not colloidal in nature and so have found no treatment in this paper.

Quite aside from this, the mere fact that a plausible explanation has been given to the action of the bromides, it would seem that medical interest would be centered in other peptizing drugs. Both the iodides and thiocyanates have this property to a greater degree than the bromides. The iodides cannot be employed very well due to their unfavorable effect on the thyroid. However, the thiocyanates offer many interesting possibilities both in the treatment of epilepsy and drug addiction that would justify a very careful and comprehensive study.

The bromides do not stand alone as examples of peptizing agents employed in medicine. The iodides have a limited application in the treatment of certain metallic poisonings, notably lead, mercury, and arsenic. As has already been indicated, the mental disturbances brought about by some poisons are similar to those shown in insanity. Clevenger[3] observed a case of lead

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[1] MacLeod: Brit. Med. J., April 15 (1899).

[2] N. Y. Med. J., 71, 904 (1900).

[3] Nervous and Mental Disease, 11, 308 (1884).

poisoning in which the symptoms of mute depression, observable in ordinary melancholia and epileptiform convulsions were present. He treated the patient with potassium iodide and in a short time the patient was discharged as fully recovered. He points out that "had the cause of this attack been unascertained, the patient would have died insane." Osler[1] gives a short summary of the use of the iodides in the treatment of cases of lead, arsenic and mercury poisoning.

Naturally the manner in which the iodides relieve the symptoms of such cases is an interesting topic. On first thought it might seem that the iodides form insoluble iodides with the metals and thus antagonize their action. This cannot be the complete story however, for the iodide of lead, for example, is soluble to the extent of 0.0442 gms. per 100 c.c. while lead chromate is soluble to the extent of 0.000007 gms. per 100 c.c. Yet lead chromate can easily bring about lead poisoning. While the amount of lead required to bring about poisoning is not known with great exactness, Brouardel considers that 1 mg. daily is sufficient. The treatment requires 0.3 gm of potassium iodide three times daily so that it seems quite necessary that an excess of iodide be present. This excess iodide undoubtedly behaves in the body as it does in the laboratory and merely serves as a powerful peptizing agent to the coagulated colloids of the nervous tissue.

This is by no means an exhaustive treatment of the subject dealing with the effects of colloidal reagents on the nervous system; the examples may be multiplied many fold, but the basic causes always come back to the alteration from the normal state of dispersion of the cell colloids. All of the work has been carried out by medical research workers who do not take into consideration that the materials they are dealing with are the best-known colloidal systems and that the drugs they use are potent reagents that will bring about colloidal changes in the tissues. Such a state of affairs is not conducive to a rapid advancement in knowledge concerning functional disorders. It is the hope of the authors that this paper may, in a small way, stimulate such workers to recognize that there is no sharp boundary between medicine and colloid chemistry, and that their researches are incomplete if they have not either included or excluded the variations of the tissue colloids in the pathological conditions.

Summary

(1) Medicine regards the major mental disorders as organic or functional disturbances. The causes and ideas of functional abnormalities are very hazy and incomplete.

(2) It is shown that while modern histological methods are well adapted to show the usual type of organic troubles they are absolutely inadequate to demonstrate the most characteristic property of living matter, i.e. the colloidal state, and its variations.

(3) The suggestion is made that many of the "functional disorders" may be nothing more than an abnormal degree of dispersion of the nerve col-

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[1] "Modern Medicine" (1915).

loids and have erroneously been classified as functional due to the inability of the histological technique to reveal the colloidal abnormalities.

(4) A study of the effects of known coagulating agents on the normal nervous system reveals that such colloidal reagents will produce symptoms that are not unlike many of those of insanity.

(5) The effects of peptizing agents are similar in many respects to other disorders.

(6) This is definite proof of the view that there is a normal state of dispersion of the nerve colloids and that any alteration from this state will bring about abnormal mental reactions.

(7) It is suggested that disorders of over-dispersion may be benefited by coagulating agents, and disorders of decreased dispersion would be improved by peptizing agents.

(8) Some physiological symptoms of catatonia are similar to the effects produced by peptizing agents. The striking results obtained in treating catatonic patients with coagulating agents indicates that this disorder may be due to the over-peptization of the colloids.

(9) Some of the symptoms of epilepsy can be reproduced by known chemical and physical coagulating agents. Both the symptoms produced by these agents and that of epilepsy are antagonized by peptizing agents such as sodium bromide.

(10) Other disorders, due to the use of coagulating agents, such as are found in drug addiction can be relieved by means of peptizing agents.

(11) The beneficial effects of potassium iodide in lead, arsenic, and mercury poisoning is another example of disorders of decreased dispersion being improved by peptizing agents.

(12) Coagulating agents cause changes in the brain colloids from normal through irritability and insanity to sleep or anesthesia, and death. Dispersing agents cause changes in the brain colloids from normal through insanity to death.

Our thanks are given to Dr. Seymour DeWitt Ludlum[1] of Philadelphia, who is primarily responsible for our starting on this investigation.

Cornell University.

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[1] S. DeW. Ludlum and A. E. Taft: Trans. Am. Neurological Ass., 1927); Alexander's "Colloid Chemistry," 2, 695 (1928).

ROTATION AND CONFIGURATION IN THE WALDEN INVERSION*

BY WILDER D. BANCROFT AND HERBERT L. DAVIS

In the past thirty years one of the important fields of research in organic chemistry has been the investigation of the phenomena commonly grouped under the heading of the Walden inversion. In general this work is an attempt to ascertain the course of more or less common reactions in organic chemistry with the special purpose of discovering if and when one group directly takes the place of another group or when the entering group occupies some other position in the molecule than that originally occupied by the displaced group. The latter is what Fischer called the Walden Inversion because it was first observed by Walden in 1895.

Study of these phenomena and of the literature dealing with them leads one inevitably to the conclusion that the crux of the whole matter is that no one is yet able definitely to correlate the configuration of any two related compounds as this configuration is revealed by their optical rotation. As long as there is a lack of such knowledge it will be impossible to tell *when* a Walden inversion takes place, to say nothing about studying the conditions which tell *why* or *how* such an inversion proceeds. That this problem is of great importance is testified to by Stewart[1] who says: "In the whole field of stereochemistry, no more puzzling phenomena are known than those grouped under the head of the Walden Inversion, and at the present time we still await a solution of the problem. The data are so complicated that it would be impossible to deal with them fully here."

The present paper proposes a return to, and more rigid adherence to, the criteria laid down by van't Hoff to govern the observation of the rotatory power of a substance. It offers also a method of correlating optical active substances with one another and with their rotatory power, and finally applies these criteria to some of the more common substances and reagents employed in the Walden inversion, classifying them into substances and reagents whose reactions are or are not characterized by Walden inversions.

Much of the work on the Walden inversion has been done with the hydroxy acids, and the examples selected will be of that type, although nearly all types of optically active compounds have been at one time or another the object of this sort of investigation. Early in the discussion it should be emphasized that there is no immediate connection between the sign of rotation and the configurations of two related compounds. Thus, merely because the chlorosuccinic acid derived from l-malic acid possesses the opposite rotatory power, one is not justified in assuming that an inversion took place during the reaction. The inversion is solely a matter of changed configuration and

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*This work is part of the programme now being carried out at Cornell University under a grant from the Heckscher Foundation for the Advancement of Research established by August Heckscher at Cornell University.

[1] Stewart. "Recent Advances in Organic Chemistry," 2, 16 (1927).

as yet we do not know that in this case a changed configuration is associated with a change in sign. It will be shown later that this is probably so in the malic acid series, but generalization is not simple. This all leads to an immense amount of confusion and the custom has grown up, following Fischer's sugar work, of designating compounds not merely "*l*" or "*d*" but we find various compounds called "*l*(+)", "*l*(−)", "*d*(+)", *or* "*d*(−)". This means that a given compound may belong to the "*l*" series so far as configuration is concerned and possess either dextro or levorotation. In the designation of the series to be used, most authors agree in selecting natural *l*-malic acid as the typical example of the "*l*" series configuration while natural tartaric acid is the type compound of the "*d*" series, and most determinations of configuration go back to these compounds or their derivatives as the starting point. The great difficulty of this method of representation is that the conclusions reached by any single investigator are not those of any other, and consequently the letter designating a given compound may vary from author to author while the sign of the rotation will usually be the same, if observations were made under similar conditions. This all appears, and is, very perplexing, but no remedy for the situation is in sight unless we can agree on some criteria to correlate the configurations as is attempted here.

In order to make the problem as concrete as possible a typical case involving the Walden inversion, and the first one discovered, will be outlined. It is from the malic acid series.

$$\text{(I) } l\text{-malic acid} \xrightarrow{PCl_5} \text{d-chlorosuccinic acid} \xrightarrow[\text{aq. solution}]{\text{in acid}} \text{d-malic acid}$$

$$\text{(II) } l\text{-malic acid} \xrightarrow{PCl_5} \text{d-chlorosuccinic acid} \xrightarrow[\text{aq. solution}]{\text{in alkaline}} l\text{-malic acid}$$

Case (I) represents the simplest case of a Walden inversion for there can be little doubt that the two oppositely rotatory malic acids possess opposite configurations, or are antipodes. The doubt in this case comes when one attempts to answer the question, "In which of the two reactions did the inversion occur?". Case (II) will be explained if there is either no inversion in either reaction, or there is inversion in each of the reactions; in case (I) there can be inversion in only one of the two reactions. There are two possible solutions to the problem; the one is that the action of the PCl_5 is normal and without inversion and that the d-chlorosuccinic acid is of the same configuration as the l-malic acid and that consequently the hydrolysis in acid solution is accompanied by inversion while that in alkaline solution is normal and without inversion. The other solution, and the one which in view of other evidence seems more probable, is that the replacement of hydroxyl by chlorine is here accompanied by inversion and that the acid hydrolysis is normal while the alkaline hydrolysis is abnormal. It is now seen that the final solution of this typical problem of the Walden inversion will not be reached until we are able to say definitely that d-chlorosuccinic acid is of the same configuration as *l*-malic acid, or is of the opposite configuration. Since there will be always at least two reactions between an optically active substance and its antipode, as in this case, this question will arise in every investigation of the Walden inversion. The fundamental importance of the correlation between optical rotation and the configuration of these compounds is obvious.

There have been several criteria proposed to establish this correlation and a few of them will be briefly reviewed. For many years Freudenberg has studied this problem, principally by means of reactions in which the groups directly attached to the asymmetric carbon atom were not replaced as a whole but were altered in steps. In one of his later papers[1] he expresses his conclusions to the effect that natural (+) lactic (sarcolactic), (−) halopropionic acids, (+) alanine, (−) malic, (−) monohalosuccinic acids, and (+) asparaginic acid all belong to the l-series. If this conclusion that l-malic acid is of the same configuration as l-chlorosuccinic is accepted, then it follows that the reaction involving phosphorus pentachloride proceeds with inversion, that is, the chlorine goes in at a different position in the molecule from that just vacated by the hydroxyl group. Correspondingly, hydrolysis in acid solution proceeds normally while inversion attends the hydrolysis in alkaline solution. This is in accord with the conclusions reached by applying the criteria of this paper, as indeed are the rest of Freudenberg's classifications.

Another method of configuration determination was proposed by Hudson in relation to the amides. This rule proposed that those hydroxy acids whose amides are dextrorotatory be designated "*d*" acids. Freudenberg amended this rule to read that all such acids are to be designated as d-acids of which the amides have a higher dextrorotation than the free acids. This amendment was made to permit the inclusion of l-mandelic acid in this series.

Some d-acids.

d-Lactic	−2.5° to −4°	d-Lactamide	+ 22°
d-Glyceric	−2.1°	d-Glyceramide	+ 66°
d-Malic	+3° to −3°		
d-Malamidic	+9.3°	d-Malamide	+ 40°
d-Tartaric	+6 to +14°		
d-Tartramidic	+64°	d-Tartramide	+106°
levo-Mandelic	−153°	levo-Mandelamide	−95.5°
Hexahydro-levo-Mandelic	−26.6°	Hexahydro-levo-Mandelamide	+41.7°

Freudenberg[2] made the inclusion of the mandelic acid after the preparation of the last-named acid and its amide, arguing that the hydrogenation of the mandelic acid would have no effect on the configuration and that since the hydrogenated acid was of the d-series according to the rule of Hudson, so also was the original mandelic acid. Thus the replacement of the carboxyl

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[1] Freudenberg and Lux: Ber., 61B, 1083 (1928).

[2] Freudenberg, Brauns, and Siegel: Ber., 56, 193 (1923).

hydroxyl group by the amino group produced a change in rotation ranging from 6° to 68° in the dextrorotatory direction. Similar substitution in l-malic acid produces a comparable increase in levorotation. It will be shown more at length later in this paper that the lactic acid which is here classified as d-lactic acid gives the levorotations here listed in aqueous solution but gives dextrorotatory salts and esters which show the acid to be truly of the d-configuration. In the same way d-malic acid in concentrated solutions gives the levorotation here mentioned, while in dilute solutions the dextrorotation becomes evident. The inclusion of the mandelic acid will also be justified later.

One of the first attempts at correlation of the forms of optically active substances was made by Fischer, who concluded that dextro-tartaric, dextromalic, and levo-aspartic acids were configurationally related. More recently Freudenberg and Braun have converted d-tartaric into d-malic acid and l-malic into d-glyceric and further into dextrolactic acid (should be l-lactic). As a result of these experiments it appears that d-tartaric, d-malic, l-glyceric, and l-lactic (the two last should be d-) all belong to what is called the *"d"* series. Hudson and Levene have extended the work of Fischer to the sugar acids and simpler aliphatic acids, using the amide rule as one method of attack.

Some very extensive investigations of this problem have been based by Clough on the assumption that substances of similar configuration would exhibit similar changes in specific rotation under the influence of the same external conditions such as temperature, solvent, the presence of foreign substances such as inorganic halides, and certain substituents either on the asymmetric carbon atom or in another group such as the carboxyl group in the molecule. In this work Clough[1] agreed with the previous workers in regard to the four acids just named and added to that list some other hydroxy acids. His classification is made because the acids, their salts and esters and some derivatives behave similarly, in that rise in temperature makes them more strongly dextrorotatory, dilution of the aqueous solution increases the rotation, the sodium and potassium salts are more dextrorotatory than the free acids, and inorganic halides affect them in the same way—making them more levorotatory. None of these tests can be applied too strictly and Clough himself says there are some important exceptions to the rules. For instance, the rule provides that the substance show a positive coefficient of rotation with rise in temperature and yet such important substances as methyl and ethyl tartrates show diminishing rotatory power with rise in temperature. These same esters in the presence of salts show increasing rotations as does free tartaric acid itself.

A review of the literature on these relationships and of his own important work on them has been made by Levene[2] who finds general agreement on the configuration of the hydroxy acids but comes to different conclusions regarding the chlorosuccinic acids. He agrees with Holmberg[3] in designating the

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[1] J. Chem. Soc., **113**, 526 (1918).

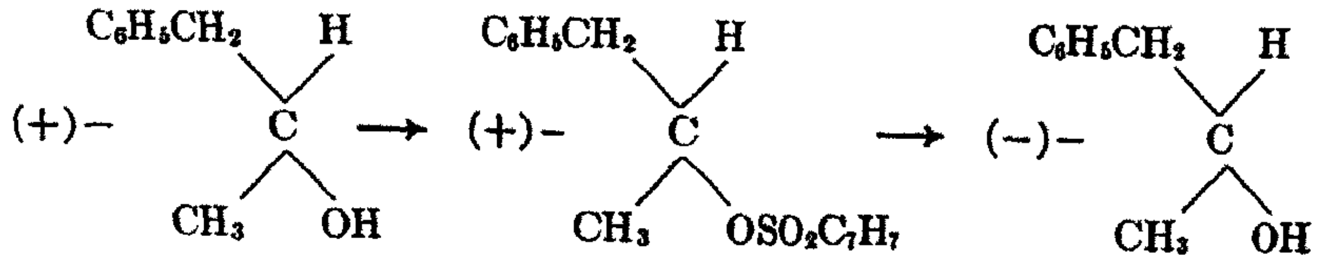
[2] Levene: Chem. Rev., **2**, 179 (1925).

[3] Holmberg: Svensk. Kem. Tid., **41**, 60 (1929); Chem. Abs., **23**, 3441 (1929).

levorotatory halosuccinic acids as of the d-configuration while Freudenberg calls them of the l-configuration. Holmberg concludes that so far there is no general method available for ascertaining the configuration of mirror image isomers. Those offered are objectively unsatisfactory and allow subjective evaluation of evidence leading to conflicting results.

Before leaving these attempts to establish relative configurations, it might be well to point out that just as we know that many of the reactions involving the groups attached to the asymmetric carbon atom proceed with inversion and that therefore such reactions are of very doubtful value in determining whether an inversion took place or not, so also there is some evidence to the effect that even when the reaction does not affect the asymmetric carbon atom directly but only involves change on groups attached to a neighboring atom, still change of configuration may occur. Fischer[1] attempted to answer this question through successive reactions interchanging two groups on the asymmetric carbon atom and thus producing the optical antipode to the original substance. According to this the configuration of the asymmetric center remained unaffected by substitutions.

Quite otherwise, however, is the evidence in the esterification and subsequent hydrolysis[2] of the (+) benzyl-methylcarbinol which produced the oppositely rotatory product.



Wittig, in his discussion of this case, says that this reaction, although the formula recognizes no substitution on the asymmetric carbon, may nevertheless be brought into the series of the Walden inversion if one assumes that the mechanism of the reaction is such as to separate the ester group directly from the asymmetric carbon:

$$>C\ \underline{|OSO_2C_7H_7 + H|}\ OH$$

and not from the oxygen atom:

$$>CO\ \underline{|SO_2C_7H_7 + HO|}\ H$$

A summary of several such cases has been made by Kuhn[3] which indicates that, while such reactions are not common, they are by no means impossible.

After thirty years of the most extensive investigations of the Walden inversion it seems a pity that we are no nearer being able to tell when an inversion takes place. We know they do take place; indeed Werner claimed that the inversion was the ordinary method for reaction to proceed and that

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[1] Fischer: Ber., 47, 3181 (1914).

[2] Phillips and Kenyon: J. Chem. Soc., 127, 399 (1925); cf. Hückel: Z. angew. Chem., 39, 842 (1926).

[3] Kuhn: Ber., 58, 2088 (1925).

direct replacement was the exception. That does not appear to be well founded and most of us still look upon the inversion as an abnormal course for a reaction to follow—possibly because up to the time of Walden's observations that was the only possibility that had been thought of. Most of us still continue to try to divide these reactions into the normal and the inversion reactions.

This attempt meets with several specific difficulties. It is not always easy to decide just what the rotation of a given compound is. Natural malic acid is dextrorotatory in the fused state or in concentrated aqueous solution; its dilute solutions, salts and esters are levorotatory. It is called l-malic acid. The opposite is true of natural tartaric acid and it is called d-tartaric acid, these two being taken as prototypes of configuration. This difficulty of having the rotation of an acid in concentrated or even in moderately dilute solutions in the opposite sense to that of its salts and esters is a common one. It is even more troublesome in the case of the amino acids. The amino acids of the succinic and propionic series are weakly rotatory and their rotation and solubility are both enhanced in acid solution where, of course, salts may form. Therefore they are usually examined in acid solution. Natural aspartic acid is dextrorotatory in aqueous solution or in acid solution but in alkaline solution it is levorotatory and its esters are levorotatory. The same things are true of alanine, or alpha amino propionic acid. With all this uncertainty these same amino acids are most common and often used in the Walden inversion. Many of these substances show widely varying rotatory powers depending on the state in which they are observed, as liquid esters, etc., or in varying concentration in varying solvents. One of the first necessities should be to establish some common state in which these substances may show their true activity in order that we may arrive at some logical conclusion concerning their configuration. This was done years ago by van't Hoff[1] and some quotations from him should make clear the necessity of adopting such standards. Chapter VII of this treatise is entitled, "Numerical Value of the Rotatory Power," and some quotations will be selected from this chapter.

Factors recognized as affecting the rotation include the wave-length of light, the solvent, and the temperature. Then, p. 134;

"It is certainly inadmissible to use simply the figures obtained by an examination of the substance without special precautions, because the size of the molecule is then uncertain, and the magnitude of the rotation seems to be specially influenced by every change in constitution. In this connection it is important to remember the fact recently discovered by Ramsay, that, of fifty-seven liquids examined, no less than twenty-one possessed double molecules, among them the alcohols, acids, nitro-ethane, acetonitrile, and acetone. Another objection is that the rotation is generally influenced by the solvent, and, indeed, by every solvent differently, perhaps in consequence of the four groups attached to carbon being differently attracted. If the substance be used alone, without solvent, its own molecules may be supposed to exert a

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[1] van't Hoff: "The Arrangement of Atoms in Space," (1899).

similar influence, an influence displayed most prominently in the formation of crystals, and which, in the case of strychnine sulphate, e.g., leads to the almost complete annihilation of the rotation.

"The objections mentioned disappear completely only when the substance is examined in the state of rarefied gas. As this is impracticable, we are driven to adopt some other means, and thus arrive naturally at the state of dilute solution. It is also indispensable, of course, to take into account the molecular weight, which can then easily be determined; while the comparability of the results will evidently be by far the greatest when the same solvent is chosen for the different cases.

"The influence of wave-length and of temperature seems not to be important if the circumstances of each case are duly taken into account. The anomalous rotation-dispersion in the case of, say, tartaric acid in aqueous solution—which is such that the rotation changes its direction with the color—is evidently connected with the phenomena of equilibrium which affect the tartaric acid in the solution; it was also found by Biot in a mixture of right and left-handed substance[s]. The same holds for the great alteration in the rotation of tartaric acid when the temperature, the concentration, or the solvent is changed. All these phenomena are connected together and only make necessary a careful use of the figures obtained, but are no argument against the existence of relations between rotation and constitution in general."

In the next section, van't Hoff shows the applicability of the law of Oudemans-Landolt, according to which the rotations of the various salts of an optically active acid or base extrapolate to the same value for the rotation of these salts in dilute solutions.

"In these investigations the theory of electrolytic dissociation is a valuable guide; it enables the Oudemans-Landolt law to be predicted, and sees in the equality of rotation of the different salts the consequence of the existence of the same ions."

From a table van't Hoff selected the following numbers as representing the specific rotation of the ions in question.

Tartrate	43°	Diff. 14
Acid tartrate	29°	
Malate	14°	
Acid malate	9°	
Glycerate	22°	
Methoxysuccinate	15°	Diff. 14
Acid methoxysuccinate	29°	
Ethoxysuccinate	23°	Diff. 14
Acid ethoxysuccinate	27°	

"From this we see at once that, when the rotation alters on dilution, only the values at the limit are to be taken, and doubtful cases may be decided by a determination of the conductivity—i.e. of the molecular weight—accompanying the observation of the polarization."

The next section deals with the "Rotation of Imperfect Electrolytes. Organic Acids" and we find, p. 141:

"These substances demand separate treatment because, representing as they do the transition stage between electrolytes and non-electrolytes, they exhibit—in aqueous solution at least— complicated phenomena, which, however have already been partially accounted for. In view of the alteration of the molecular conductivity and of the lowering of the freezing-point with the concentration of their solutions, it is evident that water effects a fundamental change in their molecular structure—dissociation, in fact. The salts, especially those of strong acids and bases, show this at degrees of dilution which admit of an optical examination, and then Oudemans' law holds. With the acids this is not the case."

Van't Hoff then gave data to show that while the non-electrolyte sugar and the electrolyte disodium tartrate show relatively slight changes in rotatory power as the solutions are diluted, the imperfect electrolytes tartaric and malic acids showed very large changes, in the case of malic acid a change from right to left being observed as the solution is diluted. He proceeded to deduce five laws governing these complex phenomena.

"1. The alteration in rotation effected by change of concentration is parallel with that effected by change of temperature, dilution and rise of temperature acting in the same direction, as in general both have the same effect on dissociation. For sugar and the tartrates the alteration with the temperature is scarcely perceptible. With tartaric acid, warming like dilution effects a rise. In the case of malic acid, Pasteur found in the dilute left-handed solution an increase of rotation to the left on warming, which is the result Schneider obtained by dilution. With mandelic acid Lewkowitsch observed a decrease in the rotation on diluting and on warming; with rhamnose Tollens found the same thing.

"2. The change of rotation with the concentration is parallel with that effected by the solvent, so that the rotations in other solvents approximate to those in concentrated aqueous solution. Tartaric acid, which in water gradually rotates less to the right as the concentration increases, exhibits in other solvents now a weak right-handed rotation, now even left-handed rotation as in alcohol.

"3. The change of rotation on dilution is in the direction of the numbers obtained for the [acid] salt, and appears to be limited by these numbers. It is again, in the case of tartaric acid that the subject has been most thoroughly investigated." Data show this to be true of tartaric acid and of malic acid. "Lactic acid, the right rotation of which is diminished by dilution (21.24 per cent. $(a)_D = 2.66$; 15.75 per cent. $(a)_D = 2.06$), possesses accordingly left rotation in its salts."

"4. The acids which undergo no change of rotation on dilution are also those which rotate as strongly as their acid salts. Methoxy- and ethoxy-succinic acids exhibit rotations which scarcely alter with the concentration and these rotations are almost the same as those obtained for the acid salts." The same situation prevails with quinic and shikimic acids.

"The hypothesis of electrolytic dissociation explains these facts to this extent, that it demands that dilution of an acid and salt formation shall bring about equal activity, since both cause the formation of the same ion. For dibasic acids the same holds for the acid salts, because dilution of these acids first liberates a single hydrogen atom.

"Evidently, however, there is something else concerned beside electrolytic dissociation, and that is the point of attack offered to the carboxyl group in another part of the molecule, as appears from the following.

"5. Great change of rotation on dilution manifests itself especially with the oxy-acids. Malic acid is remarkable in this respect. The change of rotation which we have observed to characterize this acid is no longer found in methoxysuccinic acid and in the corresponding ethyl derivative, nor in chlorosuccinic and acetylmalic acids. Thus when the hydroxyl group disappears, the rotation becomes more constant. The peculiar part played by this group is, however, still more plainly manifested in the gradual change which often occurs in oxy-acids after a change of concentration or of temperature. This was first observed in the case of lactic acid, the rotation of which decreased on simple standing of the freshly prepared solution; it was recently proved in the case of glyceric acid, and is due to etherification or lactone formation, as Wislicenus showed. This will be considered in the next section.

"In the oxy-acids, then, the alteration of the rotation on dilution may be due to a phenomenon akin to lactone formation, which also is probably influenced by electrolytic dissociation. Finally, several acids, and not oxy-acids only, possess a double molecule, and accordingly on changing the concentration they make break up in a way which will affect the optical examination. *Comparable results for acids are therefore scarcely to be obtained except by an investigation of dilute solutions of the alkali salts.*"

We shall at once make use of these criteria. In the case of malic acid (hydroxysuccinic) there is little doubt that the levorotation of the dilute solutions, of the salts, and of the esters fixes the true rotation of the malate ion as levorotatory. Aspartic (aminosuccinic) acid on the other hand offers more difficulties in that its rotation free in aqueous solution is dextro as is also the case for the acid solutions. But the levorotation of its salts and esters fixes this form of the natural aspartic acid as actually levorotatory. The statement of Holmberg that the natural dextrorotatory aspartic acid and the natural levorotatory malic acid are of the same configuration then takes on some meaning and when supported by other evidence to be offered later will be seen to be true. This is the aspartic acid which with nitrous acid gives l(-)malic acid and with nitrosylchloride gives l(-)chlorosuccinic acid.

The situation in the propionic acid system is similar. Natural or sarcolactic acid is dextrorotatory in aqueous solution, and its salts and esters give levorotations. This is the form which Walden properly wished to call l-lactic acid but there seems to be no real agreement to follow his suggestion even though it does represent the facts. The general form of the dilution-rotation curves for lactic and for malic acid is similar. The difference lies in the fact that in the lactic acid we are not able to follow the change into levorotation while with malic acid this is easy. The literature of alanine (aminopropionic acid) is less clear but it seems certain that the so-called d-alanine should actually be called l-alanine since it gives levorotatory esters and produces with nitrous acid a lactic acid whose zinc salt is levorotatory and with nitrosyl bromide a levorotatory α-bromopropionic acid.

The halogen-substituted acids of these two series present no problems for in as much as their rotations differ little with concentration, so also do the salts and esters present the same direction of rotation as the acids themselves.

Now that it has been established just what acids we are thinking about, we may take the next step and correlate the configurations in each series. The reactions just mentioned for the acids will not serve for this purpose since we do not know whether or not they involve the Walden Inversion or are examples of normal direct replacement. To correlate the configurations we shall return to the treatment of van't Hoff and employ a criterion which even in his day was known to have exceptions and weaknesses but which did serve in numerous cases. We offer this, therefore, as a first approximation and justify it empirically until a better criterion be found.

This citerion is that the rotation of an optically active molecule can be expressed in terms of some characteristics of the four different groups attached to it. The theories of Guye and of Crum Brown were expressed by van't Hoff in the equation;

$$P = (g_1\text{-}g_2)\ (g_1\text{-}g_3)\ (g_1\text{-}g_4)\ (g_2\text{-}g_3)\ (g_2\text{-}g_4)\ (g_3\text{-}g_4),$$

where P is the product of asymetry, determining the rotation, and g_1-g_4 are the group-weights in question, p. 155.

"This expression is not a necessary consequence of Guye's conception, but only a formulation of it upon certain assumptions made for the sake of simplicity. It is to be regarded as a special case of the view of Crum Brown, according to which K and g are identical. Finally, we may repeat that the essential requisite, that $P = 0$ when two groups are identical, is fulfilled; and that if two groups, g_3 and g_4, e.g., change places, the sign of P is simply reversed, its numerical value remaining the same.

"From this view the following novel and essential consequences result. If the groups are in the following order:

$$g_4 > g_3 > g_2 > g_1,$$

and the substance is, say, right-handed, then when g_4 is replaced by smaller and smaller groups, we may expect:

1. Diminution of the right rotation for $g_4 > g_3$;
2. Inactivity when $g_4 = g_3$;
3. Left rotation, increasing to a maximum and then diminishing, when $g_3 > g_4 > g_2$
4. Inactivity when $g_4 = g_2$;

5. Right rotation, increasing to a maximum and then diminishing, when $g_2 > g_4 > g_1$;

6. Inactivity when $g_4 = g_1$;

7. Left rotation, increasing when $g_4 < g_1$.

"Thus when one of the groups gradually passes from the maximum to the minimum the sign of the rotation will change four times." [*Three appears to be the correct number*].

We are fully aware of the exceptions to this criterion which led the early investigators to set aside the theory of Guye and of Crum Brown as complete expressions of the relationship between the composition of a molecule and its optical activity. Despite these defects no better method has been devised and the application of this method promises more advance than merely indefinite guesses as to the relationships which may exist. It appears very probable that factors other than the mass of the attached groups may influence the optical rotation of an asymmetric carbon atom; but no one knows what these properties are nor how to evaluate their influence into some other number which might be introduced into some such mathematical expression for rotation as was given by van't Hoff. Levene has proposed his idea in his chapter on Stereochemistry.[1]

"The question of the relationship of chemical structure has been discussed by Levene and Haller, who reached the following general conclusions. The optical rotation of a substance is the resultant of several factors, of which three have been definitely pointed out: first, the respective masses of the radicals attached to the asymmetric carbon atom; the polarity of the groups; and third, the distance of the polar groups from the asymmetric carbon atom. The effect of unsaturation and of branched chains have also been studied but sufficient data have not yet been obtained to warrant general conclusions. It can be said, however, that the influence of the double bond on the optical rotation of normal secondary carbinols depends on its position in the lighter or heavier group and on its distance from the asymmetric carbon atom."

In spite of the addition of these other factors many of the correlations of Levene would be arrived at also by the criterion here suggested so that it appears that, if mass of the groups is not the only factor, it still remains the most important factor governing optical rotation. This does not rule out the possibility that in some cases the effect of polarity or unsaturation or some other factor may not appear and influence the optical rotation. Such an effect would appear to be Fischer's[2] resolutions into active components of propyl, isopropyl cyanacetic acid. The literature indicates that unsaturated groups such as $C=O$, $C=S$, and especially $C=C$ have larger effects on rotatory power than do saturated groups in the same relative position with respect to the asymmetric carbon atom. This is not hard and fast rule for exceptions are known and the $C\equiv C$ bond appears to have less effect than the double bond. It will be shown that the introduction of the phenyl group directly attached to the asymmetric carbon as in mandelic acid has an effect different

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[1] "Annual Survey of American Chemistry," 4, 260 (1928-29).

[2] Fischer and Flatau: Ber., 42, 2981 (1909).

from that observed in the malic acid series on the one hand or the beta hydroxy butyric acid series on the other. Correspondingly the position of the carboxyl group one step removed from the asymmetric carbon atom as in the last acid mentioned brings about different properties from those observed in the malic acid series or the lactic acid series.

In the second place the applications of the criteria developed by van't Hoff are made more difficult not only by the existence of factors other than mass which have their effect, but also by the varying conditions under which the experimental data which make up the literature of the Walden inversion were gathered. It is now obvious that the course of any replacement reaction will be dependent on three major factors; (the conditions of the reactions such as temperature, concentrations, etc., being selected so as to minimize the racemization which is so likely to occur during such reaction). These factors are: the starting-out material and, to a lesser extent, the product; the reagent added and its relative concentration; and, finally, the solvent medium. Undoubtedly all three of these factors affect the course of the reaction greatly and the present survey can only make the implicit assumption (made by all other students of the phenomena) that the reactions in question have been carried out under such conditions that the data are really comparable. Thus, to take but one case, the reaction between the amino acids and nitrous acid has in general been carried out under practically the same conditions each time, since they are the only conditions in which we know the reaction to proceed. We know, however, in such a simple case as this appears to be, that the effect of decreasing the acidity of the reaction medium has a marked effect on the mixture of malic acids produced. This has been shown recently by Holmberg[1] who investigated the diazotization of natural dextrorotatory aspartic acid to give natural levorotatory malic acid. By adding increasing amounts of nitric acid the acidity of the solution was increased while the activity of the malic acid decreased.

Normality of nitric acid	0	0.25	0.50	1.0N
Specific rotation of the malic acid in uranyl nitrate	−40.3°	−54°	−306°	−405°

The first solution was acid only with the acidity of the aspartic acid. The phenomena are exactly comparable with those observed in the hydrolysis of chlorosuccinic acid except that there the observations could be continued beyond the point of neutrality (or the point at which equal amounts of the two forms of malic acid were produced which is certainly not at pH 7). The diazotization cannot be carried out in alkaline solution so far as we know; but, if it could, it seems quite probable that dextrorotatory malic acid would be the product in increasing proportions as the alkalinity is increased. Holmberg remarks merely that at the lower hydrogen ion concentrations another reaction mechanism enters which give rise to dextrorotatory malic acid or racemic malic acid. The latter was not the case in the hydrolysis experiments

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[1] Holmberg: Ber., **61**, 1893 (1928).

and does not now appear reasonable. In comparison with Holmberg's best value −436° for malic acid under such conditions, the N HNO_3 system gave a product which is about 96% l-malic while that obtained without the addition of nitric acid is 55% l-malic and 45% d-malic acids. The complications entering into this reaction, probably one of the most simple reactions used in studying the Walden inversion, show the need for caution in accepting all the published results as comparable. We[1] have already shown the character of the similar complications in the hydrolysis of chlorosuccinic acid, where hydrolysis in acid solution produces a malic acid of the same sign of rotation as the original chlorosuccinic acid while alkaline hydrolysis gives a malic acid of the opposite sign. Probably the mystery of the Walden inversion will not be fully cleared until we are able to work with data that were obtained under strictly comparable conditions since many of the reactions used are far more troublesome than the diazotization discussed above. The racemization which accompanies nearly every such reaction betrays the existence of a reaction mechanism opposite to that of the principal one, and, which mechanism shall predominate will depend on several factors, the most important of which appears to be the added reagent in most cases.

The applications of the van't Hoff criteria to the reactions of the Walden inversion are somewhat hampered by the fact that the relative amounts of reagent and starting-out material have an effect in some cases. Thus in the discussion of the hydrolysis of chlorosuccinic acid above referred to we have shown that a deficiency of silver oxide leads to one type of malic acid while the presence of more than the equivalent amount of silver oxide favors the formation of the opposite malic acid. In this particular case we consider that the acidity of the medium in which the reaction takes place is the deciding factor, the presence of more silver oxide favoring the alkaline solution reaction because a larger portion of the hydrolysis takes place at the surface of the suspended oxide. But it appears quite possible that the relative amounts of the substances employed may be decisive factors in some of the common reactions employed. The present paper therefore can classify the reagents on the assumption that comparable conditions were observed in this respect too. This classification will then indicate that under the conditions commonly employed these reagents produce Walden inversions while those do not. A justification of the classification is that it shows that the reactions of two similar groups of compounds, the malic acid and the lactic acid series behave alike in that the same reagents fall into the same classes in both series of compounds. In the latter series of compounds differences of composition, particularly the presence of the phenyl group make the classification different but not less sharp. This, then, supports the contention that the added reagent alone does not determine the course of the reactions but that the properties of the starting-out material may be such as to influence the mechanism of the replacement process.

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[1] Bancroft and Davis: J. Phys. Chem., 35, 1253 (1931).

The Application of These Criteria

In the application of these criteria there will in general be three steps to be taken. In the first place the actual rotations of the compounds studied and the conditions under which the rotations were observed must be definitely known. This is especially true of the alpha hydroxy and alpha amino acids and in these cases, only the rotations of the alkali salts or of the esters may be taken as representing authentically the rotation of the actual substance. Secondly, since we are here studying the effects of the varying reagents added, the conditions under which the reactions proceed and especially the relative amounts of reagents involved must be known. Thus the mere statement that a given halogen acid was hydrolyzed in the presence of silver oxide is not sufficient, for we know that a deficiency of silver oxide brings one result while a sufficient excess of silver oxide may produce exactly the opposite product. Finally the relation between the group weights must be considered. This will indicate whether or not direct replacement by the entering group will produce a change in the sign of rotation. This may be shown best by a concrete illustration from the malic acid system. In this compound the groups attached to the asymmetric carbon atom and their respective weights are;

H	OH	COOH	CH_2COOH
1	17	45	59

If the hydroxyl group be replaced by some other group such as $NH_2 = 16$, or $Cl = 35.5$, whose weight lies between 1 and 45, we should expect no change of sign on direct replacement. If change of sign results, it indicates that the replacement is not direct but is attended by a Walden inversion. But if the entering group be between 45 and 59, direct replacement will be accompanied by a change in sign and in this case the retention of the sign of rotation of the original compound will show a Walden inversion. Finally, if the hydroxyl group of the original malic acid be replaced directly by a group whose weight is greater than 59, such as $Br = 80$ or $I = 127$, the resultant compound will again have the same sign of rotation as that of the original malic acid and again a change of sign will indicate a Walden inversion. In the direct replacement criterion in this last case, it is as though the change in the group weight were sufficient to bring about two reversals of the sign (each time the group weight became equal to 45 and 59 respectively) and these two reversals neutralize each other, the final result being the same sign of rotation as the original hydroxy acid.

We are now in a position to apply these criteria to the more common examples of the Walden inversion. The first one to be worked out and still the best known one is that of the derivatives of succinic acid. We employ the chart given by Walden and find that the designations there given are the proper ones to employ. This constitutes no problem for the chlorosuccinic acids which in all dilutions in aqueous solutions show a nearly constant rotation which is the same as that of the salts and esters. In the same way there is general agreement as to just which acid is l-malic acid and this has been discussed above. The aspartic acid offers more need for caution. Natural asparagine, on boiling with hydrochloric acid, gives an aspartic acid which is dextro-rotatory (about +5°) in aqueous solution and in acid solution, but which in alkaline solutions is levorotatory and which in the forms of its esters is likewise levorotatory. This aspartic acid should therefore be called l-aspartic and is the acid which with NOCl gives levorotatory chlorosuccinic acid and with nitrous acid gives l-malic acid. It would appear quite reasonable that this last reaction should proceed without inversion for one would expect the replacement of the NH_3 (= 16) group by the OH (= 17) group, in view also of the chemical similarities of the groups, to produce a compound of just about the same optical rotatory power and direction. The rotatory power of the two compounds is just about the same and the retention of the same sign of rotation lends support to the conclusion that no Walden inversion takes place in the reaction. Now this chart shows the interrelation of the amino, hydroxy, and chloro compounds and the application of the method above shows that the weights of all these groups fall between 1 and 45 so that we conclude that in normal replacement, all these compounds of the same sign have the same configuration. Change of sign will therefore indicate abnormal replacement. These same considerations apply also to the bromo or iodosuccinic acids. We find therefore that in the malic acid series;

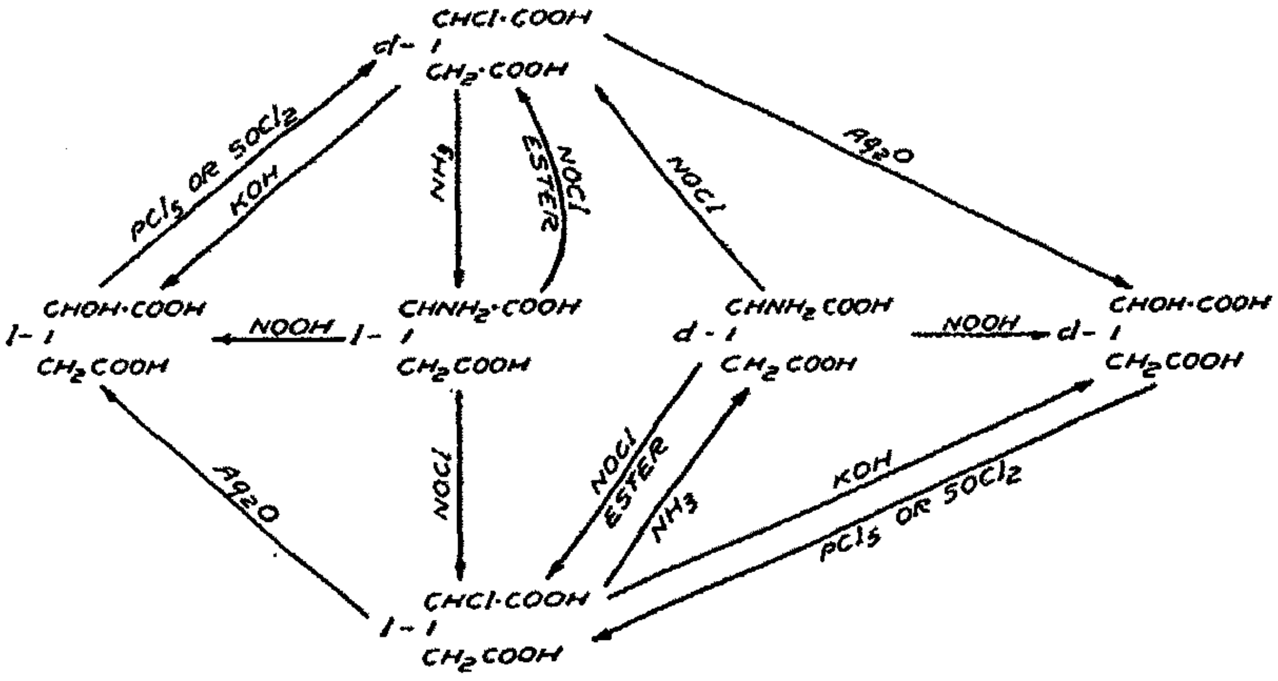

Fig. 1
Malic Acid

Normal reagents are; HNO_2, Ag_2O, NOCl.

Abnormal reagents are; PCl_5, $SOCl_2$, KOH, NH_3.

In this first example it is found that the amino acids and their esters appear to work oppositely toward nitrosylchloride. In the case of the amino ester the group weights are;

H	NH_2	$COOC_2H_5$	$CH_2COOC_2H_5$
1	16	73	87

Replacement of the amino group by the chlorine atom will not change the order of group weights any more than it did in the acid and we should predict no change in the sign of the rotation. That a change in the sign of rotation results from the action of nitrosyl chloride on the ester indicates that there a Walden inversion takes place. This may be attributed to the lesser acidity of the ester or, what seems more probable, to the effect of the ring or lactone structure involving the NH group, just as malic acid has been shown to have such a structure involving the oxygen ring. In the free acid or in the presence of other acids this "lactide" ring is present and by virtue of its more rigid stabilizing power is able to force direct replacement while in the esters the lack of such a ring permits the principal action to be one of abnormal replacement.

The second common example of the Walden inversion that has been investigated is the lactic acid series. In this series both the lactic acid and the amino acid, alanine, possess rotations in aqueous solutions or acid solutions opposite to the rotations of their alkaline solutions or esters and no end of confusion has arisen in the literature on this point. This has been particularly the case when lactic acid was compared to some other compound with a view to establishing configurational relationships. A recent example of this was the reply of Clough[1] to a criticism by Levene. Levene and Haller had claimed as a result of their reactions that an optically active form of 2-hydroxybutyric acid, $CH_3{\cdot}CH_2{\cdot}CH(OH){\cdot}COOH$, which is dextrorotatory in aqueous solution at ordinary temperatures but which yields levorotatory salts and esters, possesses the same configuration as d-lactic acid or l-tartaric acid. Levene and Haller called this the dextro acid, which is of course the wrong designation, and they then pointed out that Clough had reached opposite conclusions to their own. Clough protests that he agrees with their conclusion but not with their designation, and continues: "In order to distinguish the enantiomorphus forms of a compound from one another, the conventional symbols d and l have been assigned to them in a somewhat arbitrary manner. Thus d-lactic acid is the form which is dextrorotatory in aqueous solution at ordinary temperature but which gives rise to levorotatory salts and esters, while l-aspartic acid which may be prepared from natural l-asparagine, is dextrorotatory in aqueous solution. Guye and Jordan who resolved 2-hydroxybutyric acid into its optically active forms, termed that variety of this acid, the salts and esters of which were levorotatory, "*l'acide alpha-oxybutyric gauche*". Beilstein refers to the same compound as "*l-alpha-oxybuttersaure*". The present author also designated this compound l-alpha-hydroxybutyric acid and expressed the view that it was configurationally related to l-tartaric acid." In view of the criteria outlined by van't Hoff and applied in this paper we see at once that there is no real difference of opinion here and, if the lactic acid in question be given its true designation as l-lactic acid, true agreement is arrived at.

Walden[2] is clear on this point for he says: "For the optical designation of the active lactic acids we will indicate that acid whose salts and esters are levorotatory as l-lactic acid. Sarcolactic acid produces levorotatory salts

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[1] Clough: J. Biol. Chem., 75, 489 (1927).

[2] Walden: "Optische Umkehrerscheinungen," 48 (1919).

and esters and is therefore designated as l-lactic acid." The reasons given for this view are essentially those of van't Hoff and need not here be repeated. Suffice it to say that in the chart, Fig. 2, Walden gives the lactic acids the proper designations.

This is not the case with alanine, although exactly the same considerations apply as were applied to the hydroxy acid. A sample of alanine whose hydrochloric acid solution showed [a] = 9.4° and whose esters and salts are levorotatory gave on treatment with nitrous acid a lactic acid whose zinc salt showed [a] = −8.0°. This alanine should therefore be known as l-alanine and the action of nitrous acid produced l-lactic acid exactly as in the case of the conversion of l-aspartic acid into l-malic acid. In using these letters thus for these compounds we have reference to the real rotation of the acid in question when that rotation is no longer influenced by any type of anhydride formation or condensation, and not to the actual rotation observed in water alone or under some other incidental condition. The rotation of alanine is so small that it is not recorded; practically always it is converted to its hydrochloride or hydrochlorate and observed thus. It is clear that such rotations are in the opposite direction to the true designation of the alanine studied.

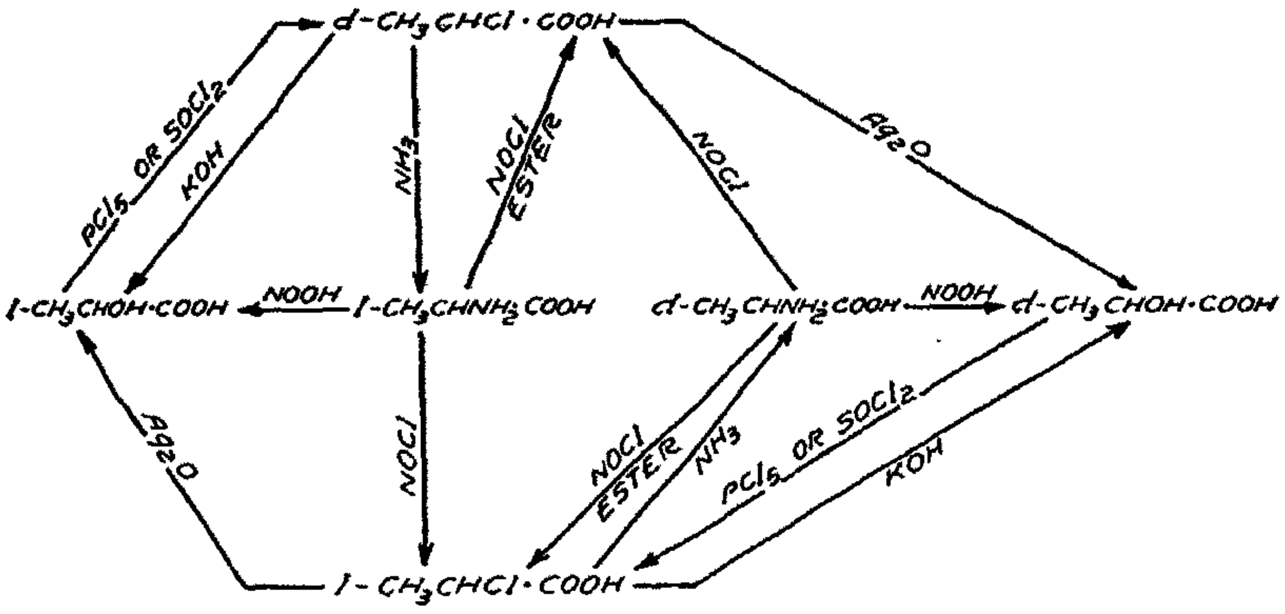


Fig. 2
Lactic Acid

The group weights in the lactic acid series are:

H	CH_3	OH	COOH
1	15	17	45.

Therefore, as in the malic acid series, the amino, chloro, and hydroxy compounds having the same sign will also have the same configuration, and again, after the proper designations are assigned, change of sign indicates a Walden inversion. In this series the reagents are;

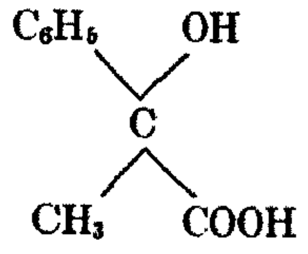
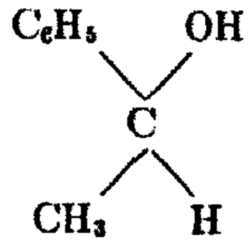
Normal: HNO_2, Ag_2O, NOCl.

Abnormal reagents are: PCl_5, $SOCl_2$, KOH, NH_3.

Comparison of the reagent classes in the lactic and the malic acid systems will show that they are identical. This is as it should be if our criteria are reliable, for the same reagents on such similar compounds should produce or be free from inversion on both compounds and we find this to be the case. As these criteria are applied to other series of compounds, the influence of the various compounds becomes felt, so that a reagent which proved normal in the two systems above may produce inversion in other systems. We have not as yet been able to work out methods for predicting definitely the course of a reaction in a given case but it appears that the presence of phenyl groups in the molecule and the relative position of the asymmetric carbon with respect to the carboxyl group, as well as the character of the groups attached to the asymmetric carbon atom all have their effects on the course of the reaction with a given added substance. Our purpose here is to enable the detection of a Walden inversion when one has taken place in order that subsequent study may be then directed to the finding out why the inversion took place.

Without going into the details of the applications we here present the results of applying these criteria to the principal systems selected by Walden for inclusion in his latest book (1929). In this table I means that the reaction indicated is accompanied by inversion, while N shows that normal replacement takes place.

TABLE I

System	HNO_2	Ag_2O	NOCl	PCl_5	$SOCl_2$	KOH	NH_3
Malic acid $COOH\cdot CH_2\cdot CH(OH)\cdot COOH$	N	N	N	I	I	I	I
Lactic acid $CH_3\cdot CH(OH)\cdot COOH$	N	N	N	I	I	I	I
beta-hydroxybutyric acid $CH_3\cdot CH(OH)\cdot CH_2\cdot COOH$	I	I	I	I			
Mandelic acid $C_6H_5\cdot CH(OH)\cdot COOH$	I	I	I	I	N	N	I
alpha-hydroxy-alpha-phenyl-propionic 	I	I		I	N		
beta-hydroxy-beta-phenyl-propionic $C_6H_5\cdot CH(OH)\cdot CH_2\cdot COOH$	I	I	I	I	N		
Phenylmethylcarbinol 	I	I	N	I	N	I	

The data in this table are not so nearly comparable as could be wished, chiefly because the need of control of reactions and of more definite attention to the relative amounts of substances reacting has not been recognized by the people who made the observations. We may select a single instance to make this clear. The work on the beta-hydroxybutyric acid was done by Fischer and Scheibler[1] who showed that the hydrolysis of the chloro acid to the hydroxy acid in presence of silver oxide went with a change of sign, which applying the criteria, indicated an inversion. This is opposite to the behavior in the case of lactic and malic acids and it was of interest to know if the existence of the beta-hydroxy asymmetric carbon atom group was responsible for the change. This idea did not prove correct for it was found that the reaction proceeded in the presence of four equivalents of silver oxide per mol of chloro acid. As we have shown in the malic acid series, a far smaller excess than this is sufficient to give the same effect as a strongly alkaline hydrolysis with the oppositely rotatory product to that usually obtained in the presence of a deficient amount of silver oxide. In most of the tables of the Walden inversion, the action of silver oxide reported is that of a deficiency of silver oxide, and, in the case of the malic acid series, is a normal replacement, while an excess of silver oxide brings about a Walden inversion. It is probable that this is true also of beta-chlorobutyric acid and that the action of silver oxide on this acid also should be listed as normal. Since no data are available for the hydrolysis of this acid in the presence of deficient silver oxide, this point can not be proved conclusively. It should prove possible in a few years to prepare such a table as this with some assurance that the data are really comparable. By that time we may be able to evaluate the forces which direct these reactions in such a way as to show more rigid correlation between the reagents used and their effects than is now possible.

For the present we might make a few observations on the table as it stands. The identity of the reactions in the lactic acid and malic acid series is to be expected from the similarities of the compounds themselves and may serve as confirmation of the existence of similar anhydride-type compounds in both series. On the other hand the evidence above indicates that the beta-hydroxybutyric acid is like malic acid in respect to the silver oxide hydrolysis; but in this case a distinctly acid hydrolysis produced the same effect as the excess silver oxide. For the present no conclusions can be drawn, for it may appear that both beta- and alpha-hydroxycompounds react similarly. It does appear that the beta-ring is broken more easily and such compounds are more prone to inversion. Finally the introduction of the phenyl group directly attached to the asymmetric carbon atom induces a complete change in the reaction process, only phosphorus pentachloride retaining its power of inversion through the whole series. At the same time thionyl chloride substitutes directly in such compounds while nitrosylchloride is able to do so on the carbinol where the acidity is low. This effect of the phenyl group has been noted recently by Kenyon, Lipscomb, and

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[1] Fischer and Scheibler: Ber., 42, 1227 (1909).

Phillips[1] who report that although thionyl chloride on the hydroxy acids and esters produces compounds of the opposite rotatory power as has been discussed here for malic acid and lactic acid, the products of the same reaction when the compounds used have a phenyl group directly attached to the asymmetric carbon atom are chloro acids and esters of the same sign of rotation as the original hydroxy acid. If however the ester such as ethyl mandelate is dissolved in a tertiary base (pyridine, quinoline, isoquinoline) the action of $SOCl_2$ again produces a chloro compound of the opposite sign to that of the hydroxy acid. They conclude: "There can be little doubt that the mechanism of the interaction of $SOCl_2$ with hydroxy-compounds is modified by the presence of a tertiary base. The work now described suggests, however, that such modification only determines the sign of rotation of the resulting chloro-compound when a phenyl group is directly attached to the asymmetric carbon atom."

Another interesting confirmation of the criteria here offered and a guide to their application is found in the action of PCl_5 and PBr_5 on alpha-hydroxybutyric acid. Walden[2] gives the data and remarks that it is surprising to find that these reagents produce halogen esters of the opposite sign.

$$\begin{tikzcd}
 & \text{PCl}_5\ \text{l-CH}_3\cdot\text{CH}_2\cdot\text{CHCl}\cdot\text{COOC}_4\text{H}_9 \\
 & (a) = -10.5^\circ \\
\text{l-hydroxybutyricisobutyl ester} \arrow[uur] \arrow[dr] & \text{PBr}_5\ \text{d-CH}_3\cdot\text{CH}_2\cdot\text{CHBr}\cdot\text{COOC}_4\text{H}_9 \\
(a) = -7.7^\circ & (a) = +6.7^\circ
\end{tikzcd}$$

The groups in the free acid are;

H	OH	CH_3CH_2	COOH
1	17	29	45

and it is obvious that the substitution of Cl for OH will change the position of that group by one step with a resultant change of sign. But since PCl_5 is, so far as we now know, always an inverting reagent, this reaction should proceed without change of sign, as it does. But the introduction of bromine involves a double change in the weight position and should result on normal replacement in no change of sign. Now PBr_5 is sufficiently like PCl_5 that we should expect it also to be an inverting reagent and to produce the change of sign which is actually observed. The opposite sign of the products is therefore clearly a result of the relation between the masses of the groups attached to the asymmetric carbon atom, the two halogen compounds having the same configuration, which is opposite to the configuration of the hydroxy acid.

This has been worked out on the basis of the acid group weights and would not follow if the ester weight were introduced. This, therefore, raises the question as to whether the acid ought not always to be taken as the norm for calculation. In all but very rare exceptions the rotations of the esters are in the same direction as the true rotation of the acid even though the group weights may have changed in order. By strict application of the group

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[1] Kenyon, Lipscomb, and Phillips: J. Chem. Soc., 1930, 415.

[2] Walden: "Optische Umkehrerscheinungen," 59 (1919).

weight relation, methyl lactate ought to work oppositely in the presence of PCl_5 and PBr_5, but it does not. These considerations indicate that here is an example where the chemical character of the attached group, in this case the carboxyl group, is a more powerful determinant than the group weights alone, and that the criteria are still valid if properly applied to the free acids. The reactions above will surely produce the same divergent results if the free acids are used instead of the esters.

The Relation of Some Common Hydroxy Acids

It has now been shown how the criteria developed above may be used to correlate the configurations and rotations of the acids which may be converted into one another by simple reactions. These same criteria will also make clear the relationships existing between the various series themselves. For convenience we select the natural lactic acid as the standard of comparison. It has already been shown above that this acid, although dextrorotatory itself, belongs to the levorotatory class, because of the levorotation of its salts and esters. For purposes of comparison with other acids and to make its character clear we shall designate this the l (+) lactic acid and shall indicate the other related hydroxy acids which are of the same configuration.

In this Table II the column headed Relation shows how the criteria were applied. Thus glyceric acid might be regarded as having been obtained from lactic acid by replacing the CH_3 group by CH_2OH (oxidation?). In doing this, the group change is from between 1 and 17 to between 17 and 45. This represents one change and normal replacement would be accompanied by a change in the sign of rotation—it always being insisted that we are dealing with real rotations. In mandelic acid the methyl group is replaced by the phenyl group which represents two steps in increase of group weight or two changes of sign, which balance each other and leave the sign unchanged. All the acids in this table have three groups in common with lactic acid and can be compared with that acid directly except beta-hydroxy-beta-phenylpropionic acid which could be compared with malic acid and thus put in the table.

It has been shown earlier in the discussion of the hydroxy acids that Freudenberg and Clough, using their various methods for correlating configurations, have arrived at the same conclusions as are shown in the table with respect to the correlation of l(+) lactic, l(−)mandelic, l(−)malic, and l(−)tartaric acids. They, however, include l(+)glyceric acid as of this same form while the application of these criteria of van't Hoff indicates that d(−)glyceric is configurationally related to the four acids just named. The experimental data are not sufficient to confirm or deny the relationship of the other three acids named in the table. That the criteria are not complete is shown by the fact that the opposite conclusion is reached concerning the alpha-hydroxy-alpha-phenylpropionic acid if it be compared with mandelic acid instead of lactic acid as was done in the table. In view of the agreement with the experimental results it appears that the comparison with lactic acid is the more reliable.

TABLE II

Acid	Groups				Relation	Configuration related
Lactic acid	H	CH_3	OH	COOH	———	l(+)lactic
CH_3·CH(OH)·COOH	1	15	17	45		
Mandelic	H	OH	COOH	C_6H_5	Two changes	l(−)mandelic
C_6H_5·CH(OH)·COOH	1	17	45	77	Same form	
alpha-hydroxy-alpha-phenylpropionic	CH_3	OH	COOH	C_6H_5	Three changes	d(+)alpha-hydroxy-alpha-phenylpropionic
CH_3·C(C_6H_5) (OH)·COOH	15	17	45	77	Opposite form	
Malic	H	OH	COOH	CH_2COOH	Two changes	l(−)malic
COOH·CH_2·CH(OH)·COOH	1	17	45	59	Same form	
Tartaric	H	OH	COOH	CHOH·COOH	Two changes	l(−)tartaric
COOH·CH(OH)·CH(OH)·COOH	1	17	45	75	Same form	
beta-hydroxy-beta-phenylpropionic	H	OH	CH_2COOH	C_6H_5	One change	d(+)beta-hydroxy-beta-phenylpropionic
C_6H_5·CH(OH)·CH_2·COOH	1	17	59	77	Opposite form	
	(compared with malic acid)					
beta-hydroxybutyric	H	CH_3	OH	CH_2COOH	No change	l(−)beta-hydroxybutyric
CH_3·CH(OH)·CH_2·COOH	1	15	17	59	Same form	
Glyceric	H	OH	CH_2OH	COOH	One change	d(−)glyceric
CH_2OH·CH(OH)·COOH	1	17	31	45	Opposite form	

Finally it may be pointed out that the conclusions here reached by the application of these relatively simple standards of comparison are, for the lactic and malic acid systems, in every respect identical with those reached by Freudenberg[1] from very extensive work on the optical rotatory power of the acids in question and of their esters and other related compounds. These authors agree with the present paper in the designation of the acids and their configurational relationships, and finally, therefore, in the character of the reaction brought about by each of the reagents discussed in connection with them. Basically apparently Levene would also agree with us in the grouping of dextro-tartaric, dextro-malic, levo-glyceric, and levo-lactic into the d-series. We have already seen that as late as 1927 Levene[2] was somewhat confused on this point so that it seems reasonable to assume that by the designations above he intended to show the rotations of the acids themselves in aqueous solution and not their true character. We know that the salts and esters of levo-glyceric and of levo-lactic acids are dextrorotatory so that these acids should be shown as d(−) glyceric and d(−) lactic acids. We still cannot agree with Levene with respect to the glyceric acid but do so in respect to the other acids. In addition we also do not agree with Levene in respect to the chloroacids, for it appears that in some of the reactions employed to go from one active compound to the other an inversion is by no means impossible.

Conclusions

1. There are no generally accepted methods for the correlation of the optical rotations of organic compounds and their configurations. This is the next important step to be taken in the elucidation of the mysteries of the Walden inversion, for until it is known definitely when an inversion takes place, there is little hope for learning much about why an inversion takes place.

2. The methods previously employed often have the defect of employing reactions which may themselves include Walden inversions and they lead to contradictory results.

3. The correlation of the rotations of the optically active compounds and their configurations is possible by the use of criteria outlined by van't Hoff. These have two principal steps, the first being the ascertaining of the real rotation of the acid as of the same sign as its salts and esters. The second step is the comparison of the mass of the groups attached to the asymmetric atom as the order of these masses is affected by the introduction of different groups.

4. By the aid of the first of these standards one is able to know definitely what relative configuration is possessed by the acid under study. The application of the second comparison then indicates whether or not a Walden inversion takes place on group replacement. It is pointed out that even in

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[1] Freudenberg and Lux: Ber., 61, 1083 (1928).

[2] Levene: Chem. Rev., 2, 179 (1925).

such reactions as esterification and hydrolysis of the ester an inversion may take place although apparently no bond of the asymmetric carbon is affected.

5. The application of these criteria is attended by certain difficulties which include variations of the conditions under which reactions are carried out, variations of the relative quantities of the reagents employed, and the possibility that in some cases factors other than mass may contribute to the general effect.

6. The application of these criteria to the malic and to the lactic acid series shows that l(−)malic, l(−)chlorosuccinic, l(+)aspartic, l(+)lactic, l(+)alanine, and l(−)chloropropionic acids are all of the same configuration. In this designation the signs within the parentheses indicate the actual observed rotations of the acids in water while the l designation for each indicates that each produces levorotatory salts and esters thus showing their true character.

7. With the configurations in each series thus determined, the detection of the Walden inversion is simple. In both of these series the action of HNO_2, Ag_2O (deficient), and NOCl is by direct replacement; while the action of PCl_5, $SOCl_2$, KOH, and NH_3 is characterized by a Walden inversion.

8. These conclusions are exactly in agreement with those of Freudenberg and it appears that this is the first time that one has been able really to compare the effect of a given set of reagents on even two similar compounds series with respect to the Walden inversion. The criteria here proposed may require future amplification or revision but at least these achievements represent an advance.

9. Similar results are shown for the application of these standards to other hydroxy acid series and it is shown that the effect of the reagents named above is not always as it is in the first two series. Apparently the occurrence of the phenyl group in the molecule or the position of the asymmetric carbon in respect to the carboxyl or other group potent in affecting rotations are able to influence also the course of the reactions into which the molecule enters.

10. It is shown that the hydroxy acids themselves can also be correlated by this method and l(+)lactic, l(−)mandelic, l(−)malic and l(−)tartaric acids are shown to be of the same configuration.

11. The facts that varying the acidity of the medium or varying the relative amounts of reagents employed in the reactions here discussed, has been shown to be capable of completely reversing the course of these reactions as indicated by the products, lead to the conclusion that this may be responsible for many of the abnormalities encountered in the application of these criteria and that many of these reactions must be completely reinvestigated in order to find what they really mean.

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THE REACTION BETWEEN ARSENIOUS ACID AND IODINE*

BY HERMAN A. LIEBHAFSKY

For the purpose of obtaining additional evidence on the rate of hydrolysis of iodine, the reaction

$$H_3AsO_3 + I_3^- + H_2O = H_3AsO_4 + 2H^+ + 3I^- \tag{1}$$

so extensively studied by Roebuck,[1] is being re-investigated in this laboratory. Since the new experimental material is to be combined with the results of a series of investigations[2] not directly related to the Roebuck reaction (Equation 1), it has seemed advisable to present here certain considerations which may enhance in some measure the value of one of the classic investigations in the field of chemical kinetics.

This investigation has become classic because it represents the first complete demonstration of the relation obtaining between chemical kinetics and chemical equilibrium. The validity over a sufficient concentration range of the rate law for the forward reaction, namely

$$-\frac{d(I_3^-)}{dt} = k_3 \frac{(I_3^-)}{(H^+)\,(I^-)^2}\,(H_3AsO_3) \tag{2}$$

and of the rate law for the reverse reaction, namely

$$+\frac{d(I_3^-)}{dt} = k_5\,(H_3AsO_4)\,(H^+)(I^-), \tag{3}$$

and the equality obtained in II between the quotient k_3/k_5 and the experimentally measured equilibrium constant, K_6, of Reaction 1, establish definitely the mechanism of the Roebuck reaction. In the concentration range where Equations 2 and 3 were experimentally established, both the forward and the reverse reaction are concerned with the single rate-determining step

$$HIO + H_3AsO_3 = H_3AsO_4 + H^+ + I^-. \tag{4}$$

(Possible intermediate addition compounds will not be considered here). Equation 2 can be easily interpreted if we assume that the concentration of hypoiodous acid is governed by the relatively rapid equilibrium

$$I_3^- + H_2O \leftrightarrows H^+ + 2I^- + HIO, \tag{5}$$

which may be regarded as the sum of the equilibria

$$I_3^- \leftrightarrows I_2 + I^- \tag{6}$$

$$I_2 + H_2O \leftrightarrows H^+ + I^- + HIO \tag{7}$$

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*Contribution from the Chemical Laboratory of the University of California.

[1] (a) Roebuck: J. Phys. Chem., 6, 365 (1902); 9, 727 (1905); these papers will be designated as I and II. See also (b) Bray: 9, 573 (1905) (c) de Lury: 10, 423 (1906); (d) Washburn: J. Am. Chem. Soc., 30, 31 (1908); (e) Washburn and Strachan: 35, 681 (1913).

[2] Bray and Liebhafsky, and Bray and Caulkins, J. Am. Chem. Soc., 53, 38, 44 (1931) are the initial papers dealing with these investigations.

Since hypoiodous acid can not be consumed more rapidly in Reaction 4 than it is produced in Reactions 5 and 7, then, if—as Abel appears to have demonstrated—iodine and water react with moderate speed while tri-iodide ion does not hydrolyze directly at all,[1] the rate of hydrolysis of iodine should be the *limiting* rate realized as the concentrations of hydrogen ion and of iodide are decreased.

Roebuck chose to employ mass units rather than concentrations in expressing the experimental results of his rate measurements. The measured value of the equilibrium constant, K_6, in these units and for 1 liter of solution at 0°C. was $1.5(10^5)$; the value calculated from the specific rates is given as $8.6(10^5)$ in I (p. 396) and $1.4(10^5)$ in II (p. 743.). Professor William C. Bray has kindly called to my attention a mistake in calculation, the correction of which brings the value from I likewise into agreement with that experimentally measured for K_6. The mistake results from evaluating k_3 from a measurement of $-dx/dt$ (x is the number of *mass* units of I_3^- in the reaction mixture) for 600 cc. (I, Table XVII) and k_5 from a measurement of $+dx/dt$ for 155 cc. (I, Table XXVIII); the rate constants thus obtained were used directly to calculate K_6. If $-dx/dt$ and $+dx/dt$ for the *same* volume are employed which is of course the only correct procedure), and if the values of the corresponding specific rates are then used to calculate K_6, we shall obtain the correct value for this equilibrium constant. The values of the specific rates, however, will still depend upon the volume assumed for $-dx/dt$ and $+dx/dt$, and the conversion of these values into conventional units can be carried out only if $-dx/dt$ and $+dx/dt$ for 1 liter are used.

Thus the specific rates given in the International Critical Tables VII, p. 150 (Volume VII appeared after the writing of this paper) must be multiplied by 2 if their values in conventional units are to be obtained. This multiplication is necessary because $-dx/dt$ and $+dx/dt$ for a 500 cc. reaction mixture were used in the calculation. The corrected values agree very closely with those of this paper.

If we therefore calculate the values of $-dx/dt$ and $+dx/dt$ from I for 1 liter, and use the corresponding specific rates to calculate K_6 we obtain $K_6 = \dfrac{4.67(10^{-1})}{2.10(10^{-6})} = 2.2(10^5)$, a value in much better agreement with the experimental results.

We shall now give the values of k_3, k_5 and K_6 for 0°C in the conventional units—rates in mols/liter/min. and concentrations in mols./liter; the constants in these units are designated by k'_3, k'_5, and K'_6.

$$\text{Forward Rate:} \qquad -\frac{d(I_3^-)}{dt} = 9.4(10^{-4})(H_3AsO_3)\frac{(I_3^-)}{(I^-)^2(H^+)} \qquad (8)$$

$$\text{Reverse Rate:} \qquad +\frac{d(I_3^-)}{dt} = 6.3(10^{-3})(H_3AsO_4)(I^-)(H^+) \qquad (9)$$

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[1] Abel: Z. physik. Chem., **136**, 161 (1928) gives 0.25 as the specific rate of the iodine hydrolysis.

Equilibrium: $$\frac{(H_3AsO_4)(H^+)^2(I^-)^3}{(I_3^-)\ (H_3AsO_3)} = 1.6(10^{-1})$$[1] (10)

We may mention next a question which must have been uncertain in the time of Roebuck's work (vide I, p. 391)—the question of whether arsenic and arsenious acids, on the one hand, or their various anions on the other, are of primary kinetic importance. A consideration of the first dissociation constants for the acids[2] shows that no appreciable concentration of an anion of either acid can exist at the concentrations of H^+ (generally above .1 N) obtaining in Roebuck's reaction system; any arsenic compound added initially must react with H^+ to give the (practically) undissociated acid. In the absence of definite evidence to the contrary, therefore, it is entirely logical to assume, as Roebuck did, that only the undissociated acids or their addition products are concerned in the rate-determining step.

In the measurement of the forward rate of Reaction 1, Roebuck found it generally impossible to utilize initial concentrations in calculating the rate constant. For the forward reaction the rate during the first interval was usually greater than the rate expected by an amount beyond the experimental error; e.g. in I, Table I, k_1 for the first interval is .028 as compared with an average of .020 for the first part of the experiment. (k_1 is a first-order rate constant defined by Roebuck in I, p. 370). Even larger discrepancies were observed in this laboratory for the more rapid measurements, which were done in the following manner:

To the rest of the reaction mixture in a 125 cc. glass-stoppered flask, 1 cc. of solution containing either the arsenic acid or the iodine was rapidly added and the flask immediately shaken. Initial time was taken by another observer as the time of mixing. After the time interval for such a sample had expired, the reaction was frozen by adding .1 N thiosulfate solution from a burette in such manner that rapid mixing was secured. Final time was taken when about half the thiosulfate had been added. Approximately 1 cc. of this solution was equivalent to all the iodine initially present in a sample; in freezing the reaction, the amount of thiosulfate was so regulated that a small amount of iodine, which could be accurately determined, remained to be titrated. From the iodine consumed in initially identical reaction mixtures

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[1] The experimental values of Roebuck which were used in the above calculations are: k_3 = .26(II p. 738); $K_6 = 1.5(10^{+4})$ and $k_3/k_5 = 1.4(10^{+5})$ (II p. 743). K_6 is for a volume of 1 liter while k_3 and k_5 are both for a volume of 500 cc. The transformation from Roebuck's to the conventional units is given by:

$$(A) = 100(I_3^-) \qquad (C) = \frac{100}{3}(I^-) \qquad E = 100(H_3AsO_4)$$

$$(B) = 100(H_3AsO_3) \qquad (D) = \frac{100}{2}(H^+) \qquad x = 100(I_3^-)$$

The calculation for the reverse rate has been made by Bray: Z. physik. Chem., 54, 463 (1906); the value there given for the specific rate must be multiplied by 1/.12 to complete the correction to a volume of one liter. ($_3k$ on pp. 488 and 489 should be $_6k$).

( ) denotes "concentration of"; all electrolytes except H_3AsO_3 and H_3AsO_4 are assumed to be completely dissociated. (The equilibrium $I^-_3 = I_2 + I^-$ is, of course, assumed to be always established.)

[2] Wood: J. Chem. Soc., 93, 411 (1908) gives $K = 6(10^{-10})$ for H_3AsO_3, and Luther: Z. Elektrochemie, 13, 297 (1907) gives $K = 5(10^{-3})$ for H_3AsO_4; both dissociation constants are fr 25°C.

during varying time intervals, rate constants could be evaluated. The two chief difficulties, aside from the discrepancy mentioned above, encountered in an attempt to study Reaction 1 at concentrations where it is very fast, are oxidation of thiosulfate by arsenious acid and slowness in freezing the reaction. The experimental method finally adopted proved satisfactory; the rate of the reaction could be measured with sufficiently accuracy (estimated at ±20 percent) even when the half time was as short as five seconds. For experiments so rapid that only one point can be obtained in the course of the reaction, the above procedure may be modified thus: Add 1 cc. of I_3^- to start the reaction. Run a convenient number (say six) of samples as rapidly as is possible by the above method. Take the average of the time readings and the average of the burette readings as establishing this point. (The minimum time will be approximately 2 seconds). Run the same number of 1 cc. pipettefuls of I_3^- into a flask, titrate, and compute the thiosulfate equivalent to the I_3^- added. From this average initial thiosulfate reading and the average reading corresponding to the one point established during the course of the run, a fairly reliable value of the rate constant may be computed. The values which have been obtained for k_3 from preliminary experiments are in reasonable agreement with those of Roebuck.

In Experiment 1, Table I, 1 cc. of $H_2AsO_3^-$ solution was added to 20 cc. of a tri-iodide solution containing all the acid; in Experiment 2 the same reaction mixture was made up by adding 1 cc. of acid tri-iodide solution to 20 cc. of arsenious acid solution also containing iodide. In the first experiment the concentrations of iodide and of hydrogen ion changed on mixing; in the second, virtually no change in these concentrations took place. From Equation 8 we calculate that a decrease of 0.02 cc. in the volume of thiosulfate solution required for the titration should take place in these experiments during the twenty second interval.

TABLE I

Concentrations in mols/liter (for the reaction system after mixing):

$(H_3AsO_3) = .040$; $(I^-) = .118$; $(I_3^-) = .00375$; $(H^+) = .067$

Time (sec.)	cc. .1 N $Na_2S_2O_3$ equivalent to I_3^- remaining	
	Experiment 1	Experiment 2
0	1.53	1.44
5	1.28	1.43
10	1.30	——
15	1.29	——
20	1.26	1.41

A plausible explanation of the high rate involves the momentary establishment of a high concentration of HIO in the boundary region which exists between the arsenic and iodine solutions before the two are mixed. Since the former solution contains neither H^+ nor I^-, a shift of the hydrolysis equilibrium for iodine, Equation 7, can produce HIO in an amount sufficient to cause appreciable reaction even before complete mixing takes place. These considerations, if valid, serve to substantiate the mechanism for the oxidation of arsenious acid and to indicate the rapidity with which HIO can be produced by hydrolysis.

Equation 8 may be written

$$\frac{-d(I_3^-)}{dt} = K_1K_2k_3'' \ (H_3AsO_3) \frac{(I_3^-)}{(I^-)^2(H^+)} = k_3'' \ (H_3AsO_3)\ (HIO) \qquad (11)$$

$K_1 = \dfrac{(H^+)(I^-)(HIO)}{(I_2)}$ is the equilibrium constant for the hydrolysis of iodine;

$K_2 = \dfrac{(I_2)(I^-),}{(I_3^-)}$ the dissociation constant of tri-iodide ion; and k_3'', the true specific rate of the rate-determining step if this step is the bimolecular Reaction 4. For k_3'' as calculated from the value $k_3' = 9.4(10^{-4})$ in Equation 8, we obtain for k_3'' at 0°C. an extremely large value, $1.45(10^{14})$,[1] equal in order of magnitude to the number of collisions we should expect for many bimolecular reactions. Reaction 4 is thus probably the fastest bimolecular reaction for which a rate constant has been accurately measured; the magnitude of this specific rate is the more surprising since neither of the reacting species is ionic. k_3'', for example, is greater by many powers of ten than the specific rate for the oxidation of hydrogen peroxide by hypobromous acid,[2] and those for the oxidation of certain inorganic compounds by bromine.[3] Since the equilibria 6 and 7 are always maintained in Roebuck's reaction system, then, to obtain the heat of activation for Reaction 4, the heat change calculated directly from the temperature coefficient of k_3' must be diminished by ΔH_1 and by ΔH_2, the heats of reaction calculated from the temperature coefficients of K_1 and K_2. Roebuck gives 3.5 as the temperature coefficient of k_3' between 0°C. and 10°C. (I p. 381); the corresponding heat change is +19,300 calories. For ΔH_1 we calculate the value +22,700 calories; for ΔH_2, +4320 calories. For the heat of activation of Reaction 4 we have, therefore, the unexpected value $Q = -7{,}700$ calories; from this figure we find that the rate of Reaction 4 at 10°C. is approximately three-fourths its rate at 0°C. Since Roebuck has obtained agreement between the temperature coefficient of the equilibrium (Equation 1), as calculated from the temperature coefficients of the specific rates, and the equilibrium temperature coefficient as experimentally measured, a serious error in the value 3.5 employed above would seem unlikely. The values of K_1, however, can be regarded only as approxi-

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[1] Those values of equilibrium constants at different temperatures, which were used in calculating specific rates and heats of reaction, are:

$K_1 = 3(10^{-13})$ at 25°C.; Bray: J. Am. Chem. Soc., **32**, 914 (1910).
$K_1 = 9(10^{-15})$ at 0°C.; Jones: J. Am. Chem. Soc., **37**, 24 (1915).
$K_2 = 1.40(10^{-3})$ at 25°C.
and $K_2 = 7.2(10^{-4})$ at 0°C.; Jones and Kaplan: J. Am. Chem. Soc., **50**, 1845 (1928).

[2] Bray and Livingston: J. Am. Chem. Soc., **45**, 1251 (1923), give $6.7(10^5)$ as the specific rate for the oxidation of hydrogen peroxide by hypobromous acid.

[3] Francis: J. Am. Chem. Soc., **48**, 655 (1926), has shown that ten inorganic compounds, among them titanous chloride, sodium arsenite, sodium bisulfite and stannous chloride have specific rates for oxidation by bromine in aqueous solution varying from 10^4 to 10^8 in order of magnitude at 25°C.

mate because of difficulties in the measurement and in the interpretation of the very low conductivities involved in the determination of this constant; but, since the arithmetical value of Q is over one-third that of ΔH_1, we shall consider a negative temperature coefficient for the reaction between hypoiodous acid and arsenious acid as reasonably well established.

For the negative temperature coefficient of the third-order reaction between nitric oxide and oxygen, there have been advanced three not entirely unrelated types of explanations; one of these[1] involves the decrease in duration of collisions which takes place as the temperature increases; another[2] accounts for the negative temperature coefficient on the basis of clustering caused by the van der Waals forces; and the third[3] assumes an exothermic intermediate product in equilibrium with the reactants. Of these explanations, only the last seems applicable to a negative temperature coefficient as large as the one for our reaction. To explain it we assume

$$\text{Equilibrium: } HIO + H_3AsO_3 \rightleftarrows H_4AsIO_4;\ \Delta H = -8{,}000 \text{ calories (approximately)} \quad (12)$$

$$\text{Rate-determining: } H_4AsIO_4 \longrightarrow H^+ + I^- + H_3AsO_4 \quad (13)$$

This mechanism must be regarded as tentative until the negative temperature coefficient has been established beyond question by a more accurate determination of ΔH_1 and by a measurement of the rate of the forward reaction over a larger temperature range. Rate measurements at the higher temperatures can be done most conveniently by the experimental method outlined in this paper.

In a bimolecular reaction with a specific rate at ordinary temperatures as large as k_3'', practically every collision between molecules of the reacting species must be effective; in other words, such a reaction must have a heat of activation very nearly equal to zero. Using an equation given by Tolman,[4] we may calculate the molecular diameter which must be assumed for a bimolecular gas reaction proceeding with a specific rate of $1.45(10^{14})$ and zero heat of activation. The result, $\sigma = 2(10^{-7})$ cm., is in rough agreement with the value obtained from a similar calculation in another aqueous reaction system.[5] If the rate-determining step in Reaction 1 is the unimolecular Reaction 13, then this value of σ is the smallest which can be assumed for our reaction system; for the bimolecular reaction forming H_4AsIO_4 must be pro-

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[1] Bodenstein: Z. physik. Chem., 100, 68 (1922).

[2] Kassel: J. Phys. Chem., 34, 1777 (1930).

[3] Trautz and Schueter: Z. anorg. allgem. Chem., 136, 1 (1924).

[4] Tolman: "Statistical Mechanics etc." 242 (1927), equation (543); No. of mols colliding/cc./sec. $= \left[10^{28.4427}\ C_1C_2.\ \sigma^2\sqrt{T\frac{M_1+M_2}{M_1M_2}}\right]$; C_1 and C_2 are concentrations in mols/cc.; σ is the average diameter of the colliding molecules, T the absolute temperature, and M_1 and M_2 are the ordinary molecular weights. This total number of mols colliding is equated to the experimentally measured rate; the equation is solved for σ. Orientation factors and effect of solvent on the number of collisions are not considered.

[5] The other reaction for which such calculation was made is the reduction of iodate ion by hydrogen peroxide. Liebhafsky: J. Am. Chem. Soc., 53, 896 (1931).

ceeding at a rate even greater than that corresponding to k_3'' as calculated if the equilibrium (Equation 12) is to be maintained. The specific rate of Reaction 13 cannot be calculated definitely; it is probably very large also. A reaction similar in many respects to the oxidation of H_3AsO_3 by iodine is the oxidation of hydrogen peroxide by that same substance. Without discussing here the complexities of the latter reaction system, we may briefly mention that certain preliminary experiments have indicated the possibility of studying this reaction at different temperatures with the hydrolysis equilibrium of iodine (practically) established and the single rate-determining step

$$HIO + H_2O_2 \longrightarrow H^+ + I^- + O_2 + H_2O. \qquad (14)$$

If this reaction can be isolated, comparison of the resulting data with those for the arsenious acid case should prove interesting.

Calculations of the kind we have just outlined should advance the knowledge of the more intimate mechanisms of reactions in solution. Such calculations employing the extensive data already existing should be valuable first of all in establishing empirically the relation between the number of collisions in solution and the number in a gas; or stated in another way, they should indicate what collisional diameter must be assumed in order that quantitative application of the Arrhenius hypothesis to aqueous reaction systems can be made. If such a diameter is found to be rather widely applicable, it may be generally used to calculate plausible values for heats of activation. Between reactants and resultants in a chemical reaction there must always be an intermediate addition product of short, but indeterminate, life. If the calculated and the measured values of the heats of activation agree, we should conclude that our rate measurements were concerned with the rate of formation of this intermediate complex; and if not, that they were concerned with its rate of disappearance.

We may mention finally that Roebuck established the kinetics of the reverse reaction only in dilute solution: as hydrogen ion and iodide ion concentrations are increased, the simple rate law (Equation 9) is no longer valid; and the reaction tends to become second order with respect to each of these substances. In the absence of more comprehensive experimental evidence, we shall not advance an explanation. It seems probable, however, that a re-investigation of this reaction, employing perchloric instead of sulfuric acid as a source of hydrogen ion, will show, after salt effect corrections have been made, that the increase in order with respect to hydrogen ion is related to the similar increase for iodide.

Summary

An examination, incidental to a re-investigation of the Roebuck reaction, of the original experimental results has yielded some interesting conclusions, which have been presented here. An initial discrepancy in experiments on the forward reaction has been eliminated and explained.

Berkeley, California,
January 6, 1931.

THE WATER CONTENT OF BENZENE

BY ALAN W. C. MENZIES

Studies of the degree to which intensive desiccation affects the physical properties of substances have led to results which are notoriously discordant.[1] Vapor pressure of a desiccated substance has not infrequently been selected for study in preference to other properties as yielding results that are perhaps least equivocal. The earliest publication on this phase of the subject was that of Smith and Menzies[2] on dried calomel; while the latest is at present the interesting work of Greer[3] who studied especially benzene below 50.6°.

It was shown by Greer that the small quantity of water present in a sample of benzene that had been distilled from phosphorus pentoxide within a closed glass apparatus was sufficient to raise the total vapor pressure by several millimeters of mercury higher than that of another portion of the same benzene dried by silica gel. So many precautions were taken to avoid the presence of water that the impression remains that the benzene sample of higher total pressure must itself have been typical of very well dried benzene. We believe, however, that very much drier benzene can readily be obtained, and studied in a glass apparatus, with far fewer precautions. If this is so, the other workers in this field may after all have operated on benzene samples which were initially so well dried that Greer's explanation of their anomalous findings would be inapplicable.

1. In 1910, Menzies[4] had shown that the boiling point of benzene dried over sodium is found by static and dynamic methods respectively with values identical within 0.001°. It might, however, be argued that any abnormal behavior, due to water if present, would be identical for the two methods.

2. More recently, Wright and Menzies[5] studied near 80°, by their method of isothermal distillation, samples of benzene dried by sodium and transferred in a dry pipette to a glass apparatus dried without extreme precaution. The change in vapor pressure on distilling off as much as half of the sample did not exceed 0.2 mm. of mercury. It would appear from the experimental work described under (3) below that lowering of vapor pressure due to removal by distillation of dissolved water from benzene must manifest itself before even one-fourth of the liquid has been fractionated off. The amount of water in our sample, therefore, was so small as not to affect the normal boiling point of benzene by over 0.01°, which is the temperature change corresponding to 0.2 mm.

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[1] Much of the literature of this subject may be found cited in the work of J. W. Smith: "The Effects of Moisture on Chemical and Physical Changes" (1929).

[2] Z. physik. Chem., 76, 713 (1911).

[3] J. Am. Chem. Soc., 52, 4191 (1930).

[4] J. Am. Chem. Soc., 32, 1616 (1910).

[5] J. Am. Chem. Soc., 52, 4699 (1930).

3. In these circumstances, and because other workers in the field of intensive desiccation had studied benzene at 80° and above, it was of interest to find if the vapor pressure of benzene, as customarily handled in the organic laboratory, and near its normal boiling point, was ordinarily affected by the presence of water. For one might anticipate that, on simple distillation and even without the use of a desiccant, any water present in the benzene would pass away with the earliest fractions by reason of its relative richness in the vapor phase. Accordingly, the experiments described below are designed to test the behavior of undried benzene from which a portion has been distilled off.

Method A. The apparatus employed was that devised by Menzies for determination of molecular weights of dissolved substances by direct measurement of vapor pressure lowering of a solvent. A description of this may be found in the original article or elsewhere,[1] but Fig. 1, although drawn to illustrate Method B, will serve to recall the form of the apparatus. About 130 cc. of a good grade of commercial "C.P. crystallizable benzene conforming to the standards of Murray" was charged into the outer bulb A and boiled for ten minutes under reflux. About 15 cc. were then distilled off through the condenser in a non-reflux position, and discarded. The first runnings were cloudy, due to water. The connection D to the condenser was closed, and a further quantity of like volume was distilled off through the gauge tube C and inner tube B, with the object of at least partially removing water adsorbed on the glass walls of these portions of the apparatus. The inner tube was then charged with a portion of the remaining benzene. To remove dissolved gases, the connection to the condenser being closed, benzene vapor was "blown through" the gauge tube and inner tube, which was then closed by stopper E, while the connection to the condenser was simultaneously opened. After thermal equilibrium had been reached, the zero reading of pressure was taken, in terms of mm. of difference of level of the benzene surfaces in the inner tube and the gauge tube. The blowing through process was repeated until the results were constant. (i) Several grams of anhydrous magnesium perchlorate were then added to the inner tube. Difficulty was anticipated in removing adsorbed gases from the large surface offered by this solid, but no such difficulty was experienced. The zero reading obtained, in the manner explained above, was identical, within the experimental error, with that obtained in the absence of the desiccant, and remained constant until the experiment was discontinued after two hours. It may be recalled that readings with this form of apparatus are not affected by slow change of atmospheric pressure.

This result pointed to the essential absence from the benzene of such an amount of water as would affect the vapor pressure of benzene at 80° by so much as half a millimeter of mercury. It may be objected that the efficiency of magnesium perchlorate as a desiccant at 80° is uncertain. (ii) Potassium hydroxide as a desiccant has been studied by Baxter and Starkweather[2]

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[1] Cf. Staehler: "Arbeitsmethoden in der anorg. Chemie," 3, 169 (1913).

[2] J. Am. Chem. Soc., 38, 2038 (1916).

at 50°, at which temperature they found that it is in equilibrium with an aqueous pressure not greater than 0.007 mm. of mercury, although possibly less.

Several grams of potassium hydroxide, freshly fused at a red heat and powdered on cooling in a pre-dried hot mortar, were introduced with a fresh sample of benzene treated as formerly, in the same manner as with magnesium perchlorate. After blowing through as before, the same constant zero reading was obtained as in the absence of the desiccant. This points to the same conclusion as in (i).

Method B. It may be objected that these desiccants are, in the presence of benzene, for some reason unable to function, or, at least, do not function in the time allowed. The same disability has indeed been imputed to phosphorus pentoxide in like circumstances. To meet this objection, the dissociation pressure of a salt hydrate pair was measured within the inner tube of the apparatus.

If no vapor is present in the benzene vapor, then the full aqueous pressure furnished by the salts should be found as a quantity additive to the pressure of benzene vapor, but if the benzene vapor already contains some water vapor, the pressure found and measured should be the difference between the true aqueous dissociation pressure of the salts and the partial pressure of water already existant in the benzene vapor before the salts are added.

As a suitable salt hydrate equilibrium to utilize for this purpose was chosen that represented the equation

$$ZnSO_4, (NH_4)_2SO_4, 6H_2O \rightleftarrows ZnSO_4, (NH_4)_2SO_4, 2H_2O + 4H_2O.$$

The pressures of this system have been measured in eleven observations by Caven and Ferguson[1] from 30.7° to 79.4°. The double salt is one of those which is readily prepared in a pure condition. At 80°, a pressure over 90 mm. of mercury is to be expected. In order to be able to measure such a high pressure in our apparatus, about 5 cc. of mercury was placed in the inner tube B, as shown in Fig. 1, in addition to the benzene. The manipulation was similar to what has already been described. About 3 grams of salt were employed, obtained by freshly efflorescing the hexahydrate in an air oven at 90° until the water content corresponded to 5.5 H_2O, and subsequently guarding against adsorption of water. Corrections to the increase of pressure observed were necessary (a) for the pressure due to liquid benzene and solid salt resting upon the mercury, and (b) for the density reduction of mercury and benzene at 80° (factors of 13.40 and 0.815 respectively) to mercury at 0°. The value of correction (a) was determined by separate experiments made outside the apparatus with tubes of similar dimensions to those forming part of the apparatus. Equilibrium was reached within an hour, and repetition of the blowing through process yielded concordant results.

The dissociation pressure found was 95.7 mm. at 80.2°. The temperature was known to ±0.1° by use of a certified mercurial thermometer of recently determined zero-point. Assuming as correct the three-constant equation

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[1] J. Chem. Soc., 125, 1307 (1924).

given by Caven and Ferguson to represent their results, ±0.1° corresponds at 80.2° to ±0.5 mm. pressure. Looking also to possible errors in pressure measurement, our value may well be in error by 1 mm. The pressure at 80.2° according to Caven and Ferguson's equation is 96.6 mm., which is 0.9 mm. higher than our value, but within our error of experiment.

A possible source of error not taken into consideration above is the alteration in the vapor pressure of benzene itself by reason of the water now dissolved in it. The amount (expressed as mol fraction) of such water will bear nearly the same ratio to the amount at saturation as its partial pressure does to that of pure water. For benzene saturated with water is in equilibrium, as to partial pressures of the components, with water saturated with benzene, whose aqueous pressure is obviously near that of pure water. The Duhem-Margules relation is not very helpful in evaluating this correction to the partial pressure of benzene, partly owing to lack of data. It may be pointed out that this relation obviously fails to hold in cases such as that of heptane and ethyl alcohol[1] where one of the partial pressure-composition isotherms passes through a maximum. Study of the published partial pressure-composition curves for pairs of non-ideal liquids leads one to anticipate a lowering by water of the partial vapor pressure of benzene much less than 2.8 mm., which is approximately that demanded in this case by Raoult's law. Liquid pairs are known where the partial pressure of the solvent (as ethyl alcohol) is actually raised by the presence of the solute (as heptane). For these reasons, no attempt was made to apply the small and uncertain correction for possible error from this cause. However, it seems unlikely that water present before the introduction of the salts influenced the pressure of the benzene used for the experiment by as much as two mm. of mercury.

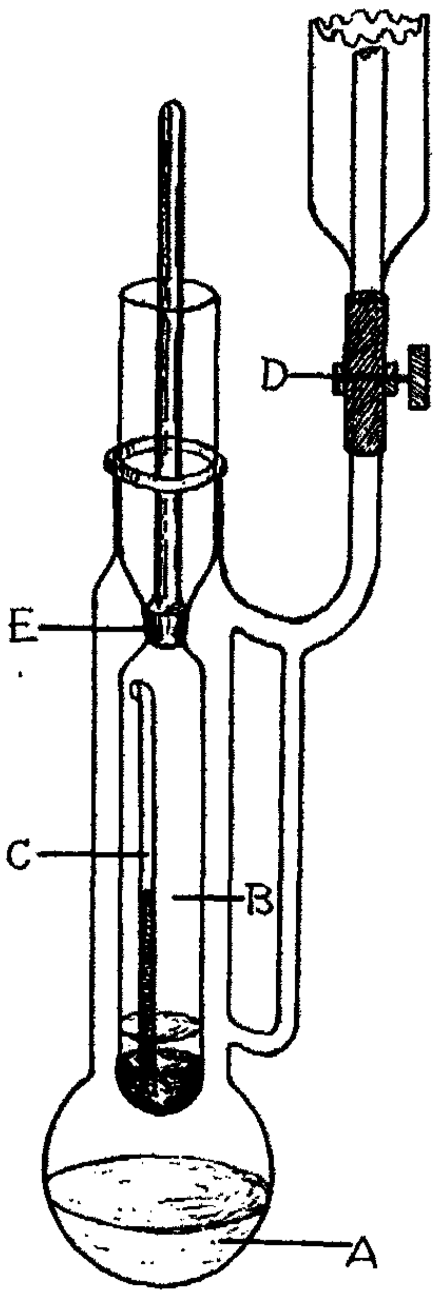

Fig. 1

The utility of the method here employed for measuring dissociation pressures of salt hydrate pairs will be referred to in an article[2] which follows.

Conclusions

From these experiments it would appear that, if ordinary undried benzene be distilled at about 80° and the first one-quarter fraction be rejected, the

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[1] Smyth and Engel: J. Am. Chem. Soc., 51, 2660 (1929).

[2] By Menzies and Hitchcock.

remaining benzene exhibits a vapor pressure that has suffered alteration from the possible presence of water in an amount not exceeding about 0.2 percent. This corresponds to a change in the normal boiling point of less than 0.1°. Beyond these limits, apparently abnormal vapor pressure results obtained by workers with intensively desiccated benzene cannot be attributed to the water content of their "ordinary" benzene, provided the latter has received even the very simple treatment of partial distillation outlined above.

Summary

It is pointed out that benzene dried by sodium and transferred to a glass apparatus has been found free from such an amount of water as would alter the normal boiling point by 0.01°.

Two methods have been described for examining the water content of the vapor of benzene at its boiling point.

It is shown that, if one-fourth of a sample of ordinary benzene, containing water, is distilled off at atmospheric pressure, the remainder contains less water than would affect the normal boiling point by 0.1°.

The bearing of this upon work with intensively desiccated benzene is pointed out.

A simple form of indirect method of measuring dissociation pressures of salt hydrates has been described.

Princeton University,
January, 1931.

MISLEADING EQUILIBRIA ENCOUNTERED IN THE MEASUREMENT OF DISSOCIATION PRESSURES IN SALT-HYDRATE SYSTEMS

BY ALAN W. C. MENZIES AND C. S. HITCHCOCK

It is only too obvious to those interested that, while the number of published experimental results in this field increases year by year, there is a regrettably large degree of discordance between the values found by different workers. It is hoped that the present communication may be of use in tending to remedy this unfortunate situation.

The errors caused by the neglect of adsorbed permanent gases which are so difficult to remove from static tensimeters are now better appreciated than in the days of Frowein, faith in whose otherwise excellent results was the cause of much interesting if nugatory speculation as to the cause of the high values yielded by the gas-current saturation method. This difficulty disappeared when it became apparent[1] that the tensimetric results of Frowein in question were themselves too low.

Apparently insignificant points of experimental technique, such as the use of glass wool in an absorption train, have been shown capable[2] of producing considerable discrepancies. Profiting by this and other constructive criticisms offered by Menzies, Partington and Huntingford[3] repeated the earlier work of Partington[4] on the aqueous pressure in equilibrium with the system $CuSO_4$, 5-3H_2O and obtained new values which were markedly higher.

In the present article a rapid method of measurement will be illustrated and shown to be applicable in difficult cases; and examples will be adduced to show that a genuine equilibrium pressure is sometimes reached which, however, is that of the vapor of water merely adsorbed upon the salts rather than an equilibrium dissociation pressure.

Methods. Two methods were employed: (1) the well-known gas current saturation method; and (2) a method whose novelty makes necessary some words of explanation.

It has often been reported that equilibrium between water vapor and a salt hydrate pair is reached more quickly if the two solid phases are in contact with a liquid in which water is at least slightly soluble; and this gain in speed is sought in several of the so-called indirect methods of dissociation pressure measurement which utilize solutions of water in such liquids as ether[5], ethyl alcohol[6] or isoamyl alcohol.[7] After the solid phases have been

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[1] Cf. Menzies: J. Am. Chem. Soc., 42, 1951 (1920).

[2] Menzies: J. Am. Chem. Soc., 42, 978 (1920).

[3] J. Chem. Soc., 123, 160 (1923).

[4] J. Chem. Soc., 99, 467 (1911).

[5] Linebarger: Z. physik. Chem., 13, 500 (1894).

[6] Foote and Scholes: J. Am. Chem. Soc., 33, 1309 (1911).

[7] Wilson, Noyes and Westbrook: J. Am. Chem. Soc., 43, 704, 726 (1921).

brought to equilibrium with the liquid, the water concentration and aqueous partial pressure of the latter are then arrived at by independent experiments.

For the work which follows, we wished to employ such a liquid in the hope of accelerating attainment of equilibrium; but we wished also (a) to be able to follow readily by the eye and without analysis the development of aqueous pressure in the system; and (b) to be able to operate far above room temperatures but without the inconvenience of a cumbersome high temperature tank thermostat. To meet these conditions, we found the method briefly outlined in the preceding article would serve admirably. With this apparatus, also, low pressures may be directly measured in terms of a column of liquid much less dense than mercury.

In general, dissociation pressure equilibria of such salt hydrate pairs as yield only a low pressure are attained only slowly, and it is especially in such cases that the results of different investigators are apt to show discrepancy. For this reason the case following was suitable for study.

1. *$BaCl_2$, 1.8 H_2O in Chloroform.* Equilibrium in the system $BaCl_2$ 2-1 H_2O and vapor is universally reputed to be difficult of attainment.[1] Baxter and Cooper, whose work is the more to be trusted because they were well aware of the difficulties, have measured this dissociation pressure at 15°, 25° and 40°, and the three-constant equation which they fit to these observations yields 56.7 mm. for the pressure at 60.1°, which was the boiling point of chloroform under the existing barometric pressure, as used by us for our method (2).

Our sample of dihydrate, Merck's "reagent" grade, was effloresced in an oven at 55° to a composition $BaCl_2$, $1.8H_2O$. Since the expected pressure would have required a column of chloroform to balance it longer than our apparatus is tall, we employed a few cc. of mercury in the inner tube of the apparatus to serve as the manometric liquid. The manipulation and corrections have already been referred to.[2] The density of chloroform at its normal boiling point was taken as 1.410.

Equilibrium was reached within half an hour, duplicate experiments yielding $57._3$ and $57._8$ mm. respectively at 60.1°. Our temperature measurement, by a Reichsanstalt certificated thermometer whose zero point had recently been redetermined, is good only to the nearest one-tenth degree. The average of these results, $57._5$, may well be in error by one millimeter, and is, therefore, in good agreement with the extrapolated value of Baxter and Cooper.

A correction, 0.3 mm., due to the lowering of the vapor pressure of chloroform within the inner tube by the water dissolved in it may be computed, assuming Raoult's law, from the following data: solubility of water in chloroform at 60°, 0.8 percent,[3] vapor pressure of water saturated with chloroform, about 149 mm. Because information is lacking on the effect of small mol

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[1] Cf. Baxter and Cooper: J. Am. Chem. Soc., **146**, 923 (1924); Schumb: **45**, 342 (1923); Partington: J. Chem. Soc., **99**, 49 (1911).

[2] See preceding article J. Phys. Chem., **35**, 1655 (1931).

[3] Extrapolated from values in I. C. T. **3**, 387.

fractions of water on the vapor pressure of chloroform, this correction was not applied, but the calculation serves to show that the value of the true correction is presumably small.

It is evident that, in this case, attainment of the true dissociation pressure presents no difficulty under our experimental conditions. We had guarded against the adsorption of water by the salts in handling, and no ambiguity was likely as to the hydrates present. A more difficult case was accordingly selected.

2. *$CuSO_4$ 1-0 H_2O.* The measurement of the equilibrium pressure for this system has presented such difficulty to various workers that it is not at all obvious what the true p-t relation really is. We have arrived at this in the following manner. The three independent investigations of Bell and Taber,[1] Foote[2] and Crockford and Warrick[3] have reached reasonably concordant values for the concentration of aqueous sulfuric acid with which these two solid phases are simultaneously in equilibrium. If we average these values for 25° we obtain a concentration of sulfuric acid about 87.8 percent. If now we suitably graph against concentration the logarithms of the aqueous pressures over sulfuric acid solutions at 25° as given in International Critical Tables, we find a pressure for 87.8 percent nearly 0.017 mm. of mercury. Siggel,[4] in Nernst's laboratory, in an effort to improve upon the work of Schottky,[5]

TABLE I

Dissociation Pressures in the System $CuSO_4H_2O \leftrightarrows CuSO_4 + H_2O$

Observers	Temp. °K.	Pressure mm. Hg Obs'd.	Calculated Siggel	Calculated M. and H.	Difference in mm. Obs'd minus Calc'd Siggel	Difference in mm. Obs'd minus Calc'd M. and H.
Averaged from three	298.1	0.017	0.019	[0.017]	−0.002	0.0
Siggel	372	6.0	6.04	5.96	−0.04	+0.04
"	383.2	12.0	11.92	11.9	+0.08	+0.1
"	403.9	38.2	37.9	38.6	+0.3	−0.4
"	410.2	53.5	52.7	53.9	+0.8	−0.4
"	420.4	90.4	88.0	90.6	+2.4	−0.2
Average of preceding five values all taken as positive					0.72	0.23
Algebraic sum of the five differences					+3.54	−0.86
Schottky	363.6	4.6		3.46		+1.14
Foote and Scholes	298.1	0.8		0.017		+0.78
Dover and Marden	298.1	1.3		0.017		+1.28
Müller-Erzbach	298.1	0.5		0.017		+0.48

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[1] J. Phys. Chem., 12, 171 (1908).

[2] J. Am. Chem. Soc., 37, 288 (1915).

[3] J. Phys. Chem., 34, 1064 (1930).

[4] Z. Elektrochemie, 19, 340 (1913).

[5] Z. physik. Chem., 64, 415 (1908).

an earlier pupil of Nernst, determined the dissociation pressure of this salt system at five temperatures from 99° to 147.4°. Siggel proposes a three-constant equation to average these results. If, however, using the above datum for 25° and an average of Siggel's data we find the constants in a two-constant equation (E) of the form $\log p = A - B/T$, where A evaluates as 11.040 and B as 3818.2, we are able to average Siggel's results considerably better than he does himself, as is shown in Table I. We have given greater weight to his two lower temperature values, in which Siggel places most trust. To this table we have appended also the values of certain other observers.

The value of Foote and Scholes[1] was obtained indirectly by equilibration with aqueous ethyl alcohol. That of Dover and Marden[2] by the transpiration method, purports to give only the apparent pressure under their experimental conditions.

(a) *Gas Current Method.* Anhydrous cupric sulfate and the monohydrate were obtained by heating the pentahydrate at about 240° and 100° respectively. Approximately equal quantities of the two salts, in granules of an average dimension of four mm., were mixed and charged into two "saturators" tubes each of 5 cm. diameter and 30 cm. length. These were immersed in a thermostat at 40° and connected by ground glass joints with two water absorption tubes containing anhydrous magnesium perchlorate, situated outside the thermostat. The weight of the second of these absorption tubes remained sensibly constant. In all, some 1500 liters of air freed from moisture by means of magnesium perchlorate were passed through the train at this temperature at a rate near 1½ liters per hour, causing the copper salts to lose some 420 mg. of water. The equilibrium pressure expected, according to equation (E), is 0.070 mm. The pressures of water found from the observed gain in weight of the absorption tubes for a metered volume of air ranged from 1.51 mm. progressively downward to 0.08 mm., at which point the bath temperature was raised to 50.0°. At this temperature the anticipated pressure is 0.167 mm. During the passage of 560 liters, the pressure measured decreased from 0.18 smoothly through the dissociation equilibrium value to 0.11 mm. when the experiment was discontinued.

In this instance, the dynamic equilibrium of dissociation is apparently very slow in both directions. During a pause in the work following the experiments at 40°, the saturator tubes had been left closed and inactive at room temperature for three summer months. The aqueous pressure within the tubes, however, remained five-fold higher than the dissociation pressure. At any particular epoch during the course of these experiments, measurements by any static method of the vapor pressure of water as yielded by this material would obviously have given concordant results. But the pressure measured would have been that of adsorbed water and not a true dissociation pressure.

In answer to the question how the copper salts in the saturator tubes acquired the water which they later yielded up as described, at least two

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[1] J. Am. Chem. Soc., 33, 1309 (1911).

[2] J. Am. Chem. Soc., 39, 1609 (1917).

replies might be made: (1) that this amount of water in the form of a thin film was in equilibrium with the aqueous pressure in the drying oven at 100°, for example; or (2) that the water was picked up at room temperature from the air of the room during the process of charging the absorption tubes. It must be recalled that the copper salts employed resulted respectively from the removal of 4 or 5 molecules of crystalline water from each "molecule" of pentahydrate of cupric sulfate and that the new specific surface so produced must be very large. A quantity of a few grams of gross analysis $CuSO_4$, 0.9 H_2O was found to gain weight on standing in the balance case containing ordinary room air at the rate of 2 percent per hour.

In those cases where the specific surface of the salts is large, where the dissociation pressure to be measured is low and where the rate of the chemical reaction is slow, the opportunity for error due to adsorbed water becomes most favorable.

(b) *$CuSO_4$, 0.9 H_2O, in Benzene.* The solid was prepared by removal of water from the pentahydrate by prolonged heating in a drying oven at 110° and was presumed to be a mixture of $CuSO_4$, H_2O and $CuSO_4$. Adsorption of water during handling was guarded against. At 80°, which is near the normal boiling point of benzene, the expected dissociation pressure for the system is 1.68 mm. of mercury, according to equation (E). The pressure found by method (2), using benzene, was 1.6 ±0.1 mm. This was reached with difficulty within an hour, the speed being increased by shaking and by use of larger quantities of the salts. Otherwise several hours might be consumed.

The error due to the effect of the dissolved water upon the vapor pressure of benzene, computed as indicated in the preceding article, would in this case reach only 0.006 mm., and is therefore negligible.

3. *$CuSO_4$, 2.9 H_2O, by Dehydration, in Chloroform.* The systems composed of vapor and cupric sulfate with five and three and with one and three molecules of water have been studied by Carpenter and Jette[1] in the ranges 25°-90° and 25°-80° respectively. While an examination of their results, which will be discussed elsewhere, points to their lower temperature values for the second system being too high, due, doubtless, to adsorbed water, their values at 60.0°, which by interpolation we find near 83.4 and 58.8 mm. respectively, are probably not far from the truth. As a desirable antecedent to our next experiment, we made two rough trials, using method (2) with chloroform, with a solid of analysis corresponding to $CuSO_4$, 4.5 H_2O, and obtained a dissociation pressure at 60.0° of $80._8 \pm 1.5$ mm. It may be recalled[2] that one molecule percent of the isomorphous sulfates of manganese, zinc and magnesium in solid solution lowers the dissociation pressure of cupric sulfate pentahydrate by 8.6, 6.2 and 2.3 percent respectively. Our copper salts gave negative tests for these and other metals.

We then prepared a sample of water content corresponding to 2.9 H_2O by allowing another portion of the material used in experiment (2b) to take up

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[1] J. Am. Chem. Soc., **45**, 578 (1923).

[2] Cf. Hollmann: Z. physik. Chem., **37**, 193 (1901).

water from the air of the laboratory over a period of two days. Using the same method, pressures at 60.0° of 73.2 and 71.0 mm. were obtained in successive experiments, pointing to a slow disappearance of adsorbed water. What is here being measured is clearly not the true equilibrium pressure of either of the systems mentioned, but that of the less hydrated system as vitiated by the presence of adsorbed water whose effect in this case disappears but slowly.

Summary

1. The method very recently proposed by Menzies is shown to yield, often within an hour, true results for the dissociation pressure of certain salt hydrates, including the difficult cases of $BaCl_2 2H_2O \leftrightarrows BaCl_2H_2O + H_2O$ and $CuSO_4H_2O \leftrightarrows CuSO_4 + H_2O$.
2. A linear equation is proposed by which to represent the pressure-temperature relation in the last-named system.
3. It is shown that, in salt hydrate systems, equilibrium pressures may be attained that are not true dissociation pressures, but rather pressures due to adsorbed water. The incidence of this source of error is discussed.

Princeton University,
January 1931.

A STUDY OF ORGANIC ACID IRON SOLUTIONS*

I. Concentrations and Colors

BY NORMAN J. HARRAR AND FRANK E. E. GERMANN

Introduction

A great variety of substances present in natural waters may act as solvents upon iron minerals. The effects of a number of these have been estimated from natural sources and sometimes tried out under artificial conditions. The solvent effects of organic acids on iron oxides were studied by Harrar[1] and it was shown that the dissolution of iron depended upon the nature of the oxide, the nature of the acid, and the nature of the resulting substance. It was found that a satisfactory explanation of this third factor could not be advanced because the precise nature of these organic iron compounds is a matter of considerable controversy.

The largest and most important contributions to the subject have been made by Weinland and his students,[2] who regard these substances as complex compounds, which dissolve in water with the formation of complex organic iron ions. This view seems to be based largely upon analyses of a great number of crystalline preparations and is supported by the work of other investigators. On the other hand, color comparisons have led Pickering[3] and others to suggest that the properties of these solutions indicate the presence of colloidal particles.

An important application of this distinction is reviewed by Thomas[4] in a recent article on the absorption of iron by plants. He states the conflicting opinions about the form in which iron must exist to be absorbed, suggests a "colloid-solution equilibrium" of

$$\text{"Colloidal } Fe_2O_3.xH_2O \leftrightarrows \text{Dissolved } Fe(OH)_3 \leftrightarrows \\ \text{Ionized } Fe^{\cdot\cdot\cdot\cdot} + 3(OH)^{-}\text{"}$$

and finally concludes that "more facts are needed" before any further progress can be made in that field.

This work had for its purpose, therefore, the collection of more information about the form in which iron exists in organic acid solutions, with particular attention to the possibilities of complex formation and of colloidal properties.

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* Contribution from the Department of Chemistry of the University of Colorado.

[1] N. J. Harrar: Econ. Geol., 24, 50 (1929).

[2] R. F. Weinland: "Einführung in die Chemie der Komplex-Verbindungen" (1919); Weinland and Reihlen: Ber., 46, 3144 (1913); Weinland and Paschen: Z. anorg. Chem., 92, 115 (1915); Weinland and Loebich: 151, 271 (1926) and many others.

[3] S. U. Pickering: J. Chem. Soc., 103, 1358 (1913); 105, 464 (1914); 109, 235 (1916).

[4] W. Thomas: Soil Science, 27, 259 (1929).

Plan of Investigation

The solutions of the complex compounds for this study were prepared by dissolving freshly precipitated ferric hydroxide in various organic acids. The quantity of the hydroxide used was an amount calculated to give about one gram of iron in 250 c.c. of solution, although in some cases, not this much could be dissolved. The acids were of normal concentrations, except as solubility limits interfered and forced the use of saturated solutions. Acids of this strength were most convenient for getting the iron into solution, and then any desired concentration could be obtained by dilution.

The selection of the organic acids was first limited to the normal series, beginning with the three simplest monobasic acids: formic, acetic, and propionic and the first four dibasic acids: oxalic, malonic, succinic, and glutaric. Then to study further the relation of dissociation constants, more of the non-substituted type were selected and a wide range of acid strengths covered.

The actual examination of the complexes produced involved a gradual development of methods and criteria to be applied. It was intended that the conclusions reached be based upon comparisons of results from a number of different angles and checked by as many acids as possible. Organic compounds, of course, offer excellent gradations in properties for this kind of work and reasoning.

Preparation of Solutions

The concentration of iron desired was one gram in 250 c.c. of one normal acid solution and it was to be dissolved as freshly precipitated ferric hydroxide. This was accomplished as follows:

A sample of Baker's Analyzed Ferric Oxide was dissolved in hot concentrated HCl, diluted with distilled water and treated with excess NH_4OH. As much water as possible was removed by suction, but it was not otherwise dried. The hydroxide was then transferred to a bottle of about 270 c.c. capacity. The solutions finally obtained were always analyzed for iron and those which did not contain within one-tenth of the required one gram in 250 c.c., were rejected.

The iron in solution was determined by titration against potassium permanganate. The latter was a Mallinckrodt Analyzed Chemical, checked against a Bureau of Standards sodium oxalate (sample no. 40 b). The usual procedure was to treat the solution with sulfuric acid, run it through a Jones Reductor and titrate at once with permanganate. In a few cases, the acid interfered with this titration and it was necessary to evaporate the solution to dryness, char the residue, and redissolve the iron in sulfuric acid.

The acids were all of C.P. grade, most of them Eastman chemicals and the others, Kahlbaum or Mallinckrodt preparations. Those which were sufficiently soluble, were weighed out in amounts calculated to give nornal solutions and the others were shaken with distilled water until nearly saturated solutions developed.

These acids were titrated against NaOH, which was checked against a Bureau of Standards benzoic acid (sample no. 39 c) and those of the readily soluble acids which were not within one-tenth of one normal concentration, were remade or rejected.

The acid solution, to the amount of 250 c.c., was added to the bottle containing the freshly prepared ferric hydroxide and the bottle stoppered tightly. It was then vigorously agitated on a shaking machine until the solid had apparently dissolved or until it appeared (after about five or six hours) that the action was practically complete. A short period was allowed for settling and the solution was ready for examination.

Concentrations

The concentrations of iron obtained in the solutions and the strengths of the acids employed are given in Table I. In all cases, preparations and determinations were made in duplicate. The results were checked still further by repeating the entire preparation and examination of each solution.

TABLE I

Acid	$K.10^4$	Normality of Acid	Grams of Fe per 250 c.c.
Formic	2.14	1.008	1.040
Acetic	.18	1.054	.958
Propionic	.14	1.008	.702
Butyric	.15	.782	.411
Oxalic	380.	.990	1.009
Malonic	16.1	.991	.941
Succinic	.66	.968	.498
Glutaric	.47	.985	.204
Adipic	.37	.315	.081
Tricarballylic	2.2	1.020	.156
Maleic	120.	.936	.923
Fumaric	10.	.126	.004
Mesaconic	7.9	.404	.014
Chloracetic	15.5	1.094	.985
Dichloracetic	500.	1.062	.947
Trichloracetic	2000.	1.049	.936
Benzoic	.66	.026	.006
Phenylacetic	.50	.129	.003
Phthalic	12.6	.087	.026
Hydrochloric	—	.976	.917
Sulfuric	—	.962	1.014

In this table the dissociation constants are expressed, for convenient comparison, as times 10^4 and for these values the tables of Landolt-Börnstein[5] and the critical work of Lunden,[6] were consulted. The figures in the last two columns were determined by the methods described above.

The tests applied to some of these solutions were rendered almost worthless by the low solubility of the acid involved or by its poor solvent effect on ferric hydroxide. It will be noted that this is true of the aromatic acids used and of fumaric and mesaconic acids. All the others dissolved at least enough iron to make possible the comparison of properties.

Colors

The colors produced by the various combinations tried were observed on at least two separate preparations and are described in Table II.

The effect of diluting these solutions was then determined, to note the colors at lower concentrations, and to obtain a measure of the intensity of the colors. The procedure was to measure off from the bottle containing the normal solution (bottle no. 1), 100 c.c. into bottle no. 2, and to add 100 c.c. of distilled water. This process was repeated and the dilution thereby, doubled and redoubled, until a solution was obtained which appeared colorless, when compared with 200 c.c. of pure water in a similar container.

The row of bottles thus obtained showed, in some cases, only a gradual fading out of the original color, but in others, definite changes in color were observed. The attempt has been made to draw up a table which will indicate the nature of the significant changes, as far as is possible to express them in words.

The first column of Table II lists the acids used and their dissociation constants expressed as in the previous table. The second column describes the color of the bottle no. 1 solution containing, if possible, one gram of iron in 250 c.c. of one normal acid. The third column states the colors produced by dilution and a careful study of the words chosen, will show where the gradual and the more abrupt changes occurred. The fourth column gives the final color to be observed and the last column contains the number of the bottle which appears colorless. The concentrations of iron and of acid at all these dilutions could be calculated and recorded, but for this table, the comparisons are made much more striking by merely listing these bottle numbers.

A careful examination of Table II will develop many interesting individual relationships and some points of general importance which may be summarized as follows:

1. The solutions with a red or orange-red color, unless very little iron has been dissolved, retain some color to about the 12th bottle. This corresponds to a concentration of .00043 grams of iron in 250 c.c. (calculated on the basis of an original one gram) and an acid normality of the same value.

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[5] Landolt-Börnstein: "Physikalisch-Chemische Tabellen" (1923).

[6] H. Lunden: "Affinitätsmessungen an schwachen Sauren und Basen" (1908).

TABLE II

Acid K.10^4	Color (no. 1)	Color changes on dilution	Final Color	Colorless Bottle
Formic	intense red			
2.14		2. red		
		3. red orange		
		4. orange		
		5. yellow	pale yellow	12
Acetic	intense red			
.18		2. red		
		3. orange red		
		4. red orange		
		5. orange		
		6. yellow		
			pale yellow	13
Propionic	blood red			
.14		2. red		
		3. red orange		
		4. orange		
		5. orange		
		6. orange yellow		
		7. yellow		
			pale yellow	13
Butyric	orange red			
.15		2. red orange		
		3. orange		
		4. orange		
		5. orange		
		6. pale orange		
		7. pale orange		
		8. pale yellow		
			pale yellow	10
Oxalic	vivid green		pale green	11
380.				
Malonic	green		pale green	6
16.1				
Succinic	orange red			
.66		2. red orange		
		3. orange		
			pale orange	9
Glutaric	red orange			
.47		2. orange		
			pale orange	9

TABLE II (Continued)

Adipic	red orange			
.37		2. orange		
			pale orange	6
Tricarballylic	red orange			
2.2		2. orange		
			pale orange	7
Maleic	orange red			
120.		2. orange yellow		
		3. yellow green		
		4. green		
			pale green	8
Fumaric	colorless			1
10.				
Mesoconic	colorless			1
7.9	(trace of yellow?)			
Chloracetic	red			
15.5		2. orange		
		3. yellow		
		4. green yellow		
		5. green		
			pale green	7
Dichloracetic	green yellow			
500.		2. green	pale green	5
Trichloracetic	very pale			
2000.	green			2
Benzoic	colorless			1
.66				
Phenylacetic	colorless			1
.50				
Phthalic	pale green			
12.6				2
Hydrochloric	green			
	(yellow on			6
	standing)			
Sulfuric	pale yellow			5
	green			

2. The solutions with a green color, all of which easily dissolve a gram of iron, become colorless at about the 6th bottle. This corresponds to a concentration of .03125 grams of iron in 250 c.c. (calculated on the basis of an original one gram) and an acid normality of the same value.

3. There are two combinations, the chloracetate and the maleate, which undergo a very definite change from red to green, merely by dilution.

4. It appears probable that the most important factor in determining the color (and, therefore, the structure) of these complexes, is the strength of the acid involved. The selection of such a large number of acids for these tests was made in order to multiply the evidence in support of this statement.

For the purpose of presenting the results of the color tests in the light of the statement just made, Table III has been prepared by arranging the data given in Table II in a different order. The acids are listed in the order of their dissociation constant values and the relation to the colors is immediately evident. The solutions which contained such small amounts of iron that no colors were seen, might have been omitted, without altering the conclusions reached, but, for the sake of completeness, they have been included.

Table III

Acid	$K.10^4$	Color (and on dilution)
Hydrochloric	—	green
Sulfuric	—	pale green
Trichloracetic	2000.	very pale green
Dichloracetic	500.	green yellow—green (2)
Oxalic	380.	vivid green
Maleic	120.	orange red—green (4)
Malonic	16.1	green
Chloracetic	15.5	red—green (5)
Phthalic	12.6	pale green
Fumaric	10.	colorless
Mesoconic	7.9	colorless
Tricarballylic	2.2	red orange—orange
Formic	2.14	intense red—yellow
Succinic	.66	orange red—orange
Benzoic	.66	colorless
Phenylacetic	.50	colorless
Glutaric	.47	red orange—orange
Adipic	.37	red orange—orange
Acetic	.18	intense red—yellow
Butyric	.15	orange red—yellow
Propionic	.14	blood red—yellow

The evidence contained in Table III is entirely in accord with the generalization that the strength of the acid involved is the prime factor in determining the color of the complex formed. One or two very obvious peculiarities of the table, however, must be explained at this point.

It will be observed that oxalic and malonic acids give green colored solutions, even in normal concentrations. Thus, when dichloracetic, maleic and chloracetic acids were selected to check further the generalization, it was supposed that they would act in a similar manner. The appearance of red colors with maleic and chloracetic acids was, therefore, quite unexpected. The color changes on dilution, however, seem to turn these examples into a confirmation of the theory advanced, as the concentration is a real factor in the dissociation of these acids. Thus, the change to green in maleic came at a greater concentration than in chloracetic, while the color in dichloracetic was almost green to begin with, as might be expected.

It seems probable, therefore, that the greens of the oxalate and malonate are not determined solely by acid strengths. As a matter of fact, the oxalate possesses a rather distinctive green color and requires much further dilution than the others before it appears colorless. The evidence obtained with the other di-basic acids seems to indicate, however, that an actual contradiction of the above principle is not involved.

It will be observed that no attempt has been made to explain the significance of the colors produced in these solutions. Thus far, the main objective of this work has been to establish the principle regarding the relations between colors and acid strengths. Before any attempt is made at an explanation, the results of some dialysis, diffusion, electrolysis and other types of experiments should be presented. The evidence obtained in these tests will be described in a subsequent article.

Summary

This study had for its purpose, the collection of more information about the form in which iron exists in organic acid solutions, with particular attention to the possibilities of complex formation and of colloidal properties.

Portions of freshly precipitated ferric hydroxide were dissolved in various organic acids, obtaining concentrations of about one gram of iron in 250 c.c. of one normal acid solutions. Standard methods of analysis were used to determine the exact amount of iron and acid present in each case. The colors of the solutions, the colors on dilution and the relative color intensities were determined for each combination.

The most general conclusion reached was that the most important factor in determining the color of any combination is the strength of the acid involved. It was shown that an arrangement of acids in the order of their dissociation constant values would permit of a definite division into two groups, strong acids with green colored solutions, weak acids with red colored solutions. Further work in support of this generalization will be presented in a later article.

COBALT SULFIDE BANDS IN SOLID SILICA GEL

BY EMIL RAYMOND RIEGEL

When silica gel containing cobalt nitrate is allowed to set, and is then overlaid by a solution of sodium sulfide, black rings of cobalt sulfide are formed in profusion. The first rings are very narrow and very numerous, the later rings become gradually broader, less numerous per unit of length and spaced further apart.

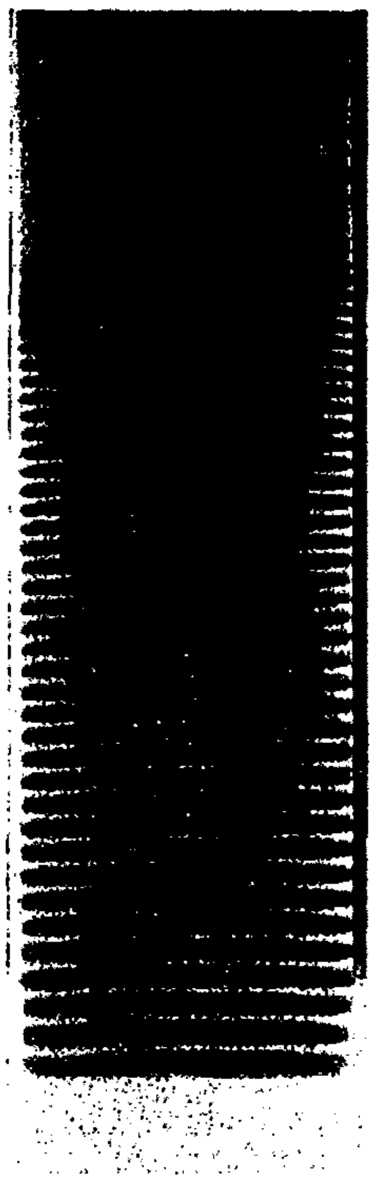

FIG. 1

Cobalt sulfide rings in silica gel. Section of the formation in a flattened pyrex tube

A suitable silica gel is made by pouring 108 cc. of 1.060 commercial sodium silicate solution into 33 cc. water to which 3.5 cc. glacial acetic acid and 0.70 grams cobalt nitrate crystals have been added previously. At once after mixing the two solutions, the resulting mixture, which is still pink, is poured into the special tubes described below, each one receiving 22 cc. The height of the liquid in the tubes is 150 mm from the bottom. The gel sets in about 3 minutes, and is overlaid at once with a 3% sodium sulfide (3% Na_2S) solution. Rings form at once and continue to form over a period of days. A portion of such a tube is shown in the accompanying photograph.

Such was the first procedure. It had the defect of involving a collapse of the upper part of the silica gel, as the solvent action of the alkaline sulfide took place. To measure the rate of advance of the black front, it was necessary to allow for the distance collapsed, which increased from day to day; the first rings were destroyed and so withdrawn from observations; the distance of the top of the gel to any point in the gel changed constantly; there were several other disturbing results so that comparative values over several days were in doubt, the worst one being that the concentration of the sulfide changed in an unknown degree. The first attempt to prevent the collapse was to place the tubes in a nearly horizontal position in a drawer; at the same time any light influence was avoided by keeping the drawer closed. The collapse and solvent action were about the same, however, and the next attempt was to make the sulfide itself into a gel, so as to immobilize the interface. This succeeded. One example follows: 4.5 cc. of 1.060 sodium silicate solution, 0.12 cc. acetic acid, and 1.5 cc. water are well mixed, and 6 cc. of 6% Na_2S solution added and the whole quickly poured on top of the solid cobalt silica gel. Some practice is required to succeed in forming this gel so that it stiffens throughout; it sets so fast that in many cases it was found best to mix the materials in the upper part of the tube itself, which provided a space holding just 12 cc. With this corrected procedure the cobalt silica gel is absolutely undisturbed and its deposits and lines may be observed and measured from a permanent interface days after they are formed. As far as we know, this is the first published example of the growth of Liesegang rings from two gels in contact. In all experiments described below, the tubes were prepared with the sulfide in such a gel, and the tubes were kept in a light tight drawer. The rate of growth of the rings is the same as with the original sulfide solution, if allowance is made for the collapse. The sulfide silica gel is a false gel, but even when partly liquefied, the cobalt silica gel suffers no attack at its upper edge.

Flattened pyrex tubes: The special tubes used were made by sealing off at one end, suitable lengths of a flattened pyrex tubing, supplied in 4′ lengths by the makers. Two sizes were sealed off, one 15 cm long, for preliminary work, the other 22 cm long, the standard length for this work. Its volume, 34 cc., was divided into the lower 22 cc. for the cobalt silica gel, and the upper 12 cc. for the sodium sulfide gel. The advantage of such a tube is twofold: First, the annoying reflection of a round tube, which meets the eye, is avoided, and second, the tube may be laid on the stage of the microscope and examined by reflected and transmitted light at any moment, with no preparation. The inside cross-sectional dimensions of the tubes were 20 by 6 mm with slight variations. All the work described may be successfully performed with round tubes, however.

Modifications studied: The effect on the pattern of various strengths of silica gel (from sodium silicate solution between 1.045 and 1.1000), of the concentration of the cobalt salt (between 0.07 and 0.21 grams crystals in standard tube), and of the concentration of the sodium sulfide, was studied. The pH was observed only casually; in modifying the amount of acetic acid used we were guided mainly by the resulting rate of setting. The more acid the mixture, the slower the set. If the acid is so low that the gel is distinctly blue, it sets before it can be poured into the tubes. The gels used generally were pink, setting in 20 minutes at the longest; or lavender, setting in as little as one minute; blue gels were made by mixing the materials in the tubes themselves. For several cases in which the gel was lavender, the pH was found to be 8.

Two examples of perfect deposition: Two tubes might be described because they illustrate the effect of raising the concentration of the cobalt salt for the same concentration of the silica in the gel, and also because the ring formation was absolutely perfect. The gel was made by pouring 144 cc. of sodium silicate solution into a mixture of 33 cc. water, 3.5 cc. glacial acetic acid and 0.82 grams of cobalt nitrate crystals. One test-tube received 22 cc. of this solution which contained 0.10 grams of cobalt crystals. A second tube was prepared with the same materials in the same proportions except that it contained 1.23 grams of crystals, or to the 22 cc. in the tube, 0.15 grams.

Each gel set in 2 minutes, and was at once overlaid with a weaker silica gel containing 3% Na_2S. The only difference between the two tubes then was the concentration of the cobalt. The daily advance of the outermost black sulfide rings was noted and plotted, giving the two curves adjoined. The higher concentration of cobalt causes a slower advance, confirming several previous results. The sulfide ion may be assumed to enter the two lavender gels at the same rate, but in the stronger (as to cobalt) gel, more sulfide is consumed per unit distance, and there is therefore less left to advance. These two tubes were remarkable in that the rings formed absolutely without fault, none was bent, all were sharp and thin. #1 tube (0.10 grams cobalt salt) gave

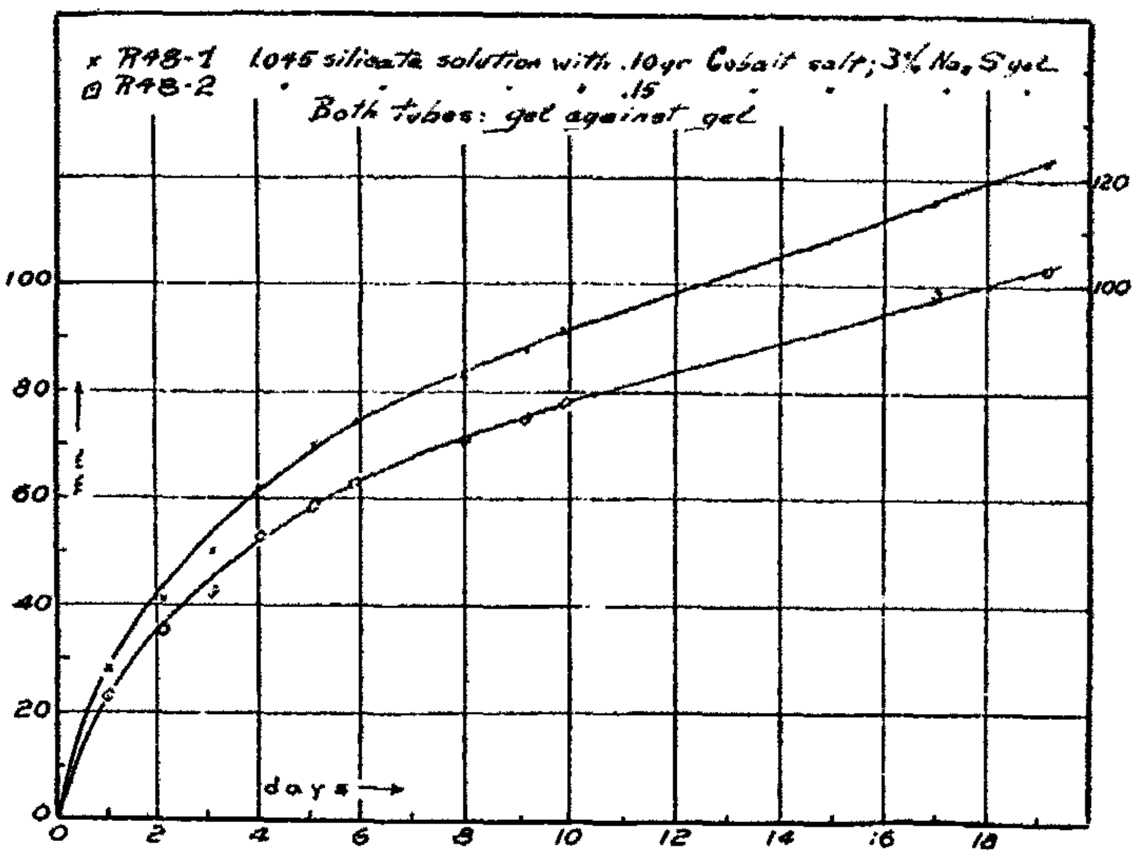

Fig. 2

over a distance of 120 mm a perfect succession of rings, numbering 150. The first ones were 0.1 mm thick, the final ones 1.5 mm in thickness. All the pink color had been drained upward so that near the bottom few rings or deposit of any kind were formed. Number and thickness of rings in #2 were very similar. It will be noted that the curve is not logarithmic, but that the advance is at the same rate from the sixth day to the nineteenth, while it is faster for the first six days. After the sixth day, there is no slackening of the rate of entry for the greater distance which the sulfide ions must cover.

The concentration of sodium sulfide was varied between 1 and 3%; the greater the concentration of the sulfide, the more rapid the advance.

For different strength of gels, made from solutions of sodium silicate between 1.045 and 1.100 in specific gravity, there was very slight differences. It was hoped that it could be demonstrated that with the more concentrated gels, the advance would be slower, and the lines finer; in general, this was the result, but all tubes did not give this result, so that it must remain in doubt.

The limits in the solution of silicates were chosen as given because solutions weaker than 1.045 gave gels that were not stiff enough, while above 1.100 the resulting gels developed fissures which interfered with the pattern growth.

As to alkalinity, a systematic study was not made; it was indicated however that the blue gels gave more numerous rings, with smaller spacings than gels with lower pH values.

Accompanying phenomena: The matter is not simply an advance of sulfide ions, a meeting with cobalt ions, deposition of cobalt sulfide, draining of the zone below by migration of the cobalt upward onto the sulfide, so that a later advance of the sulfide finds no cobalt for a certain distance, giving rise to the clear space. Several additional observations must be taken into account. (1) The ring is preceded by a brown zone which, with the front halfway down the tube, is commonly 1 mm thick. This might well be molecular cobalt sulfide too low in concentration to reach the solubility product, or colloidal cobalt sulfide not yet coagulated by some other agency. (2) There may be observed in the gels made from 1.060 sodium silicate and stronger, very faint rings barely detectable unless the observer is on his guard. These we have called phantom lines; they are described more fully further on. (3) As the gel sets, its transparency is replaced by a wax-like translucency, very apparent in the pink, lavender or blue gels. (4) Bubbles of air caught in the gel show a surprising behavior, they first grow in size, then decrease, and then completely collapse, leaving a faint trace mark. These bubbles are discussed more fully below. (5) On standing six months or a year, the black color gradually fades out if a slow drying accompanied by shrinkage is provided for. The color returns to a pink, but this gel retains the markings of each ring perfectly, showing that simultaneously with ring formation, a deformation of the gel structure took place.

The phantom rings are not colored, but seems to be merely a more intensely wax-like layer with the thickness of a faint pencil line; they are barely visible in faint reflected light against a dark background, but they are unmistakable. They number 5 to as many as 8, extend beyond the advancing front by 8 or 10 mm, and are to be found only after the front is half-way down the tube; at that stage, the pink color is very pale for these same 8 or 10 mm, and even absent for the first 3 to 4 mm. The weaker gels do not show phantom rings, as indicated in the following table:

of	3	tubes,	from	1.045	sod.	silicate	solution,	0	developed	phantom	rings
"	10	"	"	1.060	"	"	"	7	"	"	"
"	3	"	"	1.080	"	"	"	3	"	"	"
"	2	"	"	1.100	"	"	"	2	"	"	"

The dark rings form later, one dark ring always resting on a previous phantom line, and growing upward, toward the place of sulfide entry. The phantom rings may be considered due to the distension of a number of interfibrillar cavities whose walls are pressed outward by local events. The relative distribution of fibrils and water is altered so that the proportion of reflected light is greater, hence its visual detection. In a general way this idea is supported by the fact that weak gels do not possess them, while strong gels do. In the weak gel the proportion of wall substance is too small so that doubling it, let us say, should cause a visible alteration; in the stronger gel the distended walls carry with them nearby fibrils so that the aggregate is distinctly different from the average structure. Each phantom ring becomes the base of a black ring subsequently formed; no black rings form between the phanthom rings.

Bubbles in the gel: The history of some of these might be given to indicate the pertinence of the observation. In one tube (R-42-3), made from 1.060 silicate solution, containing .21 grams cobalt crystals in 22 cc., overlaid with 3% Na_2S gel, the cobalt-silica gel solution was poured in rather late, after it had become lumpy. It was hoped that the lumps would coalesce, giving the usual homogeneous gel, in which therefore the rings would grow with regularity. But on looking through it, the gel showed striae and cords; it was not homogeneous. Moreover, it contained a great many bubbles. It turned out that the rings formed with fairly regular shapes, much more so than expected.

After the front had advanced 26 mm, it was noticed that the next 6 mm were free from bubbles, whereas just before, it had contained many. The next day, the front had advanced to 35.5 mm and the region between 35.5 and 42 mm was now cleared of bubbles. From 42 on, the bubbles were numerous, thus between 42 and 47 mm 100 bubbles were counted. The next day, these were gone, while the front was at 40. The region cleared of bubbles gradually grew from 6.5 to 12, then to 14 mm, ahead of the front. It is clear that in this paler pink zone, some change other than cobalt sulfide formation was taking place in the gel: water from the upper more hydrous gel, entered in addition to the sulfide ions, swelling the gel, closing and obliterating the bubbles. The air these contained disappeared partly through chemical reaction, partly by solution under pressure. A gel made with sodium silicate of 1.100 specific gravity has such a great tendency to contract that the gel parts, and fissures form, after one or two days, within the tightly closed container. Hence if it is the normal tendency for the silica gel to contract, because for example the fibrils take up water of hydration and change it to water of constitution, it must be that the bubbles are squashed because new waters enters the neighbourhood, swelling the gel, overcoming the contracting tendency completely and reversing it, so that it becomes a swelling.

That the gel contracts is shown besides by the change in the surface of the portions poured into the flat tubes. It is at first nearly flat; after two days it becomes a deep dish (7 mm deep), with the tube closed to prevent evaporation.

The events for single bubbles of air caught in the gel were followed on the microscope:

Two bubbles in the same tube:

Measured by square-ruled micrometer, side of small square = .0814 mm.

	Large bubble	Small bubble
10.00 AM	5.5. by 5 squares	$2\frac{1}{3}$ by $2\frac{1}{3}$ squares
10.28	$6\frac{1}{3}$ by 4.8 " ; it had grown	$2\frac{1}{2}$ by $2\frac{1}{2}$ sq.; larger
10.49	7 by 5 " ; still growing	
12 noon	6 2/3 by 5 sq.; it had stopped growing	
2 PM	5.4 by 4.6 sq.; now shrinking	$2\frac{1}{2}$ by $2\frac{1}{3}$
4.45	$4\frac{1}{3}$ by $4\frac{1}{3}$	2 by 2
7 PM		1.7 by 1.7
9 PM	$4\frac{1}{2}$ by 4	.6 by .6
Next morning	gone	gone

The history of numerous other single bubbles was recorded; in all cases it agreed with that of the two noted above. The growth is due to the contraction of the gel; the shrinking is due to entering water.

It seemed likely that an explanation of the growth of the rings might be offered on the basis of sacks which are distended, with walls consisting of fibrils, coated in and out with cobalt sulfide. Before stating it more fully, an additional set of observations will be recorded.

Cobalt sulfide bands on a microscope slide: The cobalt sulfide bands in silica gel can also be grown in a thin, flat layer of the gel mix, so that all deposit dots may be observed. On a large section of thin glass a few drops of the cobalt-silicate mix are placed and immediately covered with a 20 by 20 mm cover glass which is pressed down firmly to force all but a thin layer of liquid out. The excess liquid is removed with filter paper. A dam of plastic clay is placed all around the edges of the large slide. By that time, the gel has set and a water solution of 3% Na_2S is placed around the cover glass, taking care to keep the top of the cover glass free. The deposit forms at once and is followed under the microscope, using direct light from the mirror below the stage. Bands form as fast as the sulfide enters and their genesis, growth and possible further change are followed with the low-power objective (10x) and a 17x eye piece in which a square ruled micrometer has been slipped. The duration of the experiment till the center of the cover glass has been reached from all directions is 60 minutes. Some of the details are best shown by an example:

11.56 AM	start
12 5 PM	7 fine lines (ripples) are plainly seen; growth at the rate of 1 a minute
12 10	14 bands are formed
12 19 30	watched special group of lines; sixth beginning
12 21 30	sixth and seventh finished

The time for one band or ripple to form from first faint appearance to completion is 1 minute. Such a band is shown in figure 3, with a portion of the two adjacent bands. After the previous band is finished a darkish area becomes perceptible a little distance from black edge of the previous line. The dark area deepens, begins to show detail; then the far edge sharpens like a black border being drawn. The next band appears as a faint gray area gradually growing; when the eye returns to the previous band, as quickly as possible, it is finished, not to be altered by standing. It consists of numerous dots, smaller on the sulfide entry slide, and fewer dots about 5 times larger, on the far side, as shown in the micrograph.

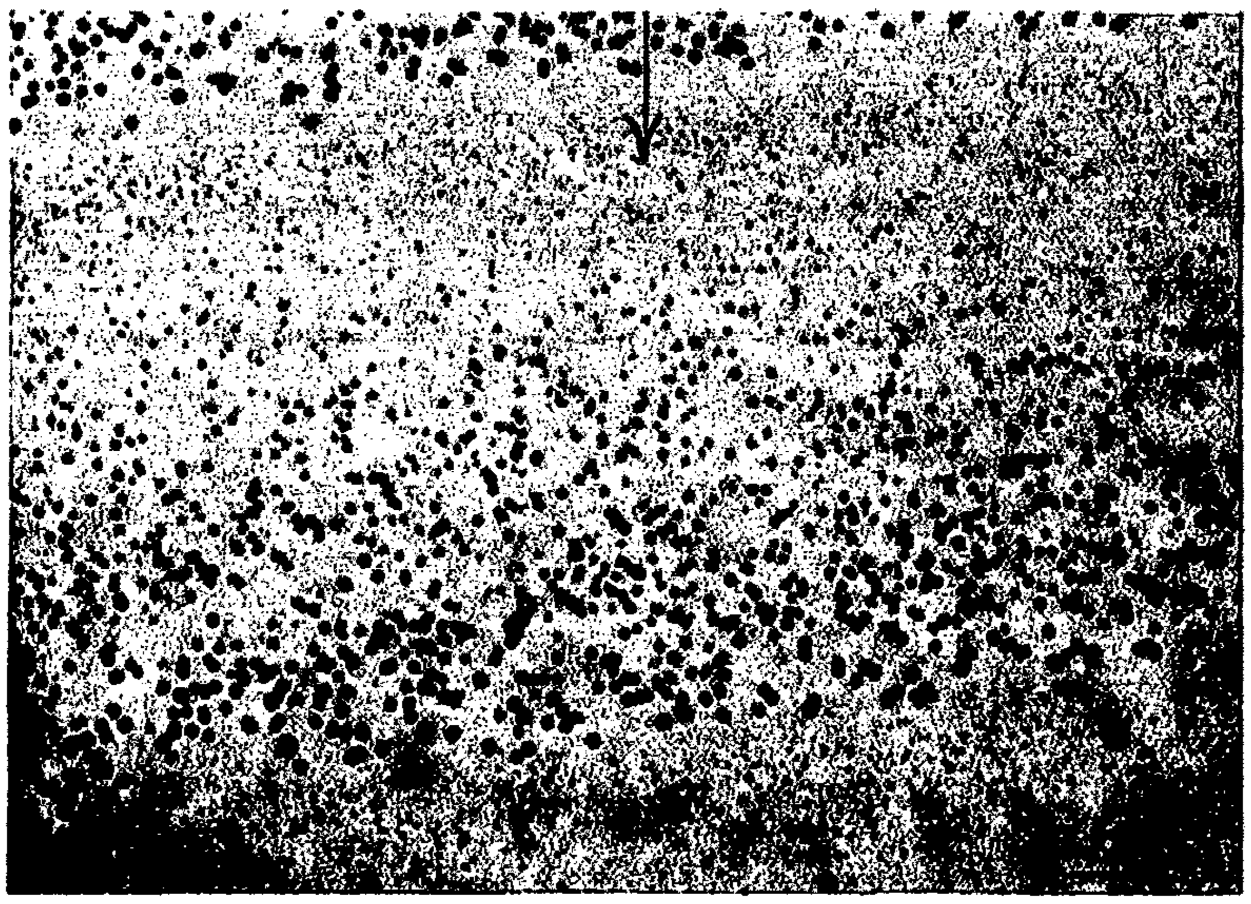

Fig. 3

Cobalt sulfide band in silica gel on a microscope slide; magnification 180 diameters. Direction of entry of sulfide shown by arrow.

The several events are explained as follows. The periodicity in the concentration of cobalt ions is the usual one. As the entering sulfide ions pass beyond the large dots of the previous band, which drain the area behind them of some of its cobalt, there are fewer cobalt ions at first. The dots which form are numerous but small. Cobalt ions drain in at a rapid rate, but arrive in time only to form, or assist in forming the rear dots. A wave of water now follows, as it reaches the nearer fine dots, these have set so hard that their walls are no longer permeable, but the water reaches the rear dots while they are still in the act of forming. Their walls are still plastic and permeable to water. The concentration of all ions in the mass of the gel is so lowered that water is drawn into the spheroidal dots, by virtue of the momentarily higher concentration within the sack. The cobalt exhausted locally, the sulfide ions pass on, while water is still being drawn into the sacks. After the first small dots of the next band are formed, the events are repeated in the same order.

Following the conception of gel structure of Arsem[1] this gel may be considered as consisting of the associated phase, the silica, arranged in an imperfect lattice, with rather large voids ("segregated gel") as compared with molecular dimensions, filled with the free phase, water. The silica is hydrated. At first, cobalt ions are distributed uniformly throughout the free phase. As the sulfide ion enters, it binds the cobalt as molecular cobalt sulfide. The concentration of ions, now lowered, allows rapid diffusion from below (the pink region) and in part, from the same level, into the chamber or sack. The work of wall building now begins. The black sulfide attaches itself to the wall, enlarging its fibrils until the wall is continuous, still highly hydrated, and soft and plastic. A wave of water lowers the concentration outside the chamber. Water is sucked in by osmotic suction, the soft walls distending, assuming a more nearly spherical shape, growing in fibril material as the walls reach the fibrils of other chambers, which failed to develop into sacks. Cobalt ions left in the free phase diffuse to the wall of the sack, there to meet sulfide ions and react to form black sulfide which enmeshes itself into the wall fibrils. Any molecular cobalt sulfide formed also reaches such walls, except perhaps an amount not detected by the microscope. The chambers are unequal; that every chamber in the lattice does not become a dot is due to the advantage which the larger size gives. The larger chambers contain more cobalt ions, and later more black sulfide per unit of wall, than the smaller chambers; later when adsorption from the outside takes place the larger sacks again have the advantage, for a greater surface is offered. The number of dots and the distance between them is a function of the distance the ions concerned migrate under the impulse of low concentration zones, and of the degree of inequalities between the chambers. In this case the distance is from 2 to 10 times the diameter of the larger dots.

Periodicity of water entry: The study of line formation on the slides has the advantage that once deposited, there is no further change. The events take place rapidly. The layer of gel mix is so thin that all the dots formed are visible and in focus. The formation of small dots on the sulfide entry side, and large dots on the far side, is well explained by the assumption that water from the outside solution enters the gel, and that this entry is periodic. That water enters the gel is established by the obliteration of the bubbles in the large flat tubes; it is reasonable to assume therefore that in the case of the band formation on the slide, there is also a water entry.

Other supporting factors: In the tall, flat pyrex tubes used, a content of 0.07 grams of cobalt nitrate crystals in the 22 cc. of cobaltic gel is not sufficient to give rings down to the bottom, a quantity of 0.10 grams is. Hence in such a tube with 0.10 grams of $Co(NO_3)_2.6H_2O$ can develop a maximum of 0.0313 grams CoS. For the 150 rings formed, requiring all the cobalt in the gel, there is available for each ring 0.00027 grams CoS. Each ring consists of numerous dots, as shown in the micrograph, Fig. 4. The average number of dots per ring is 500 at least, so that for each dot 0.0000006 grams must suf-

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[1] William C. Arsem: Gel Structure, J. Phys. Chem., 30, 306 (1926).

fice. The content of silica in the space occupied by a ring is 30 times greater. It is evident that the dots do not consist of cobalt sulfide, but rather of hydrated silica, tinted with a small amount of the black sulfide. This conclusion is strengthened by still another observation briefly stated above, but repeated more fully here. When the tubes are allowed to stand loosely stoppered for a year, the black color gradually fades out, and the pink color returns. The sulfide is oxidised by the air to the sulfate. The pink gel however retains the markings of each ring, not to be altered until the gel crumbles through loss of moisture. In the formation of the rings, an alteration in the gel structure essentially as suggested, has taken place.

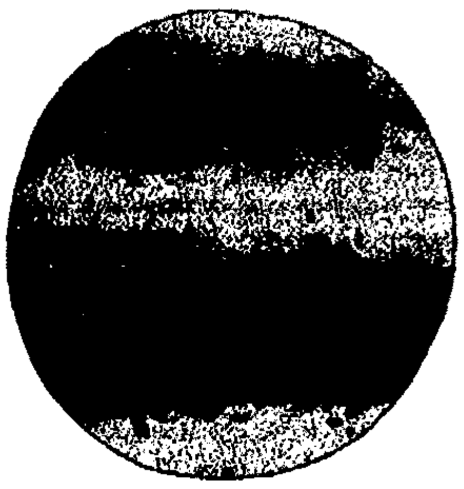
FIG. 4
Cobalt sulfide ring in the pyrex tube; × 40

Therefore the phantom rings, the changes indicated by the bubbles, the rapidity of formation of the dots in graded sizes on the slides, the small weight of sulfide available per ring, the markings in the residual faded-out gels, all fit the theory of sack formation and distension by periodically entering water, with the resulting dots consisting essentially of silica tinted black by a small amount of sulfide.

Analysis: The sodium silicate used was a commercial syrup with a silicate composition expressed by $Na_2O + 3.40\ SiO_2$, therefore fitting the table in the handbooks labelled $Na_2O + 3.36\ SiO_2$. All the solutions were taken from this single batch.

Previous work: A valuable paper has appeared describing numerous periodic stratifications of cobalt sulfide in solid gelatine gel, produced by ammonium sulfide, the entering agent, in gelatine containing cobalt-sodium nitrate.[2] As far as could be found, cobalt sulfide bands in silica gel have not been reported before.

Acknowledgments: Preliminary experiments which established the possibility of forming cobalt sulfide bands in silica gel were performed by Mr. Leo Widgoff, A.M. in 1926, in this laboratory. The method used in forming the bands on the microscope slide was devised in the course of other experiments by Mr. Melvin C. Reinhard, A.M., also in this laboratory.

Summary

Cobalt sulfide bands may be developed in solid silica gel, by overlaying the solid gel containing cobalt nitrate with sodium sulfide solution, or preferably a second silica gel, more hydrous, containing sodium sulfide. An instance is thus furnished of rhythmic bands developing from two gels in contact.

Flat pyrex tubes are described which facilitate observation on the low power microscope.

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[2] F. E. Lloyd and V. Moravek: Plant Physiology, 3, 101-30 (1928).

The behaviour of air bubbles in a gel in which Liesegang band are in process of forming is reported.

Cobalt sulfide bands on a microscope slide have been studied, an explanation is offered for the rapid formation of band formation and for the details in its structure, primarily fitting the bands grown on such slide. The same explanation may be used for the bands on the larger scale of the pyrex tubes. Essentially it presents a mechanism accounting to the visible deformation of the silica gel locally, a periodic entry of water following the periodic play of cobalt ion concentration is assumed. In the large tubes, there is in addition an entry of water before the formation of the black bands; it is this early water which destroys the bubbles.

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THE PREPARATION AND TESTING OF NICKEL CATALYSTS FOR HYDROGENATION*

BY HOMER ADKINS AND LLOYD W. COVERT

In the course of an investigation of the hydrogenation of organic compounds over nickel and other base metal catalysts it seemed desirable to compare the relative merits of different catalysts. It was then necessary to consider what characteristics of the catalyst should be used as a basis for comparison. A catalyst for hydrogenation may have merit in a number of different ways, for example, catalyst X may be better than catalyst Y in that (1) it is possible to hydrogenate at a lower temperature or (2), pressure than with catalyst Y; or (3), less of X than of Y may be required to give a certain effect; or (4), catalyst X may cause a more rapid rate of absorption of hydrogen under a given set of conditions than does catalyst Y; or (5), a given amount of X may cause complete hydrogenation of a given weight of material in less time than does the same amount of Y; or (6) less of some undesired reaction may occur with X than with Y.

The more important variables that determine the numerical values which may be assigned to these characteristics are even more numerous than the characteristics which they modify. The rate of hydrogenation over a nickel catalyst may vary with (1) the acceptor of hydrogen, (2) the impurities in the latter, (3) the temperature during hydrogenation, (4) the pressure of hydrogen, (5) the amount and (6) kind of solvent, (7) the amount of catalyst, (8) the ratio of catalyst to hydrogen acceptor, (9) the time and (10) the temperature involved in all stages of the hydrogenation experiment, (11) the thoroughness of the mixing of the hydrogen acceptor, catalyst, and hydrogen. The last of these factors is made up of at least two components, one of these being the rate or thoroughness of mechanical agitation of the reactants, and the other the ease of dispersion of the catalyst in the reaction medium.

It will appear that not only the *numerical* but also the *relative* values of the characteristics of the various catalysts are dependent upon the acceptor of hydrogen, temperature, pressure, and the other variables referred to above, which are actually used in the testing of the catalysts. It is one of the primary purposes of this paper to exhibit experimental evidence that general and sound conclusions as to the relative activities of nickel catalysts, for example, may not be reached as the result of following what may be termed a conventional method of scientific work. By this is meant the method in which each factor is in turn varied while the other factors are held constant, followed by the tacit assumption that if there are for example three variables X, Y, and Z, the effect of varying X and Y *simultaneously* may be concluded from a knowledge of the effect of varying X and Y separately.

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*A Communication from the Laboratory of Organic Chemistry of the University of Wisconsin.

For example, it will be shown that the relative merits of two catalysts are not the same for two different acceptors of hydrogen, nor for different characteristics of the catalyst, and therefore, it may be suspected that even the relative merits are not independent of the other variables, such as temperature, ratio of catalyst to acceptor, etc. which have been listed above. It has been shown in a previous paper[1] that the effect of variation in the pressure of hydrogen was rather specific for the compound undergoing hydrogenation, and it may be suspected that it differs with other variables such as the catalyst.

One may well be appalled at the amount of work involved in acquiring sufficient data to justify drawing positive conclusions on a reaction which involves six or more measurable characteristics and perhaps twice as many variables. This is especially true if the effect of simultaneous variability may not be predicted from a knowledge of the effect of the variation of one factor at a time. It is not the intention of the authors to attempt any such systematic survey but rather in the future to give especial consideration to those factors which determine the ratio of competitive or simultaneous reactions over nickel catalysts.

Preparation and Method of Treating Catalysts

In the experimental work described in this paper numerical values have been assigned to four of the characteristics of eight nickel catalysts for the hydrogenation of acetone, resorcinol, toluene, and benzyl alcohol. The temperature and the amount and ratio of catalyst to acceptor used for the hydrogenations were chosen because they gave a reasonably rapid rate of hydrogenation. The pressure of hydrogen (100 atmospheres) used is quite effective and is one that may be used without expensive equipment.[1] The rate of shaking of the reactants (41 cycles per minute) was one that has appeared to give a good suspension of the catalysts. The units for heating the bomb were of such a capacity that the contents of the bomb could be heated to 125° in 30 minutes and to 175° in 55 minutes.

Resorcinol, benzyl alcohol and acetone were hydrogenated at 125° while with toluene the temperature regulator was set for 175° but due to the rapidity of the hydrogenation the temperature of the toluene in some cases rose to about 250°. Two g. of catalyst containing approximately 16 percent of nickel was used with 1 mole of acetone, 0.62 moles of resorcinol and 0.23 moles of benzyl alcohol. Three g. of catalyst was used with 0.935 moles of toluene. Thirty five ml. of anhydrous ether was used as a solvent in the hydrogenation of resorcinol.

Seven different methods for the preparation of nickel catalysts were used in this investigation. Three of these involved differences in the source of nickel. In two of these the nickel was from nickel nitrate of varying purity and in one was from nickel chloride. Three different reagents, i.e., sodium carbonate, sodium bicarbonate, and potassium hydroxide were used for the

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[1] Adkins, Cramer, and Connor: J. Am. Chem. Soc., 53, 1402 (1931.).

precipitation of nickel on the kieselguhr support. Two different methods for mixing the reagents were used. One of these (Method A) involved the addition of the soluble nickel compound (on kieselguhr) to the precipitant, in the other (Method B) the reverse order was followed, i.e., the addition of the precipitant to the soluble nickel compound (on kieselguhr).

In the preparation of all catalysts the solution of the nickel salt was thoroughly incorporated into the kieselguhr by grinding the partly moistened powder in a mortar until it was of a cream-like consistency. This procedure which was originally suggested and used by Mr. Karl Folkers in this Laboratory, makes it possible to easily reproduce very active catalysts. The use of kieselguhr as a support for a nickel catalyst has been criticised because difficulty was experienced in reproducing the activity of catalysts. A similar difficulty was encountered in this Laboratory until Folkers' procedure was used. All catalysts were washed as previously described[1] except that they were suspended twice instead of once in 300 ml. of water. The concentration of the various precipitating solutions used with 100 g. of acid washed kieselguhr and 100 g. nickelous nitrate hexahydrate (or its equivalent) in 150 ml. of water were as follows:—120 g of sodium carbonate decahydrate in 100 ml. of water, 60 g. sodium bicarbonate in 260 ml. of water, 24 g. of potassium hydroxide in 100 ml. of water. Sodium bicarbonate as a precipitant was first used in this Laboratory by Mr. Ralph Connor who did so on the supposition that a basic nickel carbonate of more uniform composition could be obtained under certain conditions with this reagent than through the use of sodium carbonate.[2] The methods and reagents used in preparing each catalyst are indicated in Table I.

Reagents:—A "C.P." grade of nickel nitrate from the Baker and Adamson Company was used unless otherwise noted. Nickel nitrate prepared from the reaction of "C.P." grade nitric acid and pure nickel pellets from the International Nickel Company was used in the preparation of catalyst 11 Cv. The toluene b.p. 110.5-111° was C.P. grade free of sulfur. The acetone had a b.p. of 56.5 while the resorcinol was a U.S.P. grade m.p. 110°. The best grade of benzyl alcohol from the Eastman Kodak Company was further purified since rather erratic results were obtained in attempting to reduce different lots of this product. The alcohol was refluxed 12 hours with a 35 percent solution of potassium hydroxide, and then distilled through a Widmer column at 203.5-205.0°. The product was then heated for 5 hours at 100°, under 70 atmospheres of hydrogen with reduced nickel. This removed any halogen containing impurities. The nickel was prepared by the reduction of 5 g. of nickel oxide (prepared by the decomposition at 250° of nickel carbonate) for four hours at 350°. The amount of nickel so obtained was used with 150 ml of alcohol.

The products from the hydrogenation of benzyl alcohol were fractionated, toluene being collected 108-112° (740 mm) and cyclohexyl carbinol 175-185 (740 mm) by far the greater part coming over 179-180°. Cyclohexanol and

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[1] Adkins and Cramer: J. Am. Chem. Soc., 52, 4351 (1930).

[2] Cf. Gmelin-Kraut: 5, 108.

cyclohexanediol 1-3 from the hydrogenation of resorcinol were collected at 60-65° (10 mm) and 124-134 (10 mm) respectively, although in most cases at least 90 percent distilled over a 1° range. The products from the hydrogenation of toluene and acetone were methyl cyclohexane and propanol-2, respectively, and each distilled over a 1° range.

The kieselguhr used as a support for the nickel catalyst was in most cases from the Meyer Drug Company, St. Louis. However, there appeared to be no difference in activity between the catalysts on this support and those on "Filter-Cell" supplied by the Johns-Manville Company, New York.

The apparatus and method of experimentation were essentially the same as those previously described by Adkins and Cramer.

Reproducibility of Results:—The extent of variation in the data obtained in different experiments with duplicate samples of catalysts and with samples of catalysts prepared in the same way but at different times is indicated by plus and minus figures given in Tables I and II. All significant experiments were duplicated at least twice while the total number of hydrogenation experiments on which this paper is based is 145.

Comparison of Catalysts

The relative merits of catalysts may be compared in a number of different ways as noted above. Four of the characteristics of nickel catalysts will be considered in this comparison. The experimental basis for the first comparison is the time required for the adsorption of the middle 60 percent of the total amount of hydrogen absorbed. For this purpose the time for the absorption of the first and last 20 percent of hydrogen is disregarded. This comparison is thus between the activities of catalysts during the chief period of activity.

There is tabulated in Table I the time for the 60 percent of hydrogenation used as the basis for the first comparison. Limiting the comparison for the moment to the four catalysts made by the two methods through the use of sodium carbonate and sodium bicarbonate, it may be seen from the data in the table that they are all four quite active towards toluene, the differences between them being small. For acetone the bicarbonate A method catalyst (10 Cv) was distinctly inferior to the other three catalysts. The carbonate A method catalyst (8 Cv) was distinctly inferior as regards the rate of hydrogenation of benzyl alcohol and of resorcinol. The B method of preparing catalysts is better than the A method in every case for the carbonate catalysts (15 Cv) and is better than or as good as the A method in case of the bicarbonate catalysts. However, with no compound is the difference between the two methods as marked with the bicarbonate as with the carbonate catalysts.

Extending the comparisons to include the eight catalysts it may be said that potassium hydroxide may be used as a precipitant for nickel, the resulting catalyst (13 Cv) being somewhat inferior to the corresponding carbonate catalyst except for benzyl alcohol. A similar statement may be made in

TABLE I

Time in Minutes for Hydrogenations over Various Catalysts[1]

Catalyst	Toluene	Acetone	Benzyl Alcohol	Resorcinol
8 Cv ($Ni(NO_3)_2 + Na_2CO_3$) A	7.5 ±1.5 (11)	12.5 ±3 (27)	15 ±2	430 ±75 (1250)
15 Cv ($Ni(NO_3)_2 + Na_2CO_3$) B	6.5 ±2.0 (26)	11.5 ±2 (18)	8 ±1	275 (490)
10 Cv ($Ni(NO_3)_2 + NaHCO_3$) A	8.7 ±0.7 (21)	18.5 ±2 (56)	8.5 ±0.5	260 ±25 (540)
16 Cv ($Ni(NO_3)_2 + NaHCO_3$) B	6 ±1.0 (14)	13.7 ±2 (34)	8 ±2	217 ±8 (490)
13 Cv ($Ni(NO_3)_2 + KOH$) A	9.7 ±0.8 (24)	16 ±1 (37)	7 ±1	350 ±13 (900)
12 Cv ($NiCl_2 + NaHCO_3$) B	7.5 ±1.0 (20)	13.8 ±1 (30)	4.5 ±0	220 ±50 (425)
11 Cv ($Ni(NO_3)_2 + Na_2CO_3$) A	8 ±2.0 (17)	16 ±4 (31)	12 ±3	265 ±65 (715)
13 HC ($Ni(NO_3)_2 + Na_2CO_3$) A	36 ±18 (60)	40 ±10 (66)	19 ±2	562 ±12 (1410)

[1] The figures in parenthesis are the average times for complete hydrogenation, while the others are for the "middle 60 percent" of hydrogenation.

regard to nickel chloride as a source of nickel except that toward benzyl alcohol and resorcinol it was one of the most active catalysts used in this investigation.

The catalyst (11 Cv) prepared from nickel nitrate made in this Laboratory from C.P. nitric acid and C.P. nickel pellets was not much more active than that made from the Baker and Adamson nickel nitrate. The catalyst prepared by Cramer (13 HC), which was one of the most active of those used in his experimentation, was very distinctly inferior to the catalyst prepared by the modified method described in this paper.

The experimental basis for a second comparison of catalysts is the temperature at which the pressure of hydrogen reached a maximum and will be referred to as the "inflection temperature". This temperature is the one at which the rise in the pressure of hydrogen due to the rise in temperature of the bomb was compensated for by the absorption of hydrogen. Along with this may be considered the percentage of the compound which was hydrogenated before the temperature set for hydrogenation was reached. These two experimental observations in almost all cases parallel each other and both give an insight into the behavior of the catalyst in its youth. For toluene the inflection temperature was approximately 105° for 15 Cv, 10 Cv, and 16 Cv while for 8 Cv it was 130°. For acetone the inflection temperature was 80° for 15 Cv and above 100° for the other catalysts. For benzyl alcohol catalyst 12 Cv gave an inflection temperature of 90° while for the others the inflection was well above 100°. Only 15 Cv, 10 Cv, and 12 Cv gave inflection temperature, with resorcinol. In the case of 15 Cv with acetone 53 percent was hydrogenated below 125° while with other catalysts the amount so hydrogenated was usually less than 30 percent. With benzyl alcohol 83 percent of the compound was hydrogenated below 125° with catalyst 12 Cv while with most of the other good catalysts only 50 to 60 percent so reduced.

The experimental basis for the third comparison is the time required for the absorption of all the hydrogen. These values are given in parenthesis in Table I. Toluene is hydrogenated so rapidly and the reaction is so exothermic that the hydrogenations did not occur under identical temperatures. However, it should be noted that catalyst 8 Cv which was quite inactive at low temperatures gave a complete hydrogenation in the shortest time (11 minutes) as compared with the bicarbonate catalyst 10 Cv which required 21 minutes and 13 HC which required 60 minutes. With acetone the bicarbonate catalysts (10 and 16 Cv) required a distinctly longer time (34 to 56 minutes) than did the carbonate catalysts (8 and 15 Cv) (18 to 27 minutes). With resorcinol catalyst 8 Cv required 1250 minutes while 15, 10, and 16 Cv need approximately 500 minutes.

The fourth basis of comparison is only applicable to benzyl alcohol and resorcinol for it involves the ratio of products formed, i.e., toluene and cyclohexyl carbinol from the former and cyclohexanol and cyclohexanediol 1-3 from the latter compound. There is recorded in Table II the percentage yield of these products over six catalysts. Only the two products mentioned above are formed from benzyl alcohol, so that the percentages of toluene and cyclohexyl carbinol add up to 100 percent. However, in the case of resorcinol there is formed over some catalysts (notably 8, 13, and 15 Cv) considerable quantities of condensation products so that the percentages of cyclohexanol and cyclohexanediol add to 78, 87, 84, 94, and 100 percent for the various catalysts.

The carbonate catalysts gave 150 to 200 percent as much cyclohexyl carbinol as did the bicarbonate catalysts. The potassium hydroxide catalyst gave the lowest yield of the alcohol. The bicarbonate catalysts gave the better yields of cyclohexanediol 1-3 from resorcinol, the B method of catalyst preparation being very much superior. The A method with the carbonate gave the same yield of cyclohexanol as did the B method with the bicarbonate. If A and B are interchanged in the above sentence it is still true. It is rather striking that the catalyst (16 Cv) which was least active in eliminating a hydroxyl from resorcinol was the most active (of the carbonate and bicarbonate catalysts) for the removal of the hydroxyl group in benzyl alcohol.

TABLE II

Proportion of Products from Hydrogenation of Benzyl Alcohol and Resorcinol over Various Nickel Catalysts

Catalyst	Benzyl Alcohol		Resorcinol	
	Toluene	Cyclohexyl Carbinol	Cyclohexanol	Cyclohexanediol 1-3
8 Cv (Na_2CO_3) A	73 ±3	27 ±3	11 ±2	67 ±3
15 Cv (Na_2CO_3) B	70 ±1	30 ±1	22 ±1	65 ±2
13 Cv (KOH) A	90 ±2	10 ±2	16 ±1	68 ±1
10 Cv ($NaHCO_3$) A	82 ±2	18 ±2	20 ±1	74 ±1
16 Cv ($NaHCO_3$) B	85 ±2	15 ±2	11 ±1	89 ±1
13 HC (Na_2CO_3) A	66 ±2	34 ±2	8 ±1	75 ±3

It thus appears that the factors which determine the activity of a catalyst for the absorption by a hydrogen acceptor are quite different from those which determine the relative rates of what must be simultaneous and competitive reactions. For example, catalysts 15 Cv and 16 Cv gave very similar rates of hydrogenations for resorcinol while with 15 Cv the ratio of cyclohexanol to cyclohexanediol was 1 to 3 while with 16 Cv it was 1 to 8 or more. Catalyst 8 Cv and 13 HC were similar to 16 Cv in ratio (1 to 6 and 1 to 9 as compared with 1 to 8) yet the two latter catalysts were very inactive as compared to 16 Cv.

Catalysts not made by Precipitation:—The above comparison of catalysts was confined to the type in which a nickel compound was precipitated on kieselguhr, because it has seemed to us that this type of nickel catalyst was quite superior to those obtained by decomposing nickel nitrate or nickel carbonate either alone or on a support. Brown, Etzel, and Henke[1] among others decomposed nickel nitrate on kieselguhr and reduced the resulting oxide for several hours, and Bradt[2] reduced nickel carbonate. The following experimental evidence may be cited in justification of our preference for the "precipitated on kieselguhr" type of catalyst. Bradt obtained a 100 percent hydrogenation of p-nitrophenol within 120 minutes or less using a ratio of 1 part of nickel carbonate to 5 parts of p-nitrophenol at 125°, and 34 atmospheres pressure. A catalyst prepared in this Laboratory according to his directions brought about the complete hydrogenation of p-nitrophenol in 75 minutes. One part of our catalyst 16 Cv to 17 parts of p-nitrophenol induced 100 percent hydrogenation within 25 minutes, 90 percent of the hydrogenation occurring within 10 minutes. If the ratio of nickel to nitrophenol had been as great in this case as in the experiments of Bradt the nitro group would no doubt have been completely hydrogenated within a very few minutes. Catalyst 16 Cv brought about the complete hydrogenation of toluene and acetone in 14 and 34 minutes respectively while under identical conditions the catalyst prepared by Bradt's method did not give complete hydrogenation after 5 hours. Nickel catalysts prepared by reducing nickel oxide, deposited by

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[1] Brown, Etzel, and Henke: J. Phys. Chem., **32**, 633 (1928).

[2] Bradt: J. Phys. Chem., **34**, 2711 (1930).

decomposing nickel nitrate on kieselguhr as by Brown, Etzel and Henke, were very much inferior even to those prepared by Bradt's method. It should be pointed out that almost any nickel catalyst will bring about the hydrogenation of easily reducible substances such as acetone and sulfur-free nitro compounds but that the hydrogenation of toluene and resorcinol impose a more severe test upon a catalyst.

Summary

Various bases for the comparison of nickel catalysts have been suggested and experimental evidence has been given that the relative merits of catalysts may vary with the basis of comparison, as well as with the particular compound and experimental conditions under which the comparisons are made. In particular it has been shown that for nickel catalysts there is no necessary relationship between the rate of hydrogenation and the relative rates of competitive hydrogenations. Improvements in the methods for the preparation of nickel catalysts have been described and the relative values of different precipitants for depositing nickel compounds on a carrier have been measured for the rate of hydrogenation of toluene, acetone, benzyl alcohol and resorcinol. The ratio of cyclohexyl carbinol to toluene and of cyclohexanediol 1-3 to cyclohexanol produced from benzyl alcohol and resorcinol respectively has been determined for the catalysts described.

Madison, Wisconsin.

THE DETERMINATION OF SORPTION ISOTHERMALS ON CHARCOAL BY THE RETENTIVITY TECHNIQUE—EXPERIMENTS WITH CARBON TETRACHLORIDE AND WATER

BY A. J. ALLMAND AND L. J. BURRAGE

A new technique for the determination of the sorption isothermals of vapours on charcoals—the retentivity method—has recently been described.[1] It was stated that the isothermals obtained by this method showed discontinuities, being made up, in fact, of a series of loops cutting one another at definite pressures. The present paper contains details of the results obtained, and deals, in particular, with the evidence for the discontinuous structure mentioned.

The majority of the charcoals have already been described, viz. A,[2] B,[2] C,[2] G,[3] H,[3] K,[1] L.[1] The new charcoals M2, M3, and M4 are all steam activated, and made from the same raw material (palm nut kernel). They form a series of decreasing bulk density (determined on particles of 10-12 mesh, respectively 0.584, 0.478 and 0.477), to which corresponds an increasingly severe treatment during activation. M1 (bulk density 0.62) is an unactivated charcoal prepared from the same raw material by simple carbonisation, without subsequent steam treatment.

Table I contains a synopsis of certain relevant facts concerning the experimental work and the results. Column 1 gives the designation of the charcoal, column 2 the number of separate charcoal containers making up the total composite charcoal column, column 3 the initial pressure (in mm.) of vapour at which the charcoal was saturated, column 4 the number of points on the experimental retentivity curve, *i.e.* the number of times during the experiment that the air-stream was stopped and the charcoal containers weighed, column 5 the number of tangents drawn to the derived retentivity curve obtained by logarithmic extrapolation, and column 6 the number of breaks found in the derived isothermal.

Figs. 1-4 contain in detail examples of the actual isothermals obtained.

In Table II are collected the pressures in mm. at which the *three lowest breaks* have been found with different carbon tetrachloride isothermals. To these data are added the corresponding figures for the three most satisfactory experiments carried out with water vapour, *viz.* those with Charcoals G, K (after thorough previous extraction with water in order to remove hygroscopic mineral matter[4]) and M4. It will be noticed that Charcoal G gave an additional break on its water vapour isothermal at a lower pressure, 0.07 mm.,

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[1] Burrage: J. Phys. Chem., **34**, 2202 (1930).

[2] J. Phys. Chem., **32**, 452 (1928).

[3] J. Soc. Chem. Ind., **47**, 372 T (1928).

[4] See Allmand and King: Proc. Roy. Soc., **130A**, 210 (1930).

TABLE I

Nature of isothermals	1	2	3	4	5	6	Remarks
Water Vapour 25°C.	B	3	16.0	12	61	26	Very uncertain below 3 mm.
	A	4	16.0	8	41	12	Results of doubtful accuracy.
	do.	3	18.6	12	62	17	Not taken below 5 mm.
	C	4	12.8	30	65	16	Experimental work not accurate enough to justify the drawing of more tangents.
	M1	2	12.8	14	72	9	
	M2	2	12.8	10	62	12	
	M3	2	15.5	12	74	25	Accurate down to 5 mm.
	M4	2	18.6	16	167	38	The two most accurate experiments with water vapour.
	G	3	18.6	25	155	41	
	K	3	12.8	18	68	13	Early work—not very accurate.
	K (water extracted)	3	15.5	17	102	35	An accurate experiment.
	L	6	12.8	10	119	19	Early experiments. Not sufficiently accurate for more tangents.
	H	3	15.5	15	106	19	
Carbon tetrachloride vapour. 100°C.	B	3	33.0	7	183	29	Accurate below 15 mm. The two series gave practically the same extrapolation.
	do.	3	do.	11			
	B (acid extracted)	3	do.	12	115	24	Accurate below 11 mm.
	B (acid and alkali extd.)	3	do.	11	84	24	Accurate below 10 mm.
	M2	2	do.	14	131	43	A very good experiment.
	M3	2	do.	14	154	40	Exceptionally accurate below 13 mm.
	M4	2	do.	12	156	40	Good experiment, but points insufficient to define isothermal above 18 mm.
	G	2	do.	16	188	48	The best and the most accurate experiment. The two series gave identical linear extrapolations, with which two single-column experiments were also in agreement.
	do.	3	do.	16			
Carbon tetrachloride vapour 25°C.	B	4	33.0	37	237	41	All good experiments, the most accurate probably being that with Charcoal G.
	M3	3	do.	16	138	37	
	G	3	do.	15	140	43	

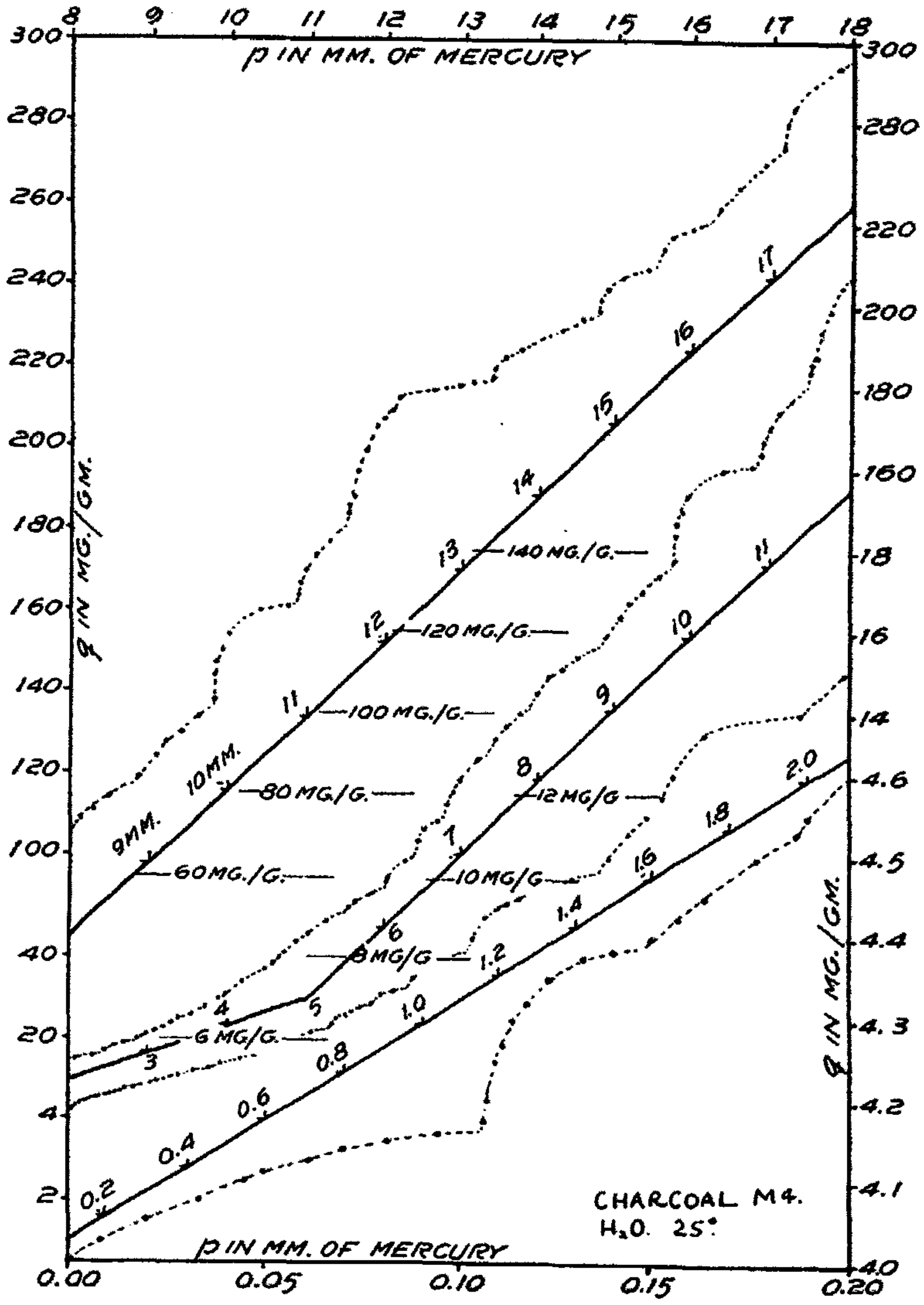

FIG. 1

than in the other cases. Several of the water isothermals showed breaks at about this pressure and some, in addition, at about 0.02 mm. We are somewhat doubtful as to their real existence.

A remarkable feature of the values of the pressures in Table II is the manner in which they appear to approximate to one or other of three fairly closely defined figures (see average values), which in turn correspond to the first three breaks. This coincidence between the pressure values is rendered still more striking by the facts (i) that the two sorbates worked with, carbon

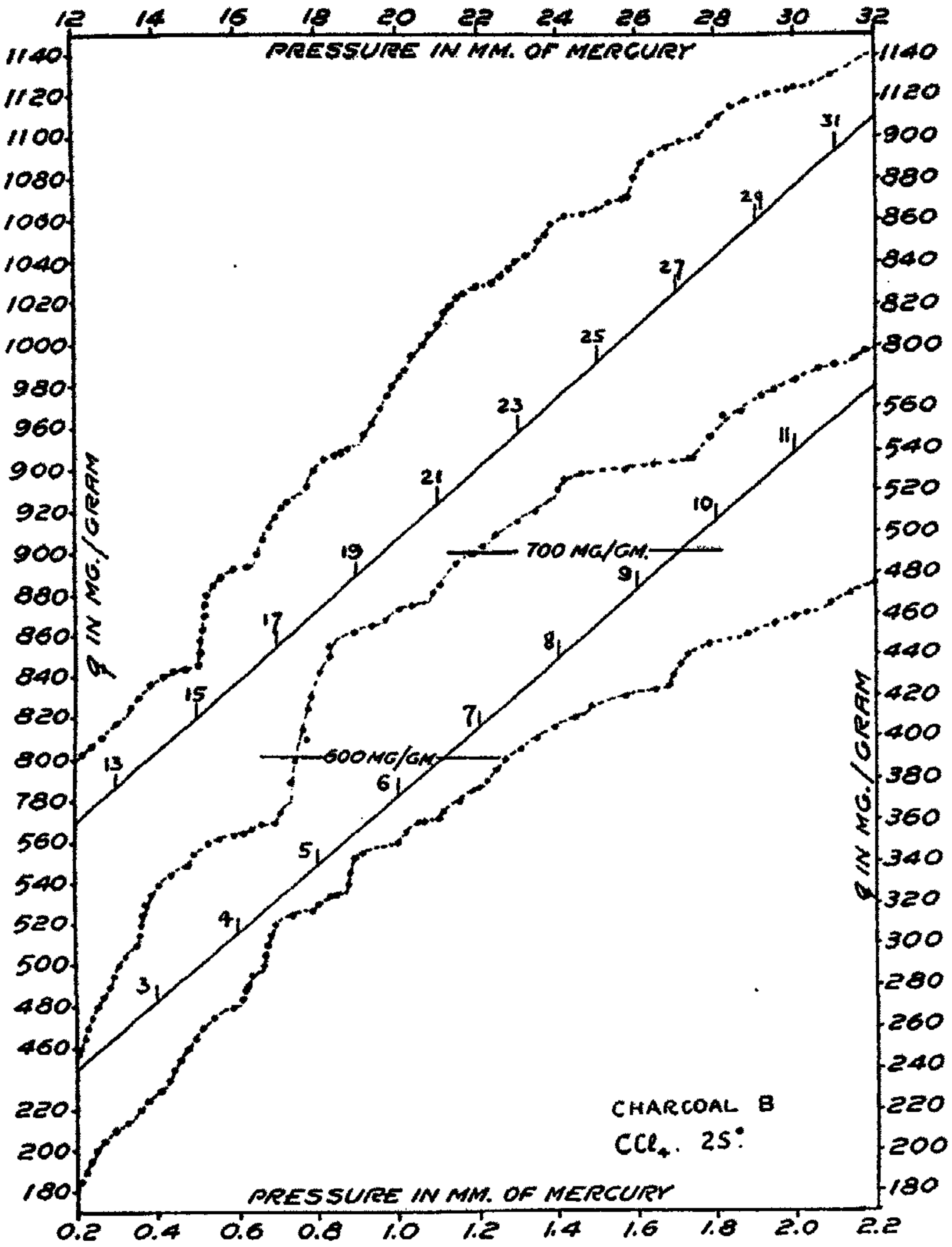

Fig. 2

tetrachloride and water, are of very different nature and furnish isothermals of quite different types and (ii) that measurements with the former substance at two different temperatures are included.

The concordance between the different pressure values very largely disappears at higher pressures. Fig. 5 contains a graphic summary of the pressures, between the limits of 5-15 mm., at which breaks have been observed during our determinations of isothermals; experiments with water vapour in which the initial charging pressure was below the latter figure are not included. The breaks are seen to vary in number from case to case, and to

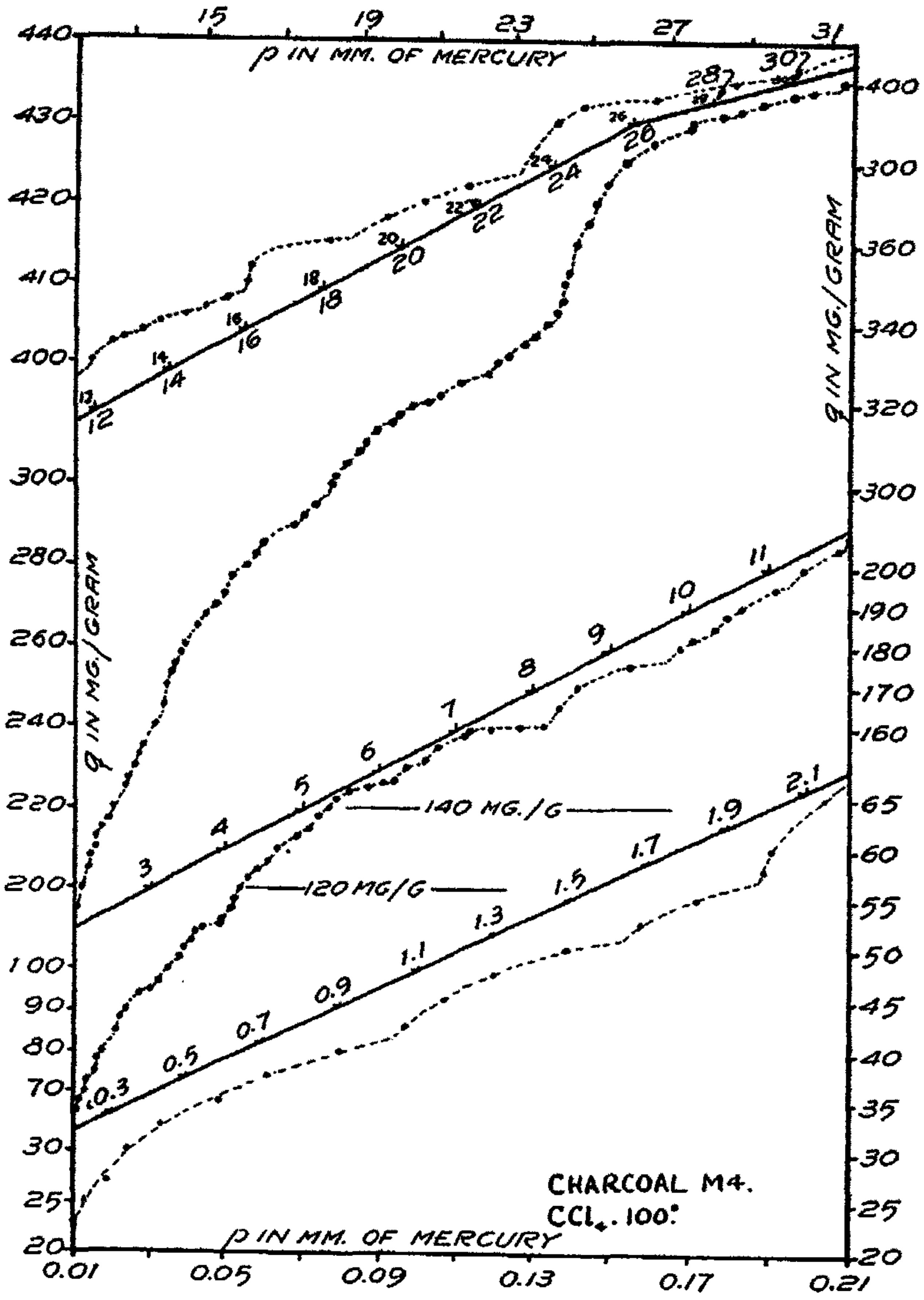

Fig. 3

be irregularly distributed. The only slight evidence of any general tendency to grouping is the fact that, above 8.9 mm., there are a number of pressure regions extending over ranges of 0.2 to 0.4 mm. within which no breaks were observed. This general lack of coincidence is emphasized by Table III (see also Fig. 4), which contains the actual data for Charcoal C over this pressure range. As far as could be judged, the experimental work appeared satisfactory in each of the three isothermal determinations concerned, and hence any

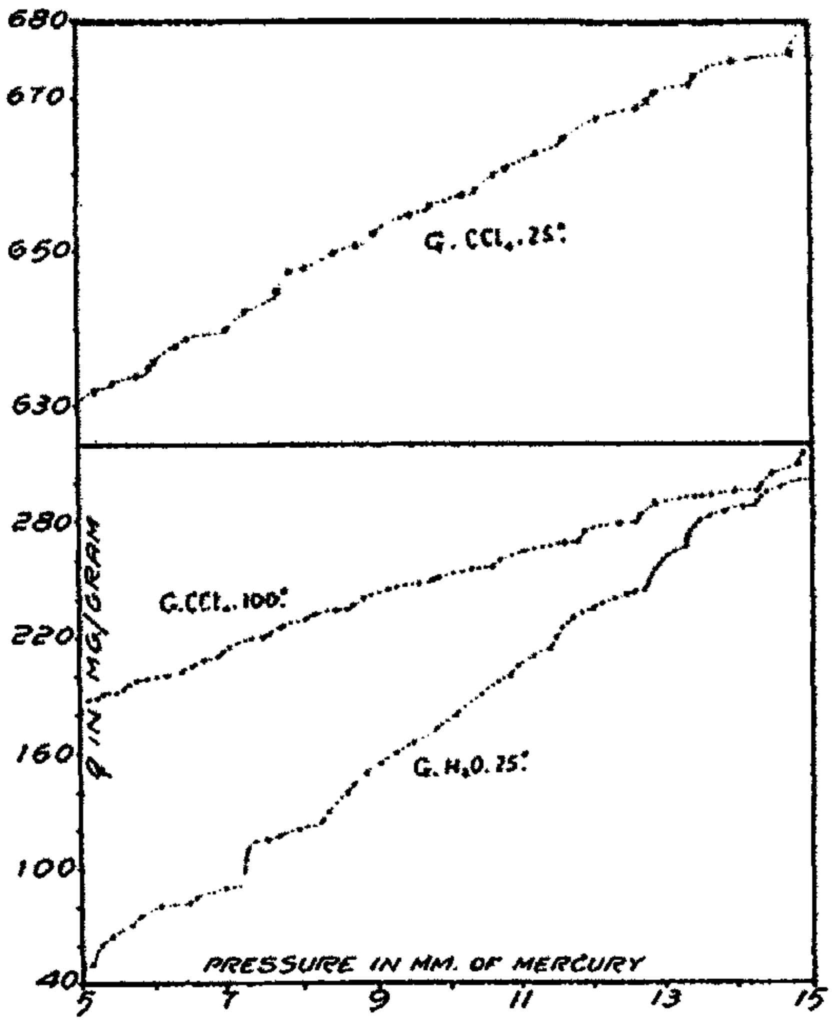

FIG. 4

TABLE II

	H_2O. 25°C.			CCl_4. 25°C.		
	G	(water K extd.)	M4	B	M3	G
(0.07)	0.10	0.10	0.105	0.10	0.094	0.10
	0.132	0.13	0.148	0.145	0.138	0.139
	0.175	0.18	0.187	0.192	0.190	0.17

CCl_4. 100°C.						
B	(acid B extd.)	(acid and B alkali extd.)	M2	M3	M4	G
0.11	0.10	0.095	0.11	0.11	0.095	0.11
0.156	0.154	0.15	0.15	0.144	0.150	0.138
0.185	0.174	0.18	0.183	0.180	0.188	0.187

Average figure and average deviation from mean	
0.102	(0.005)
0.144	(0.007)
0.182	(0.005)

TABLE III

Charcoal G. Pressures in mm.

H_2O	5.14	5.75	6.47	7.25	7.58	8.24	—	9.8
CCl_4 at 25°	5.35	5.93	—	7.0	7.7	8.22	8.9	9.75
CCl_4 at 100°	5.22	5.55	6.35	6.95	7.5	8.05	8.6	9.75
Mean value	5.24	5.74	6.41	7.07	7.59	8.17	8.75	9.77

H_2O at 25°	10.8	11.4	12.78	13.3	14.27	15.05
CCl_4 at 25°	10.4	11.6	12.8	13.4	—	14.8
CCl_4 at 100°	10.6	11.8	12.65	—	14.33	14.84
Mean value	10.6	11.6	12.74	13.35	14.30	14.9

tendency towards coincidence between the different pressure values should here be most marked. The table is arranged on the basis of the reality of such a tendency, and it will be seen to give some support to this assumption. Although the actual pressure figures in the vertical columns for the different isothermals differ from one another by amounts exceeding the experimental error, it is noticeable that none of the values in any one vertical column overlap those in adjacent columns. If these data be taken as supporting the existence of a tendency for the pressure values to group themselves around definite figures, then the obvious conclusion is that certain breaks have been "missed" during the determination of the isothermals.

Discussion

We shall discuss our results on the two working assumptions (i) that the "breaks" have a real existence under our experimental conditions and (ii) that they tend to occur at a definite series of pressures, depending to an unknown but secondary degree on the nature of the system and on the temperature. The first assumption we regard as well founded, the second as tentative and very open to question. An attempt has been made elsewhere[1] to suggest reasons for the existence of the alleged breaks; the present discussion will be confined to the experimental data.

As will be seen from the specimen isothermals reproduced in Figs. 1-4, the breaks differ to a great extent in degree of definition. About some, there can be no question of doubt, assuming the correctness of the experimental points. In other cases, it would appear necessary to justify the drawing of the isothermal as has been done.

A further point concerns the "missing" breaks (see Table III). Of these, there appear to be a large number. Fig. 5 covers the pressure region of 5-15 mm., and our unreproduced data, both for lower pressures with water and carbon tetrachloride, and for higher pressures with carbon tetrachloride, exhibit many instances of breaks shown in certain pressure regions by certain isothermals, but not by all. The point arises as to why breaks should be "missed" in some cases, if found in others.

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[1] In a paper submitted to the Royal Society for publication.

Lastly is the question of the degree of correspondence between the pressure values in cases where there is positive evidence that such correspondence may actually occur, e.g., in Tables II and III. If there is any concordance at all between the different pressure values, it would seem likely that any theory would demand a more regular spacing of the breaks than is found to exist, and in any case would require a degree of coincidence between the pressures falling within the average experimental error. In other words, the found degree of coincidence would be expected to be better if real, the presumption being that it may not be real. This last conclusion is the one provisionally suggested in the paper just referred to.

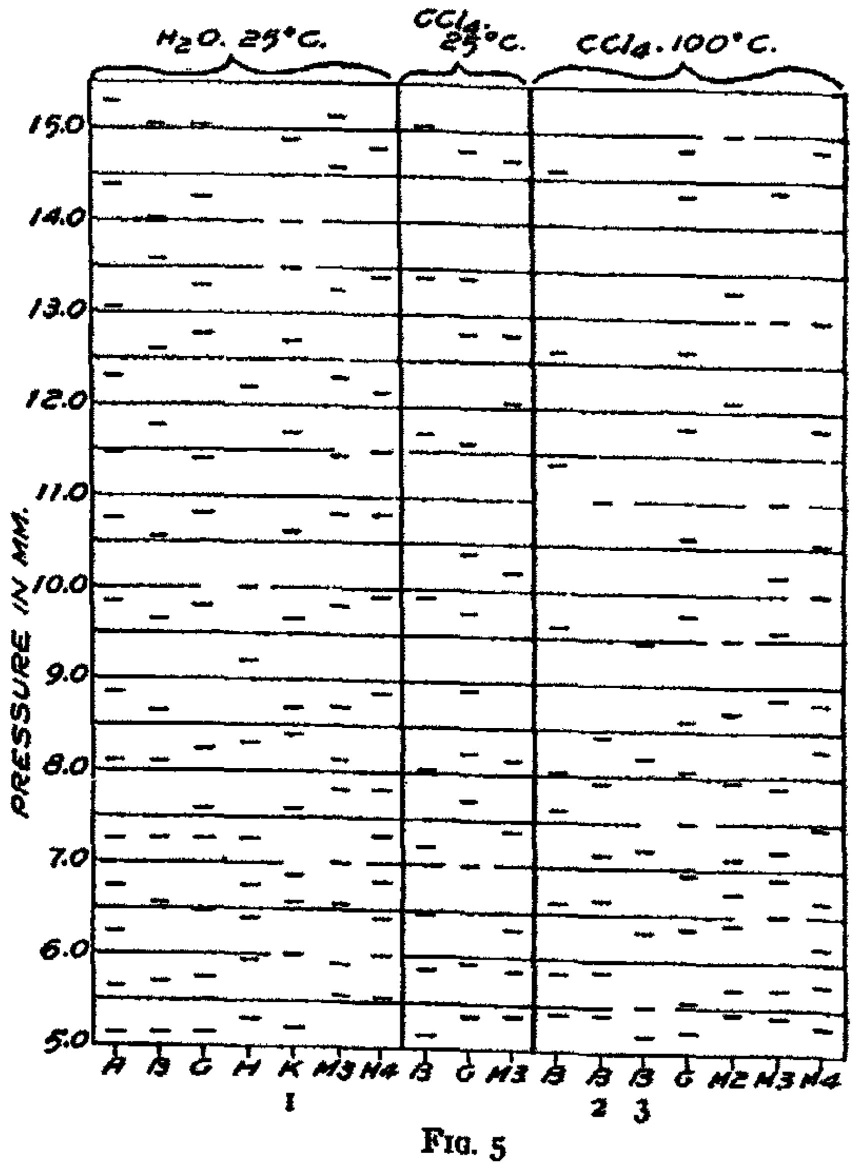

FIG. 5
(1) water extracted; (2) acid extracted; (3) acid and alkali extracted

These matters are best dealt with by a detailed analysis of the possible errors involved in our experimental method. In order to obtain the final derived isothermal, the following procedure is necessary:

(*a*) determination of the separate points in the retentivity experiment;

(*b*) their logarithmic extrapolation to figures corresponding to a column of volume 1 cc.;

(*c*) the drawing of the retentivity curve from the extrapolated data;

(*d*) the drawing and measuring of the tangents to the retentivity curve, and the construction of the derived isothermal.

These four stages will be considered in order.

(*a*) *Determination of Points in Retentivity Experiment.* The error in the weighing of the separate charcoal tubes amounted to about 0.2 mg. Expressed in mg./gram of charcoal, this is quite negligible at high q values, and insignificant even at quite low q values. The extreme limits in length of the charcoal columns were 0.5 and 12 cm. (normal figures 3-8 cm.), whilst the weight of charcoal in the separate columns normally varied between 1 and 4 grams, depending on the bulk density of the material. The times of passage of air could be determined to 0.2 second (less accurately in the earlier runs). Working at a rate of 400 cc./minute, the error for the smallest volume passed (100 cc., at the beginning of the retentivity experiment) and hence the maximum time error involved, was thus about 1.4 per cent, becoming rapidly less as the retentivity experiment proceeded. The error in the actual rate of passage of air did not exceed 2 cc./minute, or 0.5 per cent. The maximum error involved in a retentivity curve therefore amounted to about 2 per cent of the volume passed when this was small (0.1 litre), dropping to 0.5 per cent as the length of the experiment increased.

(*b*) *Extrapolation of the Experimental Points.* Each point on the final retentivity curve involves the separate weighing of the different containers which make up the composite charcoal column, and it is the results of these weighings which are extrapolated in the manner previously described. The greater that number of the charcoal containers making up the composite column, the more reliable should be the extrapolation. As will be seen from Table I, this number varied from two to six in different cases. It has been found in practice that, when once the technique of carrying out the experiments has been mastered, two columns are sufficient for a satisfactory extrapolation, the essential criterion of which is the possibility of drawing a single continuous curve through all the final points (see below).

(*c*) *The Drawing of the Retentivity Curve.* The accuracy with which this can be done depends on the number of extrapolated points obtained under (*b*), which, in its turn, depends on the number of times the retentivity experiment was interrupted for the weighing of the charcoal tubes. As will be seen from Table I, this number varied in practice between eight and thirty in the water vapour experiments, and between seven and thirty-seven in those with carbon tetrachloride. The number required to obtain a satisfactory result will of course depend on the pressure range to be covered. In the latter case, where this extended from 33 down to about 0.01 mm., we find that 16-20 points, if accurately determined, suffice for drawing a satisfactory retentivity curve, and that increasing this number makes no perceptible improvement. They must of course be suitably spaced. The fact that, in Table I, certain experiments are noted as being accurate only over certain pressure ranges, is due to faulty spacing and local inadequacy of points.

The curve itself was drawn by means of a flexible gun-metal strip, adjusted to pass through all the plotted points. If this was not possible without unnatural distortion of the strip, then an experimental error of some kind was indicated, and that portion of the curve was neglected when subsequently drawing tangents. It can not indeed be too strongly emphasized that any important error in the experimental work, leading to an uncertain extrapolation, is readily shown up when the retentivity curve is drawn.

A systematic investigation of the possible uncertainty in the final pressures (or tangent readings), due to errors in the extrapolated retentivity data of such a nature as still to permit of a continuous curve being drawn through the points, has led to the conclusion that this may conceivably amount to a *maximum* of ten per cent at low and three per cent at high, pressures. That is, a point plotted as being at 0.1 mm. may lie between 0.09-0.11 mm., and one at 30 mm. between 29-31 mm. *Neighbouring points will be subject to similar errors*, for the retentivity curve is smooth and continuous. But there is also no doubt whatever, except in the early experiments and possibly at the highest pressures, that this degree of uncertainty is usually far from being approached. On one occasion (Charcoal G; water vapour; 25 experimental points), two retentivity curves were drawn, utilising respectively the odd and even numbered extrapolated points. It was found that these curves could be superposed within experimental error. Reference may also be made to the remarks in Table I concerning the carbon tetrachloride experiments with charcoals B and G at 100.

(*d*) *The Drawing of the Tangents to the Retentivity Curve and the Construction of the Isothermal.* The actual drawing and measuring of the individual tangents involves no appreciable error if done with ordinary care. This has been amply demonstrated by constructing duplicate retentivity curves, and curves in which the extrapolated retentivity data have been plotted on more than one scale.[1] The values of the tangents to the curves at definite values of q gave pressures which were identical, or showed quite negligible differences.

It is important for absolute results to define with accuracy the initial slope of the retentivity curve, as this is a measure of the initial equilibrium pressure over the charcoal column, and subsequent pressures are calculated on the assumption of proportionality between pressure and slope. We think that our results show that errors in this initial reading are small. In any case, affecting, as they do, the pressure scale of the isothermal uniformly over its whole range, they can not account for irregular differences between the various isothermals.

One very important point however is the actual number of tangents drawn and measured. If these are not sufficiently closely spaced, as was the case in the early stages of this work, much detail in the structure of the isothermals can be missed or incorrectly plotted. In order to define the "breaks" on that part of the isothermal at intermediate pressures where its general slope is rapidly changing, some three or four points between each abrupt pressure change are necessary, and an increase beyond this number does not reveal anything fresh in the detailed isothermal structure.

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[1] Burrage: J. Phys. Chem., 34, 2214 (1930).

If this were sufficient over the whole pressure range, then 150 tangents or thereabouts would be adequate for a carbon tetrachloride isothermal between the limits of 33 and 0.1 mm. But at lower pressures, where the general slope of the isothermal (in respect of the q axis) is small, and where the breaks, on the pressure scale, are very near one another, relatively more points are necessary for exact definition, up to as many as 10-12 on each loop of the isothermal. The same is true, to a lesser extent, of breaks which occur at high pressures, where the general slope of the isothermal is steep. In this case, the pressure range covered is so considerable that three points may be insufficient to define the path of a single isothermal loop.

The numbers of tangents actually drawn per retentivity curve are shown in Table I. There is little doubt that, although in a few cases the number was excessive, in the sense that no better definition of the isothermal was achieved than would have resulted from a smaller number, in other cases it was inadequate, over at all events a portion of the pressure range.

Conclusions

The above discussion has shown that there are four factors which may have affected the form of our final isothermals to a greater or lesser degree, *viz.*

(i) errors in the measurement of the rate of passage of air during the retentivity determinations, particularly in the earlier experiments with water vapour.

(ii) errors in the extrapolation of the retentivity points.

(iii) local insufficiency of experimental points in the retentivity experiments.

(iv) local insufficiency of tangents to the extrapolated retentivity curves.

Of these factors, we think (i) to have been of significance only in the experiments stated and (ii) seldom to have been of importance. On the other hand, it is certain that (iii) and (iv) have, in certain instances, led both to breaks remaining unnoticed, and also to the pressures of detected breaks being inexactly defined.

With regard to the question of whether or not we are justified in assuming breaks to be present in certain cases where the evidence afforded for them by the position of the points on the isothermal is obviously slender, we can only say that we have been influenced by the general nature of the particular experiments and of the subsequent extrapolation which led to the final retentivity curve. In cases where these experiments and extrapolation apparently went smoothly, as judged by the absence of any obvious hitch during their course and by the well defined nature of other parts of the isothermal, we have not hesitated to assume slight breaks on the evidence afforded by the trend of three or four adjacent points on the curve. When this was not the case, we have drawn a single loop of curve through all the points concerned.

This procedure is clearly, to a certain extent, arbitrary, but, we think, justifiable. We should indeed be prepared to find that more exact experimental methods would show a number of our supposed breaks to be nonexistent. But we are inclined to think that the general result of adopting such a more refined technique would be the reverse, *viz.*, the discovery that the structure of the isothermals of vapours on charcoal is even more detailed and complex than our present work suggests it to be.

The experimental work described in this paper was carried out during the two sessions 1927-1928.

University of London,
King's College,
January 13, 1931.

THE ELECTRIC MOMENTS OF THE FIXED VEGETABLE OILS*

BY W. N. STOOPS

Introduction

Practically all the studies of dielectric polarization and electric moment of organic molecules have been carried out on pure compounds. There are, however, a large number of naturally occurring oils and resins whose chemical structure is sufficiently well established that they may be of use in furthering our knowledge of the somewhat complex relationships between molecular constitution and such properties as electric moment and dielectric constant. In addition these materials are used in the preparation of electrical insulation and hence have a practical importance.

The electric moments of these compounds were obtained from measurements of the dielectric constants and densities of dilute solutions of the oils in benzene, a non-polar solvent, the polarization at infinite dilution being calculated from them. The Debye equation may be written

$$P = \frac{\epsilon - 1}{\epsilon + 2} \cdot \frac{M}{d} = P_E + P_A + P_O$$

where P is total polarization, ϵ the dielectric constant, M the molecular weight, d the density, P_E the electronic contribution to the polarization, P_A the atomic and P_O the contribution due to the orientation of polar molecules in the applied field. P_E is the molecular refraction preferably extrapolated to that for light of infinite wave length. P_A is usually quite small[1] in comparison with P_E and is generally neglected. P_O may be obtained as the difference between P and P_E. The electric moment of the molecule is easily obtained from P_O when the other polarization values are known, since $P_O = 4\pi N\mu^2/9kT$ where N is the Avogadro number, 6.06×10^{23}; k the gas constant per molecule, 1.372×10^{-16} ergs/degree; T the absolute temperature and μ the electric moment. The applicability of the Debye equation to dilute solutions has been amply demonstrated by Smyth[2] and Williams.[3]

Experimental

The dielectric constants were measured by means of a capacity bridge. The resistance arms were non-inductively wound and carefully adjusted to the same resistance, 1049.7 ohms. The capacity arms were General Radio variable air condensers, one their precision type 222 and the other a similarly constructed condenser without the vernier adjustment. Two General Radio

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*Sci. Paper No. 487.

[1] C. P. Smyth: J. Am. Chem. Soc., 51, 2051 (1929).

[2] Smyth, Morgan and Boyce: J. Am. Chem. Soc., 50, 1536 (1928).

[3] J. W. Williams: Physik. Z., 29, 174 (1928).

variable resistances used to compensate for absorption of energy by the dielectric whose capacity was being measured were connected in series with the condensers. Each unit was individually shielded in accordance with the principles laid down by Campbell[1] and developed by the Bell Telephone Laboratories.[2]

The oscillator, built on a slightly modified Hartley circuit, was mounted in a shielded box. It was calibrated at 300,000, 600,000 and 1,000,000 cycles by means of a wave meter and the frequency checked from time to time. The detector was mounted in a separate shielded box and consisted of a crystal detector and a high sensitivity galvanometer. It was similar to the one described by Smyth, Morgan and Boyce.

The measuring condenser or cell for the measurement of dielectric constants of liquids consisted of three concentric brass cylinders, heavily gold plated and separated by small mica tabs. The condenser was mounted in a glass tube with a separate platinum wire for each cylinder coming out through capillary tubing. Three combinations giving three different capacities were possible, the only restriction being that the outer cylinder was always kept grounded to serve as a shield. This cell was calibrated with carefully purified benzene, using the value of 2.273 at 25°C for the dielectric constant[3] of benzene. The densities were measured with a pycnometer somewhat similar to that used by Isnardi.[4]

A large Dewar tube filled with toluene served as a constant temperature bath. The low temperatures were obtained by the use of liquid air[5] and those above room temperature by means of a small heating coil. The temperature of the bath was held constant to ±.05°C for ten minutes for the dielectric constant measurements and fifteen to twenty minutes for the density determinations. The probable error in the densities measured at low temperatures was 0.07% and in those above 0° not more than 0.03%. The dielectric constants were measured by direct substitution of the gold plated cell on the precision condenser. The probable error was 0.2% although the error within a given series of measurements was less. When several ohms resistance was necessary in the balancing arm to compensate for conductance or absorption in the cell the dielectric constants are probably not accurate to more than 1%. These resistances were necessary only for the pure oils at low temperatures, the dilute solutions of the oils in benzene showing no absorption. The effect of the resistance was to cause the apparent values of the dielectric constants to be too large.

Materials

Castor Oil. Baker's best grade of cold pressed castor oil was used without purification.

$d_{4^\circ}^{20^\circ} = .9613 \quad n^{27.5^\circ} = 1.4770$; (where n = refractive index)

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[1] G. A. Campbell: Elec. World, 1904, 647.

[2] W. J. Shackelton: Bell Sys. Tech. J., 6, 142 (1927).

[3] Hartshorn and Oliver: Proc. Roy. Soc., 123, 664 (1929).

[4] Isnardi: Z. Physik, 9, 153 (1922).

[5] See Walters and Loomis: J. Am. Chem. Soc., 47, 2302 (1925).

Linseed Oil. Commercial raw oil was used which had been heated for an hour at 150°C. The heating precipitates a certain amount of impurities in the oil but does not appreciably polymerize it. $d_{4°}^{20°} = .9366$; $n^{15.0°} = 1.4860$.

Tung Oil. The tung oil was the commercial product of the quality used in the electrical industry.

$$d_{4°}^{40°} = .9394;\ n^{23.0°} = 1.519$$

Tristearin. Eastman's C. P. tristearin was used without further purification.

Benzene. Fisher Scientific Company C. P. benzene was washed three times with sulfuric acid, then with dilute sodium carbonate solution and with water, dried over calcium chloride and fractionally crystallized. It was then dried over sodium and fractionally distilled.

Experimental Results

The densities, which showed only slight departure from a linear variation with temperature, were measured at 20° intervals and the dielectric constants at about 10° intervals. The densities d and dielectric constants ε in Table I were obtained at 10° intervals by graphical interpolation, and the polarizations P were calculated from them by means of the Debye equation given above. In Table II are given the mole fractions, C_2, of the polar constituents, the densities and dielectric constants of the solutions and the polarizations P_{12} and P_2 calculated from them by means of the equations

TABLE I

Interpolated values of dielectric constants and densities and the polarizations calculated from them

	Tung Oil			Linseed Oil			Castor Oil		
t°c	d	ε	P	d	ε	P	d	ε	P
−70				1.00	2.48	281	1.0242	2.55	310
−60				1.00	2.55	290	1.0172	2.65	326
−50		2.51		.9955	2.80	320	1.0102	2.79	345
−40	.9821	2.54	304	.9863	3.32	376	1.0033	3.00	372
−30	.9750	3.19	381	.9771	3.46	392	.9964	3.52	428
−20	.9680	3.33	398	.9679	3.50	399	.9893	4.12	480
−10	.9609	3.42	409	.9590	3.50	403	.9823	4.58	517
0	.9537	3.43	413	.9512	3.49	406	.9753	4.71	529
+10	.9466	3.41	414	.9436	3.45	405	.9683	4.71	533
20	.9394	3.37	413	.9366	3.40	403	.9613	4.66	533
30	.9323	3.33	412	.9298	3.35	402	.9543	4.54	530
40	.9253	3.29	411	.9229	3.31	400	.9472	4.44	526
50	.9185	3.26	409	.9159	3.26	398	.9402	4.33	522
60	.9116	3.19	407	.9090	3.22	397	.9332	4.23	519
70	.9048	3.14	405	.9021	3.17	396	.9262	4.13	515
80	.8978	3.10	403	.8952	3.13	395	.9191	4.03	511
90	.8908	3.06	402	.8883	3.08	393	.9119	3.94	507
100	.8838	3.02	400	.8814	3.04	390	.9046	3.84	502

$$P_{12} = \frac{\epsilon-1}{\epsilon+2} \times \frac{C_1M_1 + C_2M_2}{d} \text{ and } P_2 = \frac{P_{12}-P_1}{C_2} + P_1$$

Here P_{12} is the polarization of the mixture, and C_1 and C_2, M_1 and M_2, and P_1 and P_2 are, respectively, the mole fractions, molecular weights and polarizations of the two components.

TABLE II

Tung Oil. 25° C. $P_1 = 26.57$

C_2	d	ϵ	P_{12}	P_2
.003088	.8754	2.306	27.90	457
.004583	.8762	2.323	28.53	454
.006370	.8773	2.341	29.28	452
.009460	.8790	2.368	30.49	441
.012386	.8805	2.396	31.73	443
.024186	.8859	2.437	35.62	401

Linseed Oil 27°C. $P_1 = 26.59$

C_2	d	ϵ	P_{12}	P_2
.004872	.8721	2.319	28.65	450
.007782	.8756	2.351	29.81	441
.009824	.8767	2.367	30.58	432
.012442	.8778	2.391	31.69	437
.016000	.8795	2.420	33.02	429

Castor Oil 30°C. $P_1 = 26.68$

C_2	d	ϵ	P_{12}	P_2
.002695	.8702	2.312	28.09	551
.004168	.8713	2.340	28.92	564
.005760	.8733	2.366	29.75	560
.008250	.8749	2.410	31.10	563
.010293	.8764	2.442	32.17	560

Tristearin 35°C. $P_1 = 26.70$

C_2	d	ϵ	P_{12}	P_2
.003803	.8634	2.281	28.12	416.1
.004160	.8632	2.287	28.32	416.1
.004410	.8636	2.291	28.44	421.3
.004595	.8634	2.292	28.51	420.6

Discussion

The density varies practically linearly with temperature, and this same variation is assumed to hold at temperatures below the melting point, they having been obtained by extrapolation. The oils showed a marked tendency to super-cool, but had usually completely solidified at −40° or above. In Fig. 1 the dielectric constants of the three oils are plotted against temperature. The pronounced falling off in dielectric constant at low temperatures is due to the fact that the polar molecules are no longer able to orient in the field, and hence the dipole contribution to the dielectric constant disappears. For linseed oil and tung oil solidification occurs at about −25° and −10° respectively, but the freezing point is not sharp and hence the dielectric constant drops gradually from the value for the liquid to that for the solid. The points on the steepest part of the curves depend on whether they are measured on oil that is freezing or melting, indicating that the ten to fifteen minutes at constant temperature before each reading is not long enough for attaining a true equilibrium. The castor oil supercooled, and did not solidify even at the lowest temperature with the result that all parts of the curve were reproducible. Although the oil did not solidify, the increase in viscosity is sufficient to interfere with and finally to practically prevent the orientation of the dipoles. The gradual decrease in freedom of orientation of the dipoles caused by the increase of viscosity results in a smoother and less abrupt falling off in the dielectric constant than in the other two oils where solidification occurs. The polarizations of the oils exhibit almost the same variation with temperature as the dielectric constants, going through a maximum at about 10°C, then decreasing slowly at higher temperatures and rapidly at lower ones.

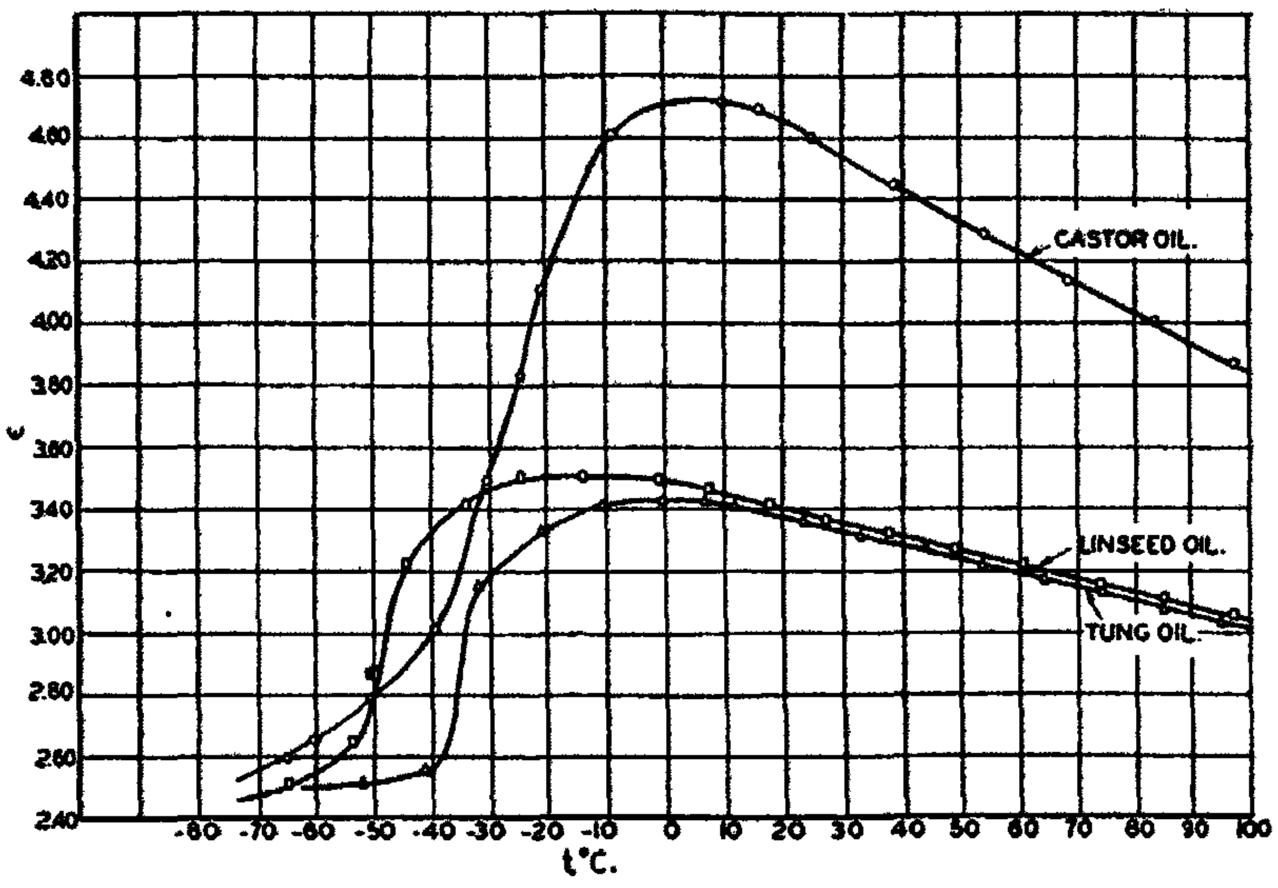

Fig. 1

TABLE III

Values of Polarization Terms

Substance	Temp.	P_∞	P_T	P_E	P_S	P_O	$\mu \times 10^{18}$
Tung Oil	25°	461	413	286	306	165	2.8
Linseed Oil	27°	457	402	260	280	187	3.0
Castor Oil	30°	564	530	276	300	276	3.7
Tristearin	35°	419		272		147	2.7

The polarization values and electric moments for the three oils and for tristearin are given in Table III. The polarization at infinite dilution, P_∞, was obtained by plotting P_2 against the concentration C_2 and extrapolating to zero concentration. The temperature given applies only to P_∞ and P_2, the polarization of the pure oils, the other terms being independent of temperature. The polarization of the solid, P_S, was calculated from the dielectric constant obtained by freezing the liquid in the cell, and from the density got by extrapolating from the liquid to the solid state, assuming the same variation with temperature. The contraction on solidification probably prevents the oil from entirely filling the space between the cylinders in the measuring condenser, and causes the measured dielectric constant to be too low. Nevertheless, it may be noted that the P_S values are all about twenty units higher than the corresponding molecular refractions, an increase which is about what we would expect for the atomic refraction P_A.[1] The molecular refractions P_E, were determined from refractive index data obtained from the literature for tristearin, and by a Pulfrich refractometer for the oils. The orientation polarization, P_O, was taken as the difference between P_∞ and the average of P_E and P_S, except in the case of tristearin for which P_S was not measured.

The magnitude of all these quantities depends of course upon the molecular weight of the material. Tristearin is a pure compound and has a definite molecular weight, but the oils are mixtures and an approximate value must be assigned. The composition of tung oil is fairly well known,[2] it being about 80-85% trielaeosterine of molecular weight 878.9 and 15-20% triolein of molecular weight 885.1. The value of 880 was used for the molecular weight of tung oil in these calculations, and cannot be much in error. The molecular weight of the linseed oil used was taken as 850. A theoretical figure assuming it to be entirely triglyceride of its various acid constituents would be 875-885, but it contains some mono- and diglycerides. An analysis of linseed oil by Eibner and Schmidinger[3] shows it to consist of triglycerides of linolic acid, 60%, linolenic 23%, saturated acids 8%, and oleic acid 5%. Linolenic acid differs from linolic (whose triglyceride is shown in Fig. 2) in that it contains three double bonds in each carbon chain instead of two. Experimentally determined molecular weights vary from 750 to 850 for raw oil. The oil used had been heated slightly (an hour at 150°-200° to remove a precipitate which forms in the early stages of heating) but not sufficiently to appreciably polymerize it. Castor oil is about 80% triglyceride or ricinoleic acid[4] with small proportions of the triglycerides of similar acids. The molecular weight was taken as 933, that of the principal constituent of the oil.

A fairly long chain acetate molecule, such as amyl, has a moment of 1.9.[5] A glyceride may be considered as three such acetate molecules connected at one end, although of course not all to the same carbon atom. If the three

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[1] C. P. Smyth: J. Am. Chem. Soc., 51, 2051 (1929).

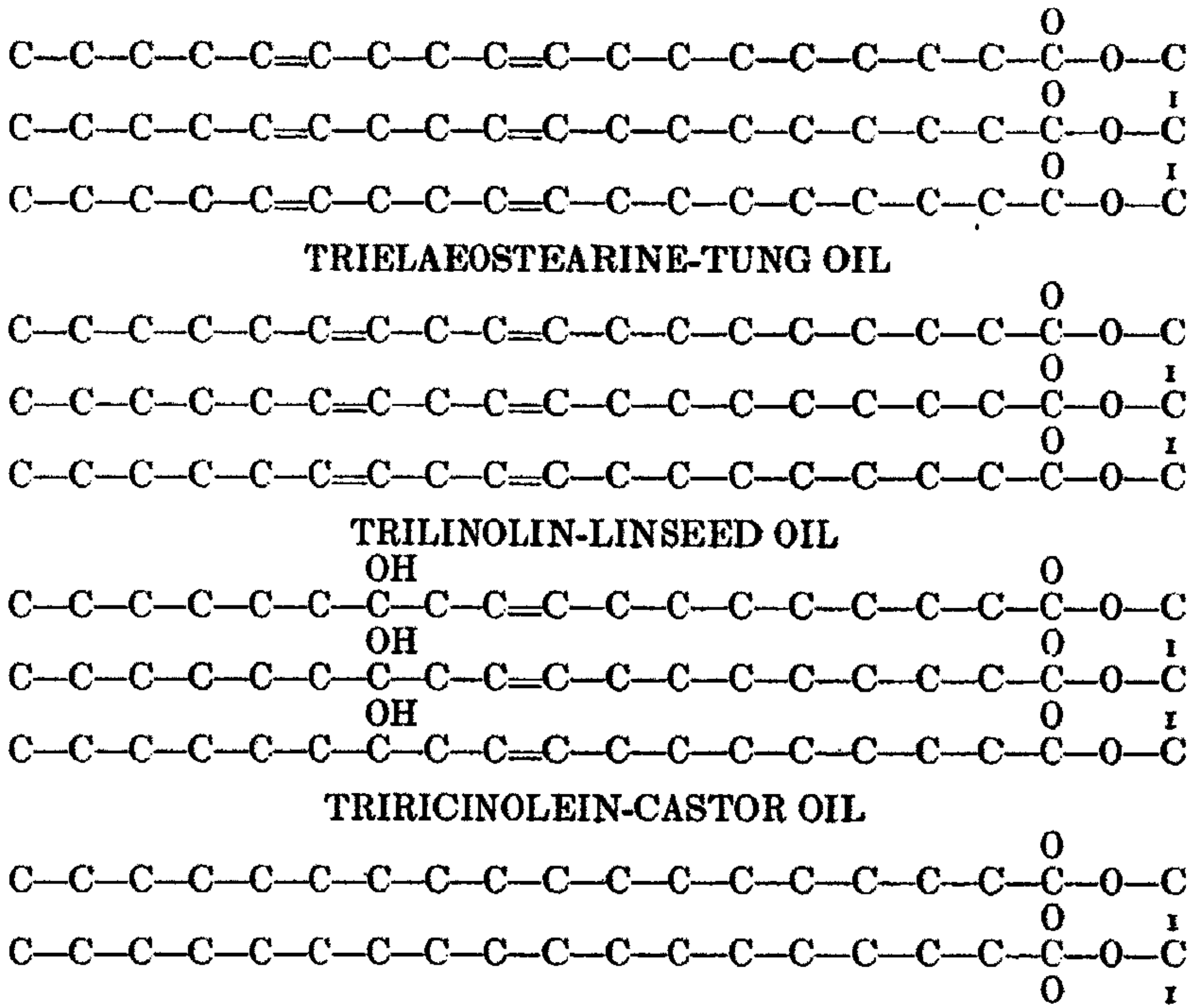
[2] Wissensch. Veröffent. dem Siemens-Konzern. Vol. IV, Pt. 2 p. 284 (1925).

[3] Eibner and Schmidinger: Chem. Umschau, 30, 293 (1923).

[4] Eibner and Munzing: Chem. Umschau, 32, 153 (1925).

[5] Müller and Sack: Physik. Z., 31, 815 (1930).

groups in the glyceride molecule lie parallel and exert no influence the one on the other a molecule such as tristearin should have a moment of 3 times 1.9 or 5.7. The moment found, 2.7, shows that the interaction of the dipoles is quite strong. Adam[1] has shown that the area per chain of tristearin as a close-packed film is the same as the area of the stearic acid molecule, indicating that the chains are parallel to each other. However in dilute solution where the molecules are comparatively far apart the repulsive forces between the dipoles must separate the chains and produce the smaller moment for the molecule as a whole.



$$\begin{array}{l} C-C-C-C-C=C-C-C-C=C-C-C-C-C-C-C-C-\overset{O}{C}-O-C \\ C-C-C-C-C=C-C-C-C=C-C-C-C-C-C-C-C-\overset{O}{C}-O-\overset{|}{C} \\ C-C-C-C-C=C-C-C-C=C-C-C-C-C-C-C-C-\overset{O}{C}-O-\overset{|}{C} \end{array}$$

TRIELAEOSTEARINE-TUNG OIL

$$\begin{array}{l} C-C-C-C-C-C=C-C-C=C-C-C-C-C-C-C-C-\overset{O}{C}-O-C \\ C-C-C-C-C-C=C-C-C=C-C-C-C-C-C-C-C-\overset{O}{C}-O-\overset{|}{C} \\ C-C-C-C-C-C=C-C-C=C-C-C-C-C-C-C-C-\overset{O}{C}-O-\overset{|}{C} \end{array}$$

TRILINOLIN-LINSEED OIL

$$\begin{array}{l} C-C-C-C-C-C-\overset{OH}{C}-C-C=C-C-C-C-C-C-C-C-\overset{O}{C}-O-C \\ C-C-C-C-C-C-\overset{OH}{C}-C-C=C-C-C-C-C-C-C-C-\overset{O}{C}-O-\overset{|}{C} \\ C-C-C-C-C-C-\overset{OH}{C}-C-C=C-C-C-C-C-C-C-C-\overset{O}{C}-O-\overset{|}{C} \end{array}$$

TRIRICINOLEIN-CASTOR OIL

$$\begin{array}{l} C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-\overset{O}{C}-O-C \\ C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-\overset{O}{C}-O-\overset{|}{C} \\ C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-C-\overset{O}{C}-O-\overset{|}{C} \end{array}$$

TRISTEARIN

FIG. 2

Formulae of tristearin and of the principal constituents of the oils.

The structural formulae of tristearin and of the chief constituent of each of the oils are given in Fig. 2, the hydrogen atoms being omitted. The oils may evidently be considered as derivatives of tristearin, tung and linseed oils differing only by the presence of six double bonds in the carbon chains, and castor oil by three double bonds and three hydroxyl groups. A small but definite polarity is known to be associated with the double bond[2] when

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[1] Adam: "The Physics and Chemistry of Surfaces," 50 (1930).

[2] Smyth and Zahn: J. Am. Chem. Soc., 47, 2501 (1925).

it is unsymmetrically located in the molecule. Hence it is not surprising that tung and linseed oils have slightly larger moments than tristearin. The slight difference in the location of the double bonds in the two oils can scarcely account for their differences in moment. Linseed oil contains several other constituents in small proportion in addition to that whose structure is given in Fig. 2 and some of them may be of a more highly polar nature. Furthermore, the molecular weight assigned to the oil may be sufficiently in error to account for the difference in moment.

Bless[1] has obtained a value of 2.19_6 for the moment of tung oil. There is not sufficient information in the abstract to determine whether the difference between this value and the one given above is due to a smaller molecular weight for tung oil or to some other cause. That tung oil should have a moment less than 2.7, that of tristearin, seems very unlikely on consideration of the close structural resemblance of their molecules.

Castor oil contains in addition to the double bond an hydroxyl group attached to each of the long carbon chains. The hydroxyl group has a moment of 1.7 and should increase the polarity of the triglyceride molecule, and the value of 3.7 is no larger than would be expected.

The so called "fixed" vegetable and animal oils and fats consist chiefly of triglycerides.[2] The most common acids from which the glycerides are formed are stearic, oleic, palmitic, linolic, and hydroxy acids. The substances studied here cover the range fairly thoroughly, castor oil containing the hydroxy and dihydroxy esters, linseed oil and tung oil the unsaturated ones and tristearic the completely saturated ester. Therefore it seems reasonably certain the moments of the other animal and vegetable oils and fats of this class will have moments in the same range, from 2.7 to 3.7, depending on the constitution of the acids of which they are composed.

Summary

The dielectric constants and densities of three vegetable oils, namely tung oil, linseed oil and castor oil, have been measured over a wide temperature range and their polarization calculated.

The electric moments of these oils and of tristearin were obtained by means of measurements on their dilute solutions in benzene and are 2.7, 2.8, 3.0 and 3.7×10^{-18} e.s.u. for tristearin, tung oil, linseed oil and castor oil respectively. The values are discussed from the standpoint of the molecular structure of the compounds.

These oils are typical of the group of fixed oils and fats of the triglyceride structure and they may all be expected to have electric moments varying from 2.7 to 3.7.

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[1] Bless: Phys. Rev., 35, 1442 (1930).

[2] See, for instance, Thorpe: "Dictionary of Applied Chemistry," 4, 645.

SURFACE TENSION OF SATURATED VAPORS AND THE EQUATION OF EÖTVÖS

BY J. L. SHERESHEFSKY

In discussing phenomena of solid-liquid or liquid-liquid surfaces it is usually emphasized that the properties under consideration belong to neither of the phases making up the interface, but to the interface proper. Thus it is made clear that the tension in a benzene-water interface is characteristic, neither of the benzene, nor of the water, but of the new phase of the interface which is made up of the latter two. But there is generally a lack of definiteness when dealing with liquid surfaces in contact with their own vapors. The properties of such surfaces are usually ascribed to the liquids concerned, without giving due consideration to the effect that the respective vapor phases undoubtedly have on these properties.

Van der Waals was the first to point out that the surface represents a third phase whose properties differ from those of the liquid or vapor. There is thus a complete parallelism between liquid-liquid and liquid-vapor interfaces. The surface tension, say, of benzene is therefore understood to refer neither to the liquid benzene, nor to the benzene vapor, but to the benzene (liquid)-benzene (vapor) interface, and is also conceived as the resultant of two effects produced by the surfaces presented by the liquid and the vapor.

The Surface Tension of Saturated Vapors

The tension in a liquid-liquid interface as determined by the method of capillary rise is given by the expression

$$\sigma = \tfrac{1}{2} r\, h\, g\, (\rho_1 - \rho_2) \tag{1}$$

where h is the height of rise, r the radius of the capillary, and ρ_1 and ρ_2 the densities of the immiscible liquids in equilibrium with each other. This expression also holds for the interface between a liquid and its vapor, ρ_1 and ρ_2 being the respective densities.

It is therefore evident that the tension of a surface formed by the contact of two fluid phases, whether they be two immiscible liquids, or a liquid and its vapor, is given by the difference of two terms, and thus is analogous to Antonoff's[1] rule, which states that the interfacial tension between two liquids is equal to the difference of the surface tensions of the liquids in equilibrium with each other. Thus, if σ is the relative, or interfacial tension, σ_1 the surface tension of liquid (1) in equilibrium with the vapor of liquid (2), and σ_2 is the surface tension of liquid (2) in equilibrium with the vapor of (1), Antonoff's rule may be expressed by the equation

$$\sigma = \sigma_1 - \sigma_2 \tag{2}$$

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[1] Phil. Mag., (6) 36, 377 (1918).

Applying this rule to an interface between a liquid and its vapor σ represents the relative surface tension, σ_1 the tension of the liquid surface proper, that is, of a hypothetical liquid surface whose vapor was momentarily removed or frozen, and σ_2 is the tension of the surface presented by the vapor. From this follows by analogy that

$$\sigma_1 = \tfrac{1}{2}\,\mathrm{rhg}\rho_1 \tag{3}$$

and

$$\sigma_2 = \tfrac{1}{2}\,\mathrm{rhg}\rho_2 \tag{4}$$

A more rigorous derivation of these equations may be obtained from considerations of equation (1) as applied to liquid surfaces in contact with vapors. At temperatures far removed from the critical the vapor density term, ρ_2, is usually omitted, since it is negligible with respect to the density of the liquid. As a result equation (1) becomes only approximate and assumes the more simplified form of

$$\sigma = \tfrac{1}{2}\,\mathrm{rhg}\rho_1 \tag{5}$$

This expression increases in accuracy at lower temperatures, and becomes exact as the vapor pressure of the liquid approaches zero. At this state of the liquid the relative surface tension, σ, becomes equal to the absolute tension, σ_1, of the liquid surface proper. Since this state also corresponds to the hypothetical liquid surface postulated above equation (5) becomes identical with equation (3), which defines the absolute surface tension of a liquid.

The surface tension of a vapor as defined in equation (4) may now be obtained by combining equation (3) with the expression for the relative surface tension of a liquid as given by equation (1), and with equation (2) expressing Antonoff's rule.

Entirely different consideration led N. Barbulescu[1] to the same conclusions.

The Surface Tension of Saturated Vapors and Temperature

To relate the surface tension of saturated vapors to temperature the following two equations are utilized.

$$\sigma = K_1 T_c V^{-\frac{2}{3}} (1 - T/T_c)^{1.2} \tag{6}$$

and

$$\rho_1 - \rho_2 = K_2 \rho_c (1 - T/T_c)^{0.3} \tag{7}$$

Equation (6) was deduced by van der Waals from his theory of corresponding states, and later modified by S. Sugden.[2] Equation (7) was suggested by D. H. Goldhammer[3] and corrected by S. Sugden[4]. Here T_c and ρ_c are the

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[1] Physik. Z., **31**, 48 (1930).

[2] J. Chem. Soc., **125**, 32 (1924).

[3] Z. physik. Chem., **71**, 577 (1910).

[4] J. Chem. Soc., **130 II**, 1780 (1927).

critical temperature and critical density respectively, V the molar volume of the liquid, and K_1 and K_2 constants which are approximately universal for all non-polar liquids.

Combining these with equations (1) and (4), we obtain the expression

$$\sigma_2 = \frac{\Delta T_c}{\rho_c^{1/3} M^{2/3}} (1 - T/T_c)^{0.9} \rho_2 \qquad (8)$$

which relates the surface tension of saturated vapors to the density of the vapor, its critical constants and temperature. The constant Δ equals K_1/K_2 and is nearly the same for all non-associated substances, M is the molecular weight, and the other terms have the designated significance.

To test the validity of this equation the surface tension of the saturated vapors of six liquids at various temperatures were calculated and compared with observed values. The agreement as shown in Tables I to VI inclusive is very good up to the critical temperature for all substances except carbon

TABLE I

Surface Tension of Saturated Vapors

Benzene

$\Delta = 1.39$ Mol. Wt. $= 78.05$; $T_c = 561.5$ $\rho_c = .3045$

I t°C	II $1 - T/T_c$	III ρ_2	IV σ_2(obs.)	V σ_2(calc.)	VI Percent Deviation
90	.353	.0036	.0904	.0935	3.43
120	.302	.0076	.1640	.1640	0.00
150	.247	.0144	.262	.260	0.76
180	.193	.0249	.357	.360	0.84
210	.140	.0421	.453	.456	0.66
240	.086	.0715	.483	.498	3.11
280	.016	.2209	.344	.340	1.16

TABLE II

Surface Tension of Saturated Vapors

Chlorobenzene

$\Delta = 1.39$ Mol. Wt. $= 112.5$; $T_c = 632.2$ $\rho_c = .3654$

I t°C	II $1 - T/T_c$	III ρ_2	IV σ_2(obs.)	V σ_2(calc.)	VI Percent Deviation
150	.332	.0054	.105	.1057	0.67
180	.283	.0102	.172	.173	0.58
210	.236	.0180	.253	.258	1.98
240	.188	.0301	.348	.353	1.44
270	.141	.0494	.433	.446	3.00
300	.093	.0778	.490	.485	1.02
320	.062	.1075	.456	.465	1.98
333	.042	.1360	.450	.415	7.78

TABLE III

Surface Tension of Saturated Vapors

Ethyl Ether

$\Delta = 1.39$ Mol. Wt. = 74.1; $T_c = 466.8$ $\rho_c = 0.2625$

I t°C	II $1-T/T_c$	III ρ_2	IV σ_2(obs.)	V σ_2(calc.)	VI Percent Deviation
20	.373	.00187	.0447	.0442	1.12
50	.308	.00508	.1037	.1013	2.32
80	.245	.01155	.1880	.1875	0.27
110	.179	.02349	.2880	.2870	0.35
140	.114	.04448	.3610	.3610	0.00
170	.049	.08731	.3280	.331	0.91
185	.017	.1320	.1960	.194	1.02

TABLE IV

Surface Tension of Saturated Vapors

Carbon Tetrachloride

$\Delta = 1.39$ Mol. Wt. = 153.84; $T_c = 556.2$ $\rho_c = 0.5576$

I t°C	II $1-T/T_c$	III ρ_2	IV σ_2(obs.)	V σ_2(calc.)	VI Percent Deviation
90	.3475	.0079	.1010	.0995	1.49
120	.293	.0163	.1770	.1765	0.28
150	.239	.0302	.2683	.2720	1.38
180	.185	.0525	.3730	.3780	1.34
210	.132	.0879	.4660	.465	0.22
240	.077	.1464	.4300	.477	10.95
270	.0225	.2710	.222	.298	34.20

TABLE V

Surface Tension of Saturated Vapors

Methyl Formate

$\Delta = 1.31$ Mol. Wt. = 60.04; $T_c = 487$ $\rho_c = 0.3489$

I t°C	II $1-T/T_c$	III ρ_2	IV σ_2(obs.)	V σ_2(calc.)	IV Percent Deviation
50	.337	.0043	.095	.0955	0.53
80	.275	.0105	.193	.1943	0.67
110	.2125	.0216	.316	.317	0.28
140	.152	.0412	.438	.447	2.06
170	.090	.0763	.497	.516	3.83
200	.028	.1524	.340	.361	6.18

TABLE VI

Surface Tension of Saturated Vapors

Ethyl Acetate

$\Delta = 1.43$ Mol. Wt. = 88.06; $T_c = 523.1$ $\rho_c = 0.3077$

I t°C	II $1-T/T_c$	III ρ_2	IV σ_2(obs.)	V σ_2(calc.)	VI Percent Deviation
90	.307	.0047	.0918	.0907	1.20
120	.248	.0103	.1645	.1643	0.12
150	.192	.0206	.260	.260	0.00
180	.134	.0388	.353	.346	2.76
210	.077	.0712	.400	.396	1.00
240	.019	.1500	.229	.237	3.49

tetrachloride. In the latter case the divergence is most probably due to the doubtful data in the neighborhood of the critical temperature. The observed values in the fourth column of each table were taken from the data of Ramsay and Shields as recalculated and corrected by S. Sugden.[1]

It is to be observed that the surface tension of saturated vapors attains a maximum value near the critical temperature, the ratio of the temperature at which the maximum occurs to the critical temperature being the same for all substances, as was shown by the author in a preceding paper.[2]

The Law of Eötvös

To express the relationship between surface tension of a liquid-vapor surface and temperature Eötvös suggested, in analogy to the gas law PV = RT, the similar equation

$$\sigma(M/\rho_1)^{2/3} = K(T_c - T) \qquad (9)$$

As this equation was only exact for low temperatures and was far from reproducing the experimental results for the whole range of temperatures up to the critical, Ramsay and Shields have introduced after an extensive investigation an arbitrary constant "d", thus modifying the equation to the form

$$\sigma(M/\rho_1)^{2/3} = K(T_c - T - d) \qquad (10)$$

This equation, while it has improved upon the Eötvös equation in accuracy, has lost its symmetry and is not consistent with the theory of corresponding states. It furthermore shares, with the original Eötvös equation, the fault that it takes no consideration of the density of the vapor, which has as it was shown above an important effect upon the surface tension of the interface.

A relationship which shall be consistent with the theory of corresponding states, and which shall also take account of the vapor density, may be developed on the basis of the conclusions arrived at in the preceeding section in this paper.

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[1] J. Chem. Soc., 125, 32 (1924).

[2] J. Phys. Chem., 34, 1947 (1930).

Combining equations (1) and (4), we obtain

$$\sigma_2 = \sigma\left(\frac{\rho_2}{\rho_1 - \rho_2}\right) \qquad (11)$$

which relates the relative surface tension, σ, with the surface tension of the vapor, σ_2. Substituting for the latter its equivalent in equation (8), we obtain

$$\sigma\left(\frac{M^{2/3}}{\rho_1 - \rho_2}\right) = \Delta \frac{T_c}{\rho_c^{1/3}}(1 - T/T_c)^{0.9} \qquad (12)$$

which in multiplying by $(\rho_1-\rho_2)^{1/3}$ assumes a form that is very similar to the original expression of Eötvös' Law, namely

$$\sigma\left(\frac{M}{\rho_1 - \rho_2}\right)^{2/3} = \Delta T_c\left(\frac{\rho_1 - \rho_2}{\rho_c}\right)^{1/3}(1 - T/T_c)^{0.9} \qquad (13)$$

A similar relationship was suggested by N. Katayama[1] as shown by equation (14)

$$\sigma\left(\frac{M}{\rho_1 - \rho_2}\right)^{2/3} = K(T_c - T) \qquad (14)$$

This equation accounts for the vapor density as well as equation (13), but is not as complete in its relationship to the theory of corresponding states, since the latter includes the critical volume as well as the critical temperature. It is also not in as good agreement with experiment, as equation (13), as is evidenced in Tables VII to XII inclusive. The values of σ calculated by

TABLE VII

The Equation of State for Liquid-Vapor Interfaces

Benzene (liquid)-Benzene (vapor)

$\Delta = 1.39$ Mol. Wt. $= 78.05$ $T_c = 561.5$ $\rho_c = .3045$

I t°C	II $1-T/T_c$	III $\rho_1-\rho_2$	IV σ(obs.)	V σ(calc.)	VI σ(calc.)
13.5	.490	.8857	29.72	29.70	
20.5	.477	.8782	28.91	28.86	
32.5	.456	.8653	27.30	27.20	
39	.445	.8581	26.36	26.40	
41.5	.439	.8553	26.08	26.00	
54.8	.417	.8400	24.28	24.38	
61	.406	.8330	23.61	23.60	
72	.386	.8207	22.15	22.70	
90	.353	.8006	20.13	20.00	19.08
120	.302	.7616	16.42	16.52	15.67
150	.247	.7166	13.01	12.98	12.37
180	.193	.6657	9.56	9.65	9.22
210	.140	.6011	6.45	6.53	6.23
240	.086	.5137	3.47	3.60	3.47
270	.033	.3696	1.05	1.09	1.06
280	.016	.2305	0.36	0.36	0.36

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[1] Tohoku Imp. Univer. Science Reports, (1) 4, 373 (1916).

TABLE VIII

The Equation of State for Liquid-Vapor Interfaces

Chlorobenzene (liquid)-Chlorobenzene (vapor)

$\Delta = 1.39$ Mol. Wt. = 112.5; $T_c = 632.2$ $\rho_c = .3654$

I t°C	II $1-T/T_c$	III $\rho_1-\rho_2$	IV σ(obs.)	V σ(calc.)	VI σ(calc.)
12	.549	1.118	34.36	34.40	
18.7	.538	1.108	33.35	33.50	
24.1	.523	1.102	32.85	32.40	
41	.503	1.083	30.78	30.85	
50	.488	1.073	29.83	29.70	
62.1	.470	1.059	28.20	28.40	
81	.440	1.039	26.10	26.25	
93	.422	1.025	24.99	24.90	
123	.373	.9910	21.63	21.53	
150	.332	.9545	18.55	18.65	17.57
180	.283	.9122	15.40	15.50	14.61
210	.236	.8622	12.16	12.38	11.71
240	.188	.8054	9.30	9.45	8.94
270	.141	.7341	6.43	6.63	6.29
300	.093	.6442	4.05	4.01	3.83
320	.062	.5628	2.39	2.43	2.32
333	.042	.4914	1.63	1.50	1.41

TABLE IX

The Equation of State for Liquid-Vapor Interfaces

Ethyl Ether (liquid)-Ethyl Ether (vapor)

$\Delta = 1.39$ Mol. Wt. = 74.1; $T_c = 466.8$ $\rho_c = 0.2625$

I t°C	II $1-T/T_c$	III $\rho_1-\rho_2$	IV σ(obs.)	V σ(calc.)	VI σ(calc.)
20	.373	.7109	17.01	16.80	16.12
50	.308	.6713	13.69	13.35	12.81
80	.245	.6286	10.25	10.20	9.71
110	.179	.5707	7.00	6.97	6.81
140	.114	.4936	4.00	4.01	3.97
170	.049	.3785	1.42	1.44	1.47
185	.017	.2698	0.40	0.40	0.46

TABLE X

The Equation of State for Liquid-Vapor Interfaces

Carbon Tetrachloride (liquid)-Carbon Tetrachloride (vapor)

$\Delta = 1.39$ Mol. Wt. = 153.84; $T_c = 556.2$ $\rho_c = 0.5576$

I t°C	II $1-T/T_c$	III $\rho_1-\rho_2$	IV σ(obs.)	V σ(calc.)	VI σ(calc.)
20	.473	1.593	26.95	26.60	25.55
33	.450	1.567	25.22	25.00	
45.9	.426	1.540	23.63	23.40	
90	.3475	1.4475	18.51	18.25	17.59
120	.293	1.3740	14.95	14.90	14.35
150	.239	1.2914	11.46	11.62	11.24
180	.185	1.1945	8.50	8.60	8.27
210	.132	1.0687	5.67	5.66	5.44
240	.077	0.8980	2.64	2.92	2.86
270	.0225	0.5955	0.49	0.66	0.56

TABLE XI

The Equation of State for Liquid-Vapor Interfaces

Methyl Formate (liquid)-Methyl Formate (vapor)

$\Delta = 1.31$ Mol. Wt. = 60.04; $T_c = 487$ $\rho_c = 0.3489$

I t°C	II $1-T/T_c$	III $\rho_1-\rho_2$	IV σ(obs.)	V σ(calc.)	VI σ(calc.)
50	.337	.9251	20.48	20.52	19.96
80	.275	.8698	15.95	16.10	15.68
110	.2125	.8048	11.77	11.80	11.55
140	.152	.7156	7.63	7.77	7.65
170	.090	.6081	3.96	4.12	4.06
200	.028	.4131	0.92	0.98	1.00

TABLE XII

The Equation of State for Liquid-Vapor Interfaces

Ethyl Acetate (liquid)-Ethyl Acetate (vapor)

$\Delta = 1.43$ Mol. Wt. = 88.06; $T_c = 523.1$ $\rho_c = 0.3077$

I t°C	II $1-T/T_c$	III $\rho_1-\rho_2$	IV σ(obs.)	V σ(calc.)	VI σ(calc.)
90	.307	.8065	15.74	15.58	15.04
120	.248	.7580	12.08	12.10	11.73
150	.192	.7005	8.85	8.84	8.56
180	.134	.6265	5.70	5.58	5.57
210	.077	.5232	2.94	2.92	2.82
240	.019	.3278	0.50	0.52	0.52

means of equation (13) are regularly lower than those calculated by means of equation (14) and those observed, particularly for the lower temperatures where the accuracy of the observations is quite certain.

The data of the third and fourth columns were taken from S. Sugden.[1] In the fifth column are given the values calculated by means of equation (13), and in the sixth—the values calculated by means of equation (14) as taken from N. Katayama.[2] Table XIII gives the constants Δ, which are approximately the same for all unassociated substances for both liquid and vapor states. In the second column of this table is also given the constant K of equation (14).

TABLE XIII

The Equation of State for Liquid-Vapor Interfaces

Constants

	Δ	K
Benzene	1.39	2.04
Chlorobenzene	1.39	2.02
Ethyl Ether	1.39	2.04
Carbon Tetrachloride	1.39	2.05
Methyl Formate	1.31	2.15
Ethyl Acetate	1.43	1.97

Summary

1. On the basis of Antonoff's rule and the capillary rise equation of surface tension, an expression is deduced which determines the surface tension of saturated vapors.

2. This expression is further developed into a form which relates surface tension of saturated vapors with temperature. The equation is tested for six unassociated vapors and found to reproduce observed results with fair accuracy.

3. The various modifications of Eötvös' law are discussed, and a new one is developed which takes account of the vapor density and is based on the theory of corresponding states. This new equation is tested against the same six compounds in the liquid state and is found to be in good agreement with observed data.

Chemical Laboratory
Howard University
Washington, D. C.
December 1930.

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[1] Loc. cit.

[2] Loc. cit.

THE INTERACTION BETWEEN NITRIC OXIDE AND HYDROGEN SULPHIDE IN THE PRESENCE OF WATER

BY H. B. DUNNICLIFF, SARDAR MOHAMMAD AND JAI KISHEN

Recently, J. A. Pierce[1] has studied the reaction between nitric oxide and hydrogen sulphide from the thermodynamic point of view. He concludes that "the assumption of Thomson[2] that nitric oxide and hydrogen sulphide react to form ammonium sulphide and nitrous oxide is obviously incorrect: absence of the former by qualitative tests being sufficient indication of this. The counterclaim of Le Conte[3] that the gases do not react at all is likewise refuted." He has established that the gases react together with formation of water, sulphur and nitrogen according to the stoichiometric equation:

$$2NO + 2H_2S = 2H_2O + 2S + N_2,$$

though the mechanism is more complex. The present work communicates a study of the reaction between the two gases in the presence of much water.

The Soluble Products of the Reaction between Nitric Oxide and Hydrogen Sulphide in the Presence of Water

Hydrogen sulphide was prepared from ferrous sulphide and hydrochloric acid and purified by passing it first over dry iodine crystals and then through a dilute solution of sodium sulphide. Nitric oxide was made by dripping a concentrated solution of sodium nitrite into an acidified solution of ferrous sulphate.[3] Nitric oxide and hydrogen were passed into water in a two-litre flask from which air had been displaced by carbon dioxide gas. Milkiness due to sulphur was observed after some time. After a few hours the solution became yellow and more sulphur was formed and deposited. The interaction appeared to take place more rapidly when traces of nitrogen peroxide were previously introduced into the solution. The atmosphere over the solution remained clear throughout the reaction and the brown colour of nitrogen peroxide was never observed inside the flask. The yellow solution immediately became white when it was exposed to the air and some of the sulphur in the solution also seemed to coagulate. Cadmium carbonate was added to remove the excess of hydrogen sulphide and to deposit sulphur. The solution gave tests for 'ammonium' but hydroxylamine was absent. A nitrite was present but no nitrate. Acetic acid, when added to the solution obtained after the passage of the gases through water for several hours, produced a transitory yellow colour which indicated the presence of some sulphur acid. Qualitative tests showed that a thiosulphate was present but tetrathionate and other thionic acids were not detected. This contradicts the result previously announced[4] where it is stated that tetrathionate is present and nitrite is absent. The results given in the present article have been often confirmed.

Quantitative Determination of the Products of Reaction in Solution

'Ammonium.' Sodium hydroxide solution was added in excess to the original solution containing colloidal sulphur. Steam was blown through the solution and the ammonia absorbed in excess of standard sulphuric acid.

Nitrite and thiosulphate were estimated by the following methods. Cadmium carbonate freshly precipitated from a solution of cadmium sulphate by ammonium carbonate was employed to remove the excess of hydrogen sulphide and to deposit sulphur from the solution.

1. (a) Excess of potassium permanganate was added to oxidise completely both thiosulphate and nitrite. Ferrous sulphate was then added in excess and the excess of ferrous sulphate was back titrated against potassium permanganate.[5]

(b). The thiosulphate was estimated by titration against a standard solution of iodine. Control experiments indicated that when the quantity of a nitrite in a mixture of a thiosulphate and a nitrite is not large, the thiosulphate could safely be determined by this method.

2). The nitrite and thiosulphate were exactly oxidised as described above. The nitrite formed as the result of oxidation was determined by the method of Bowman and Scott.[6] The results of three experiments are recorded in Table I. The amount of ammonia was always in excess of that calculated for the nitrite and thiosulphate present, both when Merck's extra pure cadmium carbonate or freshly precipitated and thoroughly washed cadmium carbonate was used. This was found to be due to small quantities of ammonia present in the cadmium carbonate. Hence, the solution which contained colloidal sulphur was used for determining 'ammonium' (V.S.).

The quantities of the products formed in the reaction are small. Errors in estimation were reduced by taking large volumes of the solutions. In the determinations of the nitrite the solution was evaporated to small bulk after oxidation.

TABLE I

The Quantitative Determination of the Products formed in Solution in the Reaction

Composition of the solution in grams per (100×10^5) c.c.

Nitrite	Thiosulphate	Total 'ammonium'		Error %
		Calculated from Nitrite and Thiosulphate	Determined	
284	121	150	152	−1.3
376	151	196	191	2.6
527	430	344	349	−1.4

The Gaseous Products of the Reaction

The apparatus for the estimation of nitrogen and nitrous oxide in the gaseous products of the reaction is described in "The Action of Hydrogen Sulphide on Solutions of Nitric Acid."[7] Nitric oxide obtained by the action of sodium nitrite on ferrous sulphate, was passed through a concentrated solution of caustic soda and then over solid caustic soda to purify it from traces of nitrogen peroxide. It was stored in the gas pipette, H_1, (Fig. 1) over water the surface of which was covered with a layer of paroleine. The tower, D, connected with the reaction flask, C, contained cupric phosphate to remove the excess of hydrogen sulphide.[8] Paraffin wax had been run through the rubber tubing used as connections to prevent the action of nitric oxide on the rubber. Before commencing an experiment, the whole apparatus was swept clean of other gases by a stream of carbon dioxide. The two gases were then admitted into the reaction flask, C, which would be easily shaken. The gases were allowed to stand for some hours and the reaction flask was occasionally shaken. When interaction appeared to be complete the gaseous mixture was swept forward through the cock F_1, and a further supply of gases was introduced into C. Any excess of nitric oxide was absorbed in a series of vessels E_1, E_2, (Fig. 1) E_3, (Fig. 2)[7] of different forms each containing a mixture of

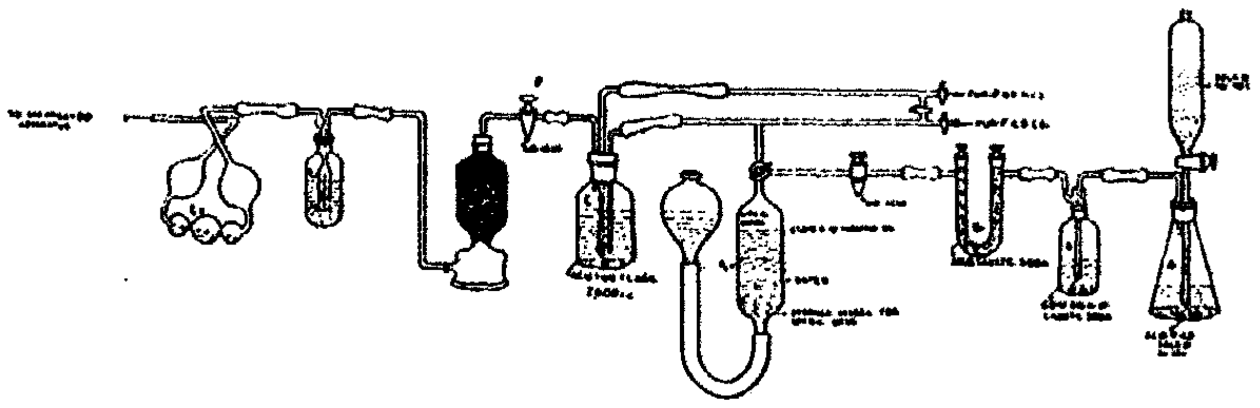


Fig. 1
(Diagrammatic)

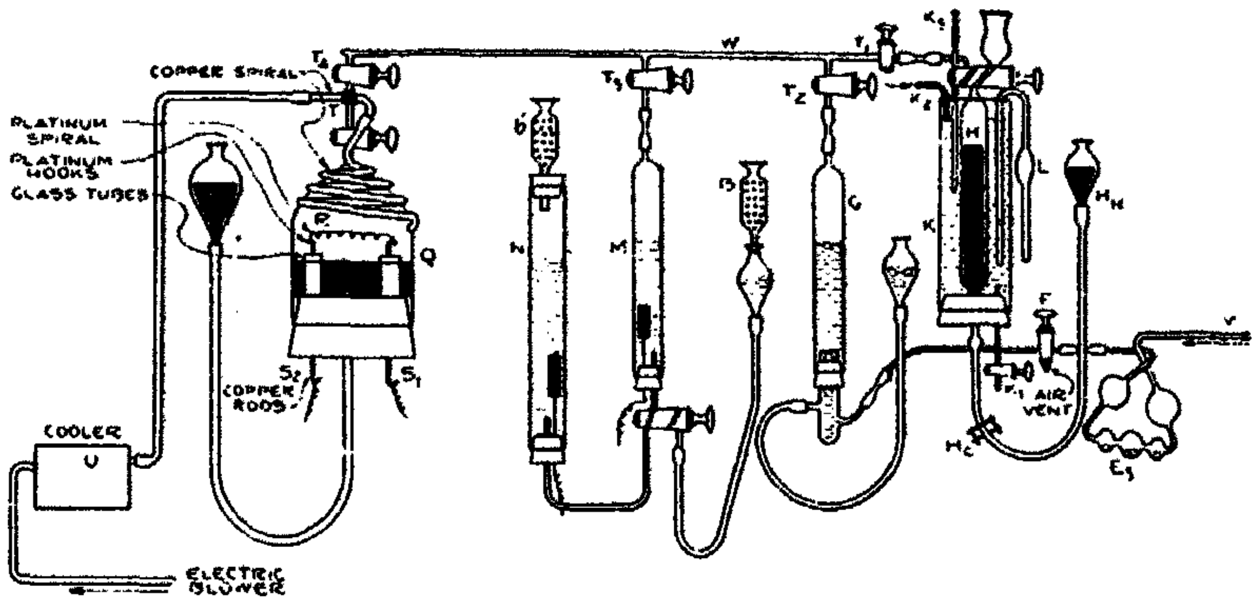


Fig. 2

five volumes of a saturated solution of potassium bichromate with one volume of concentrated sulphuric acid.[9] This mixture oxidises nitric oxide quantitatively to nitric acid and is stable at ordinary temperatures. The residual gases were finally swept out by carbon dioxide and collected over caustic potash in the tube G, Fig. 2,[7] through the cock F. The residual gases (N_2O and N_2) had then to be brought under combustion with excess of hydrogen in the pipette described in Fig. 3.[7] The contraction produced should be equal to the volume of nitrous oxide.

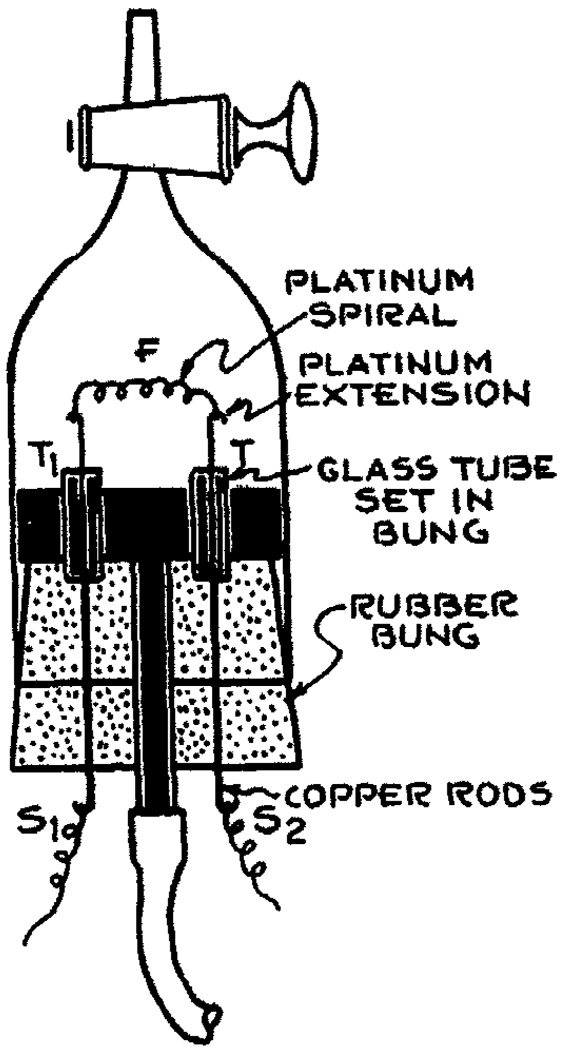


FIG. 3
Combustion Pipette

In Table II (i) and (ii) are given the results of two experiments performed under similar conditions, i.e., the whole of the gases evolved were collected, the analyses being of average samples.

In (ii), the gaseous products from the first two hours' reaction were let out through the air-vent cock F_1. Subsequent quantities of the two gases formed in the reaction were then collected in G.[7] The mixture had the same composition as the gas collected during the first two hours. This shows that the chemical change is the same during those two periods of the reaction.

In order to find out if the gases are in the same proportion in both the gas and liquid phase the gases were collected (a) from the gaseous phase above the liquid and (b) by bubbling carbon dioxide through the liquid.

It was found (vide results Table III, i and i.a) that (a) contained a lower percentage of nitrous oxide than (b) (vide Table III, ii).

This may be due to the fact that nitrous oxide, the first reduction product, is removed from the sphere of action by its relatively high solubility in water or that nitrous oxide is formed in the liquid phase either exclusively or in greater quantity than in the gas phase. This point is under investigation.

TABLE II

Analysis of the Gaseous Products of the Reaction

	Vol. of the gas c.c.	Vol. of hydrogen c.c.	Vol. after combustion c.c.	Contraction N_2O c.c.	N_2 c.c.	Composition N_2O %	Composition N_2 %
i.	13.6	31.0	42.8	1.8	11.8	13.2	86.8
i. a	24.6	40.2	61.6	3.2	21.4	13.0	87.0
ii.	32.2	43.8	71.9	4.1	28.1	12.7	87.3

TABLE III

The Gaseous Products formed when Hydrogen Sulphide and Nitric Oxide are bubbled through Water

	Vol. of the gas c.c.	Vol. of Hydrogen c.c.	Vol. after combustion c.c.	Contraction c.c.	N_2	Percentage composition N_2O	Percentage composition N_2
i. a	30.2	39.7	73.2	1.7	28.5	5.6	94.4
i.a	24.1	40.8	63.8	1.1	23.0	4.6	95.4
ii. b	30.2	41.9	64.6	7.5	22.7	24.8	75.2

The Effect of the Presence of Sulphuric Acid

The reaction in the presence of sulphuric acid is more rapid at first than when sulphuric acid is absent, but it slows down very quickly. The milkiness of the solution did not increase and only traces of ammonia were observed. The percentage composition of the residual gases is shown in Table IV.

TABLE IV

The Gaseous Products (from gas and liquid phase) formed when Nitric Oxide and Hydrogen Sulphide are bubbled through Dilute Sulphuric Acid

	Vol. of the gas. c.c.	Vol. of Hydrogen c.c.	Vol. after combustion c.c.	Contraction c.c.	N_2 c.c.	N_2O %	N_2 %
With 5% H_2SO_4							
i.	30.5	44.1	71.6	3.0	27.5	9.8	90.2
With 10% H_2SO_4							
ii.	15.8	31.6	42.9	4.5	11.3	28.5	71.5

The results indicate the formation of a higher proportion of nitrous oxide when sulphuric acid is present. If the formation of nitrous oxide takes place mainly in the liquid phase, this may be due to the greater solubility of nitric oxide in sulphuric acid than in water.

Since, after long passage of the gases (NO and H_2S) through water, the small amount of nitrite is the same as when the gases are passed for a short interval, it appears that either (a) the nitrite is a minor bye-product, or (b) that nitrite is formed as an intermediate product and systematically decomposed. The presence of sulphuric acid practically prevents the formation of ammonia in the solution. This suggests that such ammonia as is formed is not produced in the gaseous phase (when on shaking it would be found in the sulphuric acid) but in solution. This would confirm the observations of Pierce[1] who finds not only that nitrous oxide is not formed when dry nitric oxide and hydrogen sulphide are mixed, but that ammonia also is not a product of the reaction in the absence of water.

The Action of Nitric Oxide on Ammonium Nitrite and Dilute Solutions of Ammonia

(A) *Products found in the Solution.* Nitric oxide was passed into ammonium nitrite solutions of various concentrations in an atmosphere of hydrogen and the excess of nitric oxide was driven off by bubbling hydrogen through the solution. Nitrate was not detected by the most delicate tests. Titration against standard potassium permanganate showed that the amount of nitrite was unchanged. The solubility of nitric oxide in solutions of ammonium nitrite was also determined in the presence of hydrogen. The value found at 20°C agreed fairly with that given by Lunge for the solubility of nitric oxide in water. (Value determined = 0.0070 gram per 100 c.c., Lunge found 0.0068 grams per 100 c.c. at 20°C).

There was no evidence that any chemical action takes place when nitric oxide is passed into dilute solutions of ammonia in an atmosphere of hydrogen.

The Action of Nitric Oxide on Solutions of Ammonium Sulphide

The existence of a thiosulphate in the solution due to the interaction between nitric oxide and hydrogen sulphide suggests the formation of ammonium poly-sulphide (via ammonium sulphide and sulphur) as an intermediate product in the reaction.

Hydrogen sulphide was passed into a solution of ammonia in the absence of air for some time and then excess of the gas was removed from the solution by bubbling hydrogen through it. A little more ammonium hydroxide was added to tend to produce ammonium sulphide from the hydrosulphide. When nitric oxide had been passed through the colourless solution for about 15 minutes, a yellow colour developed and sulphur was thrown down. This sulphur then gradually decreased in quantity as it dissolved in the solution, ultimately giving it an orange colour. The orange colour in the case of weak solutions (approximately N/200) was removed on passing nitric oxide for about twenty hours. Freshly prepared cadmium carbonate was added to deposit sulphur. The results showed that the polysulphides formed seemed to decompose into thiosulphate or thionic acids and sulphur. Since the amount of thiosulphate found in the solutions was small if cadmium carbonate was added immediately after the reaction, it appears that the thiosulphate is produced via the polysulphide. When nitric oxide was passed into N/33 ammonium sulphide for five hours, the thiosulphate formed was 0.2 gram per litre. The amount of thiosulphate increases considerably if the solution is allowed to stand.

Only traces of nitrite were detected. When an insufficient amount of nitric oxide was kept in contact with a strong solution of ammonium sulphide over mercury for about 48 hours, the nitric oxide was completely absorbed in the solution which readily gave tests for a nitrite. There was no possibility of nitric oxide being in excess and forming nitrous acid via oxygen from the air, as it was completely absorbed in the experiment.

Traces of sulphate were present if nitric oxide was bubbled into very weak solutions for several hours when the polysulphide first formed seemed to decompose completely. This may have been due to decomposition of thiosulphate by hydrolysis

$$(NH_4)_2S_2O_3 + H_2O = (NH_4)_2SO_4 + H_2S$$

(B). *The Gaseous Products.* The experiments could not be performed in the presence of carbon dioxide as the solution was completely decomposed when the apparatus was being washed with carbon dioxide. The percentage of nitrous oxide and nitrogen determined from these experiments (N_2O = 13.0%; N_2 = 87.0%) exactly corresponded with the percentage of these gases from the reaction between nitric oxide and hydrogen sulphide in the early stages (vide Table II). This proved that the gaseous products are not obtained from ammonium sulphide and nitric oxide but probably from nitric oxide and hydrogen sulphide in the gas phase, the hydrogen sulphide being drawn out of the hydrolysed ammonium sulphide solution by carbon dioxide. To overcome the difficulty of providing an inert atmosphere over the solution, another apparatus (Fig. 4) was connected with the apparatus for the gas analysis (Fig. 2). The air from the capillary tube was completely expelled by using the same nitrometer as a pump. Nitric oxide prepared in A, by Thiels's method[3] was admitted into the nitrometer, N. A known volume of a solution of ammonium sulphide was drawn into the nitrometer from the cup, G. The nitrometer was shaken occasionally and, after the desired interval for reaction, the residual gases were driven into the apparatus for gas analysis (Fig. 2) by raising the reservoir of the nitrometer and using a current of carbon dioxide. A mixture of 50 c.cs. of N/33 ammonium sulphide solution with 10 c.c. of ammonium hydroxide of the same strength was exposed to 80 c.c. of nitric oxide. After 19 hours the contraction was 26 c.c. The gas collected over caustic potash was 11 to 12 c.c., the balance (nitric oxide) having been absorbed in the dichromate mixture. The results of two experiments performed under similar conditions are shown in Table V.

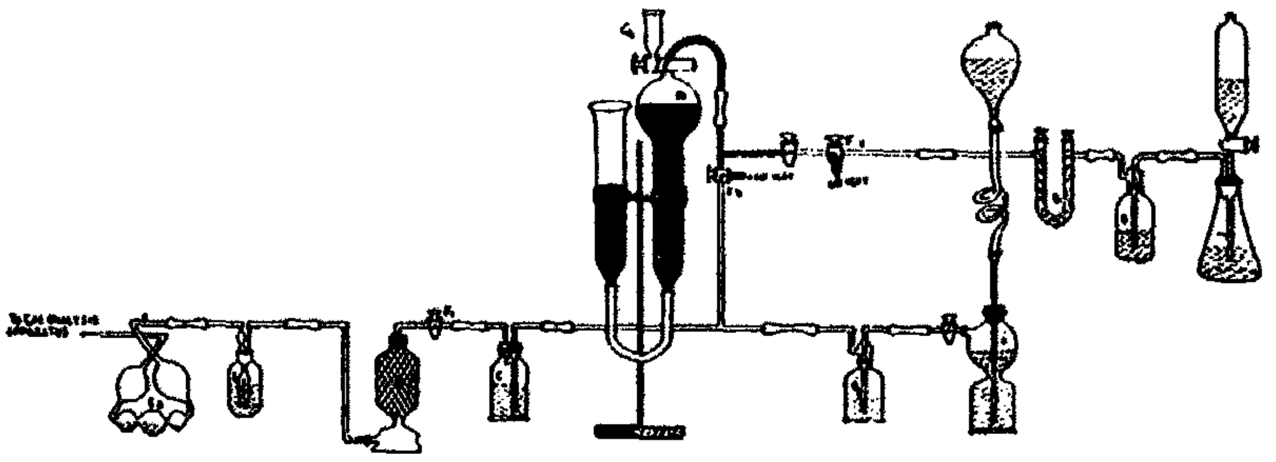


FIG. 4

TABLE V

Analysis of the Gaseous Products of the Reaction between Nitric Oxide and Ammonium Sulphide

	Vol. of the gas c.c.	Vol. of Hydrogen c.c.	Vol. after combustion c.c.	Contraction c.c.	N_2	Composition N_2O %	Composition N_2 %
i.	11.4	18.6	26.8	3.2	8.2	28.1	71.9
ii.	12.0	21.6	30.2	3.4	8.6	28.4	71.6

Nitric oxide was in excess in these experiments.

Experiments were performed in which the excess of the reducing agent i.e., ammonium sulphide, was exposed to nitric oxide. In Table VI are given the results of two experiments carried out under similar conditions in which 82 c.c. of nitric oxide, were allowed to react with 50 c.c. of ammonium sulphide solution (approximately N/10) and 10 c.c. of N/33 ammonium hydroxide. After 19 hours the residual gas, *which was free from nitric oxide*, was about 21 c.c. in the first experiment and 17.2 c.c. in the second experiment.

Table VI

Analysis of Residual Gas from the Action of Nitric Oxide with Excess of Ammonium Sulphide

	Vol. of the gas c.c.	Vol. of Hydrogen c.c.	Vol. after combustion c.c.	Contraction c.c.	N_2 % c.c.	N_2O %	N_2 %
i.	21.2	33.4	54.5	0.1	21.1	0.0	100.0
ii.	17.2	31.0	48.2	0.0	17.2	0.0	100.0

These experiments show that when an excess of the reducing agent is used, the gaseous product of the reaction consists of pure nitrogen. The percentage of nitrous oxide is increased by using an excess of the oxidising agent, i.e. nitric oxide. Bancroft[10] from a study of the reduction of nitric acid by metals arrived at the same conclusions: "In the first case there is never an appreciable concentration of the reducing agent, hence its potential is low, and the reduction will not go so far. In the second case there is always an excess of reducing agent and the reduction should go to a lower stage than in the first case. There is a little chance for nitric acid to react with the intermediate products. An excess of reducing agent will cause more complete reduction to a lower stage."

It also shows that nitric oxide is reduced to nitrogen via nitrous oxide under favourable conditions and is conclusive evidence that nitrous oxide is reduced to nitrogen by hydrogen sulphide (or ammonium sulphide).

The Action of Nitric Oxide on Ammonium Thiosulphate

(A). *The Products of the Reaction in Solution.* On passing nitric oxide into solutions of ammonium thiosulphate in an atmosphere of hydrogen, a transitory yellow colour is observed with deposition of sulphur in small quantities. The decomposition of the thiosulphate increases with the decrease in the concentration of the solutions but the amount of ammonia in a solution remains constant. Table VII shows the decomposition of solutions of ammonium thiosulphate of different strengths.

Table VII

The Decomposition of Ammonium Thiosulphate by Nitric Oxide

Composition of the solution grams per 100 c.c.

	Strength of the solutions	$(S_2O_3)''$ taken	$(S_2O_3)''$ left	Decomposition	Percentage decomposition
i.	N/6	1.867	1.858	0.009	0.5
ii.a.	N/19.7	0.568	0.540	0.028	4.9
b.	N/19.7	0.568	0.529	0.039	6.9
iii.	N/77.14	0.145	0.119	0.026	17.9

Table VIII

Showing the Formation and Decomposition of Nitrite when Nitric Oxide is passed into Mixtures of Ammonium Thiosulphate and Ammonium Nitrite Solutions. The Composition of the Solutions is given in grams per 100 c.c.

	Strength of the solution	Time of passing the gas hours	Thiosulphate Taken gram	Thiosulphate Left gram	Decomposition gram	Percentage decomposition %	Nitrite Before the reaction gram	Nitrite After the reaction* gram	Increase or Decrease gram
i.	$\frac{N}{23.87}$ $(S_2O_3)''$ $\frac{N}{32.10}$ $(NO_2)'$	1.5	0.469	0.456	0.013	2.8	0.0717	0.0825	+0.0108
ii.	$\frac{N}{24.6}$ $(S_2O_3)''$ $\frac{N}{32.1}$ $(NO_2)'$	1.5	0.456	0.442	0.014	3.1	0.0717	0.0840	+0.0123
iii.	$\frac{N}{18.48}$ $(S_2O_3)''$ $\frac{N}{16.94}$ $(NO_2)'$	4.5	0.606	0.539	0.067	11.1	0.1357	0.0801	−0.0556
iv.	$\frac{N}{49.75}$ $(S_2O_3)''$ $\frac{N}{46.62}$ $(NO_2)'$	4.5	0.225	0.211	0.041	6.2	0.0493	0.0365	−0.0128

* As calculated from permanganate titration. This would show as nitrite any nitric oxide in solution or molecular combination with any compound in solution. The matter is under further investigation.

Sulphate was found to be present in small quantities but tetrathionate was not detected. Nitric oxide was passed into N/20 ammonium thiosulphate solutions for different intervals but the nitrite formed was negligible in all the stages of the reaction. If formed, nitrite is probably decomposed in all stages of the reaction by comparatively strong solutions of ammonium thiosulphate (vide foot-note to Table VIII p. 1729). The transitory yellow colour observed throughout the reaction may be the result of interaction between the nitrite formed and the thiosulphate present.[11] However, an increase in the amount of nitrite was observed (Table VIII) in the early stages of the reaction when nitric oxide was passed into mixtures of equal volumes of ammonium thiosulphate and ammonium nitrite solutions. In the later stages of the reaction, decomposition of nitrite is noticed

When nitric oxide was passed into about N/20 ammonium thiosulphate solutions, sulphate was formed. The results shown in Table IX give the amount of change effected in different intervals of time and it will be observed that there is no regular relationship between the thiosulphate decomposed and the sulphate formed. A small but continuous decrease in the amount of ammonia was observed. The solution was alkaline to litmus after the passage of the gas for nine hours.

TABLE IX

The Amount of Sulphate formed when Nitric Oxide is passed into Ammonium Thiosulphate for different intervals

Quantities are shown in grams per litre.

		1	2	3	4
i.	Time of Passage of Gas (Hours).	1.5	2.5	4.5	9.0
ii.	Thiosulphate taken as $(S_2O_3)''$	5.654	5.654	5.654	5.654
iii.	Thiosulphate left as $(S_2O_3)''$	5.599	5.462	5.101	4.604
iv.	Thiosulphate decomposed as $(S_2O_3)''$	0.055	0.192	0.553	1.050
v.	Sulphate formed as $(SO_4)''$	0.045	0.094	0.297	0.328
vi.	$(NH_4)^{\cdot}$ corresponding to $(SO_4)''$ formed	0.017	0.035	0.111	0.123
vii.	$(NH_4)^{\cdot}$ corresponding to $(S_2O_3)''$ left	1.799	1.756	1.639	1.480
viii.	Total of (v) and (vi)	1.816	1.791	1.750	1.602
ix.	$(NH_4)^{\cdot}$ corresponding to $(S_2O_3)''$ taken	1.818	1.818	1.818	1.818
x.	Percentage. Decrease in $(NH_4)^{\cdot}$		−1.5	−3.7	−11.8

B. *The Gaseous Products of the Reaction.* About 250 c.c. of nitric oxide were kept in contact with 250 c.c. of ammonium thiosulphate solution (about N/50) for twenty hours. The volume of the residual gases collected over caustic potash was small. The results of two experiments are shown in Table X.

TABLE X

Analysis of the Gaseous Products of the Reaction between Nitric Oxide and Ammonium Thiosulphate

	Vol. of the gas. c.c.	Vol. of Hydrogen. c.c.	Vol. after combustion c.c.	Contraction	N_2	Composition	
						N_2O	N_2
i.	12.5	24.1	35.9	0.7	11.8	5.6	94.4
ii.	10.6	18.2	28.2	0.6	10.0	5.7	94.3

The Action of Nitric Oxide on Solutions of Ammonium Tetrathionate

Ammonium tetrathionate was prepared and was estimated by the method of A. Kurtenacker.[12] On passing nitric oxide into solutions of ammonium tetrathionate of various concentrations, a slight turbidity but no coloration was noticeable. The solution became acidic. (Solutions of ammonium tetrathionate become acidic also on long standing). As in the thiosulphate experiments, the total concentration of ammonia in the solution remained unchanged. The solutions did not give tests for a nitrite when the gas was passed for four hours.

TABLE XI

The Decomposition of Ammonium Tetrathionate Solution by Nitric Oxide
Composition of the solution: gram/100 c.c.

	Strength of the solution	Time in hours for passing NO	$(S_4O_6)''$ taken	$(S_4O_6)''$ left	$(S_4O_6)''$ decomposed	Percentage decomposition
i.	N/29.92	1.0	0.869	0.869	0.000	0.0
ii.	N/29.92	2.0	0.869	0.849	0.020	2.3
iii.	N/20.51	4.0	1.091	0.700	0.391	35.9
iv.	N/32.91	4.0	0.680	0.196	0.484	71.2

Nitric oxide was also passed into mixtures of ammonium nitrite and ammonium tetrathionate solutions. The results were comparable with those obtained from mixtures of ammonium thiosulphate and ammonium nitrite solutions. (vide Table XII).

TABLE XII

Shows the Formation and Decomposition of Nitrite when Nitric Oxide is passed into Mixtures of Ammonium Tetrathionate and Ammonium Nitrite Solutions

Composition of the solution: grams per 100 c.c.

	Strength of solutions	Time in hours for NO	$(NO_2)'$ taken	$(NO_2)'$ after the reaction*	Increase or Decrease
i.	$\frac{N}{21.27}$ $(S_4O_6)''$ $\frac{N}{21.94}$ $(NO_2)'$	1.54	0.105	0.127	+0.022
ii.	$\frac{N}{21.27}$ $(S_4O_6)''$ $\frac{N}{21.94}$ $(NO_2)'$	4.0	0.105	0.071	−0.034

* vide footnote to Table VIII, page 1729.

In solution tetrathionates like thiosulphates are not affected by a nitrite in a neutral medium. In the presence of an acid, the solution of a tetrathionate became yellow. For this reason the amount of tetrathionate was not determined in the above experiments as all the methods recommended for the estimation of tetrathionates involve the use of an acid. The production of a transitory yellow colour is not peculiar to thiosulphates in the presence of an acid and a nitrite as stated by Falcoila.[11]

The Action of Hydrogen Sulphide on Nitrous Oxide

It appears from the results given in Tables II, III and IV that nitric oxide can be reduced through nitrous oxide to nitrogen. To confirm this pure nitrous oxide was collected over hydrogen sulphide solutions in the nitrometer N (Fig. 4) in the presence of water. An analysis of the residual gases after 30 hours is given in Table XIII. Quantitative reduction of nitrous oxide to nitrogen was recorded in both experiments.

TABLE XIII

An Analysis of the Gas which results when Nitrous Oxide reacts with Hydrogen Sulphide Solutions

	Vols. of the gas c.c.	Vol. of H_2 c.c.	Vol. after combustion c.c.	N_2 c.c.	N_2 %
i.	20.4	32.4	52.6	20.4	100
ii.	20.0	32.0	52.2	20.4	100

The liquid phase contained sulphur and readily gave tests for ammonia. This reaction is under further investigation.

The Action of Hydrogen Sulphide on Solutions of Ammonium Nitrite

Bagster[13] observed that hydrogen sulphide acts slowly upon ammonium nitrite converting it into ammonia. Small quantities of nitrogen are also evolved when solutions of ammonium nitrite are kept in contact with hydrogen sulphide for a number of days. The residual gases consisted of nitrogen only.

Summary and Discussion

1). Nitric oxide reacts with hydrogen sulphide solution giving ammonium thiosulphate, ammonium nitrite, sulphur, nitrous oxide and nitrogen.

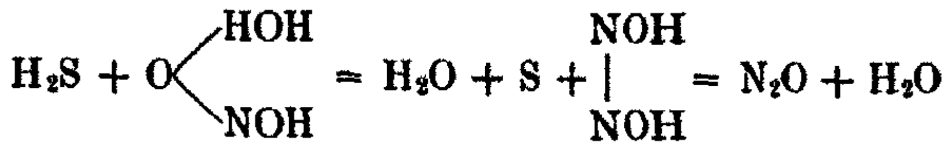
2). Ammonium sulphide solution is decomposed by nitric oxide forming polysulphides of ammonium and small amounts of ammonium thiosulphate and nitrous oxide and nitrogen are evolved. Excess of the reducing agent gives pure nitrogen but excess of the oxidising agent increases the yield of nitrous oxide.

3). Saturated hydrogen sulphide solution completely reduces nitrous oxide to nitrogen and ammonia.

4). Nitric oxide slowly converts dilute solutions of ammonium thiosulphate into ammonium sulphate. Small quantities of nitrogen are formed.

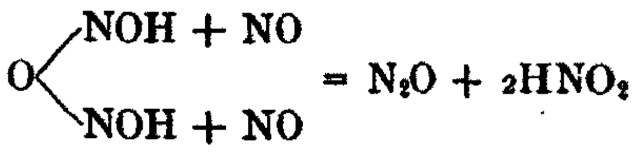
5). Bagster observed that hydrogen sulphide slowly converts ammonium nitrite into ammonia. It has been shown that small amounts of nitrogen are also evolved.

Pierce stated that dry hydrogen sulphide and dry nitric oxide react giving nitrogen and not nitrous oxide. The formation of nitrous oxide is probably due to the water present. Zimmermann[14] observed that aqueous solutions of nitric oxide have a greater conductivity than pure water. He considered that the solution is in part a chemical process giving ionisable substances one of which is possibly Angeli's acid $H_2N_2O_3$ (i. e., $H_2O + 2NO$), derivatives of which are known and which, upon acidification, give nitric oxide. This Angeli's acid may be supposed to react upon hydrogen sulphide.[4]

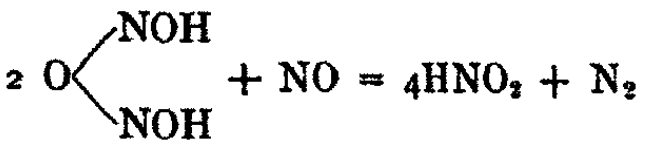


$$H_2S + O\left\langle\begin{matrix}HOH\\ NOH\end{matrix}\right. = H_2O + S + \begin{matrix}NOH\\ |\\ NOH\end{matrix} = N_2O + H_2O$$

Previous investigators[15] have found that nitric oxide with water gives not only nitrous acid and nitrous oxide but also nitrogen. Assuming Angeli's acid as an intermediate compound, their formation may be expressed by the equations:[16]



$$O\left\langle\begin{matrix}NOH + NO\\ NOH + NO\end{matrix}\right. = N_2O + 2HNO_2$$



$$2\ O\left\langle\begin{matrix}NOH\\ NOH\end{matrix}\right. + NO = 4HNO_2 + N_2$$

F. Hefti and W. Schidt[17] found that hydrogen sulphide reacts with nitrous acid to give thiosulphate, sulphur and ammonia. This leads directly to the conclusion that nitrous acid may be the source of all the products obtained by experiment. Bagster has reported the formation of nitrous oxide and nitrogen from the same reaction.

Evidence of the hydration of nitrous oxide to hyponitrous acid is given by Nichols and Derbigney[18] who show a great increase in conductivity of distilled water when nitrous oxide is dissolved in it. The subsequent reduction of the hyponitrous acid by reducing agents probably plays an important part in controlling the amounts of the final products of the reduction of nitric oxide and nitrous oxide:

$$N_2O + H_2O = H_2N_2O_2\text{—reduction}\rightarrow\left[\begin{matrix}2H_2O + N_2\\ 2NH_3 + 2H_2O\end{matrix}\right.$$

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[1] Pierce: J. Phys. Chem., 33, 22 (1929).

[2] Handbuch der anorganische Chemie, 2, 256 (1907).

[3] I. Thiele: Ann., 253, 246 (1889).

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[6] Bowman and Scott: J. Ind. Eng. Chem. **7**, 766 (1915); Cumming and Kaye: "Quantitative Analysis," 84, (1928).

[7] Dunnicliff and Mohammad: loc. cit., pp. 1345 and 1354 (1929).

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RAMAN EFFECT IN THE ULTRAVIOLET REGION

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The Raman spectra of organic substances have recently been the subject of a large number of investigations. The comprehensive papers of Dadieu and Kohlrausch deserve special mention in this connection. These authors have attempted to correlate Raman lines corresponding to various frequency shifts with the characteristic vibration between the different parts of a molecule. Thus for example a Raman shift of 2900-2950 cm^{-1} is ascribed to the vibration between (C-H) a carbon and a hydrogen atom in an aliphatic compound. The importance of such attempts to find out the frequency of vibration between different parts of a molecule for an accurate elucidation of molecular structure can easily be appreciated.

The investigations have mostly been carried out in the visible region of the spectra and the exciting lines have mostly been the following wavelengths in the spectra of mercury lamp:—4358.3, 4347.5, 4339.2, 4108.1, 4077.8 and 4046.8 Ångstroms. The results are in some cases of doubtful accuracy as regards the exact magnitudes of Raman shifts, because of the want of monochromacy in the exciting radiations. In some recent investigations by the students of Raman an attempt has been made to use monochromatic radiations having wavelengths 4358.3, 4347.5 and 4339.2 Å.U. by circulating a solution of didymium chloride round the liquid under excitation.

In the ultraviolet spectrum from a quartz mercury lamp there are two strong lines 3131.7 and 3125.7 of comparable intensities and the nearest strong lines from these, are 3341.5 Å.U. and 3021.5 Å.U. with a frequency difference of 2000 and 1000 cm^{-1}, approximately. The Raman lines due to the scattering of these two wavelengths by a liquid can be easily picked out because there would be a constant frequency difference of 61.5 cm^{-1}. Hence the Raman shifts produced by a liquid exposed to radiation could be unequivocably determined. Apart from this intrinsic interest in the investigation of Raman effect by ultraviolet light from a mercury lamp, it was hoped that new lines which were too feeble when produced by longer wavelengths might be detected in scattering due to shorter wavelengths. In this paper are described the results of an investigation on Raman radiation in the ultraviolet produced by the following substances, the references referring to work on the Raman spectra in the visible:—

(1) Water,[1] Methyl alcohol.[2]

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[1] Daure: Compt. rend., 186, 1833 (1928); Rao: Ind. J. Phys., 3, 123 (1928); Venkateswaren and Karl: Z. Physik, 3, 123 (1928).

[2] Venkateswaran and Karl: Z. physik. Chem., B. 1, 466 (1928); Ganesan and Venkateswaran: Ind. J. Phys., 4, 195 (1929).

(2) Formic acid, Ethyl formate,[3] Sodium formate, Acetic acid,[4] Ethyl acetate,[5] Sodium acetate,[6] Ethyl benzoate,[7] Benzoic acid, Sodium benzoate, Trichloroacetic acid, Sodium trichloroacetate, Monochloroacetic acid, Sodium monochloroacetate, Malonic acid, Sodium malonate and Ethyl malonate.[8]

Experimental Method

Preparation of pure substances:—It is of importance that the substances to be used should be chemically the purest available. In most cases Merck's extra-pure substances were taken for the purpose and in some cases also Kahlbaum's pure chemicals. They were purified by repeated distillations until they were very clear, free from dust and other fluorescent impurity.

The method of illumination is similar to that advocated by Wood.[9] A quartz tube with two side tubes and flat ends fused into it was used for containing the liquid under investigation. The tube was placed horizontally in front of the slit of the quartz spectrograph and was immersed in water contained in a glass tank with two quartz windows.

The open ends of the side tubes were always above the water level. A horizontal quartz mercury lamp was suspended above the glass tank, as close to the quartz tube as possible. The water in the glass tank was frequently renewed. The slit of the spectroscope was shielded from direct illumination by the quartz lamp by suitable screens and practically the whole of the light that entered the spectrograph was due to scattering at right angles.

The spectrum of the scattered light was photographed with a Hilger E_2 quartz spectrograph using Ilford Isozenith plates (H and D 700). The time of exposure varied from three to five hours for different substances. In order however to obtain the fainter details, exposure of ten to twelve hours was given.

The wavelengths of the lines appearing in the spectrogram were calculated with a Hilger travelling micrometer. Hartmann's simplified interpolation formula $\lambda = \lambda_0 + \frac{c}{n - n_0}$ was used with the neighboring mercury lines as standards of reference. The Raman lines falling on the incident mercury lines are not measured.

Experimental Results

In Table I are given the wavelengths, the corresponding frequencies expressed as wave numbers per cm. in vacuum and the notations of the exciting mercury lines.

Raman spectrum of redistilled water. The Raman spectrum of water has been investigated by a large number of workers in the visible region and is

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[3] Pal and Sen Gupta: Ind. J. Phys., **5**, 13 (1930); Dadieu and Kohlrausch: Sitzungsber. Akad. Wiss. Wien., **138**, 41 (1929).

[4] Dadieu and Kohlrausch: loc. cit.; Venkateswaran: Phil. Mag., **7**, 597 (1929); Ganesan and Venkateswaran: Ind. J. Phys. **4**, 195 (1929).

[5] Dadieu and Kohlrausch: loc. cit.

[6] Dadieu and Kohlrausch: Sitzungsber. Akad. Wiss. Wien., **138**, 635 (1929).

[7] Dadieu and Kohlrausch: Sitzungsber. Akad. Wiss. Wien, **138**, 799 (1929).

[8] Dadieu and Kohlrausch: loc. cit.; Pal and Sen Gupta: Ind. J. Phys., **5**, 73 (1930).

[9] Phil. Mag., **6**, 729 (1928).

TABLE I

λ in I.A.	4358.34	4347.50	4339.23	4108.08	3077.83
ν in cm.$^{-1}$	22938	22995	23039	24335	24516
Notations	e	f	g	h	i
λ in I.A.	4046.56	3983.96	3906.40	3663.28	3654.83
ν in cm^{-1}	24705	25094	25592	27290	27353
Notations	k	l	m	o	p
λ in I.A.	3650.15	3341.48	3131.7 (mean)	3125.66	3021.50
ν in cm^{-1}	27388	29918	31922	31984	33087
Notations	q	r	s	t	u
λ in I.A.	2967.28	2925.41	2893.60	2803.48	2752.78
ν in cm^{-1}	33691	34173	34549	35660	36316
Notations	v	w	x	y	z
λ in I.A.	2652.04 (group)				
ν in cm^{-1}	37673 (mean)				
Notations	z_1				

characterised by its broad bands. In the ultraviolet region it behaves in a manner very similar to that of the visible region.

The most conspicuous band is the one shifted from the exciting lines 3132 and 3126 by about 3400 wave-number and extends from λ3524.3 to 3479.0. Even on close examination the surface of the band is very difficult to ascertain but however it exhibits more or less well defined edges. The central portion of the band is of maximum intensity and is at a distance of 3444 wave-numbers from the exciting lines.

TABLE II

Methyl alcohol—CH_3OH

Wave No. of the Raman lines (Vac.)	I	Exciting lines and Δν	Wave No. of the Raman lines (Vac)	I	Exciting lines and Δν
28979	2	s-2943	30952	4	t-1032
29042	0	t-2942	31606	2b	x-2943
30143	5d	u-2944	31714	1	x-2835
30255	5	u-2832	32621	0	?
30458	3	s-1464	32708	2	w-1465 (y)
30519	3	t-1465	32814	2	w-1359
30737	5b	t-1247 v-2954	33372	1	z-2944
30858	5vb	v-2833	34732	2vb	z_1-2941
Line corresponding to s merged into 30858			34844	2vb	z_1-2829

Δν 1032 (4); 1247 (0); 1359 (2); 1465 (3); 2832 (5); 2943 (5d).

Another faint band appears from λ3327.76 to λ3287.44, probably excited by the line 2967.3.

Note:—In the tables that follow the abbreviations used are given below—d—diffuse, b—broad, vb—very broad. It appears at first sight strange that a strong Raman line 30952 cm^{-1} produced by t should be unaccompanied by a line due to s. A closer examination will show that the line 30858 is a very broad one and contains in it unresolved a Raman line having frequency difference 1032 cm^{-1} from the s line.

TABLE III

Sodium formate—HCOONa

This substance was studied in a conc. aqueous solution.

Wave No. of the Raman lines (vac)	I	Exciting lines and $\Delta\nu$	Wave No. of the Raman lines (vac)	I	Exciting lines and $\Delta\nu$
21593	3	e-1345	30641	3	t-1343
21886	1	e-1052	30865	1	v-2826
21962	0	e- 976	31725	1	s- 197
30263	1	u-2824	31789	1	t- 195
30579	3	s-1343			

$\Delta\nu$: 196 (1); 976 (0); 1052 (1); 1344 (3); 2825 (1).

TABLE IV

*Ethyl formate—$HCOOC_2H_5$

Wave No. of the Raman line (vac)	I	Exciting line and $\Delta\nu$	Wave No. of the Raman line (vac)	I	Exciting line and $\Delta\nu$
21226	3	e-1712	23693	3	k-1012
21483	3	e-1455	23865	4	k- 840
21563	3	e-1375	24150	1	m-1442
		i-2953	24411	1	p-2942 (q)
21737	5	k-2968	30155	1d	u-2932
21775	6	k-2930	30477	0	s-1445
21840	1	e-1098	30542	0	t-1442
21940	1	e- 998	30763	2b	ν-2928
22104	2	e- 834	30926	0	s- 996
22165	1	l-2929 (f)	31085	0	s- 837
22329	1d	e- 609	31150	0	t- 834
22540	0	?	31375	0	u-1712 (t)
22681	1	m-2911	31585	0	x-2964
23259	0	k-1446	31642	0	u-1445
23617	1	k-1088	32677	0	v-1014

$\Delta\nu$: 609 (1d); 836 (4); 997 (1); 1013 (3); 1093 (1); 1375 (3); 1446 (3); 1712 (3); 2932 (6); 2966 (5).

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* The peculiar characteristic of the liquid is that a strong continuous spectrum appears in the visible and ultraviolet region when it is studied in a quartz tube. In the visible region it almost disappears when the quartz tube is replaced by a glass one. Owing to the presence of this continuous spectrum the faint Raman lines in the ultraviolet region can not be studied.

Formic acid—HCOOH. This liquid has been investigated by various workers in the visible region. Attempts were made to investigate it in the ultraviolet but the experiments were not successful as formic acid decomposes by the ultraviolet rays.

Table V

Sodium Acetate—CH_3COO-Na

(concentrated aqueous solution)

Wave No. of the Raman lines (vac)	I	Exciting line and Δν	Wave No. of the Raman lines (vac)	I	Exciting line and Δν
30510	2	s-1412	30763	2	v-2928
The line with shift 1412 excited by t remains unresolved with the line below.			31002	0	s- 920
30557	2	s-1345	31061	0	t- 923

Δν : 922 (0); 1345 (0); 1412 (2); 2928 (2);

Table VI

Ethyl Acetate—$CH_3COOC_2H_5$

Wave No. of the Raman lines (vac)	I	Exciting line and Δν	Wave No. of the Raman lines (vac)	I	Exciting line and Δν
28990	8	s-2932	30814	2	s-1108
29051	8	t-2933	30874	2	t-1110
30133	4d	u-2954	31070	2	s- 852
30177	3	s-1745	31133	2	t- 851
30240	3	t-1744	31278	3	s- 644
30462	4	s-1460	31339	3	t- 645
30526	4	t-1458	31539	3	s- 383
30704	4	v-2987	31600	3	t- 384
30754	7	v-2937	32698	0	u- 389

Δν : 385(3); 645(3); 852(2); 1109(2); 1459(4); 1745(3); 2934(8); 2954(4d); 2987(4).

Benzoic acid in methyl alcohol. This liquid has been investigated by Dadieu and Kohlrausch[1] in the visible region. Attempts were made to investigate it in the ultraviolet region but without success, as the substance being highly fluorescent absorbs the ultraviolet rays.

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[1] Sitzungsber. Akad. Wiss. Wien., **138**, 799 (1929).

TABLE VII

Acetic acid—CH_3COOH

Wave No. of the Raman lines (vac)	I	Exciting line and Δν	Wave No. of the Raman lines (vac)	I	Exciting line and Δν
28979	5	s-2943	30747	4	v-2944
29040	5	t-2944	31033	4	s- 889
30145	3	u-2942	31096	4	t- 888
30250	2	s-1672	31300	2	s- 622
30314	2	t-1670	31364	2	t- 620
30486	0	s-1436	31617	2vb	t- 367 x-2932
Very feeble line, not measurable and may be due to t.			31696	0	t- 288?
			32689	1	v-1002
30646	0	s-1276	32803	2	v- 888

Δν : 288(0); 367(0); 621(1); 888(4); 1002(1); 1276(0); 1436(0); 1671(2); 2943(5).

TABLE VIII

Ethyl Benzoate—$C_6H_5COO\text{-}C_2H_5$

This liquid being highly fluorescent can not be investigated in the ultraviolet region

Wave No. of the Raman lines (vac)	I	Exciting line and Δν	Wave No. of the Raman lines (vac)	I	Exciting line and Δν
21216	7	e-1722	Here the Raman lines excited by p and 9 with 3075 have fallen on an incident Hg line which has become very broad.		
21336	10	e-1602			
21485	2b	e-1453			
21640	10b	e-1298 (k)			
21729	4b	k-2976 (f)			
21835	3	e-1103			
21939	7	e- 999	25685	5	o-1605
22087	3	e- 851	25748	4	p-1605
22323	3	f- 672	25784	8	q-1604
22609	3	e- 329	26016	4	o-1274
22747	3	e- 191	26078	4	p-1275
23099	6	k-1606	26115	7	q-1273
23484	4	i-1032	26507	3	p- 846
23538	4b	k-1167	26543	3	q- 845
23596	3	k-1109	The Raman line due to o with shift 618 coincides with Hg line		
23696	10	k-1009			
23855	6	k- 850			
24088	5	k- 617	26735	1	p- 618
24215	3	o-3075	26773	3	q- 615

Δν : 191 (3); 329 (3); 617 (5); 672 (3); 848 (6); 1004 (10); 1032 (4); 1106(3); 1167 (4b); 1274 (7); 1298 (10b); 1453 (2b); 1604 (10); 1722 (7); 2976 (4b); 3075 (3).

Table IX

Sodium benzoate—C_6H_5-COONa

This substance is studied in a concentrated aqueous solution

Wave No. of the Raman lines (vac)	I	Exciting line and $\Delta\nu$	Wave No. of the Raman lines (vac)	I	Exciting line and $\Delta\nu$
28855	3	s-3067	30918	4	s-1004
28016	3	t-3068	30981	4	t-1003
30320	6	s-1602	31074	1	s- 848
30382	6	t-1602	31138	1	t- 846
30520	5	s-1402	31304	1	u-1783?
30583	5	t-1401	31484	1	u-1603
30765	2	v-2926			

$\Delta\nu$: 847 (1); 1004 (4); 1402 (5); 1602 (6); 2926 (2); 3068 (3).

Table X

Sodium malonate—NaOOC-CH_2-COONa

(Concentrated aqueous solution)

Wave No. of the Raman lines (vac)	I	Exciting line and $\Delta\nu$	Wave No. of the Raman lines (vac)	I	Exciting line and $\Delta\nu$
30154	0	u-2933	30548	0	s-1374
30301?	00		30675	0	s-1247(t)

$\Delta\nu$: 1374 (0); 1247 (0); 2933 (0).

Table XI

*Malonic acid—COOH-CH_2-COOH

(Concentrated aqueous solution)

Wave No. of the Raman lines (vac)	I	Exciting line and $\Delta\nu$	Wave No. of the Raman lines (vac)	I	Exciting line and $\Delta\nu$
30244	od	t-1740	31075	0	t- 909
30756	2	v-2935	31353	1	u-1734
31023	0	s- 907	32731	1	v- 960 (u- 356)

$\Delta\nu$: 908 (0); 960 (1); 1737 (1); 2935 (2).

* The faint Raman lines in malonic acid cannot be studied owing to the presence of strong continuous spectrum.

Table XII

Ethyl malonate—C_2H_5-COO-CH_2-COO-C_2H_5

Wave No. of the Raman lines (vac)	I	Exciting line and $\Delta\nu$	Wave No. of the Raman lines (vac)	I	Exciting line and $\Delta\nu$
28984	2vb	?	30533	1	t-1451
30147	0	u-2940	30719	0	v-2972
30469	1	s-1453			

$\Delta\nu$: 1452 (1); 2940 (0); 2972 (0).

TABLE XIII

*Sodium trichloroacetate—CCl_3COONa
(Concentrated aqueous solution)

Wave No. of the Raman lines (vac)	I	Exciting line and Δν	Wave No. of the Raman lines (vac)	I	Exciting line and Δν
22518	4	e- 420	24280	1	k- 425
22658	2	e- 280	31500	1	s- 422
23773	2	i- 743	31563	1	t- 421
23852	1	i- 664			

Δν: 280 (2); 422 (4); 664 (1); 742 (2).

* Trichloroacetic acid, its sodium salt and monochloracetic acid, its sodium salt (Tables XIII-XVI) are all investigated in the visible region with a glass plate in between the mercury lamp and the quartz tube.

TABLE XIV

Trichloroacetic acid—CCl_3COOH
(Concentrated aqueous solution)

Wave No. of the Raman lines (vac)	I	Exciting line and Δν	Wave No. of the Raman lines (vac)	I	Exciting line and Δν
22102	1	e- 836	24275	3	k- 430
22240	1	f- 755	31508	4	s- 414
22508	4	e- 430	31570	4	t- 414
22652	2	e- 286			
		k- 842	31658	2	s- 264
23863	2	i- 653	31721	2	t- 263
24143	1	m-1449			

Δν: 264 (2); 286 (2); 414 (4); 430 (4); 653 (2); 755 (1); 836 (1); 1449 (1).

TABLE XV

Monochloroacetic acid—$CH_2ClCOOH$
(Concentrated aq. solution)

Wave No. of the Raman lines (vac)	I	Exciting line and Δν	Wave No. of the Raman lines (vac)	I	Exciting line and Δν
21514	0	e-1424	30200	1	s-1722
21745	2	k-2960	30264	1	t-1720
22132	2	e- 806	30500	0	s-1422
23901	1	k- 804(s)	30709	1	v-2982
23992	0	m-1600 (l-1102)	31117	3	s- 805
28960	5	s-2962	31178	3	t- 806
29022	5	t-2962	31490	0	s- 432
30124	2	u-2963	31550	0	t- 434

Δν: 433 (0); 805 (3); 1423 (0); 1600 (0); 1721 (1); 2962 (5); 2982 (1).

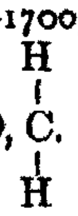
TABLE XVI

Sodium monochloroacetate—CH_2Cl-COONa
(Concentrated aq. solution)

Wave No. of the Raman lines (vac)	I	Exciting line and $\Delta\nu$	Wave No. of the Raman lines (vac)	I	Exciting line and $\nabla\nu$
21565	1	i-2951	30133	1d	u-2954
21756	1	k-2949	30518	2	s-1404
22160	0	e- 778	30582	2	t-1402
23782	1	k- 923(i)	31132	1	s- 790
23927	1	k- 778	31193	1	t- 791
28970	2d	s-2952	31681	0	u-1406
29031	2d	t-2953			

$\Delta\nu$: 778 (1); 791 (1); 923 (1); 1404 (2); 2952 (2d).

Discussion of Results

Dadieu and Kohlrausch have ascribed the frequency shifts 2900-3000, 1600-1700, 1350-1450 respectively to the following vibration bonds —C—H, C=O,  $\overset{H}{\underset{H}{C}}$. Most of the lines whose frequency shifts are less than 1070 are due to vibration between the radicals forming the molecule. Thus the frequency shifts between 1000-1070 are supposed to be due to the vibration between the CH_3 or OH group against a residual group containing CH_2. The frequency shifts between 700 and 1000 are due to vibration between two parts of an organic molecule at C-C linkage. These suggestions are very interesting but they still lack convincing proof. Some of the results described here do not support in its entirety the hypothesis of Dadieu and Kohlrausch. For example formic acid, sodium formate and sodium benzoate give frequency shifts lying between 1340-1405 though they do not contain a CH_2 linkage. It is very probable that this frequency shift may be also due to a C-(OH) vibration. Again the frequency shifts 1600-1700 are given by all acids containing COOH group, except trichloroacetic acid which is a strong acid. The sodium salts of all the acids studied here do not give the frequency shift 1600-1700 though they all contain the C=O linkage. Only in the case of sodium acetate a very faint line having frequency shift 1649 (I=00) have been observed by Dadieu and Kohlrausch. This is most probably due to the presence of a trace of free acetic acid due to hydrolysis. It is clear therefore that the frequency shift 1600-1700 is suppressed when the C=O linkage forms part of a negative ion (the frequency shift 1602 in sodium benzoate is due to the benzene ring.)

Kohlrausch and Dadieu calculate 832 cm^{-1} as the frequency for the vibration C-Cl. Bhagavantam and Venkateswaran found 750 cm^{-1} in the Raman spectra of all organic compounds containing chlorine with the exception of isopropyl chloride. In trichloracetic acid we find both the shifts 836 cm^{-1} and 755 cm^{-1} while in its sodium salt only the frequency shift 743 cm^{-1} is observed. In mono-chloracetic acid we obtain the frequency shift 805 cm^{-1}, but in sodium salt the shift is somewhat less, 778, 791. This diminution in the frequency shifts as we pass from the halogen substituted acids to their sodium salts is rather remarkable.

It is noteworthy that under the influence of ultraviolet rays between 2000 and 3000 Å, formic acid undergoes decomposition, and the halogen substituted acids undergo hydrolysis. We have not been able to observe any Raman shift by scattering of mercury lines of wave-length greater than 3000 Å from these substances, when the exciting light also contained wave-lengths between 2000-3000 Å. If the radiations between 2000-3000 Å from a quartz mercury lamp are removed by the interposition of a glass plate, Raman shifts characteristic of these substances by the scattering of mercury lines of lower wave-lengths are observed. We are therefore led to the conclusion that a molecule cannot produce Raman lines by scattering light of a lower frequency if it is simultaneously exposed to high frequency radiations which are capable of decomposing it. Further investigations on this point are in progress.

Chemical Laboratory,
University of Dacca,
November 15, 1930.

STUDIES ON PHOSPHORIC ACID*

IV. Oxonium Salts of Ortho Phosphoric Acid with Certain Organic Compounds

BY G. BROOKS KING[1] AND JAMES H. WALTON

The purpose of this investigation was to study the formation of oxonium salts of phosphoric acid with various organic compounds, further, to make a comparison of phosphoric and sulfuric acids with regard to their ability to form addition compounds with organic substances.

The present work was suggested by an investigation in this laboratory by Walton and Kepfer[2] in which the solubility of several organic acids in solutions of ortho phosphoric acid was studied. Using solutions of phosphoric acid of various concentrations they found indications of compound formation with the following organic acids: oxalic, succinnic, malic, citric and iso-valeric. The solubility of phenol was also determined and a compound indicated. No attempt was made to determine the composition of these compounds. It was of interest to investigate the formation of these substances by means of a phase rule study of the freezing point curves of mixtures of the pure components.

A phase rule study of phosphoric acid with other compounds is mentioned only a few times in the literature and only one case was found where an organic compound was used as one of the components. Rabinow and Jakubsohn[3] determined the freezing point curves of mixtures of phosphoric acid with ethyl ether and found that two compounds were formed; $(C_2H_5)_2O \cdot 6H_3PO_4$ and $(C_2H_5)_2O \cdot 4H_3PO_4$. However, numerous compounds of phosphoric acid and organic compounds have been isolated by Klages,[4] Allendorf,[5] Raikow[6] and others.

Kendall and Carpenter[7] studied the addition compounds of sulfuric acid with organic substances by means of freezing point curves, with a view of getting some insight into the probable mechanism of various sulfonation reactions. Kendall concluded that the greater the difference in acidic strength between two substances, the greater the tendency for addition compound formation. Kendall regards such addition compounds as true oxonium salts, of the following type:

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*Contribution from the Laboratory of General Chemistry of the University of Wisconsin.

[1] The material presented here is a portion of that to be used by G. B. King in his dissertation to be presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Wisconsin.

[2] J. Phys. Chem., **34**, 543 (1930).

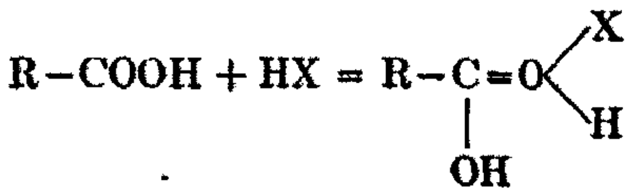
[3] Z. anorg. Chem., **129**, 55 (1923).

[4] Ber., **35**, 2313-2315 (1902).

[5] Ber., **31**, 1298-1301 (1898).

[6] Chem. Ztg., **24**, 367 (1900); **25**, 1134 (1901).

[7] J. Am. Chem. Soc., **36**, 2498 (1914).



$$R-COOH + HX = R-\underset{\displaystyle OH}{\underset{|}{C}}=O\begin{matrix}\diagup X\\ \diagdown H\end{matrix}$$

In the present work a similar study has been made with ortho phosphoric acid and organic substances.

Experimental

Pure ortho phosphoric acid was prepared and dried according to the Ross and Jones[8] method, modified by Walton and Weber.[9] The acid so prepared gave a melting point of 42.5° and 42.6°, taking as the melting point the temperature at which the last crystal disappeared when the temperature was slowly raised. By supercooling some of the fused acid to 40° and then seeding, the acid crystallized and the temperature rose to 42.3°. As this method was used in taking freezing points the above value, 42.3°, was taken as the freezing point of pure ortho phosphoric acid and this value was used in plotting the curves.

Most of the organic compounds used in this investigation were those prepared by Eastman, and in only a few cases was any special purification necessary.

The method of experimentation in the present work is essentially that used by Kendall and his collaborators in their study of freezing point curves. However a freezing point was taken rather than a melting point, as the latter proved unsatisfactory in this work due to the very viscous nature of the phosphoric acid. A Beckmann freezing point apparatus was employed consisting of a 1" × 8" hard glass test tube fitted with a rubber stopper, thermometer, stirrer, and a tube for the passage of dry air. A tube with a side arm was employed when the material to be added was a solid. This freezing tube was fitted into a larger test tube which served as a jacket.

Phosphoric acid was weighed out as rapidly as possible in a stoppered weighing bottle and introduced into the freezing tube. Dry air was passed over the mixture in the freezing tube at all times except in the case of benzaldehyde when dry hydrogen was used. The organic substance, if a solid, was introduced into the tube in the form of pills; if a liquid it was weighed out in a weighing pipette and introduced directly into the top of the freezing tube. The solution after being thoroughly stirred was cooled slowly until the solid phase began to separate; in most cases it was necessary, however, to seed the solution. As the solid phase began to separate the temperature rose slightly and the highest temperature was taken as the freezing point of that particular mixture. An approximate freezing point was first run in each case so as to regulate the bath to an appropriate temperature. Freezing points taken by this method must necessarily be slightly low because of supercooling.

Because supercooling was very marked experimental difficulties were very great in the examination of these systems especially near the eutectic on

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[8] J. Am. Chem. Soc., 47, 2165 (1925).

[9] Unpublished results.

the phosphoric acid side of the system; moreover the mixture would sometimes solidify to a jelly-like mass with no definite point of fusion and it was necessary to remelt and repeat the operation until crystallization took place. This latter difficulty was encountered when supercooling was most marked. In some systems where the freezing point of the mixture was low the phosphoric acid became very viscous and stirring produced minute air bubbles which rendered the solution turbid, making it impossible to detect the formation of minute crystals. In such cases the solution was seeded, cooled, and the lag in temperature, which was always followed by a slight rise, carefully noted. This gave a means of obtaining freezing points in the region of the eutectic with a fair degree of accuracy. As the percentage of phosphoric acid was decreased the freezing point was more definite after the eutectic was passed and the supercooling less marked. Points in the region of the maxima on all curves were very definite but the points in the region of the eutectic are not accurate to more than a degree. In some cases the solutions became so deeply colored that an examination was impossible. If a compound with a congruent melting point is formed in a two component system, a maximum appears in the curve, and from this maximum the melting point and composition of the compound can be obtained.

Tabulation of Results

I. ACIDS.

1. *Acetic acid:* the compound $CH_3COOH \cdot H_3PO_4$ was obtained; stable at its maximum; melting point 33.8°. The compound is white and crystallizes very readily. Some of the crystals were separated from the mixture and gave a melting point slightly lower than the one recorded above. See Fig. 1, Curve II.

Solid phase H_3PO_4

% H_3PO_4	100	90.8	85.9	84.9
F. T.*	42.3	27.0	14.8	14.0

*Freezing temperature.

Solid phase $CH_3COOH . H_3PO_4$

% H_3PO_4	80.0	77.4	74.8	73.1	72.5	67.5	64.4
F. T.	18.9	21.7	25.6	27.9	29.6	32.7	32.7
% H_3PO_4	63.6	57.4	56.7	51.0	42.6	38.0	
F. T.	33.8	31.6	32.7	30.3	23.0	14.5	

2. *Propionic acid:* no compound was indicated in this system in the region studied. The runs were not carried below −3°.

Solid phase H_3PO_4

% H_3PO_4	100	90.6	84.5	82.4	78.1	74.6	73.0	70.4
F. T.	42.3	33.2	26.3	20.3	12.7	6.2	2.0	−2.(±1°)

3. *n-Butyric acid:* no compound was indicated in the region studied.

Solid phase H_3PO_4

% H_3PO_4	100	87.7	77.8	70.0
F. T.	42.3	34.2	25.8	16.5

On adding more butyric acid the mixture froze around 0° solidifying to a jelly without any definite point of fusion. The runs were discontinued at this point.

4. *n-Caproic acid:* no compound was found in this system. A mixture of the two components was light brown in color.

Solid phase H_3PO_4

% H_3PO_4	93.8	88.6	80.0	72.5	66.4	61.5	56.7	53.9
F. T.	40.9	39.9	38.2	35.8	32.8	30.4	23(±1°)	24.0

5. *Benzoic acid:* no compound was obtained from this system. After the addition of about fifteen per cent benzoic acid, separation into two layers took place and the temperature of fusion remained constant. Also the acid sublimed so readily that any degree of accuracy was impossible.

Solid phase C_6H_5COOH

% H_3PO_4	99.1	98.1	97.1	96.3	95.4	94.3	92.6	90.0
F. T.	44.0	73.0	84.5	92.7	98.0	101.3	106.0	112.0
% H_3PO_4	87.2	84.9	82.6	20.5	17.2	15.4	6.0	0.0
F. T.	113.8	115.5	115.8	116.4	116.5	116.9	119.0	122.3

6. *Pyruvic acid:* the compound $CH_3COCOOH \cdot H_3PO_4$ was obtained; stable at its maximum; melting point 36.4°. Fig. 1, Curve III.

Solid phase H_3PO_4

% H_3PO_4	100	87.6	82.9	77.1
F. T.	42.3	28.0	21.5	16.6

Solid phase $CH_3COCOOH \cdot H_3PO_4$

% H_3PO_4	70.4	69.1	62.7	61.7	54.3
F. T.	24.(±1°)	26.4	33.6	34.4	36.4
% H_3PO_4	52.9	45.7	38.9	30.0	24.3
F. T.	35.8	35.2	33.7	30.6	26.5

7. Several other acids were used as one component with phosphoric acid. Succinnic acid decomposes slowly when heated with phosphoric acid as is evidenced by a slow effervescence. Tartaric acid deepens to a dark brown color with phosphoric acid. Cinnamic acid reacts vigorously with decomposition. o-Toluic acid is insoluble in phosphoric acid. Oxalic acid decomposes rapidly when heated with phosphoric acid. Malic acid is also decomposed readily.

8. *Monochloro-acetic acid:* no compound was indicated in this system. Fig. 1, Curve IV.

Solid phase H_3PO_4

% H_3PO_4	100	96.0	86.5	76.9
F. T.	42.3	38.8	32.1	26.6

Solid phase $CH_2ClCOOH$

% H_3PO_4	66.0	61.5	60.0	58.2	54.0	51.6	46.4
F. T.	38.4	41.1	43.4	44.3	46.6	47.4	49.7
% H_3PO_4	43.4	43.2	35.3	31.6	26.0		
F. T.	50.8	50.6	52.2	54.2	55.0		

9. *Phenylacetic acid:* no compound with phosphoric acid was indicated in a phase rule study of this system.

Solid phase $C_6H_5CH_2COOH$

% H_3PO_4	87.0	79.0	68.1	64.9	60.0	53.0	44.7	27.8
F. T.	45.1	50.7	56.2	58.1	60.0	62.0	64.2	68.3
% H_3PO_4	17.3	9.6	0.0					
F. T.	70.2	72.0	76.7					

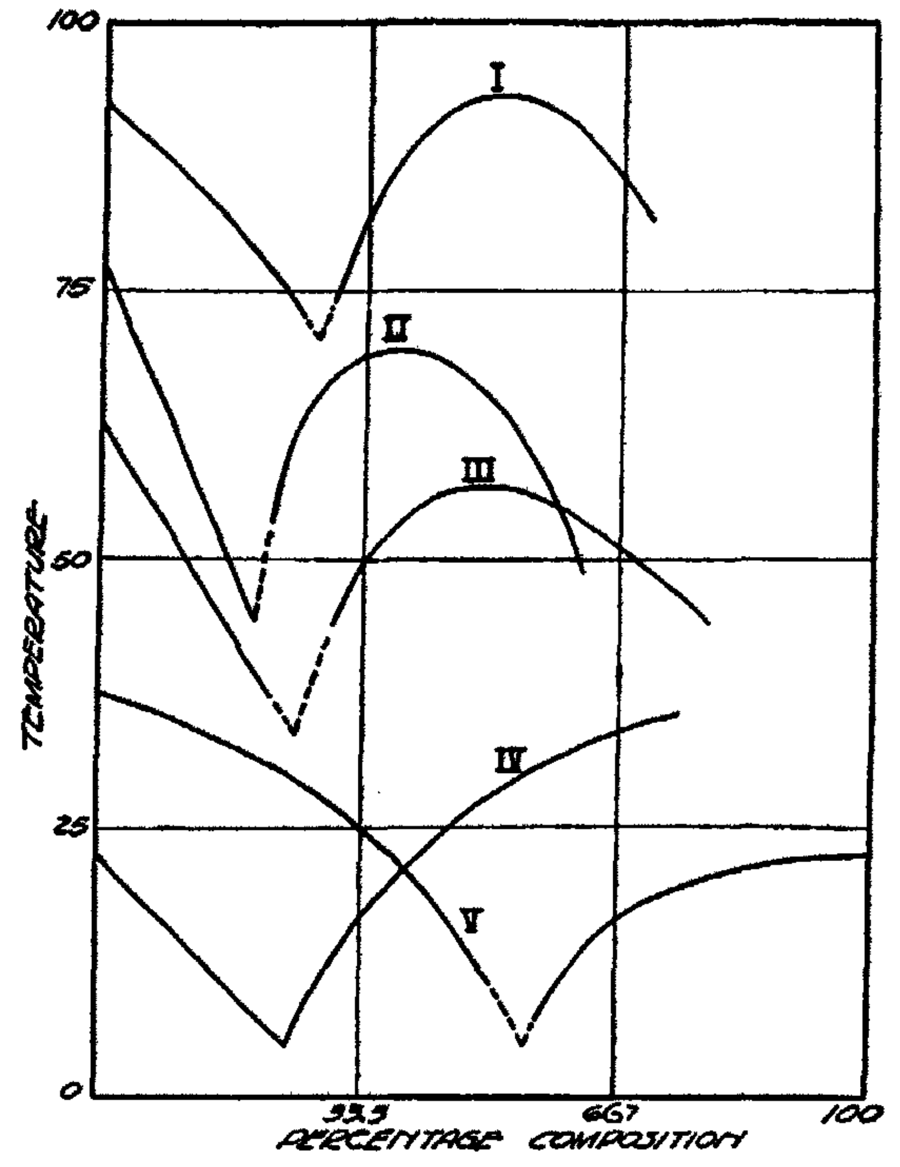

FIG. 1

I. Benzaldehyde and H_3PO_4. Subtract 50 from temp. scale.
II. Acetic acid and H_3PO_4. Subtract 35 from temp. scale.
III. Pyruvic acid and H_3PO_4. Subtract 20 from temp. scale.
IV. Monochloracetic acid and H_3PO_4. Add 20 to temp. scale.
V. Guaiacol and H_3PO_4. Add 5 to temperature scale.

II. ALDEHYDES.

1. *Benzaldehyde:* the compound $C_6H_5CHO \cdot H_3PO_4$ was obtained; stable at its maximum. Melting point 43.0°. The solution of the two components was a light orange in color. Dry hydrogen was passed through the freezing tube at all times to prevent oxidation of the aldehyde. Crystallization was brought about with some difficulty, it being necessary to first freeze the mixture and then preserve a crystal in the upper part of the tube for later crystallization. The freezing point of a mixture which was allowed to stand over

several days varied from that of the original, indicating a probable condensation. Raikow[6] reports the isolation of this compound. Fig. 1, Curve I.

Solid phase H_3PO_4

% H_3PO_4	100	86.0	83.8	76.5	76.0
F. T.	42.3	34.2	32.0	24.9	23.7

Solid phase $C_6H_5CHO \cdot H_3PO_4$

% H_3PO_4	71.3	66.2	65.4	62.5	55.5	54.9	48.0	47.4
F. T.	24.0	31.4	33.6	36.0	40.7	42.6	43.0	42.2
% H_3PO_4	44.7	40.8	35.0	30.7				
F. T.	42.0	40.2	36.3	34.1				

2. *Furfural* which had been freshly distilled, when added to phosphoric acid turned a very dark red, almost black color, rendering an examination of this system impossible.

3. *Anisaldehyde:* the compound $CH_3OC_6H_4CHO \cdot H_3PO_4$ was obtained; stable at its maximum; melting point 83.6°. The mixture of the two components gave a red colored solution.

Solid phase H_3PO_4

% H_3PO_4	100	92.3	90.5	84.7
F. T.	42.3	36.7	34.5	27.5

Solid phase $CH_3OC_6H_4CHO \cdot H_3PO_4$

% H_3PO_4	80.0	77.0	76.0	74.0	72.9	68.0	66.	
F. T.	26(±1°)	40.3	47.6	52(±1°)	52.6	58(±2°)	63(±1°)	
% H_3PO_4	59.2	56.1	52.0	49.5	46.1	43.6	40.0	39.0
F. T.	71(±1°)	74.8	80.5	81.7	83.4	83.4	83.6	83.2
% H_3PO_4	33.0	32.5	30.0	22.0	17.6			
F. T.	81.2	81.5	80.9	76.9	73.7			

III. KETONES.

1. *Benzalacetone:* an examination of this system was impossible as the two components gave a solution almost black in color.

2. *Acetophenone:* the compound $C_6H_5COCH_3 \cdot H_3PO_4$ was obtained; stable at its maximum; melting point 87.9°. Considerable difficulty was encountered on the phosphoric acid side, due to the fact that the solution became a deep green in color and it was difficult to obtain an accurate freezing point. The portion of the curve on the phosphoric acid side before the eutectic was reached is at best only approximate. Klages[4] and Allendorf[5] report the isolation of this addition compound. Fig. 2, Curve I.

Solid phase H_3PO_4

% H_3PO_4	100	99.2	95.8	92.8
F. T.	42.3	40.6	39.0	37.5

Solid phase $C_6H_5COCH_3 \cdot H_3PO_4$

% H_3PO_4	92.5	83.6	76.0	64.4	60.0	55.9	52.3	46.3	41.1
F. T.	36.9	44.8	55.7	73.0	79.3	81.5	87.3	87.9	87.8
% H_3PO_4	33.1	30.0	28.4	22.1	17.6	12.3	3.9	2.4	1.9
F. T.	85.2	83.8	83.5	80.1	77.9	74.5	56.9	52.9	18.7

Solid phase $C_6H_5COCH_3$

% H_3PO_4	0.0
F. T.	18.3

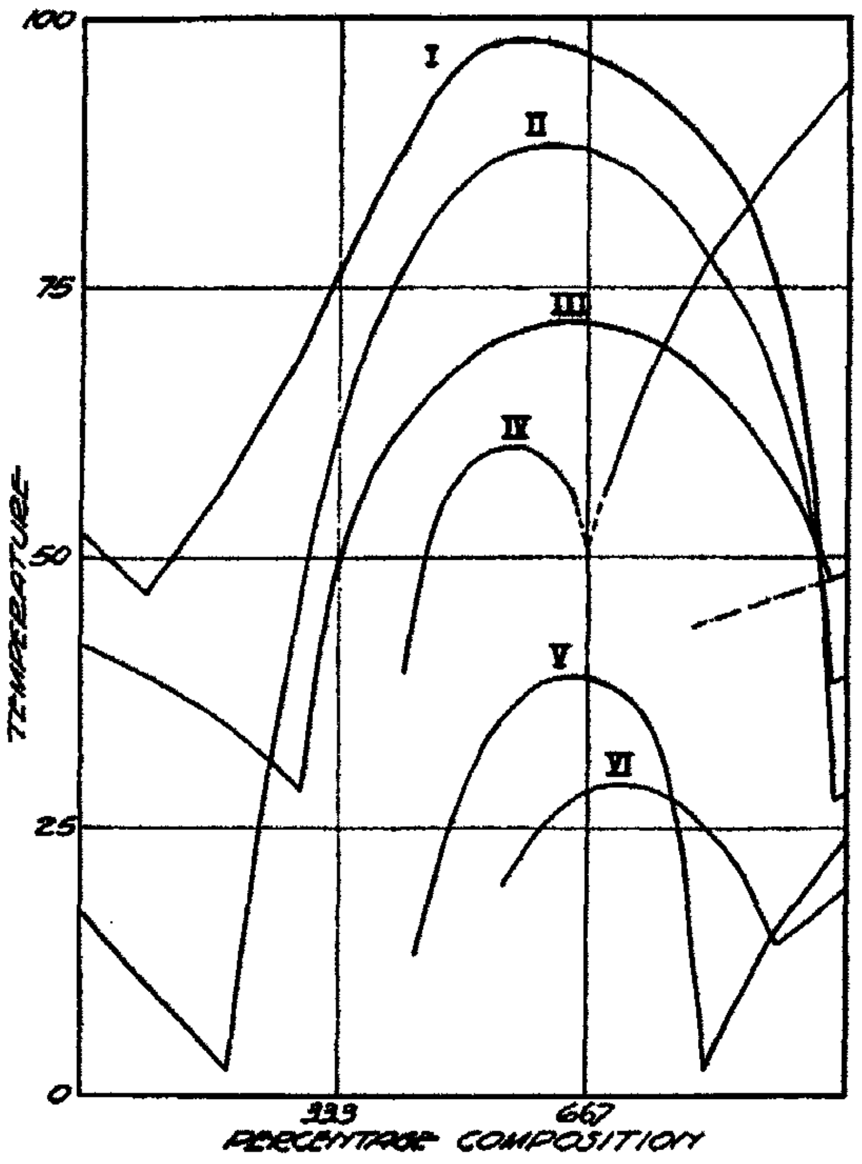

FIG. 2

I. Acetophenone and H_3PO_4. Subtract 10 from temp. scale.
II. Coumarin and H_3PO_4. Add 25 to temperature scale.
III. Benzophenone and H_3PO_4.
IV. *Coumarin and H_2SO_4. Subtract 25 from temp. scale.
V. *Benzophenone and H_2SO_4. Add 25 to temp. scale.
VI. *Acetophenone and H_2SO_4.

* Taken from data of Kendall: J. Am. Chem. Soc., **36**, 2498 (1914).

3. *Benzophenone:* the compound $C_6H_5COC_6H_5 \cdot H_3PO_4$ was found; melting point 71.3°. It was possible to cool below the eutectic of the compound with benzophenone, indicating a metastable state. Fig. 2, Curve III.

Solid phase H_3PO_4

% H_3PO_4	100.	97.6	95.3	93.6	91.5	89.3	88.0	86.0
F. T.	42.3	39.5	39.0	38.5	37.9	37.5	36.7	36.3
% H_3PO_4	84.2	82.3	79.5	76.9	74.3	71.3		
F. T.	35.8	34.9	32.9	32.5	30.1	28.5		

Solid phase $C_6H_5COC_6H_5 \cdot H_3PO_4$

% H_3PO_4	65.9	64.7	63.4	59.6	56.3	52.4	49.4	46.6
F. T.	59.1	57.7	61.0	62.9	64.4	66.1	67.4	68.8
% H_3PO_4	44.2	43.0	40.0	37.0	35.6	32.5	33.0	30.6
F. T.	68.9	70.2	70.9	71.3	71.3	71.0	71.2	70.8
% H_3PO_4	28.0	27.9	24.3	24.1	21.3	21.1	18.1	18.1
F. T.	70.4	70.4	69.6	70.2	69.1	69.0	67.8	66.5
% H_3PO_4	16.3	12.6	9.8	4.1				
F. T.	67.0	65.9	63.4	58.6				

Solid phase $C_6H_5COC_6H_5$

% H_3PO_4	*18.1	*14.2	*6.8	1.7	1.6	0.0
F. T.	43.8	45.4	46.9	47.9	47.8	48.0

* Metastable state.

IV. PHENOLS.

1. *Phenol:* Hoogewerff and van Dorf[10] report the isolation of the compound $C_6H_5OH \cdot H_3PO_4$. From the freezing point curve of the components the composition of the compound can not be determined because of the flatness of the curve, indicating a high degree of dissociation of the compound into its components.

Solid phase $C_6H_5OH \cdot H_3PO_4$

% H_3PO_4	93.4	81.1	73.1	63.5	55.7	45.	36.5
F. T.	67.5	70.2	70.3	70.3	70.3	69.9	69.4

2. *Guaiacol:* no compound was indicated in the study of this system. Good checks on freezing temperatures could not be obtained at the lower temperatures; the solution was very viscous and crystallization slow. Fig. 1, Curve V.

Solid phase H_3PO_4

% H_3PO_4	100	81.1	73.8	68.0	58.7	51.5	
F. T.	42.3	37.0	34.3	31.3	24.1	15.5	
% H_3PO_4	44.9	34.6	25.4	15.8	9.0	4.0	0.0
F. T.	12(±1°)	20.9	24.5	26.5	26.9	27.3	27.5

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[10] Rec. Trav. chim., 21, 349 (1902).

3. Other phenols: p-cresol, naphthol, thymol, p-nitro-phenol were almost completely insoluble in pure phosphoric acid. Although resorcinol was soluble in phosphoric acid, the solution colored so deeply that no examination was made.

V. ANHYDRIDES.

1. *Benzoic anhydride:* the components in this system were only partly miscible. No compound was indicated in the region which could be investigated.

2. *Coumarin:* the compound $C_9H_6O_2 \cdot H_3PO_4$ was obtained; stable at its maximum; melting point 113.4°. Fig. 2, Curve II.

Solid phase H_3PO_4

% H_3PO_4	98.8	96.3	93.8	93.0	90.7	88.8	87.1	84.4	82.2
F. T.	39.8	37.1	35.0	33.7	32.3	30.9	29.3	26.6	27.7

Solid phase $C_9H_6O_2 \cdot H_3PO_4$

% H_3PO_4	80.0	78.4	76.2	68.8	62.8	56.5	50.5	46.5
F. T.	40.8	54.8	63.7	84.6	95.9	104.9	109.7	111.8
% H_3PO_4	40.1	39.5	33.1	30.6	28.1	26.1	22.8	14.4
F. T.	113.4	112.5	111.6	109.0	108.1	107.1	105.0	99.7
% H_3PO_4	11.8	9.2	4.7	2.4				
F. T.	97.7	93.8	86.0	73.3				

Solid phase $C_9H_6O_2$

% H_3PO_4	1.7	1.0	0.0
F. T.	67.9	68.1	68.8

VI. ESTERS.

1. *Methyl Salicylate* and *Phenyl Benzoate* are insoluble in phosphoric acid.

Discussion

The nature of the addition compounds of ortho phosphoric acid with organic compounds is probably that of true oxonium salts. The general rule of Kendall which states that compounds are readily formed from two components of widely different acidic strengths seems to be borne out in the present study. The fact that all the addition compounds contained equimolar quantities of the components indicates that the primary dissociation of phosphoric acid is monobasic, that is

$$H_3PO_4 \rightleftarrows H^+ + H_2PO_4^-$$

The dissociation constants of phosphoric acid are given by Abbott and Bray[11] as follows:

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[11] J. Am. Chem. Soc., 31, 729 (1909).

$$H_3PO_4 \rightleftarrows H^+ + H_2PO_4^- \qquad K_1 = 1.1 \times 10^{-2}$$
$$H_2PO_4^- \rightleftarrows H^+ + HPO_4^{--} \qquad K_2 = 1.96 \times 10^{-7}$$
$$HPO_4^{--} \rightleftarrows H^+ + PO_4^{---} \qquad K_3 = 3.5 \times 10^{-13}$$

It is evident from the above that the first acid is much stronger than the other two. Therefore the tendency for compound formation is greatest between the first acid and the organic compound in question. The latter two acids are too weakly acidic to form addition compounds with organic compounds as evidenced by the results in this paper.

Further confirmation of Kendall's rule is evident when we consider the strength of the organic acids used. Acetic acid is a very weak acid, having a dissociation constant of .0000180 as given by Ostwald,[12] and it readily forms a compound with the much stronger phosphoric acid. Likewise with pyruvic acid. Propionic and butyric acids are slightly weaker than acetic acid and would therefore be expected to form similar addition compounds. Because of the necessity of using low temperatures in the study of these acids, thus resulting in very viscous solutions, only a part of the system of each acid was studied. No compounds were indicated in the regions studied. Although addition compounds would be expected, it may be that because of the nearer approach of the organic acid to a hydrocarbon, the influence of the carbonyl group towards acids may be affected in such a manner that no reaction takes place. Monochloro-acetic acid, which has an ionization constant of .00155 does not form an addition compound. Since it is much stronger than acetic acid, the tendency of compound formation should be less. Phenylacetic acid, which is also more acidic than acetic acid does not form a compound with phosphoric acid.

Phosphoric acid has been compared with sulfuric acid with regard to the ability to form addition compounds with organic substances. The results for sulfuric acid are taken from Kendall's data. The curves for the two inorganic acids with the same organic compound are given in Fig. 2. It is to be noted that in all cases the phosphoric acid compounds have a much greater range of stability than the corresponding compound with sulfuric acid. The compounds with sulfuric acid are much less dissociated at the maximum as is evidenced from the sharp breaks in the curves. Both sulfuric and phosphoric acids form equimolecular compounds with coumarin and benzophenone. While acetophenone forms the compound $C_6H_5COCH_3 \cdot H_3PO_4$ with phosphoric acid, it forms the compound $2C_6H_5COCH \cdot H_2SO_4$ with sulfuric acid.

The ability of phosphoric acid to form addition compounds with organic substances seems to be much less than the ability of sulfuric acid to combine with the same compounds. This is readily explainable on the basis of Kendall's rule of acidity, as sulfuric acid is a much stronger acid than phosphoric acid.

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[12] Z. physik. Chem., 3, 418 (1889).

Summary

1. In a series of freezing point determinations, thirty-one organic substances, including acids, esters, aldehydes, ketones, phenols, and acid anhydrides have been investigated with ortho phosphoric acid as one component.

2. Eight addition compounds have been found to exist with the above compounds, their general formula being $=C=O \cdot H_3PO_4$.

3. Kendall's rule of acidity holds in all systems examined.

4. Phosphoric acid forms addition compounds less readily with organic compounds than does sulfuric acid.

5. A comparison of the freezing point curves of the two acids has been made.

Madison, Wisconsin.

THE SOLUBILITY OF NAPHTHALENE IN SOME DERIVATIVES OF FURFURAL*

ARTHUR A. SUNIER

Of late years several investigators[1] have expressed the view that polarity and internal pressure effects were largely responsible for deviations from Raoult's law; and quite recently Sidgwick[2] has emphasized that solubility data often throw considerable light on the nature of the bond in chemical compounds; in particular, such data assist in distinguishing between polar and non-polar bonds.

Naphthalene is believed to be a non-polar compound; it can be readily prepared in a high state of purity; its melting point is rather low, and its latent heat of fusion is known with a fair degree of certainty. Considerations such as these have led several investigators to determine the solubility of naphthalene in a rather large number of solvents. Thus far, however, no determinations have been recorded for derivatives of furfural, no doubt because such compounds have only lately become commercially available. Since furfural is a ring compound containing double bonds and oxygen in the ring it was felt that solubility studies of some of its derivatives might prove of general interest in connection with the general subject of valence mentioned above, as well as of interest to anyone working more directly with these compounds. In the present paper the solvents used were furfuryl alcohol, furfuryl acetate and methyl, ethyl, n-propyl, n-butyl furoates.

Experimental

The synthetic method of Alexejew[3] was employed in making the solubility determinations recorded in the paper. The method consists in heating a sealed tube containing weighed quantities of solvent and solute and noting the highest temperature at which but few small crystals of solute remain in equilibrium with the solution. Ward[4] has described precautions which must be taken to assure the attainment of equilibrium conditions at the solubility temperature. The whole matter has been studied rather thoroughly in this laboratory; the results of this study are to be found elsewhere.[5] The apparatus and procedure were essentially those of Sunier and Rosenblum[6]

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* Contribution from the Chemical Laboratory of the University of Rochester.

[1] Hildebrand: "Solubility" (1924); Proc. Nat. Acad. Sci., 13, 267 (1927); J. Am. Chem. Soc., 51, 66 (1929); Ward: J. Phys. Chem., 30, 1316 (1926).

[2] Sidgwick: "The Electronic Theory of Valency" (1928).

[3] Alexejew: Wied. Ann., 28, 305 (1886).

[4] Ward: J. Phys. Chem., 30, 1316 (1926).

[5] Sunier: J. Phys. Chem., 34, 2582 (1930).

[6] Sunier and Rosenblum: J. Phys. Chem., 32, 1049 (1928).

which in turn are only slight modifications of the apparatus and procedure used by Ward. In the present research four units were built in close proximity to one another and all stirred and shaken from one motor; it was therefore possible to make four determinations at once. In two of the units were placed bi-metallic thermo-regulators, capable of keeping the two four liter baths to 0.01°; these regulators could be easily adjusted at the end of an hour or half hour period to the next tenth degree (the procedure adopted by Sunier and Rosenblum); this facilitated matters considerably. A two-unit outfit possessing certain advantages is described and discussed in another paper.[1]

The tubes were made up in much the same way as described earlier. With the solvent furfuryl alcohol a slight momentary flash was noted on sealing tubes containing considerable quantities of liquid; this did not, however, cause a loss in weight of more than two milligrams.

The thermometers used were compared, before and after most of the runs were completed, with thermometers recently standardized by the Bureau of Standards.

Materials

All materials were obtained from the Eastman Kodak Company and were their best grades.

The naphthalene was recrystallized from methyl alcohol and care was taken[2] to remove adsorbed solvent from the crystals. The melting point of the recrystallized material was 80.12° when determined carefully in the manner recommended by the Bureau of Standards[3].

None of the solvents was purified further. It would seem desirable to give the physical constants supplied by the manufacturers at the time the materials were purchased:

Furfuryl	Alcholol	B. P.	75– 76° / 17 mm.
"	Acetate	"	84– 85° / 25 mm.
Methyl	Furoate	"	83– 84° / 25 mm.
Ethyl	"	M. P.	30– 33°
n-Propyl	"	B. P.	105–107° / 25 mm.
n-Butyl	"	"	118–120° / 25 mm.

Results

The experimental results are given in Table I. The weight of solute is given first, then the weight of solvent, then the calculated mol fraction and finally the solubility temperature in degrees centigrade.

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[1] Sunier: J. Phys. Chem., 34, 2582 (1930).

[2] Sunier: J. Phys. Chem., 34, 2582 (1930).

[3] Bureau of Standards, Sci. Paper No. 340.

TABLE I

Solvent: Furfuryl Alcohol

Weight $C_{10}H_8$	Weight Solvent	Mol Fraction	Solub. Temp.
1.486	0.4045	0.738	71.4
1.639	0.344	0.785	72.6
1.309	0.617	0.619	68.3
1.011	0.606	0.561	67.2
0.862	0.792	0.455	64.3
0.712	1.649	0.249	53.0
0.826	1.273	0.332	58.7
0.643	2.159	0.186	46.3
0.4667	2.910	0.1094	32.4
Solvent: Furfuryl Acetate			
1.638	0.404	0.816	70.0
1.261	0.703	0.662	61.4
0.941	0.732	0.584	56.2
0.712	0.870	0.472	48.3
1.076	0.438	0.729	65.2
0.541	0.922	0.378	40.9
0.746	0.935	0.466	48.3
0.660	0.925	0.438	46.2
0.798	1.688	0.341	37.4
0.4226	1.902	0.196	19.4
Solvent: Methyl Furoate			
1.462	0.992	0.592	56.8
1.854	0.515	0.780	67.9
1.119	1.035	0.516	51.8
0.887	1.355	0.392	42.3
0.765	1.652	0.313	35.0
0.647	1.927	0.2484	27.7
Solvent: Ethyl Furoate			
1.340	0.423	0.776	66.8
1.177	0.495	0.723	63.5
1.150	0.825	0.604	55.5
1.039	1.280	0.470	44.9
0.812	1.624	0.353	33.8
0.452	1.223	0.288	25.6

TABLE I (Continued)

Solvent: n-Propyl Furoate

Weight $C_{10}H_8$	Weight Solvent	Mol Fraction	Solub. Temp.
1.656	0.525	0.791	67.9
1.201	0.698	0.674	60.1
1.027	1.035	0.544	50.2
1.059	1.376	0.481	45.3
0.953	1.772	0.393	36.4
0.684	1.895	0.303	25.6

Solvent: n-Butyl Furoate

Weight $C_{10}H_8$	Weight Solvent	Mol Fraction	Solub. Temp.
1.234	0.530	0.754	64.9
1.134	0.934	0.615	54.9
1.264	1.514	0.523	47.7
1.093	1.873	0.434	39.2
0.587	1.241	0.383	33.9
0.541	1.810	0.232	21.3

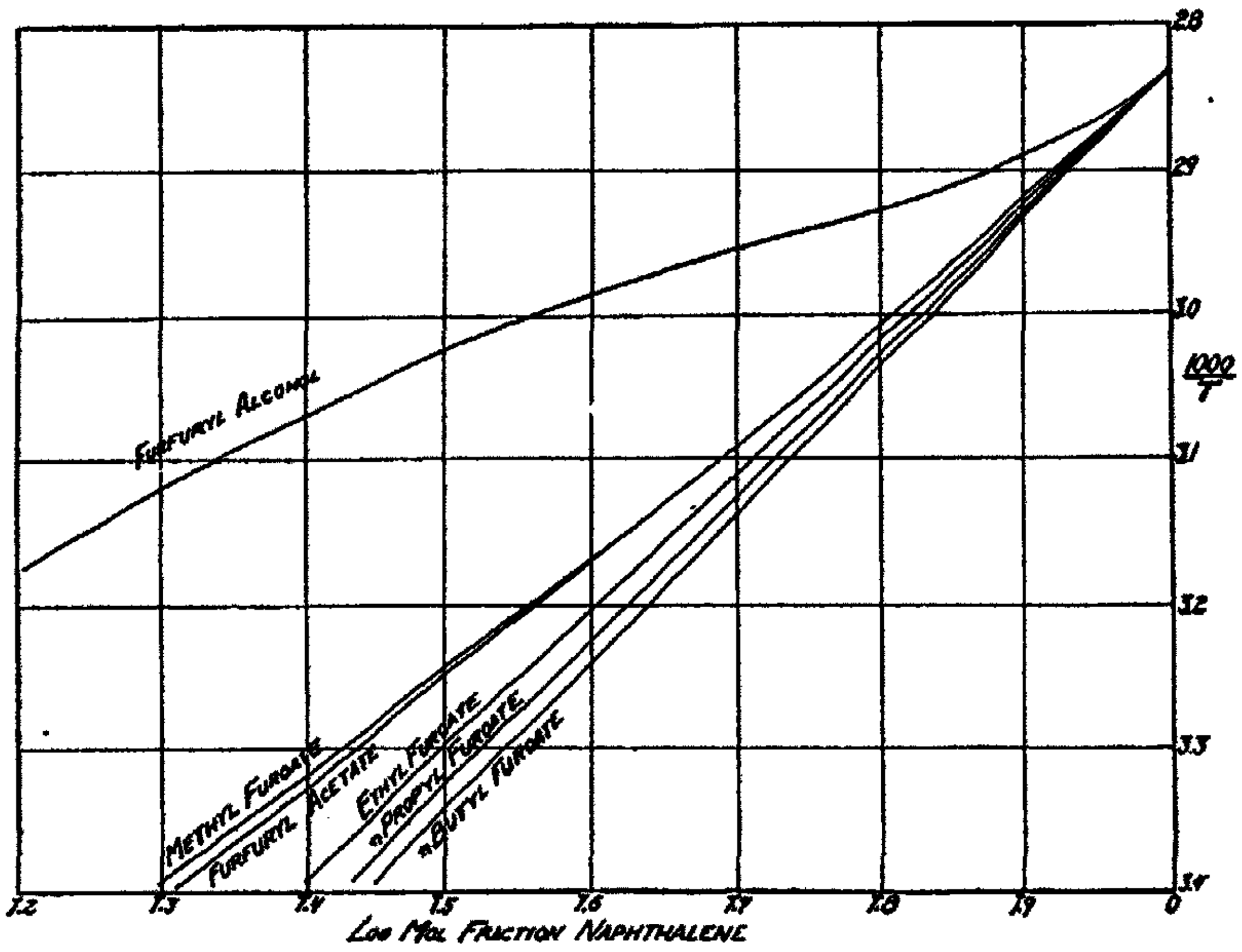

FIG. 1

The results have been plotted in Fig. 1 in the customary way—log N vs 1/T. Large plots were constructed and the mol fractions at rounded temperatures were read off; these values are found in Table II.

TABLE II
Solubility of Naphthalene in Derivatives of Furfural at Rounded Temperatures, expressed in Mol Fractions of Naphthalene

Temp.	Furfuryl Alcohol	Furfuryl Acetate	Methyl Furoate	Ethyl Furoate	n-Propyl Furoate	n-Butyl Furoate
75	0.857	0.900	0.900	0.908	0.910	0.913
70	0.684	0.811	0.811	0.824	0.826	0.830
65	0.474	0.726	0.726	0.747	0.750	0.753
60	0.352	0.644	0.644	0.668	0.678	0.684
55	0.275	0.565	0.565	0.597	0.607	0.618
50	0.219	0.491	0.491	0.531	0.543	0.555
45	0.1758	0.425	0.425	0.471	0.483	0.498
40	0.1446	0.367	0.366	0.415	0.430	0.445
35	0.1194	0.316	0.313	0.365	0.379	0.379
30	0.1048	0.272	0.267	0.321	0.338	0.351
25	0.0849	0.233	0.227	0.281	0.297	0.309
20	0.0728	0.199	0.192	0.246	0.260	0.272

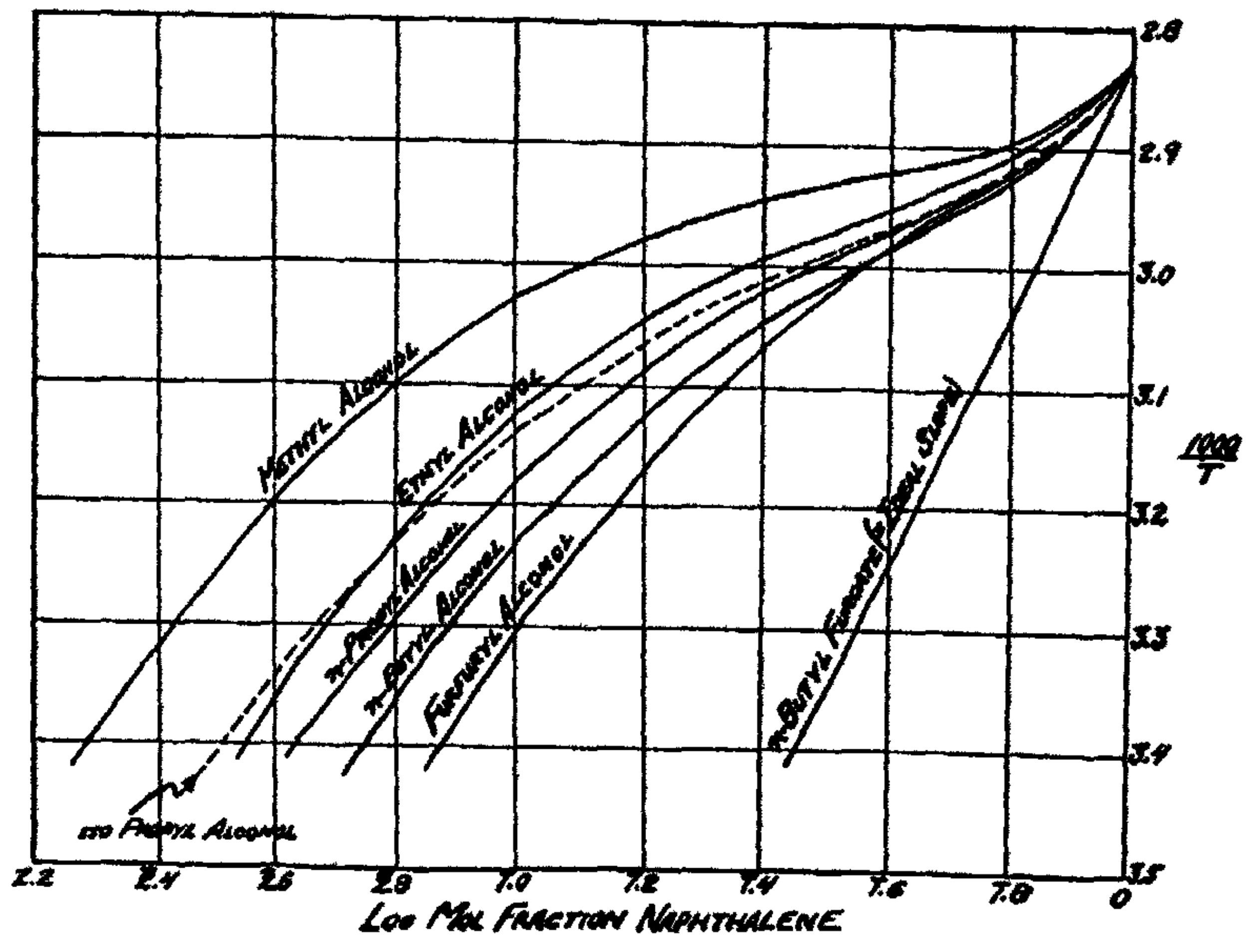

FIG. 2

Discussion of Results

As has been mentioned earlier no recorded data could be found in the literature bearing on these systems; comparison with previous results is thus impossible. In an earlier paper[1] it was shown that errors in the solubility temperature as large as 0.1° were not likely to occur if only fine crystals were

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[1] Sunier: J. Phys. Chem., 34, 2582 (1930).

present in the tube and if the rate of heating was 0.01° per minute or less; since these two precautions were taken it is thought the recorded temperatures are accurate to ±0.1°. However it is realized that various impurities might have been present in the solvent, but it would seem quite likely that the shapes of the curves relative to one another would not be greatly changed by the presence of some common impurity.

Furfuryl alcohol is the poorest and n-butyl furoate the best solvent for naphthalene of any of the materials under consideration. The curve for the former solvent approximates that of n-butyl alcohol[1] as can be seen from an inspection of Fig. 2 which compares data on various aliphatic alcohols. The curve for the latter solvent is very near, if not equal to, that shown by an ideal system such as naphthalene and chlorobenzene[2] or naphthalene and ethylidene bromide.[3] The solubilities of furfuryl acetate and methyl furoate appear to be identical from 80 down to 40°; below this the latter substance dissolves a little less naphthalene.

The influence of methyl, ethyl, n-propyl and n-butyl groups is clearly seen in Fig. 1; a very regular increase in the solubility is noted for these substances. It would be of interest to study the longer chained derivatives to see if a solubility greater than the ideal would be obtained; if such were the case it is quite likely that solvation effects must be operative as Hildebrand[4] has pointed out.

It seems rather remarkable that furfuryl alcohol, containing five carbon atoms, has a solubility one might expect for normal pentanol; the former compound has a ring structure containing two double bonds and oxygen, the latter is of course a straight chain compound. It would appear that n-butyl furoate is a non-polar compound. In an earlier paper[5] the subject of polarity and solubility is discussed briefly and reference is there made to the work of Debye,[6] Smyth[7] and Stewart.[8] Further discussion does not seem necessary at this time.

Summary

The solubility of naphthalene in six derivatives of furfural has been determined at a variety of temperatures. Certain regularities have been pointed out.

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[1] Sunier: J. Phys. Chem., **34**, 2582 (1930); Ward: **30**, 1316 (1926).

[2] Ward: J. Phys. Chem., **30**, 1316 (1926).

[3] Sunier and Rosenblum: J. Phys. Chem., **32**, 1049 (1928).

[4] Hildebrand: "Solubility" (1924).

[5] Sunier: J. Phys. Chem., **34**, 2582 (1930).

[6] Debye: "Polar Molecules" (1929).

[7] Smyth: Chem. Reviews, **6**, 549 (1929).

[8] Stewart: Chem. Reviews, **6**, 483 (1929).

KINETICS OF TRANSITIONS IN POLYMORPHIC SOLIDS*

BY ARTHUR F. BENTON AND RAYMOND D. COOL

Introduction

It is well known that in chemical changes in which at least one of the reactants and one of the products is a solid phase, the reaction is commonly autocatalytic. After a longer or shorter period of "incubation," the rate increases (induction period), reaches a maximum and then decreases, finally falling off to zero when the reaction is complete. The phenomenon is interpreted on the assumption that reaction proceeds more readily at the interface between the two solid phases than elsewhere, and that the rate of reaction is proportional to the extent of this interface. The only necessary condition for the appearance of this type of autocatalysis appears to be the occurrence of a separate solid phase on each side of the reaction equation. It has been observed[1] in reactions in which one solid produces a second solid and a gas (decomposition of Ag_2O, $AgMnO_4$, $Ag_2C_2O_4$, various metallic carbonates, etc.), and in those in which a solid and a gas react to form a second solid and a gas (reduction of CuO, NiO, Ag_2O, etc., by hydrogen or carbon monoxide); it is occasionally observed in reactions in which a solid and a gas react to form a second solid (hydration of salts, oxidation of metals at low temperatures, etc.).

In addition to these three, a fourth type of reaction is available for study, namely, those in which all the participants are in the solid state. An example is the transition of a polymorphic solid, involving nothing but one solid reactant and one solid product. It appears that this case might be less complex, especially from the theoretical stand-point, than any of the other three cases cited.

Observations of allotropic transformations have indicated that in certain cases at least, reaction proceeds more readily at the boundary between the two solid phases than elsewhere.[2] It appears, however, that little attention has been given to the kinetics of allotropic changes as a function of the quantity of material transformed. Estimates of the velocity of transformation have been obtained dilatometrically in a few cases, but the assumption is usually implied that at a given temperature the rate is independent of the extent to which reaction has proceeded. Furthermore, in these experiments the solid under study was always in contact with the dilatometer liquid, which through solubility or adsorption effects might have considerable influence on the rate of reaction. In certain cases a marked effect has been observed.[3]

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* Contribution from the Cobb Chemical Laboratory, University of Virginia, No. 72.

[1] For a discussion of the results obtained in this field, see Taylor: "Treatise on Physical Chemistry," 2nd Ed., **2**, pp. 1067-9.

[2] See, for example, Cohen and coworkers: Z. physik. Chem., **30**, 601 (1899), **63**, 625 (1908); Bridgman: Proc. Am. Acad. Arts Sci., **52**, 57 (1916); Early and Lowry: J. Chem. Soc., **115**, 1387 (1919).

[3] Cohen: Z. physik. Chem., **14**, 53; Cohen and Bredig: 535 (1894).

In view of these facts it was decided to study the kinetics of certain allotropic transformations by employing a dilatometer in which the volume changes are transmitted by means of an inert gas rather than by a liquid.

Experimental Method

Apparatus.—The dilatometer consisted of a glass bulb sealed at the top to a capillary tube leading to a 3-way stopcock, one arm of which was open to the atmosphere, and the other was connected to a closed vacuum manometer of 2 mm. glass capillary. The adjustment of the mercury levels in the manometer was effected by means of a mercury well and glass plunger so that the redistilled mercury was never in contact with rubber. The manometer levels were read with the help of a wood scale sliding in brass guides and counterbalanced so as to remain in any desired position. The scale carried two pointers, exactly 760.0 mm. apart, which were illuminated by small electric lights mounted on the scale. Two small mirrors, set at an angle of 45°, were also attached to the scale, one at the level of each pointer. By this device the image of the upper mercury level and pointer was brought down to the lower mirror and there reflected to the eye at the height of the lower level and pointer, thus facilitating simultaneous reading of the two levels. This somewhat complicated manometer was resorted to only after preliminary experiments with an open manometer had shown that even small fluctuations in barometric pressure were sufficient to vitiate the results.

Careful temperature control is also essential if reliable results are to be obtained. To this end, the bulb was surrounded by an electrically heated vapor bath, jacketed with asbestos paper, and tightly closed at the top with a cork stopper cemented with litharge-glycerine cement. This stopper carried a calibrated thermometer graduated to 0.1°, a narrow capillary tube by means of which air could be bubbled through the bath liquid, when necessary, to prevent bumping, and a reflux condenser. The latter was in turn connected to a 3-way stopcock so that the vapor bath could be opened to the air, or connected to a device for maintaining a constant pressure. The pressure regulator was similar to the one described by Scofield.[1]

Procedure.—A liquid whose boiling point was above the transition temperature was used in the vapor bath. For transitions from the high temperature form to the low temperature form, the bath was at first closed off from the pressure regulator, and run at atmospheric pressure to convert the sample into the high temperature form. After a suitable time the bath was connected to the regulator, in which in the meantime the pressure had been adjusted to give the temperature at which the measurement was to be made. As soon as this temperature was approximately attained, the sample, which had previously been open to the air through a calcium chloride tube, was connected to the manometer. With the mercury levels kept 760 mm. apart to insure constancy of pressure in the bulb, the rate of reaction was followed by reading the height of the mercury column in the calibrated arm of the manometer

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[1] Schofield: Ind. Eng. Chem., **18**, 717 (1926).

at five-minute intervals. For transitions from the low temperature form to the high, the procedure was the same, except that the preliminary heating with the bath at atmospheric pressure was not required.

Materials.—The experiments to be reported here deal with the transitions of mercuric and of thallous iodides. These substances were chosen because their transitions occur at convenient temperatures and are accompanied, in both cases, by pronounced color changes. Samples 1-3 of mercuric iodide were used only in preliminary experiments, and their preparation need not be described. Samples 4 and 5 were made from recrystallized mercuric chloride and potassium iodide according to the procedure given in U.S. Pharmacopoeia, 8th Revision, p. 237. Sample 4 was also recrystallized from alcohol, and both samples were dried for about 100 hours in an oven at 110°.

Thallous iodide was prepared from C. P. potassium iodide and thallous nitrate. The resulting precipitate was carefully washed and dried before use.

The liquids used as vapor baths were not especially purified. Those most largely employed were water, amyl alcohol, aniline, xylene, acetic acid and benzaldehyde.

Results

Reliability of the Method.—At different times a number of trials were made to determine how closely manometer readings could be checked by displacing the mercury columns and then restoring them to a difference of 760 mm. In these trials readings could be regularly reproduced within 1 mm., and consequently in following reaction rates the manometer was read to this degree of precision only.

Table I indicates the extent to which the rate of reaction is reproducible in experiments carried out under identical conditions. In each of these runs the sample (No. 4) was first heated for one hour at 137° to convert it into the yellow form, and the rate of transition to the red form measured at 120.2°. It should be mentioned, however, that the reproducibility was by no means always so satisfactory as in Runs 31-4, owing to slight fluctuations in the temperature of the vapor bath. Fortunately, this difficulty was serious only when water or benzaldehyde was used as bath liquid.

Table I

Reproducibility of Rate Measurements

Run	Time to reach max. rate (min.)	Rate at max. (cm/5 min.)	Time for complete reaction (min.)	Total reaction (cm.)
31	35	1.0	75	7.4
32	35	1.1	75	7.7
33	35	1.2	65	7.9
34	35	1.1	75	7.8

In order to secure reliable information regarding the early stages of reaction, careful studies were made to determine the time required for temperature equilibrium to be established throughout the sample after the temperature of the bath had been suddenly changed. This was accomplished by observation of the manometer when the temperature was changed to the same extent as in a regular run, but without passing through the transition temperature, and also, in some cases, by comparison of the readings of the thermometer in the vapor bath with a second thermometer inserted in a well at the center of the sample. It was found that equalization of temperature required 15 min. for mercuric iodide, Sample 4 (bulb 13 cm. long and 1.8 cm. in inside diameter), 5 min. for mercuric iodide, Sample 5 (bulb 132 cm. long and 0.5 cm. in diameter, wound in a spiral), 10 min. for thallous iodide, Sample 1 (bulb 1.5 cm. in diameter), and 10 min. for thallous iodide, Sample 2 (bulb consisting of three branches, each 12 cm. long and 1.5 cm. in internal diameter).

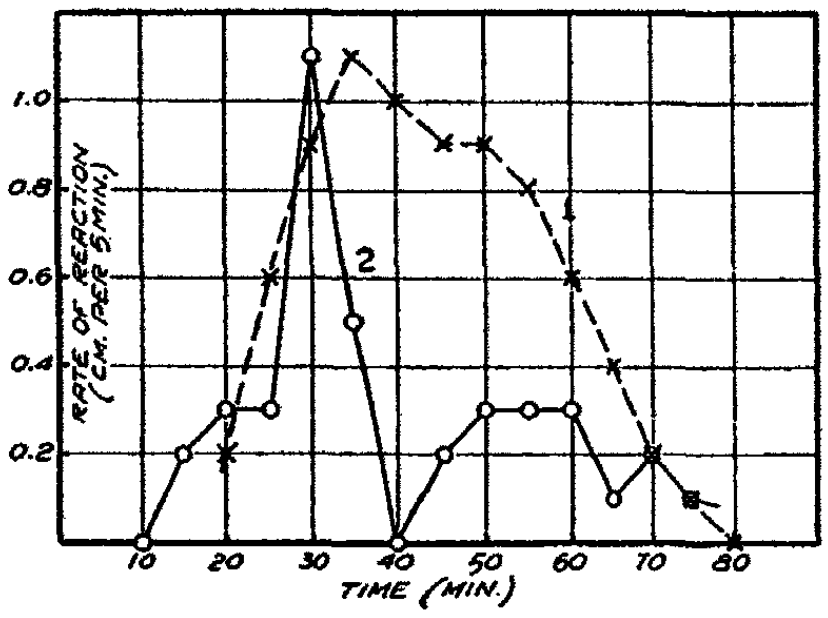

FIG. 1

Rate of transition of mercuric iodide.
Curve 1: Sample 4, yellow to red at 120.2°;
Curve 2: Sample 5, red to yellow at 130.0°.

Autocatalytic Nature of the Reactions.—Typical data from runs made under the best conditions are plotted in Figs. 1 and 2. Fig. 1 shows the rates of transition of mercuric iodide in both directions; Curve 1 represents the change, yellow to red, for Sample 4 (76.50 g.) at 120.2°, and Curve 2 represents the change, red to yellow, for Sample 5 (67.85 g.) at 130.0°. In Fig. 2 similar data are shown for thallous iodide; Curve 1 is the change, red to yellow, for Sample 1 (48.21 g.) at 142.0°, and Curve 2 is the change, yellow to red, for Sample 2 (107.61 g.) at 180.5°. On each curve the initial plotted point represents the first reading unaffected by temperature lag.

It will be seen that these transformations are autocatalytic in nature, and give curves of the same type as those for other systems involving two separate solid phases. The rate increased rather rapidly to a maximum and then fell off much less abruptly, so that only about 20-30% of the total change had occurred when the maximum rate was reached. This behavior ordinarily indicates that the reaction started and spread from a comparatively large number of centers. That this was the case was evident from visual observation of the colors of the samples as reaction proceeded. The process was never observed to start in only one or two places and spread from these, but spots of the stable form appeared throughout and then continued to grow in size, finally merging into one another. In line with these observations also is the fact that the period of "incubation" was usually very short or entirely absent, except when the subsequent rate was very slow.

Rate of Reaction and Temperature.—The rate of reaction was found to increase with increasing distance from the transition temperature, both above and below. The relative rates are indicated in three ways: (1) time required for rate to reach the maximum, (2) the rate of change at the maximum, and (3) time required for completion of the total change. Table II contains typical data for the yellow → red transition of mercuric iodide (Sample 4), where the preliminary treatment of the sample was approximately the same in each case. (The transition temperature is near 127°).

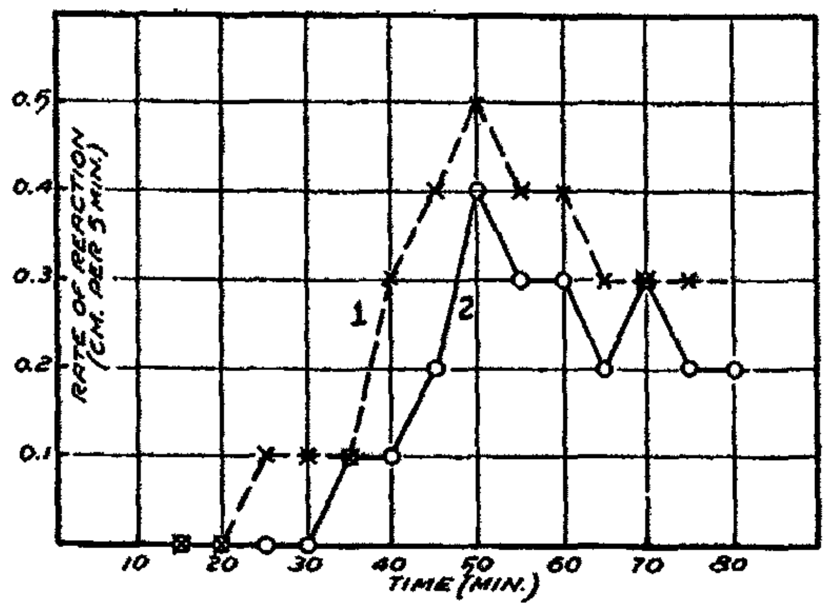

Fig. 2

Rate of transition of thallous iodide, Sample 1
Curve 1: red to yellow at 142.0°;
Curve 2: yellow to red at 176.0°

Table II

Yellow to Red Transition of Mercuric Iodide.

Run	Temp. °C.	Time to reach maximum (min.)	Rate at maximum (cm./5 min.)	Time for total reaction (min.)
23	98.5	<15	>8.0	25
24	116.0	45	1.0	85
30	120.2	55	0.9	105

Although changes at temperatures far removed from the transition temperature were too rapid for quantitative study, they could be followed qualitatively by observing the color change. The yellow form (Sample 1), on cooling to 50°, changed completely to red in less than 15 minutes. On cooling the yellow form (Sample 3) from 137° to 20°, it became completely red in less than 10 minutes, and a similar result was obtained on cooling it from 180° to 20°. At 122.8° this sample was less than one-third converted to the red form in 2.5 hours.

For the conversion of mercuric iodide to the high temperature form, it was found that at 129.5° Sample 3 changed to yellow only very slightly in 10 hours; at 136.7° the change required 40 minutes for completion, while at 181° reaction was complete in 10 minutes.

For thallous iodide the effect of temperature over the corresponding range is even greater. Table III shows results obtained with Sample I for the change, red to yellow. The preliminary treatment was substantially the same in each case. (The transition temperature is probably between 160° and 170°).

TABLE III

The Red to Yellow Transition of Thallous Iodide

Run	Temp. °C.	Time to reach maximum (min.)	Rate at maximum (cm./5 min).	Time for total reaction (min.)
22	131.2	Too fast to measure		20
23	142.0	45	0.5	150
26	150.0	460	0.5	>790

On cooling from 180° to 25° this sample changed completely in 2 minutes.

Data for the change of the same sample of thallous iodide in the reverse direction are given in Table IV.

TABLE IV

The Yellow to Red Transition of Thallous Iodide

Run	Temp. °C.	Time to reach maximum (min.)	Rate at maximum (cm./5 min.)	Time for total reaction (min.)
11	174.0	125	0.2	>720
20	176.0	50	0.4	>145
18	177.8	25	1.0	65
15	180.2	15	2.0	25

A number of workers[1] have found that the velocity of certain transformations from the high to the low temperature form passes through a maximum as the temperature is lowered. We have obtained qualitative evidence that the same is true of the cases under consideration. Thus when samples of mercuric iodide, sealed in tubes approximately 3 × 120 mm., were converted into the yellow form by heating and then immersed in liquid air, the yellow color immediately faded to white, but no further change occurred in 70 minutes at this temperature. On then permitting the tubes to warm up in a bath of petroleum ether, the salt gradually acquired its normal yellow color at −160° to −140°, and at the same time specks of the red form began to appear at numerous points. On reaching this stage, one sample was again cooled in liquid air, with the result that the progress of the transformation was completely stopped, the yellow portions fading to white and the red parts to orange.

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[1] Gernez: Compt. rend., 100, 1343, 1382 (1885); Tammann: "Kristallisieren und Schmelzen," (1903); Cohen and coworkers: Z. physik. Chem., 30, 601 (1899); 33, 57 (1900), 35, 588 (1900).

It is evident that the rate of conversion at −191° is very small, if not zero, and that the rate must pass through a maximum somewhere between this temperature and 20°.

Effect of Preliminary Treatment.—The rates of reaction of all samples were found to increase with the number of transformations previously undergone. This increase was very marked during the first few runs with a given sample. Thus for Sample 5 of mercuric iodide, with all other factors constant, the maximum rate was five times as great in the sixth run, and seven times as great in the ninth run, as in the first. However, the activity changed less and less in successive experiments, and finally reached a constant value.

The rate of reaction was also affected by the time and temperature of heating previous to a given transformation, as may be seen from the data in Table V, which refer to Sample 4 of mercuric iodide. Previous to these experiments the sample had attained its constant maximum activity.

TABLE V

Effect of Preliminary Treatment

Run	Time of heating at 137°(hr.)	Temp. of run	Time to reach maximum (min.)	Rate at maximum (cm./5 min.)	Time for total reaction (min)
28	14	120.6°	85	0.4	>205
29	1	120.6°	35	0.9	125
30	5	120.2°	55	0.9	105
31	1	120.2°	35	1.0	75

Since the conversion of the red form to the yellow at 137° required less than 30 minutes for completion, the retarding effect of heating at this temperature for times in excess of one hour may be ascribed to growth of the crystals and gradual elimination of their imperfections, a process which would be facilitated by the appreciable volatility of the material. We have obtained no evidence either for or against the applicability of Smits theory of allotropy,[1] which postulates the existence in each allotropic modification of an inner equilibrium changing with temperature.

Effect of Different Gases on Rate of Transition.—Although the large majority of the runs were carried out in the presence of air, a few experiments were made with thallous iodide in atmospheres of carbon dioxide or nitrogen. Since the results were the same within experimental error for all three gases, it is concluded that the adsorption of gas by the iodide, if it occurs at all, is a negligible factor in the rate of transition.

Transition Temperatures and Changes of Volume.—While no special effort has been made in this work to determine the exact location of the transition temperatures, the results definitely place them within certain limits. Thus the transformation of mercuric iodide at atmosphere pressure must occur between 123° and 129.5°. Most of the values in the literature are 126° to 127°, but figures as high as 130° have been reported. We have found that the

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[1] Smits: "The Theory of Allotropy," (1922).

transition point of thallous iodide lies definitely between 150° and 174° and probably between 160° and 170°. The values recorded in the literature vary from 150° to 190°.

From observation of the total displacement of the mercury level in the manometer when reaction was complete, and from its volumetric calibration (0.028 cc. per cm.), the change of volume accompanying these transitions was obtained, as follows: mercuric iodide, 0.0028 cc. per gram; thallous iodide, 0.003 cc. per gram. These differences in specific volume are exceptionally small. The red form has the greater density in each case.

Summary

A dilatometric method has been developed for measuring the rates of polymorphic transitions of solids in presence of an inert gas. The method eliminates the spurious effects that occur when liquids are used in the dilatometer to transmit the volume changes.

The transitions of mercuric iodide and thallous iodide have been found to be autocatalytic in both directions. The kinetics are similar to those observed in numerous other systems in which one of the reactants and one of the products is a solid phase.

Above the transition point the rates increase very rapidly with increasing temperature. For the change in the reverse direction, the rate at first increases as the temperature is lowered, but then passes through a maximum, and decreases to very small values at liquid air temperature.

The rate is markedly affected by the duration and temperature of heating of the sample previous to conversion.

Approximately equal rates are found in the presence of air, carbon dioxide or nitrogen.

University, Virginia.

REDUCTION OF SILVER HALIDES BY SODIUM SULPHITE AND NITRITE IN PRESENCE OF INDUCTORS AND A CHEAP DEVELOPER IN PHOTOGRAPHY

BY RAM BEHARI LAL VERMA AND N. R. DHAR

In previous publications[1] from these laboratories it has been shown that sodium sulphite, which readily undergoes oxidation in air or oxygen initiates or accelerates the oxidation of sodium nitrite, potassium oxalate, ferrous sulphate, cuprous, nickelous, ferrous and other hydroxides.

In photography, sodium sulphite has been largely used since its introduction by Berkeley, to prevent stains produced by the oxidation of developers in alkaline solutions. The exact function of the sulphite in development has not yet been cleared up.[2]

In this paper, the reactions between sodium sulphite and different sparingly soluble silver salts have been studied in presence of various organic and inorganic developers and an attempt has been made to find out the real mechanism of the sodium sulphite added in photographic development. The reactions, however, differ from the usual induced reactions of sodium sulphite in the fact that the oxidation of sodium sulphite is not the primary change here but a secondary one. In fact, the developers used in photography, appear to induce the reduction of the sparingly soluble silver salts by sodium sulphite.

The following reactions have been investigated:

Reduction of (1) silver chloride, (2) silver bromide, (3) silver iodide, (4) silver thiocyanate by sodium sulphite in presence of

(a) Hydroquinone.
(b) Pyrogallol.
(c) Metol.
(d) Hydroxylamine hydrochloride.
(e) Hydrazine sulphate.
(f) Ferrous sulphate.

Experimental Procedure

20 cc. of a standard solution of silver nitrate (N/99.5) were added to 20 cc. of a standard solution of sodium chloride (N/99.5) taken in a bottle and silver chloride was precipitated. 20 cc. of a standard solution of the developer was then added and the volume was made up to 100 cc. The mixture

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[1] Dhar: J. Chem. Soc., 111, 694 (1927); Proc. Akad. Wet. Amsterdam, 29, 1023 (1921); Z. anorg. Chem., 128, 207 (1923); J. Phys. Chem., 28, 943 (1924); Mittra and Dhar: Trans. Faraday Soc., 17, 676 (1922); Z. anorg. Chem., 122, 146 (1922); J. Phys. Chem., 29, 376; Palit and Dhar: 799 (1925); 30, 939 (1926); 32, 1663 (1928); 34, 711 (1930).

[2] Compare, "Photography as a Scientific Implement," 150 (1923).

was shaken for 20 minutes and filtered. The experiments were carried on at 30°. The precipitate remaining on the filter paper was washed several times with distilled water and nitric acid was added to it to dissolve out the silver formed by reduction. The filter paper was washed and the filtrate titrated against a standard potassium thiocyanate solution using ferric sulphate as an indicator. From this the amount of silver reduced was calculated.

In the case of silver bromide, sodium bromide was used and in the case of silver iodide, potassium iodide was used for the precipitation of the silver halides. Silver thiocyanate was precipitated with potassium thiocyanate.

In all the cases the strength of sodium sulphite was N/24.3. Tables I-III show the experimental results:

TABLE I

Hydroquinone M/200

Na_2SO_3 present cc.	AgCl present gm.	Ag. obtained gm.
0	0.02881	0.00144
5	"	0.00621
10	"	0.00909
15	"	0.01170
20	"	0.01674

TABLE II

Hydroquinone M/400

Na_2SO_3 present cc.	AgCl present gm.	Ag. obtained gm.
0	0.02881	0.00126
5	"	0.00450
10	"	0.00810
15	"	0.01008
20	"	0.01125

TABLE III

Hydroquinone M/800

Na_2SO_3 present cc.	AgCl present gm.	Ag. obtained gm.
0	0.02281	0.00099
5	"	0.00342
10	"	0.00657
15	"	0.00729
20	"	0.00872

From the foregoing results we see that the amount of AgCl reduced decreases as the concentration of the solution of the developer decreases but increases in all the cases as the amount of Na_2SO_3 increases.

Exactly similar results have been obtained with other developers and various silver salts.

The above results show that silver chloride is reduced by the developer solution even in the absence of sodium sulphite. Similar results are obtained with other silver salts also. The greatest reduction is observed with metol and the least with ferrous sulphate.

The results in Table IV will show that in the absence of sodium sulphite, the reducing power of the developer is in the following decreasing order:

Metol >Pyrogallol >Hydroquinone >Hydrazine sulphate >Hydroxylamine hydrochloride >Ferrous sulphate.

TABLE IV

M/200	Amount of Ag. reduced from AgCl	AgBr	AgI	AgCNS
Metol	0.00216	0.00359	0.00054	0.00045
Pyrogallol	0.00207	—	0.00045	0.00027
Hydroquinone	0.00144	0.00351	0.00045	0.00022
Hydrazine sulphate	0.00063	0.00063	0.00013	—
Hydroxylamine hydrochloride	0.00027	0.00054	—	0.00018
Ferrous sulphate	—	0.00052	0.00009	—

As has been mentioned before, if no developer is used, sodium sulphite does not reduce the silver salts and hence the silver salts are the actors. From the results it will be seen that even without the sodium sulphite the developers reduce the silver salts (though to a slight extent), and hence are called the inductors. Sodium sulphite in its turn is the acceptor.

It is remarkable that in the presence or in the absence of sodium sulphite, the reduction of silver salts with the organic developers is greater than with the inorganic developers of the same concentration.

If the reduction by sodium sulphite be considered in presence of the inductors the inducing powers of these inductors come out in the same order in which they reduce the silver salts in the absence of sodium sulphite:—

Metol >Pyrogallol >Hydroquinone >Hydrazine sulphate >Hydroxylamine hydrochloride >Ferrous sulphate.

The results in Table V will illustrate this point.

The results quoted in Table V are those in which 20 cc. of sodium sulphite were used.

Another thing to be noted from the results is that the greatest reduction is in the case of chlorides and the least in the case of iodides i.e. the order is AgCl > AgBr > AgCNS > AgI. The reason for this may be that silver iodide is the least soluble and silver chloride is the most soluble of the silver salts investigated.

These results show that the reduction of the silver salts by sodium sulphite can take place only in the presence of substances which themselves can reduce the silver salts. It appears that these inductors in being oxidised

TABLE V

Salt	Inductor	M/200	M/400	M/800
AgCl.	Metol	0.02133	0.01935	0.01782
	Pyrogallol	0.02052	0.01611	0.00792
	Hydroquinone	0.01674	0.01125	0.00872
	Hydrazine sulphate	0.01377	0.00918	0.00729
	Hydroxylamine hydrochloride	0.00981	0.00549	0.00270
	Ferrous sulphate	0.00675	0.00486	0.00270
	II			
AgBr.	Metol	0.01872	0.01782	0.01269
	Pyrogallol	0.0144	0.00846	0.00450
	Hydroquinone	0.00999	0.00702	0.00477
	Hydrazine sulphate	0.00369	0.00342	0.00306
	Hydroxylamine hydrochloride	0.00369	0.00306	0.00288
	Ferrous sulphate	——	0.00261	0.00153
	III			
AgI.	Metol	0.0009	0.00085	0.00072
	Pyrogallol	0.0009	0.00063	0.00054
	Hydrazine sulphate	0.000315	0.000270	0.000225
	Hydroxylamine hydrochloride	0.00045	0.000270	0.000225
	IV			
AgCNS.	Metol	0.01449	0.01251	0.00909
	Pyrogallol	0.00576	0.00261	0.00198
	Hydroquinone	0.00198	0.00117	——
	Hydrazine sulphate	0.00036	0.00027	——
	Hydroxylamine hydrochloride	0.00036	0.00027	——

start the oxidation of sodium sulphite by the silver salts and when once the oxidation of sodium sulphite is started, it goes on reducing the silver salts when its concentration is increased.

For instance metol reduces the silver salts thus:

Metol + silver chloride = silver + oxidation product of metol.

This primary reaction starts the oxidation of sodium sulphite according to the following equation:

$$Na_2SO_3 + 2AgCl + H_2O = Na_2SO_4 + 2Ag + 2\ HCl,$$

the reduction by sodium sulphite being a secondary change. Similarly for the other reactions primary and secondary reactions occur.

In all these cases, the primary change, i.e. the oxidation of the easily oxidisible substances, pyrogallol, metol etc. takes place and this primary change induces the secondary or the induced reaction i.e. the oxidation of sodium sulphite by the silver salts. The view that hydroquinone can act as an inductor and sodium sulphite as the acceptor has also been advanced by Bancroft.[1]

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[1] J. Phys. Chem., 33, 1188 (1929).

We have observed that sodium nitrite can also behave as an acceptor in a similar way in the reduction of the silver salts in the presence of inductors such as metol, hydroquinone and pyrogallol. Sodium nitrite alone does not reduce the silver salts. The experimental results are given in Table VI.

TABLE VI

N/200 $NaNO_2$ added cc.	AgCl present gm.	Ag. reduced gm.
	I. M/100 Hydroquinone	
0	0.02881	0.00189
5	"	0.00324
10	"	0.00387
15	"	0.00432
20	"	0.00486
	II. M/200 Hydroquinone.	
0	.02881	0.00144
20	"	0.00369
	III. M/400 Hydroquinone.	
0	0.02881	0.00108
20	0.02881	0.00270

The results with Metol are given in Table VII.

TABLE VII

$NaNO_2$ added cc.	AgCl present gm.	Ag. reduced gm.
	M/100 Metol	
0	0.02881	0.00252
5	"	0.00360
10	"	0.00423
15	"	0.00468
20	"	0.00540
	M/200 Metol	
0	0.02881	0.00216
20	"	0.00423
	M/400 Metol	
0	0.02881	0.00171
20	"	0.00324

This result very well bears out the observation of Dhar[1] that one chemical change will either promote or induce another chemical change of the same nature. The reduction of the silver salts by metol, etc. brings about their reduction by sodium nitrite.

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[1] Proc. Akad. Wet. Amsterdam, 29, 1023 (1921).

The reduction may be represented in the following way:

$$AgCl + \text{metol} = Ag + \text{oxidation product of metol (primary change)}$$
$$2\,AgCl + NaNO_2 + H_2O = 2Ag + NaNO_3 + 2\,HCl \text{ (secondary change)}$$

It is interesting to note from the results that of all the organic developers the best inductor is metol and this is followed by pyrogallol and hydroquinone. This is probably due to the side chain present in metol.

Of the inorganic developers hydrazine sulphate is more reducing than hydroxylamine hydrochloride or ferrous sulphate.

We have carried on some experiments to prove the practical use of the reduction of silver salts by sodium sulphite. We have tried to show experimentally that sodium sulphite plays an important part in the development in photography. It has been observed that the efficiency of the developer is well maintained even when the amount of metol is considerably decreased and the amount of sodium sulphite is largely increased. Photographic plates were used and the developing solutions containing different amounts of sodium sulphite were utilised.

The developing solution used in practice has the following composition:

$$\text{I.}\quad \left.\begin{array}{l}\text{1 gm. metol}\\ \text{4 gms. hydroquinone}\\ \text{25 gms. } Na_2SO_3\end{array}\right\}\ \text{in 500 cc. water}$$

II. 25 gms. Na_2CO_3 " " "

Equal volumes of the solutions from the two are taken and the plate is developed in the mixture.

In our experiments two photographic plates were exposed for the same time and the one developed in the above solution and the other developed in the solution consisting of

$$\text{I.}\quad \left.\begin{array}{l}\text{0.5 gm. metol}\\ \text{50 gms. } Na_2SO_3\end{array}\right\}\ \text{in 500 cc. water}$$

II. 25 gms. Na_2CO_3 do.

It is found that in the case when the amount of the metol is reduced to one half, hydroquinone eliminated altogether, and sodium sulphite being doubled, the development is as satisfactory as in the previous case but it is a bit slow.

Another proportion was tried with the following combination:

$$\text{I.}\quad \left.\begin{array}{l}\text{0.5 gm. metol}\\ \text{2 gm. hydroquinone}\\ \text{37.5 gms. } Na_2SO_3\end{array}\right\}\ \text{in 500 cc. water}$$

II. 25 gms. Na_2CO_3 do.

This formula worked quite well, though the development was again a bit slow.

The cause of the slow development, in cases where more sodium sulphite is due to its retarding influence on the reduction of silver salts by hydroquinone or metol.

It has been established by Dhar,[1] Moureu and Dufraisse[2] and others that many negative catalysts in oxidation reactions actually take place in the chemical changes with the oxidizing agents. It appears, therefore, that sodium sulphite can very well partially replace the expensive developer metol or hydroquinone.

Summary

1. The reduction of AgCl, AgBr, AgI and AgCNS by Na_2SO_3 in presence of organic substances like metol, hydroquinone, pyrogallol and inorganic substances like hydroxylamine hydrochloride, hydrazine sulphate and ferrous sulphate has been studied.

2. It has been observed that in the absence of metol, pyrogallol etc., there is no reduction of the silver salts by sodium sulphite alone but metol, pyrogallol, etc., are capable of reducing silver salts in the absence of sodium sulphite. The reducing power is in the following decreasing order:

Metol > Pyrogallol > Hydroquinone > Hydrazine sulphate > Hydroxylamine hydrochloride > Ferrous sulphate.

3. The reduction of the silver salts is increased both by increasing the concentration of the developers as well as that of sodium sulphite. The inducing action of the developers on the reduction of silver salts by sodium sulphite has been shown to follow the same order as was obtained for the reduction of silver salts by the developers alone.

4. Of all the silver salts the greatest reduction has been observed in the case of chlorides and the least in the case of iodide, the order being AgCl > AgBr > AgCNS > AgI.

5. The mechanism of these reactions has been explained.

6. Reactions of a similar type have also been carried out by using sodium nitrite instead of sodium sulphite.

7. It has been shown by exposure and development of plates that in the existing formula for developers, the amount of such expensive substances as metol, hydroquinone etc. can be profitably diminished if the quantity of Na_2SO_3 is increased.

8. It has been observed that as the quantity of the Na_2SO_3 is increased the rate of the reduction of the photographic plates is diminished owing to the fact that acceptors like Na_2SO_3 begin to act as marked negative catalysts when used in higher concentrations.

Chemical Laboratory,
Allahabad University,
Allahabad, India,
January 29, 1931.

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[1] Proc. Akad. Wet. Amsterdam, 29, 1023 (1921).

[2] Compt. rend., 179, 237 (1924).

REDUCTION REACTIONS IN SILICA GELS

BY DALLAS S. DEDRICK

Gels of the silicic acid type have been characterized[1,2] as rigid, transparent systems having a continuous but very porous solid phase; a continuous liquid phase fills the interstices of the solid. The liquid phase may exist as free liquid or as liquid adsorbed on the surface of the solid phase, or as part of the crystal lattice itself. Diffusion of solute takes place readily through this liquid phase. The chemical composition of the solid phase does not affect diffusion or reaction phenomena within the system.[3]

Clark[4] points out that, in general, freshly prepared silica gels are in a mesomorphic state. They show a paracrystalline structure which on standing undergoes slow changes by means of a regular orientation which must be due to the progressive arrangement of the silicon dioxide molecules into a crystal lattice. Hence, in time, the very small capillary structure must slowly disappear in favor of the regular crystalline structure. This statement is borne out by Röntgen analysis of old silica gels.

Reactions in gels are interesting because the gel structure affords a medium in which no convection currents are produced by the diffusion of the reagents into the system. The purpose of the present investigation was to study oxidation and reduction reactions in an alkaline gel system and to note the influence of the concentrations of the reactants as well as the influence of the gel structure itself on the nature and behavior of the products formed.

Materials and Methods

Because of its slight change in solubility with temperature a silicic acid gel cannot be prepared by cooling a hot solution, but it must be made by the interaction of an acid with a soluble silicate either directly or by dialysis. The gels used in this study were basic in their reaction. Owing to the fact that gelation takes place rapidly from an alkaline solution, it is necessary to mix the reagents directly in the reaction tubes. Calculated quantities are admitted by means of burettes and care is taken to insure thorough mixing and removal of air bubbles before the system sets. The quantities of the reagents used must be very carefully regulated since it was noted that very slight variations from the calculated amounts produce unsatisfactory gels. The gels were prepared and observed in eight inch tubes.

Two concentrations of sodium silicate were used in the preparation of the gels, one having a specific gravity of 1.10 and the other 1.06. They were

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[1] Jordan Lloyd: Biochem. J., 16, 530 (1922).

[2] van Bemmelen: Z. anorg. Chem., 20, 265 (1902).

[3] Dreaper: J. Soc. Chem. Ind., 32, 678T (1913).

[4] Clark: Applied X-rays," 174 (1927).

prepared by diluting ordinary commercial "water glass." All other reagents were either of C.P. quality, or they were specially purified before use. The sulfur dioxide solutions were prepared by passing the gas into distilled water at 0°C. immediately before use.

Throughout this work gelation was produced by sulfuric acid in which calculated amounts of copper sulfate had been dissolved. Gels of three types were prepared using 3N, 1.5N, and 0.75N sulfuric acid, respectively. The copper sulfate concentrations were 1 g., 0.5 g. and 0.25 g. in 30 cc. gel.

After the gels had stood for a day a 10 cc. portion of the reducing agent was added to each tube. The speed of diffusion of the reagent was obtained by noting from time to time the distance through which the reaction band had moved. The readings were made by means of a gauge and are accurate to within less than 1 mm.

The possibility of untrustworthy comparisons caused by non-uniform handling was carefully avoided. In the analysis of the products standard qualitative analytical methods were used.

Results

A distinct qualitative difference is noted in the reducing properties of two percent and one percent aqueous solutions of hydroxylamine hydrochloride. The reaction product in either case is composed of a mixture of red cuprous oxide and minute copper crystals which give a decided metallic luster to the precipitate. The more pronounced effects are noted when the one percent solution is allowed to diffuse through the system. Here, the reduction products are invariably precipitated in the form of Liesegang's rings. No evidence of the banding of the reaction products is observed in the case of the systems reduced by the two percent hydroxylamine solution.

Gels made from the more dilute solution of sodium silicate were invariably more satisfactory. Variation in the concentration of the cupric ion or the concentration of the acid used in making the gel appear to have little influence.

Gels through which a 1 M aqueous solution of sulfur dioxide is diffusing show quite interesting phenomena. Within a few minutes after the addition of the reducing agent there appears a distinct brownish-yellow band containing cuprous oxide. This band moves progressively downward through the gel. Tables I and II show the movement of this band measured in representative gels prepared from sodium silicate with a specific gravity of 1.06. Among the gels listed in these Tables are those prepared by means of three different concentrations of acid and also containing three different concentrations of cupric sulfate. The curves in Fig. 1 are obtained by plotting the mean values of the movement of the band against the time in hours. The results for the dilute gel are shown graphically by Curve 2 Fig. 1. The rate of movement through the concentrated gels is shown in Table III and in Curve 1 of Fig. 1. The two curves lie quite close together. It is to be noted that during the first twenty hours, the diffusion is faster in those gels prepared from the more concentrated silicate solution. After this the curves lie parallel to one another, indicating equal rates of diffusion.

TABLE I

Distance moved by Ring in Cms.

Hours			14	39	63	87	111
No.	Conc. Acid	Conc. $CuSO_4$					
18	3 N	1.00	2.1	3.6	4.5	5.1	5.7
23	3 N	0.50	2.2	3.8	4.7	5.3	5.9
28	3 N	0.25	2.2	3.8	4.6	5.3	5.9
48	1.5 N	1.00	2.1	3.5	4.5	5.2	5.8
53	1.5 N	0.50	2.3	3.6	4.7	5.3	5.9
58	1.5 N	0.25	2.2	3.7	4.8	5.2	5.7
78	0.75N	1.00	2.2	3.5	4.5	5.2	5.8
83	0.75N	0.50	2.2	3.6	4.6	5.2	5.7

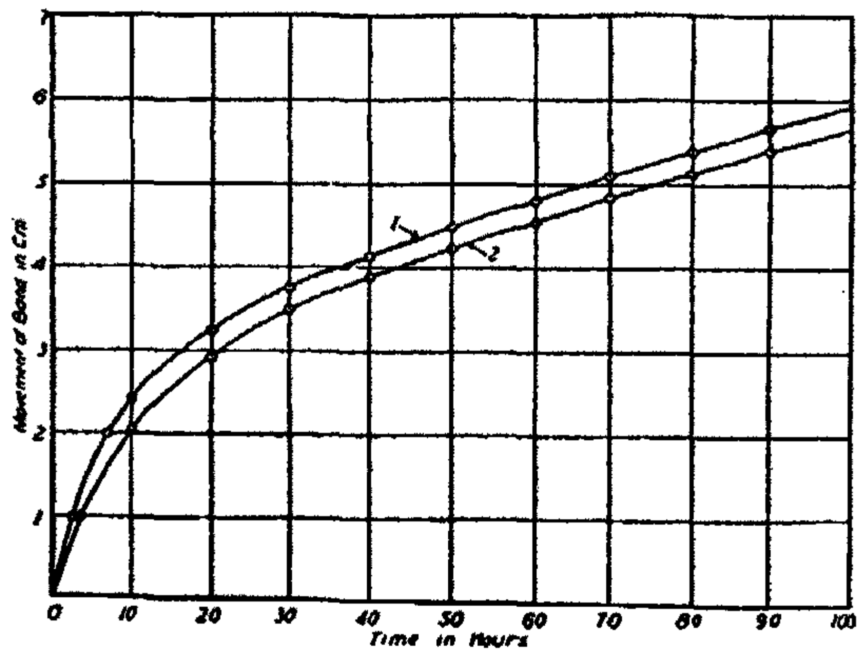

FIG. 1

TABLE II

Hours			.75	18.5	30.5	45.5	76
No.	Conc. Acid	Conc. $CuSO_4$					
106	1.5N	0.4	0.7	2.9	3.5	4.0	4.7
107	1.5N	0.4	0.7	2.9	3.5	4.1	5.0
108	1.5N	0.4	0.7	2.9	3.5	4.1	5.1
109	1.5N	0.4	0.7	3.0	3.7	4.2	

TABLE III

Hours			7.5	25.5	37.5	52.5	83
No.	Conc. Acid	Conc. $CuSO_4$					
101	1.5N	0.7	2.4	3.8	4.0	4.9	5.9
102	1.5N	0.7	2.2	3.3	3.9	4.5	5.3
104	1.5N	0.7	2.2	3.6	4.0	4.6	5.7
105	1.5N	0.7	2.2	3.7	4.0	4.8	5.8

After about four days the formation of small crystals of cuprous oxide was observed in the area through which the sulfurous acid had already passed. These crystals differ from those first formed in that they are red instead of yellowish brown and that they are promiscuously scattered throughout the gel. The crystals grow quite rapidly and they are well defined; they are always more numerous and larger near the bottom of the tube. Initially the crystals have the form of a cross, but as they grow larger other appendages appear until the full-grown crystal is composed of eight well defined projections. Fig. 2 gives a view of the unordered arrangement of the crystals in the gel. Fig. 3 is a view of a typical crystal magnified twenty times.

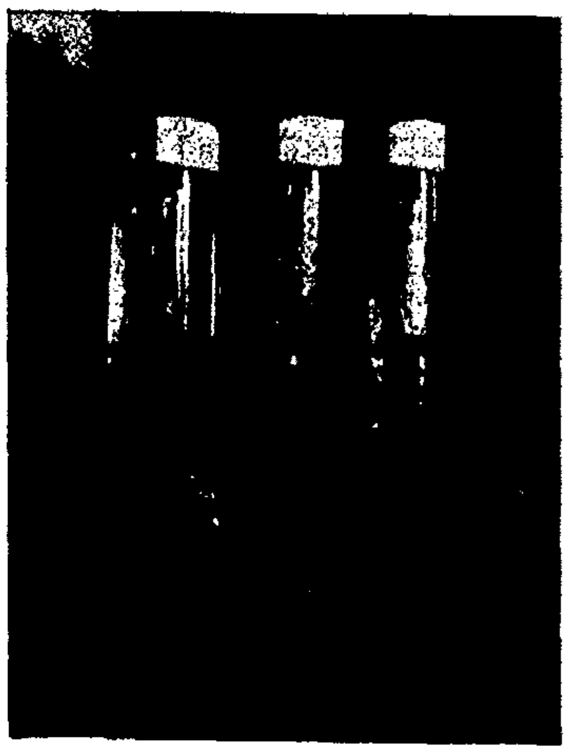

Fig. 2

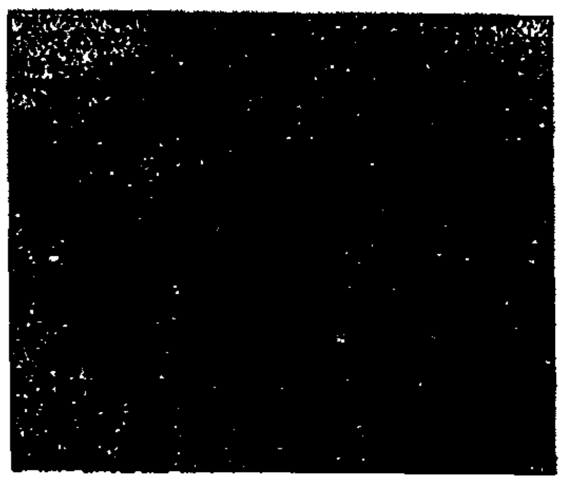

Fig. 3

The crystals belong to the orthorhombic system. Under the microscope they appear to be distinctly fibrous. Analysis shows them to be cuprous oxide. They differ structurally, however, from cuprite which is the most common natural form of cuprous oxide. After a period of two years these crystals under an atmosphere of sulfur dioxide have disintegrated into crystal groups of metallic copper. These small crystals are so arranged that the group has the same geometrical shape as the crystal of cuprous oxide from which it was formed.

A distinct Fehling's test is observed as a result of the diffusion of a 5 percent glucose solution into those gels made from the more dilute solution of sodium silicate. The product consists of yellow cuprous oxide. No reaction is noted upon the addition of the glucose solution to those gels made from the more concentrated sodium silicate.

Discussion

The fact that the more dilute solution of hydroxylamine gives a banded structure while the more concentrated solution does not is in agreement with the results obtained by Holmes[5] and by Bradford.[6] According to

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[5] Holmes: J. Am. Chem. Soc., 40, 1187 (1918).

[6] Bradford: Biochem. J., 10, 169 (1915).

Bradford, striations in gels are formed only by interaction of dilute reagents. Since the reaction product is precipitated from a supersaturated solution it is necessary that the reagents be dilute in order to allow any distance between areas of supersaturation.

Better results are observed throughout when the more dilute solutions of sodium silicate are used in the preparation of the gels. This is due to the fact that the gels so prepared become homogeneous more quickly. A gel so prepared is less brittle than a gel made from a more concentrated silicate solution and is less affected by the stresses incident to gelation. It is quite possible that the paracrystalline state postulated by Clark[4] is more prolonged in the case of the gels made from the more concentrated silicate solution. This would account for the more rapid initial rate of diffusion through a gel so prepared. As is shown by the curves, after the first twenty hours the rates of movement of the reaction bands are equal for both types of gels. This indicates that the molecular or crystal arrangements are quite comparable in the two gels after that time.

An indication as to the structure of the gel is given by the fact that a 5 percent glucose solution will diffuse into a gel made from a sodium silicate solution with a specific gravity of 1.06, but will not diffuse into a gel prepared from the more concentrated silicate solution, this is shown by the absence of the Fehling's test in the tube. This phenomenon indicates that there must be interstices in the one gel which are of a diameter sufficiently large to allow passage of the glucose molecules while in the other there are not. The failure of glucose to diffuse into the more concentrated gel cannot logically be attributed to differences in concentrations which would affect the osmotic relations. According to Pringsheim,[7] osmotic forces are exerted through the medium of a very thin film of precipitate. The reaction stops at the surface if the solutions are isotonic. There is no indication of a reaction in either the supernatant glucose solution or in the gel itself. No reaction occurs when salts are added to the glucose solution to insure its being hypertonic with respect to the cupric surface in the gel. Hence, it is evident that the failure to react within the gel is not due to an isotonic condition.

From a study of the vapor pressures of different liquids absorbed in silica gels, Anderson[8] calculates the diameters of the largest capillaries to be of the order of 5×10^{-6}cm. According to Patrick,[9] we must assume that the pores must approach molecular magnitudes in order to account for the pronounced lowering of vapor pressures above silica gels. However, there is no data at hand showing the effect of different concentrations of gel on the vapor pressure lowering. It does not appear illogical, however, to postulate a pore diameter in the gels made with the more concentrated sodium silicate solution which is smaller than the diameter of the glucose molecule.

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[7] Pringsheim in Alexander: "Colloid Chemistry," 790 (1926).

[8] Anderson: Z. physik Chem., 88, 191 (1914).

[9] McGavick and Patrick: J. Am. Chem. Soc., 42, 946 (1920).

The apparent movement of the reaction bands downward through the gels in those cases where sulfur dioxide solution is the diffusing agent is due to alternate precipitation and solution. The reduction products in alkaline solution are soluble in the acid that diffuses through the gel after the base has been neutralized. The diffusion curves for sulfurous acid are parabolic in shape which is in agreement with the findings of Moravec.[10]

The product of the alkaline reduction of cupric sulfate with sulfurous acid is the yellow hydrated cuprous oxide. This precipitate is quite stable in air, even at elevated temperatures. At higher temperatures the gel-free precipitated cuprous oxide samples fused into copper globules in the reducing flame and changed to a mixture of black cupric oxide and red cuprous oxide in the oxidizing flame. This yellow form of the oxide is quite soluble in sulfurous acid. For this reason the reaction band is never very wide because solution takes place almost as rapidly as precipitation.

The cuprous oxide crystals form with no apparent relation to each other and in no sense could they be considered to form banded structures in the gel body. Obviously, the conditions which bring about the crystallization are not the same as those which caused the original banded precipitates. There is undoubtedly a diffusion of cuprous ion in the wake of the moving sulfurous acid which tends to concentrate the cuprous ion in the lower half of the tube. The crystal formation is, therefore, due to precipitation from a supersaturated solution of cuprous oxide.

Summary

A study has been made of the reduction of cupric ions in silica gels.

Hydroxylamine reduces the cupric ion to the cuprous ion and metallic copper. A one percent solution causes the formation of well defined crystals in banded rings. The two percent solution does not form banded precipitates.

Evidence is presented that in a five percent glucose solution the molecules are of such magnitude as to be larger than the interstices of a gel prepared from sodium silicate having a specific gravity of 1.10. The molecules are smaller, however, than the interstices of a gel prepared from the more dilute silicate, (1.06).

A solution of sulfur dioxide in water diffuses rapidly into the alkaline gels causing the precipitation of a band of yellow, metastable cuprous oxide. This oxide is soluble in the sulfurous acid which diffuses through the gel after the precipitation of the product. In acid solution, the oxide is reprecipitated as well-defined crystals of red cuprous oxide.

During the first twenty hours the rate of diffusion of sulfur dioxide solution into the more concentrated gel is greater than the rate of diffusion of an identical solution through a gel prepared from the more dilute silicate solution. After approximately twenty hours the rates of diffusion are equal.

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[10] Moravec: Kolloid-Z., 49, 39-46 (1929).

This indicates that at the beginning the more concentrated gel is structurally different from the more dilute gel, but that after that time, the two gels become structurally comparable. The general shape of the curve is in agreement with that found by Moravec.

Variations of factors other than the concentration of the sodium silicate produce no effect on the rate of diffusion of sulfur dioxide solution through the gels. A variation due to concentration changes would undoubtedly be noted if the reagents were more dilute.

Acknowledgment is made to Dr. J. L. Whitman, now of Texas Christian University for suggestion and supervision of the problem.

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THE ADSORPTION OF HYDROGEN BY NICKEL POISONED WITH CARBON MONOXIDE*

BY T. A. WHITE AND ARTHUR F. BENTON

Introduction

It has been recognized for some years that the reactions which occur at the surface of a solid catalyst are intimately connected with the nature and extent of the adsorptions of the reacting substances and products by the catalyst. While all gaseous reactions involve two or more gases, adsorption studies have largely been concerned with one gas at a time. In order to have a complete picture of the process occurring at the solid surface, all the gases involved should be considered simultaneously. This has been done to some extent with catalytically inactive materials, and to a lesser extent with active catalysts.

One of the most interesting facts concerning the catalytic activity of a substance is the inhibiting action which a small amount of a foreign gas can have on the activity of the catalyst. The inhibitory action of carbon monoxide on various metallic catalysts[1] has been known for a long time. Pease and Stewart[2] have studied the poisoning effect of carbon monoxide on the hydrogen-ethylene reaction with a copper catalyst. In studying the effect of small amounts of carbon monoxide on the adsorption of hydrogen and ethylene by copper, Griffin[3] found that adsorptions were increased at lower pressures and decreased at higher pressures.

Since nickel is a very active hydrogenation catalyst, it appeared to us that it would throw considerable light on the adsorption problem if the effect of carbon monoxide on the hydrogen adsorption of nickel was studied. It is known that carbon monoxide is a marked poison to a nickel catalyst.[4] By making such a study we hoped, also, to see if the effect Griffin observed was peculiar to copper or if it was a property of all catalysts.

Experimental Method and Apparatus

The initial results were obtained with the usual type of apparatus, which has been described by Pease;[5] a new apparatus, in which stop-cocks are largely eliminated, was employed in obtaining the later results. The details of apparatus, procedure, materials, constant temperature baths and free space determinations have previously been described.[6]

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* Contribution from the Cobb Chemical Laboratory, University of Virginia, No. 70

[1] Henry: Phil. Mag., 65, 269 (1825).

[2] Pease and Stewart: J. Am. Chem. Soc., 47, 1235 (1925).

[3] Griffin: J. Am. Chem. Soc., 49, 2136 (1927).

[4] Green: "Industrial Catalysis," p. 305.

[5] Pease: J. Am. Chem. Soc., 45, 1197 (1923).

[6] Benton and White: J. Am. Chem. Soc., 52, 2325 (1930).

The small amounts of carbon monoxide that were used were always placed in the adsorption bulb, which was at the required temperature, half an hour before the regular run was started. Between runs the adsorbent was evacuated for about two hours, at 200° in the case of the first adsorbent, and at 250° for the second of the two used. The first adsorbent, which was the same as the first adsorbent already used by us,[6] weighed 23.68 g., and the second weighed 23.03 g. Both were prepared from the nitrate as previously described. Helium, assumed to be unadsorbed, was used as a reference gas. Carbon monoxide was prepared by the reaction of formic acid with sulphuric acid and purified by passage over soda-lime and phosphorus pentoxide.

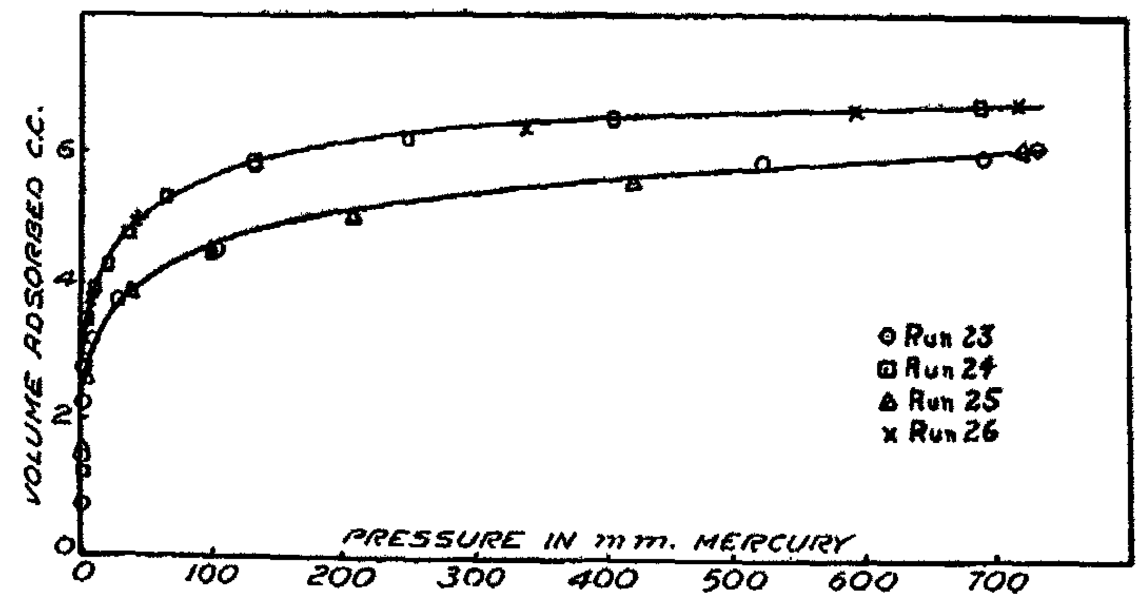

FIG. 1

Adsorption of hydrogen by nickel poisoned with carbon monoxide at 0°. Run 23, hydrogen with no CO; Run 24, hydrogen with 0.038 cc. CO; Run 25, hydrogen with no CO; Run 26, hydrogen with 0.038 cc. CO.

The small amounts of carbon monoxide were measured in two ways, both of which were essentially the same. In the earlier apparatus, it was possible to measure volumes as small as 0.038 c.c. by knowing the volume of the bore of a given stop-cock and filling it with carbon monoxide at a known pressure and temperature. In the later form of apparatus, the volumes of carbon monoxide were measured in the calibrated capillary tube,[6] F, at a known pressure and temperature.

Expermental Results

Fig. 1 shows a series of isotherms for Sample 1. While the same effect was obtained with other samples of nickel, none of them gave such a marked increase in adsorption, all along the isotherm, when carbon monoxide was used. This increase could only be obtained with a fresh sample of nickel which had not previously been exposed to carbon monoxide. It was impossible to be sure that the carbon monoxide was pumped off after a given run. For example, Run 25 checked Run 23, both of which were made with pure hydrogen; and Run 26 checked Run 24, in each of which 0.038 c.c. of carbon monoxide had been taken up by the adsorbent. But Run 27, which was supposed to be a pure hydrogen run, checked Runs 24 and 26, indicating that the carbon monoxide might have remained adsorbed in spite of the evacuation following Run 26. This same type of thing was encountered with Sample 2; an increase was obtained at first, but could not be checked in subsequent runs.

Larger amounts of carbon monoxide, close to a tenth of a cubic centimeter, produce no marked effect on the hydrogen adsorption. The isotherms of pure hydrogen and those with approximately 0.1 c.c. of carbon monoxide present lie so close to each other that it is doubtful if the differences exceed the experimental error. However, it may be that there is a slight increase in the hydrogen adsorption all along the isotherm when this quantity of carbon monoxide is used.

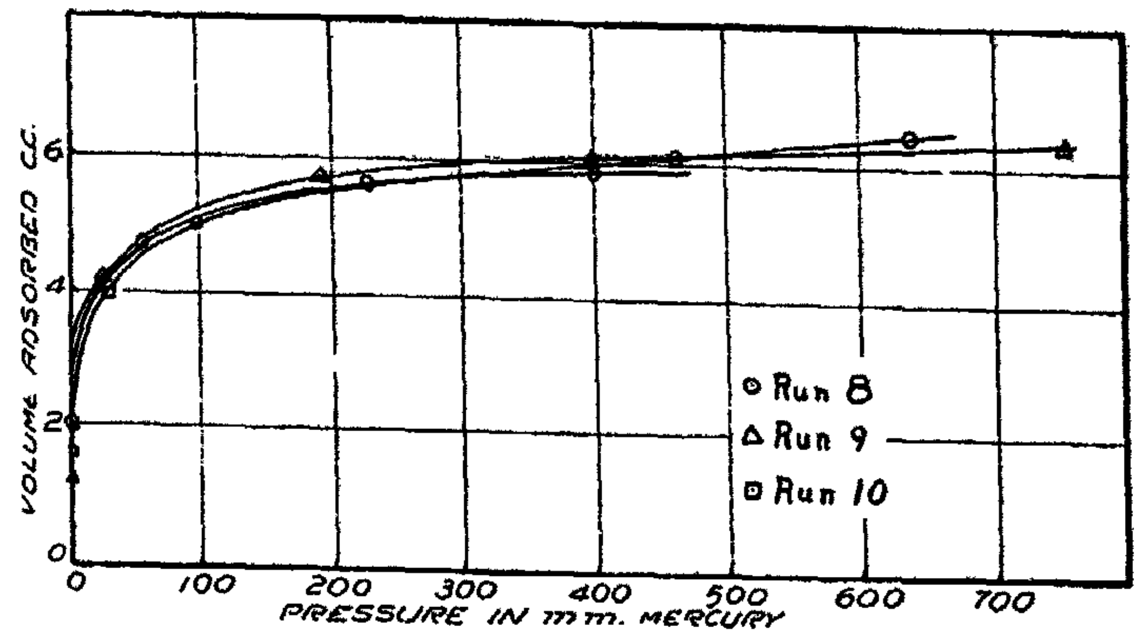

Fig. 2

Adsorption of hydrogen by nickel poisoned with carbon monoxide at 0°. Run 8, hydrogen with 0.3 cc. CO; Run 9, hydrogen with 0.8 cc. CO; Run 10, hydrogen with 1.6 cc. CO.

The isotherms given in Fig. 2 show the effect of larger amounts of carbon monoxide on the hydrogen adsorptions of Sample 2. Run 9 agrees very closely with the pure hydrogen isotherm. Runs 1-7 were made with small amounts of carbon monoxide, and checked satisfactorily the results obtained with Sample 1. It will be noticed that larger amounts of carbon monoxide produce no striking changes in the type of isotherm or in the amounts adsorbed. However, the rate at which equilibrium is reached in these last three cases is slower the greater the amount of carbon monoxide employed.

These experiments were extended to lower temperatures, at −183°, but no quantitative results could be obtained. While each isotherm determined at that temperature was probably as accurate as those obtained at 0°, it was impossible to obtain satisfactory checks. On the other hand, it may be stated qualitatively that the hydrogen adsorptions, in the presence of carbon monoxide at −183°, are decreased by an amount which is approximately equal to the amount of carbon monoxide already present.

Due to the fact that carbon monoxide reacts with nickel, a complete isotherm was never made with that gas at 0°. The amount of carbon monoxide adsorbed at −183° is far in excess of the amount of hydrogen adsorbed at that temperature. Some qualitative experiments indicate that the amount of carbon monoxide adsorbed at 0° is at least equal to, and probably greater than, the amount of hydrogen adsorbed at the same temperature and pressure.

Discussion of Results

It will be noticed at once that the results differ considerably from those obtained with copper by Griffin.[3] On the other hand, at least one point is common to both copper and nickel; namely, a very small amount of carbon monoxide increases the hydrogen adsorption. In the case of copper the increase is noted only at low pressures, for the poisoned isotherm crosses the pure hydrogen isotherm at relatively low pressures; but with nickel the increase can be observed at all pressures up to one atmosphere, when very small amounts of carbon monoxide are employed.

Since it takes only a very small amount of carbon monoxide to cause the increased adsorption, one would hardly expect that such a few molecules could of themselves attract and hold so many more hydrogen molecules. In explaining this increased adsorption, then, it must be assumed that the carbon monoxide changes the surface activity of the adsorbent in some way so as to make more areas available for hydrogen adsorption. There are three ways by which this may be accomplished. Either the carbon monoxide can increase the activity of the already most active areas, or it can stimulate those areas which do not function until higher pressures, or it can create entirely new areas. In view of the fact that only small amounts of carbon monoxide give this effect, the first of the above three ways seems most reasonable to us, because the most active areas have the carbon monoxide adsorbed on them. Therefore, it may be assumed that the increased adsorption is due to an enlargement of active areas, which are produced by having very small amounts of carbon monoxide adsorbed on them.

Griffin explained the decrease of hydrogen adsorption at higher pressures on copper, poisoned with carbon monoxide, by assuming that the carbon monoxide prevented the solution of hydrogen in copper. No decrease in hydrogen adsorption with nickel was observed. However, since the isotherms shown in Fig. 1 draw together at higher pressures, it seems reasonable to assume that at some pressure greater than atmospheric pressure the two isotherms may cross. This drawing together from 1.0 c.c. at 40 mm. pressure to 0.8 c.c. at 700 mm. pressure could be explained by assuming a slight amount, 0.2 c.c., of solubility of hydrogen in nickel. In view of the results of Sieverts[7] this amount does not seem unreasonable.

With the exception of the rate with which equilibrium is reached, it would be difficult to distinguish between the isotherms obtained when larger amounts of carbon monoxide are employed from a pure hydrogen isotherm. Since there seems to be practically no solubility of hydrogen, and in view of the same hydrogen adsorption with or without carbon monoxide present, we must

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[7] Sieverts: Z. physik. Chem. 60, 170 (1907).

assume that either the carbon monoxide increases the hydrogen adsorbing areas by the amount of carbon monoxide present in each case, or the hydrogen is adsorbed on top of the carbon monoxide as a second layer. In view of the fact that amounts of carbon monoxide in the neighborhood of 0.1 c.c. produce only a very slight increase, if any, in adsorption, we believe that, when larger amounts of carbon monoxide are used, the hydrogen is adsorbed either directly as a second layer, or indirectly through the carbon monoxide as some sort of a surface complex. One might expect this second layer to be taken up slowly, and hence anticipate the much slower, observed adsorption.

In conclusion, then, the inhibiting action of carbon monoxide on the hydrogen adsorption of nickel may be pictured in some such manner as this. Extremely small amounts of carbon monoxide produce a slight increase in the hydrogen adsorption; slightly larger amounts, in the neighborhood of 0.04 c.c., produce a maximum increase in the hydrogen adsorption; larger amounts, up to 1.0 c.c, produce decreasingly smaller increases in the adsorption; and still larger amounts of carbon monoxide produce decreases in the hydrogen adsorption. The inhibiting action of carbon monoxide towards the adsorption of hydrogen by nickel might be likened to that group of drugs which have an optimum dose for stimulating body activity, but which produce death in larger amounts. It should be stated, however, that the catalytic activity of a reduced metal does not follow such a course.

It has frequently been pointed out that the relative amounts of gas adsorbed at ordinary pressures by different solids can not be used as a measure of catalytic activity. It has been assumed that only the gas adsorbed at very low pressures is sufficiently activated for catalytic reactions to occur. This hypothesis implies that the more firmly the gas is held, the greater is the degree of activation produced thereby. From the present work and the similar studies of Griffin on copper it might have been expected that carbon monoxide, the presence of which, in very small amount, increases the adsorption of hydrogen at low pressures, would act as a promoter of the activity of the metal, rather than as a poison. Since the reverse is the case, it seems necessary to conclude that the hydrogen, though more strongly adsorbed in the presence of carbon monoxide, is less activated. This must mean that the valence of the hydrogen is largely saturated by the formation of a rather stable surface complex with the carbon monoxide. The poison acts, not by preventing the adsorption of hydrogen on the active areas of the catalyst, but rather by forming a surface compound with those hydrogen molecules which would otherwise have been activated. Depending on the stability of this compound under the given conditions, the action of the poison is more or less pronounced. It should be noted, however, that while the above situation may be fairly general, it can not be universal, since Pease[8] has shown that the adsorption of hydrogen by copper is markedly decreased by poisoning with a small quantity of mercury.

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[8] Pease: J. Am. Chem. Soc., 45, 2296 (1923).

In absence of additional data it would be idle to speculate on the relation between the observations here reported and the peculiarities of copper and nickel as catalysts for the various possible reactions between hydrogen and carbon monoxide.

Summary

A study of the effect of both small and moderately large amounts of carbon monoxide on the hydrogen adsorptions of two samples of reduced nickel has been made at 0° and at −183°.

At 0°, 0.038 c.c. of carbon monoxide increases the hydrogen adsorption at all pressures up to one atmosphere; amounts in the neighborhood of 0.1 c.c. seem to produce only a very slight increase, if any, in the adsorption; and amounts from 0.3 c.c. to 1.6 c.c. have scarcely any effect on the amount of adsorption but decrease the rate of adsorption.

The qualitative result at −183° is that the amount of hydrogen adsorption, at all pressures up to one atmosphere, is decreased by an amount approximately equal to the amount of carbon monoxide employed.

An effort is made to reconcile these results with the known poisoning action of carbon monoxide on the catalytic activity of nickel in hydrogenation reactions.

University, Virginia.

THE APPLICABILITY OF EINSTEIN'S LAW OF PHOTOCHEMICAL EQUIVALENCE

BY B. K. MUKERJI AND N. R. DHAR

We have studied in detail the energetics of fourteen photochemical reactions. From the results now obtained as well as by critically examining the literature on the subject it becomes apparent that Einstein's Law of equivalence fails in the majority of photochemical reactions.

The following fourteen reactions have been investigated with a view to determine the quantum efficiency (number of molecules decomposed per absorbed quantum) in each case at different ranges of the visible and infrared regions of the spectrum and at different temperatures.

(1) Potassium oxalate and iodine; (2) the bleaching of dicyanin; (3) sodium formate and mercuric chloride; (4) quinine sulphate and chromic acid; (5) sodium formate and iodine; (6) potassium permanganate and oxalic acid; (7) ferrous sulphate and iodine; (8) sodium nitrite and iodine; (9) chromic acid and oxalic acid in presence of manganous sulphate and sulphuric acid; (10) sodium potassium tartrate and bromine; (11) mercuric chloride and ammonium oxalate in presence of eosin as sensitiser; (12) the oxidation of iodoform; (13) sodium malate and iodine; (14) sodium citrate and iodine.

The experimental arrangements were the same, as described by Bhattacharya and Dhar.[1]

The following are the experimental results:

(1) *Potassium oxalate and iodine.*

Mean wave length in A°	Quantum efficiencies at		
	20°C	30°C	36°
4725	18.6	40	74.8
5650	3.6	14.9	23.6
7304	3.7	7.5	74

(2) *The bleaching of dicyanin.*

Mean wave-length in A°	Quantum efficiencies at		
	25°	30°	40°
4725	0.258	0.207	0.33
5650	3.36	1.6	2.12
7304	0.29	0.66	0.89

(3) *Sodium formate and mercuric chloride.*

Mean wave-length in A°	Quantum efficiencies at	
	20°	30°
4725	1.2×10^2	6.5×10^2
5650	0.7×10^2	5.6×10^2
7304	0.273×10^2	0.68×10^2

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[1] Z. anorg. allgem. Chem., 169, 381 (1928).

(4) *Quinine sulphate and chromic acid.*

Mean wave-length in A°	Quantum efficiencies at		
	25°	30°	35°
4725	4.3	18.15	3
5650	4	2.66	1.53
7304	2.3	0.45	2.58

(5) *Sodium formate and iodine.*

Mean wave-length in A°	Quantum efficiencies at		
	20°	25°	30°
4725	39	43.8	112
5650	86	14.6	11
7304	54	92	110

(6) *Potassium permanganate and oxalic acid.*

Mean wave-length in A°	Quantum efficiencies at		
	8.5°	14.5°	24.5°
4725	93.8	133	245
5650	38	89	71
7304	39	36	36

(7) *Ferrous sulphate and iodine.*

Mean wave-length in A°	Quantum efficiencies at		
	24.5°	30°	34.5°
4725	18.64	28.4	127.5
5650	16.8	25.7	106
7304	8.34	14.2	52.7

(8) *Sodium nitrite and iodine.*

Mean wave-length in A°	Quantum efficiencies at		
	20°	25°	30°
4725	61.7	190	208
5650	38	81	93
7304	32	68	77

(9) *Chromic acid and oxalic acid.*

Mean wave-length in A°	Quantum efficiencies at	
	21°	31°
4725	53	58.7
7304	3	9.5

(10) *Sodium potassium tartrate and bromine.*

Mean wave-length in A°	Quantum efficiencies at		
	20°	25°	30°
4725	29.4	47	75.3
5650	33.4	36.8	53.3
7304	24.4	26	59

(11) *Ammonium oxalate and mercuric chloride in presence of eosin as sensitiser.*

Mean wave-length in A°	Quantum efficiencies at		
	26°	36°	46°
4350	35.2	45.4	48
4950	85.1	100.4	154
5400	37.7	42.4	58

(12) *Photo oxidation of iodoform in (a) Amyl alcohol.*

Source of light	Quantum efficiencies at		
	19°	29°	39°
1000 watt lamp	3.4	3.54	4.05

(*b*) *in benzene medium.*

Source of light	Quantum efficiencies at		
	24°	34°	44°
1000 watt lamp	450	480	530

(13) *Sodium malate and iodine.*

Mean wave-length in A°	Quantum efficiencies at	
	30°	40°
4725	27.5	59.7
7304	1.5	5.6

(14) *Sodium citrate and iodine.*

Mean wave-length in A°	Quantum efficiencies at	
	23°	33°
4725	11.5	14.9
7304	2.6	11.2

Discussion

From the foregoing results, it will be seen that in general, the following two important issues have been dealt with in all these experiments:

(I) The dependence between the photochemical yield and the wave-length of the light employed and (II) the relationship between the quantum efficiency and the temperature of the reacting system.

From the experimental results recorded in this paper it will be seen that the reactions in which Einstein's law of photochemical equivalence is approximately valid are the bleaching of dicyanin and the oxidation of quinine by chromic acid. It seems likely, therefore, that in these two reactions simply the molecules activated by the absorption of energy react and there is no other complicated secondary reaction. We have calculated the heats of reaction of some of these changes from the existing thermochemical data and they are as follows:

(1)	Sodium nitrite and iodine	37661	calories
(2)	Potassium oxalate and iodine	131300	"
(3)	Mercuric chloride and sodium formate	61057	"
(4)	Mercuric chloride and ammonium oxalate	156894	"
(5)	Sodium formate and iodine	55638	"
(6)	Chromic acid and oxalic acid in presence of manganese sulphate and sulphuric acid	294848	"
(7)	Ferrous sulphate and iodine	116151	"

It is clear therefore, that most of these reactions which deviate markedly from Einstein's law are highly exothermal in nature.

Of late years stress has been laid on the importance of the emission of ions and electrons in chemical changes in explaining the mechanism of chemical reactions. From some preliminary experiments we are of the opinion that emission of ions takes place in the oxidation of sodium sulphate by air and experiments are in progress in this laboratory to find out if electronic emissions actually take place in some of the reactions studied in this investigation.

Basing on these observations the following mechanism has been suggested for a bi-molecular reaction.

$X_2 + hv = X_2$ (active .... (I)

X_2 (active) $+ Y_2 = 2XY +$ electron $+$ heat energy .... (II)

Electron $+ X_2 = X_2$ (active) .... (III)

Thus, this view of activation can satisfactorily explain the abnormally large photochemical yield in exothermal reactions.

From our experimental results it will be seen that in most cases the quantum efficiency at different temperatures increases with the frequency of the incident radiation.

It seems probable that this is due to the fact that the total energy of the absorbed quantum goes on increasing with the frequency of the incident radiation and one quantum may activate more than one molecule.

Our results show that in general, the quantum efficiency increases with the increase in the temperature of the reacting substances.

Mukerji, Bhattacharya and Dhar[1] have carried on measurements of the extinction coefficients of some of the reacting mixtures studied in this paper. In every case they found that the absorption of radiation markedly increases with increase in temperature. These results are of importance because they can be utilised in explaining partially the increase of quantum yield with increase in temperature.

Summary

1. The quantum yield of fourteen photochemical reactions have been determined at different temperatures and under radiations of different wavelengths.

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[1] J. Phys. Chem., 32, 1834 (1928).

2. The Einstein law of photochemical equivalence fails in almost all the cases investigated in this paper.

3. From the experimental results it will be evident that the quantum efficiency gradually increases with the frequency of the incident radiation.

4. The experimental results show that in general, the quantum efficiency increases with increase in the temperature of the reacting substances.

5. It has been proved that those reactions which markedly deviate from the law of photochemical equivalence are highly exothermal in nature.

6. An explanation for the abnormally large photochemical yield has been offered from the point of view of the emission of electrons during chemical changes.

Chemical Laboratories,
University of Allahabad,
Allahabad, November 12, 1930.

THE THERMAL DECOMPOSITION OF CARBON TETRABROMIDE

BY H. AUSTIN TAYLOR

The number of homogeneous gas reactions involving relatively simple inorganic molecules, which up to the present have been shown to occur unimolecularly is extremely small in comparison with the rapidly accumulating number involving complex organic molecules. Two alone in fact are at present known: the decompositions of nitrogen pentoxide[1] and nitryl chloride.[2]

The decomposition of carbon tetrabromide has been shown[3] to occur according to the following equations:

$$2CBr_4 = C_2Br_6 + Br_2$$
$$C_2Br_6 = C_2Br_4 + Br_2$$

with a further possible reaction yielding hexabrom-benzene:

$$3C_2Br_4 = C_6Br_6 + 3Br_2$$

There seems to be some doubt whether the latter possibility does occur; and, if at all, it is certainly to a small extent, the main product being tetrabromethylene. The possibility presented itself that a study of the complete decomposition might yield on analysis a complex rate made up of two consecutive reactions, the first being probably bimolecular and the second, the decomposition of hexabromethane, possibly unimolecular. In view of the work of Stewart and Edlund[4] on the bromination of ethylene, a completely heterogeneous reaction, it was suspected that the decomposition here involved might be in part at least heterogeneous but it was hoped that a measurement of the rate with known surface of contact would allow an estimation to be made of the extent of homogeneity if any were present and permit thereby an analysis of another homogeneous unimolecular reaction. The reaction however was found to be completely heterogeneous and apparently, approximately of first order. The latter is to be expected for a catalysed reaction in which the true order is the second.

The method of following the reaction was essentially a colorimetric one. Measurements were made of the times taken for a known sample of the carbon tetrabromide to yield concentrations of bromine vapor at the temperature of the experiment, sufficient to match certain color standards, the color comparison being made by use of a Lummer-Brodhun photometer head. The color standards were made up from bromine in carbon tetrachloride solution, yielding concentrations in the ratio of 1:2:3 up to six in the six comparative standards used, covering the range of bromine intensity developed by an average amount of carbon tetrabromide. Two sixty-watt lamps were used as

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[1] Daniels and Johnston: J. Am. Chem. Soc., 43, 53 (1921).

[2] Schumacher and Sprenger: Z. Electrochemie, 35, 653 (1929).

[3] Merz and Weith: Ber., 11, 2235 (1878). See Edgar: Diss. Minnesota (1927).

[4] J. Am. Chem. Soc., 45, 1014 (1923).

sources of illumination, one for the reaction vessel and one for the standards, operated from the same electrical source so that any variation in line voltage would affect each to the same extent.

The reaction vessel consisted of a pyrex tube of 120 ccs. capacity with flat ends and carrying a small entrance tube at the side through which the solid carbon tetrabromide could be introduced. The reaction vessel was located in the center of a long tubular furnace lying horizontally so that the light passed down the length of the reaction tube to the photometer. Suitable circular diaphragms served to cut out from the light beam entering the photometer, any light passing down the furnace between the sides of the reaction vessel and the sides of the furnace. A glass cell similar to those containing the color standards, but holding carbon tetrachloride alone was used to balance the light intensity passing through the empty reaction tube, the positions of the two light-sources being arranged to this end.

The complete procedure was then to weigh the reaction tube empty, introduce a suitable quantity of carbon tetrabromide,[1] remove the air by evacuation with a hyvac pump for five minutes (longer evacuation was found only to result in removal of the bromide), seal under vacuum at a previously constricted point, and reweigh the tube together with the remainder of the side arm now removed. The difference between the two weights after due allowance is made for the air removed gives the weight of bromide taken. Experience showed that by having the furnace rheostat regulated for the temperature required for the experiment but with the furnace some twenty degrees higher at the moment that the cold reaction vessel was put in place, the furnace was so rapidly cooled and the vessel warmed to the temperature required that little further control was needed to maintain a temperature constant to within ±1.°

The time at which the tube was placed in the furnace was noted as also the succeeding times at which the bromine intensity developed by the reaction balanced each of the six standards. The latter were mounted on a smooth sliding carriage so that each in turn could be moved rapidly into position. By plotting these observed times as ordinates against six equidistant points as abscissae a smooth curve was obtained which cut the time axis at a point close to the origin. The deviation was noted and used as the time required to heat the tube to the temperature in question and vaporize the carbon tetrabromide. This time, in other words, was taken as the starting point of the reaction, the observed time intervals being reduced accordingly. The values quoted are these corrected time intervals.

The results obtained at 300° C. are given in Table I and show the variation of the rate of reaction with amount of the bromide taken.

To determine the approximate order of the reaction the usual test for the time of a certain percentage decomposition may be applied. The times taken for the bromine developed by reaction to reach a certain standard, correspond,

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[1] The author is indebted to Prof. H. G. Lindwall for the sample used, prepared by the bromination of acetone.

TABLE I

Temperature 300°C

Weight of bromide taken	0.3260	0.4488	0.6240	0.9740g.
Standard	Time Intervals in mins.			
1	5.0	4.5	2.0	1.0
2	11.75	9.0	4.0	2.0
3	22.0	16.5	8.5	3.5
4	42.0	29.5	14.0	5.5
5	77.0	45.5	20.5	8.0
6	—	65.0	28.0	10.5

These data are plotted graphically in Fig. 1.

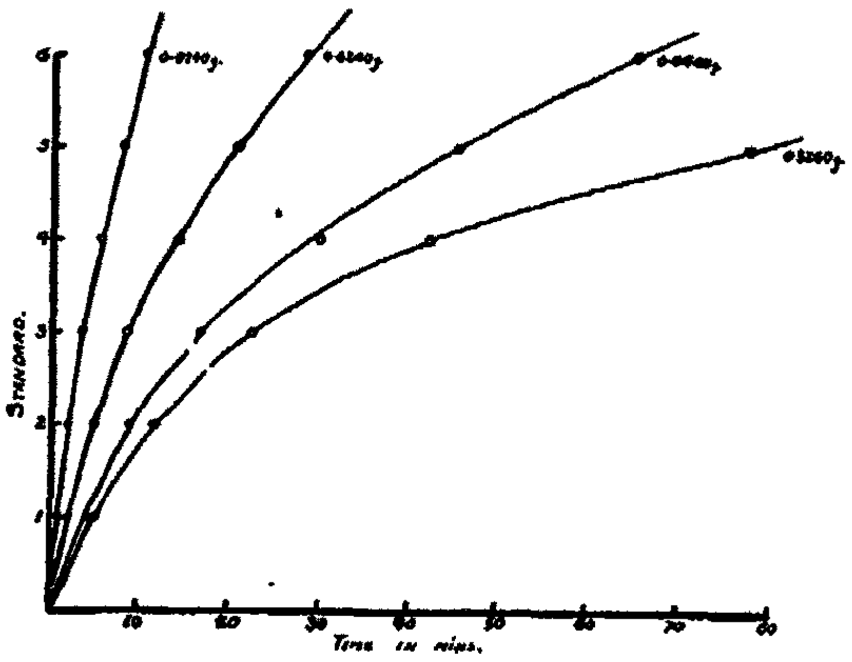

FIG. 1

however, to different total amounts of reaction, when different initial weights of carbon tetrabromide are used. A comparison has therefore to be made between the time taken for one standard to be reached in one case, with the time taken for a different standard in another case depending on the initial amount of reactant used and its rate of reaction. Assuming the reaction to be unimolecular the rate and therefore the concentration of bromide, will be proportional to the initial amount. That is, the amount of decomposition corresponding to the first standard in the first case cited above will be equal to Standard 0.4488/0.3260 = 1.38 in the second case and so on. These times read from the plotted results are in the four cases, 5.0, 6.0, 4.5 and 4.0 minutes respectively, or with standard 2 in the first case and its equivalent in the other cases, 11.75, 13, 12.5 and 11.0 minutes. The order of magnitude of these figures is obviously the same, indicating the correctness of the assumption of first order for the rate. That the agreement is not better is no doubt due to the fact that the reaction is not a simple one and by a disadvantage inherent in the method, the above times correspond to a high percentage total reaction. For measurements to be made early in the course of reaction, extremely dilute standards must be used when the error involved in a photometric balancing becomes largely increased.

The fact that the reaction is not simply that given by the stoichiometric equation soon became obvious after a number of runs had been made in the same tube. The surface of the tube became somewhat blackened with a deposit which was not removed by the ether used to clean out the other products after each reaction. The deposit, probably carbon, negligible in a single reaction, became visible therefore, only after a series of runs had been made in the tube. It was found that after thoroughly cleaning the tube with chromic acid solution, the next reaction tried was several times slower than the ones previously made. It was thought at first that this might be due to some catalytic effect of the carbon deposit. The complete absence of any autocatalytic trend in the rate curves however was significant and the cause was finally shown to be due to reaction between the bromine liberated and the alkali in the glass with the result that the time taken to develop a given visible bromine concentration was increased and the rate apparently reduced. By rinsing the reaction tube, after cleaning with chromic acid and water, with a bromine solution in carbon tetrachloride, reproducible rates could be obtained.

To determine the presence of heterogeneity in the reaction, a thin layer of powdered pyrex was introduced into the reaction tube and after treating with bromine as mentioned above a rate measurement was made. The rate found was so rapid, that it was almost impossible to get a single match with any one of the six standards accurately. The extent of surface was therefore increased less drastically by the introduction of small lengths of glass tubing. The internal surface of the reaction vessel was found to be 190 sq. cms. and an additional surface area of 200 sq. cms. was introduced, the volume being reduced from 120 to 110 ccs. The surface-volume ratio therefore was slightly more than doubled. Table II gives one example of a series of measurements made with this increased surface, the data from Table I using approximately the same initial amount of bromide are included for comparison.

TABLE II

Temperature 300°C.

Weight of bromide taken	0.4325 (increased surface)	0.4488g.
Standard	Time intervals in mins.	
1	2.0	4.5
2	4.0	9.0
3	8.5	16.5
4	14.5	29.5
5	22.5	45.5
6	33.0	65.0

TABLE III

Weight of carbon tetrabromide used = 0.4488g.

Temperature Standard	300	310	320	330
	Time in mins.			
1	4.5	2.0	0.9	0.4
2	9.0	4.0	1.7	0.8
3	16.5	7.0	3.0	1.3
4	29.5	12.4	5.5	2.4
5	45.5	19.0	8.0	3.6
6	65.0	26.3	11.5	5.0

It can readily be seen that the reaction is practically entirely heterogeneous, since a doubling of the surface has doubled the reaction rate.

The effect of temperature on the reaction rate may be seen from the data given in Table III which are the time intervals observed at four different temperatures using approximately the same amount of carbon tetrabromide, corrected proportionately, on the basis of the unimolecular relationship shown above, for the small difference in initial amount taken. The values given therefore are comparable for the mass of bromide stated.

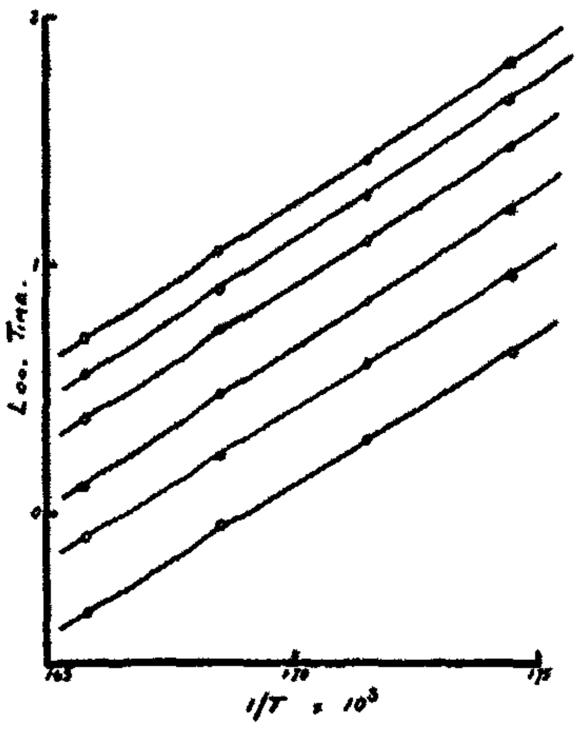

FIG. 2

Fig. 2 shows the linear relation obtained by plotting the logarithms of these times against the reciprocals of the absolute temperatures. The average energy of activation calculated from the above data by means of the Arrhenius equation is 57,200 calories. The value appears to show a slight increase as the reaction proceeds. The average value calculated from the times to the second standard is 55,500 calories whilst that for the sixth standard is 58,300 calories. This would suggest a probably higher activation energy for the secondary reaction than for the primary one, namely for the decomposition of the hexabromethane, which however must also be heterogeneous.

Summary

The thermal decomposition of carbon tetrabromide is shown to be a heterogeneous reaction of apparent first order over the temperature range 300 to 330°C. with an activation energy of 57,200 calories.

Nichols Chemical Laboratory,
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New York, N. Y.

CAESIUM TETRAIODIDE

BY NORMAN RAE

In 1930 a paper was published by Briggs, Greenawald and Leonard[1] on the ternary system caesium iodide, iodine and water at 25°C.

They establish the existence of two polyiodides CsI_4 and CsI_3, and show that the pentaiodide described by Wells and his co-workers[2] does not exist at 25°C.

They call attention to the fact that all other workers in the same field, including the present writer, have followed Wells and assumed that the higher polyiodide is the pentaiodide.

Referring to my paper[3] they say: "Rae studied quantitatively the rate at which iodine is lost by evaporation from the supposed pentaiodide prepared in accordance with the directions of Wells and Wheeler. He gives curves of weight loss against time and shows that the loss virtually ceased, unless the temperature was raised, when the material attained a weight corresponding to the tri-iodide CsI_3. For some unaccountable reason, however, Rae shows no actual experimental data for the first thirty days during which the supposed pentaiodide was losing iodine, nor does he give analyses of the pentaiodide at the beginning of the experiment. Nevertheless, if his weight curve be extrapolated back to zero time, the original composition does come close to CsI_5, but the actual points as given on the curve start out from a stage corresponding almost exactly to a tetraiodide."

The explanation is that the object of the experiment referred to was to show that the break in the volatilisation curve occurs at the point corresponding to the formula CsI_3. Wells and Wheeler give three analyses of their compound in which the percentage of caesium varies from 15.20 to 20.96; from this and the description given, the writer concluded that the supposed pentaiodide was a much more unstable substance than it really turns out to be, and that it would not be possible to prepare the pure dry CsI_5 to give the initial point on the curve. This point was not a necessary one for the object in view and it was a much simpler thing to obtain the composition for the points on the curve from the composition at the end point when only caesium iodide was left.

No attempt was therefore made to analyse the moist product prepared by Wells and Wheeler's method; but, instead, it was placed in the glass weighing bottle in a small desiccator over sulphuric acid to dry for thirty days before transferring to the desiccator containing caustic soda and starting the weighings. The writer was in error in assuming from Wells and Wheeler that the substance was the pentaiodide and that it was more unstable than it really is

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[1] J. Phys. Chem., 34, 195 (1930).

[2] Am. J. Sci., 44, 43 (1892).

[3] J. Chem. Soc., 107, 1286 (1915).

and, at the time, thought that the pentaiodide had lost iodine over the sulphuric acid at about the same rate as it subsequently did over caustic soda and so the first thirty days were included in the diagram although the curve was not drawn for this period.

It now appears that the tetraiodide is not a very unstable substance, for the original data are still available and show that after drying for thirty days over sulphuric acid the composition was

	found	calculated for CsI_4
caesium iodide	40·76	40·56
extra iodine	59·24	59·44

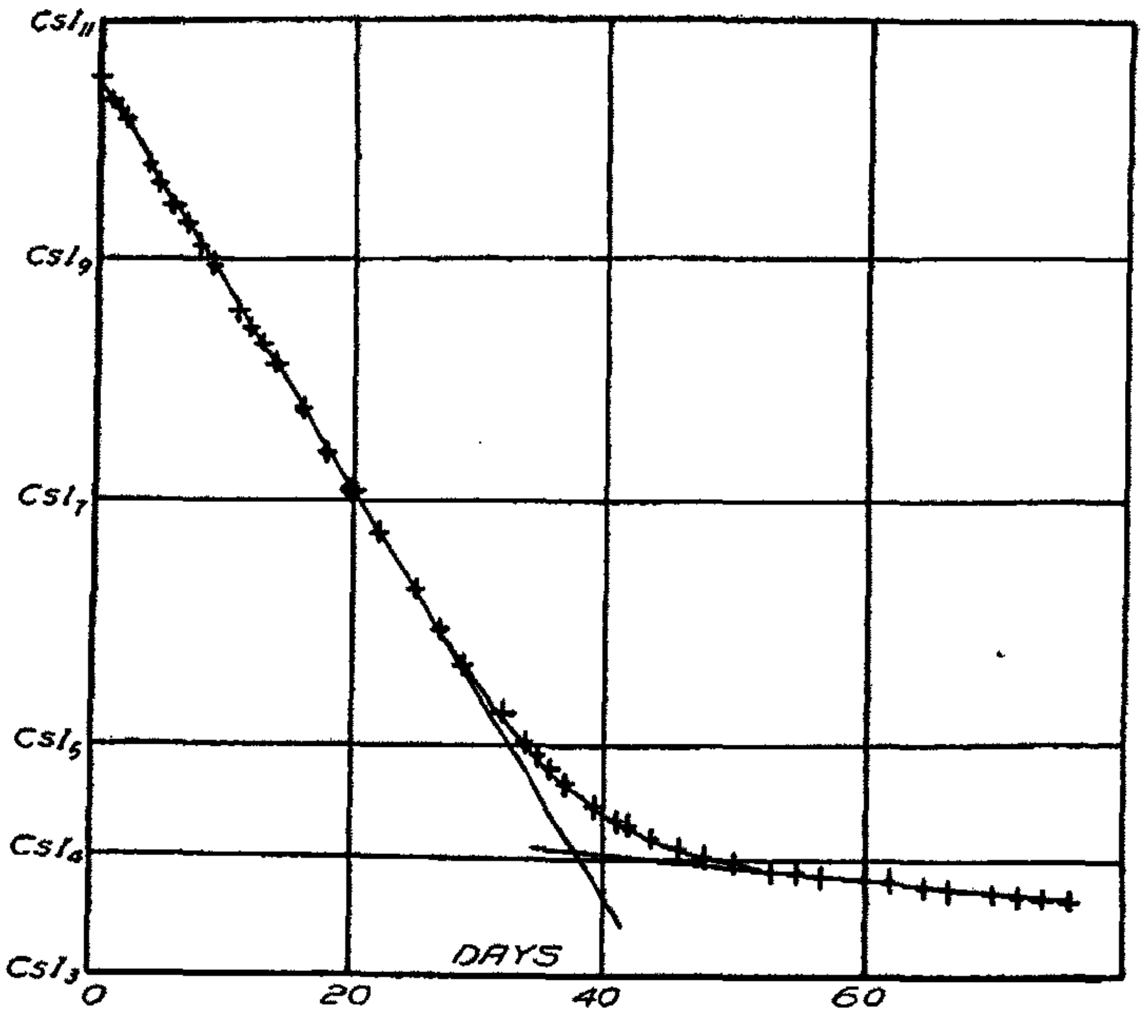

Fig. 1
Caesium Tetraiodide

The authors quoted above also say: "Rae's curves are not very reliable evidence concerning the formulas of the unstable higher polyiodides, since a mixture of iodine and tetraiodide—the supposed pentaiodide—might lose iodine as vapour only very little faster than the tetraiodide alone"; while Wells and Wheeler, in their paper, (loc. cit.) state: "It (CsI_5) loses iodine on exposure about as rapidly as iodine itself volatilises."

To test this statement and also the reliability of the volatilisation method for indicating the existence of a polyhalide, a further experiment has now been made.

Wells and Wheeler found that the higher polyhalide melts at 73°C. and also that artificial mixtures of caesium tri-iodide and iodine, representing compositions varying from CsI_4 to CsI_9, all melt at a uniform temperature of 73°C.

1·7817 grams of caesium iodide were weighed in a flat form weighing bottle, excess of iodine was added, the stopper placed on and the mixture was heated in an electric oven at 80°C. till it had all melted: it was then cooled overnight and weighed to get the weight of iodine added: this was 8.4419 grams. The solid mixture therefore had a composition between CsI_{10} and CsI_{11}. This was placed in a desiccator over caustic soda and was weighed at intervals of two or three days. The caustic soda was renewed three times to ensure that it was not becoming exhausted or coated, thereby affecting the rate of loss. Altogether forty-four weighings were made and these all lie on a very smooth curve which is shown in the diagram. This curve shows a very definite break at the point corresponding to the tetraiodide CsI_4 and also shows that the vapour pressure of the polyiodide is much less than that of free iodine. The average loss per day in the first stage was 0.153 grams and that in the last stage 0.011 grams, that is about fourteen times slower.

Summary

The volatilisation method confirms the correctness of the formula CsI_4 for the higher polyiodide of caesium and shows that its vapour pressure is much less than that of iodine.

University College,
Colombo,
Ceylon.
January 26, 1931.

SOME OBSERVATIONS ON THE COLOUR OF COLLOIDAL SOLUTIONS OF ARSENIC TRISULPHIDE

BY S. S. BHATNAGAR

The paper by Weiser[1] on the subject of the colour of arsenic trisulphide is of considerable interest. It refers in extenso to a paper published by Bhatnagar and Rao.[2] On account of a number of mistakes in translation (as our original paper was written in English) the impression that is left in the mind of the reader is that we consider the red colloidal solution to be definitely As_2S_2. What we actually showed was that the composition of the reddish variety was given approximately by the empirical formula As_2S_2,x H_2S and that at one stage of the removal of H_2S, the composition of the precipitate was more nearly As_2S_2 rather than As_2S_3 when the coagulum was obtained out of contact with air. The presence of air as a result of the oxidation of H_2S always increases the percentage of sulphur. The air was avoided in the preparation of our solutions, which does not appear to be the case in the experiments of other authors. Besides the quantities of As_2O_3 originally taken by us for the preparation of colloidal solution are different from those employed by Weiser. That concentrations affect profoundly the physical and chemical character of the coagula is well known (cf. P. P. von Weimarn and others). Moreover this view of ours is in line with the work of Linder and Picton who showed that the results of the analysis of a colloidal solution of arsenious sulphide always gave results for sulphur too low for As_2S_3. Somewhat similar observations were made by Clermont and Frommel.[3] The results of the analysis (mean of several not quite concordant readings) quoted in our paper (loc. cit.) were obtained by Mr. B. L. Rao, M.Sc. and there is no reason to believe that they are wrong in as much as they show a distinctly less amount of sulphur in the composition than would be the case if the precipitate was As_2S_3 entirely.

The senior author of this paper realised long ago that the simplicity of the analytical results obtained by B. L. Rao did not exclude the possibility of their being explained on a formula more complicated than the one proposed in our previous paper. In a thesis (entitled Studies in Magneto-Chemistry submitted by S. L. Bhatia for the D.Sc. degree of the Punjab University, 1928-29) Bhatnager and Bhatia have shown from magnetic data that the formula of the precipitated colloid is more complicated than that originally given by Bhatnagar and Rao.

The author is unable to share the view that the colour of the colloidal solution is due only to variation in the physical character of the precipitated salt. The reasons for this are as follows:—

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[1] J. Phys. Chem., 34, 1021 (1930).

[2] Kolloid-Z., 33, 159 (1923).

[3] Compt. rend., 87, 330 (1879).

1. That even a solution of H_2S in water is not of simple composition, but contains sulphur, pentathionic acid, etc. The presence of these things would certainly add to the complexity of the arsenious sulphide as ordinarily obtained in colloidal form.

2. Winter, Bhatnagar and Rao and Semmler have all noticed evidence for chemical change.

3. The hydrolysis of As_2S_3 or the oxidation of H_2S which result in the ultimate separation of sulphur gives sulphur as well as As_2O_3 a chance to form adsorption complexes which are chemically different from As_2S_3.

4. W. Pauli and A. Semmler[1] regard the colloid as having the constitution $(xAs_2S_3, H_2As_2S_4, HAs_2S_4)H^{\cdot}$.

These views seem to find support from the conductivity and other physical data (W. Pauli: loc. cit). The case is not unique with As_2S_3. Pauli and his co-workers[2] have shown that even colloids like ferric hydroxide have complex chemical composition when their coagula are chemically analysed.

The main thesis of the paper by Bhatnagar and B. L. Rao was to show the complexity of the so-called As_2S_3 solution. While not contesting the experimental work of Weiser, the author ventures to suggest that purely physical aggregates do not explain the complexity or colour changes of those solutions and that the author, as a physical chemist distinctly inclined towards physics, explored the view of Weiser in 1922 without success.

The reason why this work was repeated by Bhatnagar and Bhatia (Thesis, loc. cit.) from the stand-point of other physical properties was that the quantities of the precipitate obtained were so small that more reliance could be put on physical rather than on the purely analytical methods.

The author believes that the aqueous origin of realgar-like material is to be explained along the lines suggested by Bhatnagar and Rao and by Pauli and that chemical complexes are formed and that realgar of aqueous origin is not exactly As_2S_2 but more complex in character, a fact which is borne out by analyses given in books on mineralogy. As_2S_2 formed by igneous methods is sharply to be distinguished from that obtained in the form of aqueous deposits in caves in nature.

University Chemical Laboratories,
University of Punjab,
Lahore, India.

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[1] Kolloid-Z., 34, 145 (1924).
[2] Kolloid-Z., 35, 131 (1924).

NEW BOOKS

1 + 2

Radiations from Radioactive Substances. *By Ernest Rutherford, James Chadwick and C. D. Ellis. 23 × 16 cm; pp. xi + 588. New York and London: The Macmillan Company; The University Press, 1930. Price: $6.50.* The chapters are entitled: radioactive transformations; the alpha rays; absorption of the alpha rays; some properties of the alpha particle; theories of absorption of alpha rays; secondary effects produced by alpha rays; general properties of the radiations; the scattering of alpha and beta particles; the collisions of alpha particles with light atoms; the artificial disintegration of the light elements; the radioactive nuclei; beta ray and gamma ray spectra; the disintegration electrons; the passage of beta particles through matter; the scattering and absorption of gamma rays; intensity problems connected with the emission of gamma rays; atomic nuclei; miscellaneous.

When discussing radioactive transformation, the authors say, p. 18: "The theory of Cases 2 and 4 has been worked out on the assumption that there is a permanent equilibrium between the successive products of transformation. This is impossible to realise completely in practice, since the amount of every radioactive substance is always decreasing with time. No sensible error, however, is introduced when the *primary* source is transformed so slowly that there is no appreciable change in its amount in an interval of time required for the later products to attain approximate equilibrium with the primary source. This condition is very nearly fulfilled, for example, in the case of radium and its product radon, where the period of the former is 1600 years, and of the latter 3.82 days. The latter approaches its equilibrium value very closely after the radon has been supplied continuously from the radium for an interval of 2 months. During this time, the fraction of the radium transformed is only about 7/100,000, so that for the interval under consideration it may be regarded as a constant source without sensible error. It is convenient to apply the term 'secular' equilibrium to this and similar cases.

"Consider next the important case of radon and its products, radium A, B and C. A stage of equilibrium between radon and its products is reached after the radon has been stored about 5 hours, and the amount of each of the products finally decays exponentially with the period of radon. This is a case of 'transient' equilibrium, for the amounts of the products are changing comparatively rapidly. The amount of radium A, B or C at any subsequent time is always appreciably greater than the amount of secular equilibrium when the supply of radon is kept constant," p. 18.

"The origin of actinium and of its parent protactinium has always been a question of great interest and importance and it is still unsettled. Boltwood early showed that in uranium minerals the quantity of actinium was always proportional to the amount of uranium, indicating that a genetic relation existed between them. On the other hand, the activity of actinium with its whole series of α ray products in a uranium mineral is much less than that shown by a single α ray product of the radium series. The discovery of the new product uranium Y led to the suggestion that it might prove to be the head of the actinium series, for it was present in about the required amount. On this view, the more recently discovered product protactinium is the missing link between uranium Y and actinium. On the other hand, it has also been suggested that actinium has its ultimate origin not in a branch product of the uranium series but in an isotope of uranium existing in small relative amount. It is, however, very difficult to reach a definite decision on these points with the data at present available. Much light may be thrown on this question if it proves possible to purify either actinium or protactinium in sufficient quantity to determine its atomic weight with accuracy. This seems likely to be done for protactinium in the near future, for it exists in uranium minerals in quantity comparable with that of radium and chemical methods of purification have already been devised. When the atomic weight of protactinium is known, the atomic weight of all other members of the actinium series can at once be deduced from a knowledge of the radiations emitted by each product.

"Important new evidence on the problem of the origin of actinium has been recently obtained by Aston (Nature, March 2, 1929, p. 313), by examining with a mass-spectrograph the isotopic constitution of lead obtained from a uranium mineral. A sample of lead, separated by Mr. Piggot of Washington from the radioactive mineral Norwegian bröggerite, was compared with the spectrum of ordinary lead. The mass spectrum of the lead from the mineral showed a strong line 206, a faint line 207, and a still fainter line 208. The line 206 is no doubt due to uranium-lead, but the line 207 cannot be due to the presence of ordinary lead as an impurity or to thorium-lead, for in the mass spectrum of ordinary lead the line 208 is about twice as strong as 207. Aston concludes that the line 207 must be in part due to the end-product of the actinium series, actinium-lead. This, if correct, fixes the atomic weight of all the members of the actinium series. Since six α particles are expelled in the transformation of protactinium into actinium lead, the atomic weight of protactinium should on this view be 231. The atomic weights of the actinium series, given in the table of the radioactive elements, have been calculated on this basis. The evidence indicates that protactinium must arise from an isotope of uranium. The simplest assumption to make is that this isotope, number 92, which will be termed actinium, has a mass 235, and is transformed by the emission of an α particle into a β ray product number 90 which gives rise to protactinium. The β ray product is probably to be identified with uranium Y," p. 32.

"In addition to the groups of α particles which have been assigned to a definite product in the radioactive series, there have been found associated with the complex bodies radium C and thorium C a few particles of abnormally long range. The first observation of these long-range particles was made by Rutherford and Wood in 1916. When absorbing screens sufficient to stop completely the α particles of 8.6 cm. range were placed between a thorium C source and a zinc sulphide screen they still observed a small number of scintillations, which they attributed to an unknown group of long-range α particles. The range of these particles was found to be about 11.3 cm. in air, and their number was about 100 for every 10^6 α particles emitted from the source. They obtained indications that roughly one-third of these particles had a range of about 10 cm., but the evidence was not definite.

"Later Rutherford observed, during the investigations which led to the discovery of the artificial disintegration of nitrogen, that the α particles of radium C were accompanied, in their passage through nitrogen and oxygen, by a small number of particles which had a range in air of about 9 cm. On account of their small number—about 28 in 10^6 of the normal α particles—it has been difficult to fix with certainty the origin and nature of this group of long-range particles. For various reasons Rutherford at first concluded that these particles were not emitted by the source of radium C but arose in the volume of gas exposed to the collisions of the α particles, and suggested that they might prove to be atoms of nitrogen and oxygen set in rapid motion by close collision with an α particle. In later experiments he examined the deflection of these particles in a magnetic field and concluded from his results that the particles probably had a mass of 3 and carried a double positive charge, and that they were indeed isotopes of the ordinary α particles. Subsequently, however, similar measurements of the magnetic deflection of the more numerous long-range particles from thorium C showed that these particles had a mass of 4, that is, were ordinary α particles. This result threw grave doubt on the former conclusions about the nature of the particles from radium C, and further investigation showed that these also were α particles, and, moreover, that most probably they were emitted by the source of radium C and were not produced by collision in the gases traversed by the α particles," p. 87.

"It was observed by Rutherford and subsequent investigators that it was unexpectedly difficult to follow the reduction of velocity below about 0.40 V_0, where V_0 is the maximum velocity of the α particles from radium C, corresponding to a range of α particles of 4 or 5 mm. in air. This difficulty was in part due to the marked heterogeneity of the issuing beam, which caused a broad diffuse band of α particles in a magnetic field, but mainly to the influence of another effect which has only recently been recognised, namely the rapid capture and loss of electrons by low velocity α particles. This effect only manifests itself clearly in a high vacuum, when the issuing beam splits up into three distinct groups of α particles corresponding to neutral, singly charged, and doubly charged particles. With the addition of a small quantity of gas in the path of the rays, these three bands disappear and give place to one main band which is less deflected than the group of doubly charged particles," p. 102.

"We have so far referred to observations on the distribution of He_+ and He_{++} particles after passing through mica and other absorbing screens. An unexpected effect was noted when observations were made with bare sources of platinum wire coated with the active deposit of radium by exposure to radon. Within the limit of experiment, the number of He_+ particles corresponded to an equilibrium distribution. This could not be due to some of the radioactive atoms being driven by recoil into the metal, for a similar effect was observed when a polished metal wire was coated with a surface deposit of radium C by electrolysis. This result is surprising when we consider that on the average the deposit is not one molecule thick and that the mean free path for capture for such velocities corresponds to 3 to 4 mm. of air. It seems probable that the distribution observed is to be ascribed to the radioactive matter itself.

"It is very difficult to believe that these He_+ particles come directly from the nucleus and, even if this be assumed, it is a curious coincidence that the number should be about that required for equilibrium between He_+ and He_{++} in their passage through mica. It was at first thought that a partial equilibrium is set up by the passage of the α particles through the dense distribution of the electrons around the nuclei from which they are expelled. This peculiar effect can, perhaps, be explained by taking into account some recent observations made by Mlle Chamié on the distribution of active matter whether deposited by the action of the emanation or by chemical action. She has obtained definite evidence that the active matter is not uniformly distributed but collects together in granules which may contain as many as a million atoms. Similar results have been obtained by Harrington. Under such conditions, it is easily seen that an approximate equilibrium between singly and doubly charged particles will be set up by the passage of the α particles from the interior of the granules to the surface. The average thickness of these granules is sufficient to lead to an approximate equilibrium between He_+ and He_{++} in the issuing beam of particles," p. 129.

"Taking into account the reduction factor employed in calculating the secondary ionisation, and using the data of Lehmann, it can be estimated that the total ionisations δT per cm. for an α particle of speed corresponding to 1000 electron volts in hydrogen, helium, and air are in thousands of ions 2.9, 2.15, 9.1 respectively, while the observed values are 4.6, 4.6 and 22 respectively. On the average the ionisation calculated in this way is about one-half the observed for all three gases. This indicates that the number of collisions which lead to ionisation are about twice as numerous as those calculated on the Henderson theory, and about 1.5 times the number on the revised theory. A similar result has emerged from a comparison of theory with observation for absorption and straggling of the α rays. The analyses of these different data are thus consistent among themselves and lead to the general conclusion that for the lighter gases the number of effective collisions giving rise to the liberation of δ particles of different speed is about twice as great as that calculated from simple classical considerations, when no account is taken of the orbital velocity of electrons.

"If the classical considerations of the transference of energy between the α particles and electrons are substantially correct for close encounters, the difference must be due to the probability of transfer of considerable quanties of energy in more distant collisions, which on the classical theory gives only a small energy transfer. Such interchanges are possible on the new wave-mechanics and a more complete solution will no doubt ultimately be given along these lines," p. 146.

"The recoil of the atom due to the expulsion of an α particle is clearly observable in a Wilson photograph when the expansion chamber contains a radioactive gas. Photographs of this kind have been obtained by C. T. R. Wilson, Bhose and Ghosh, Kinoshita, Akeuti and Akiyama, and Dee. At ordinary pressure, the recoil track is shown by a knob at the end of the track. As the pressure is reduced, the recoil track becomes longer and often shows evidence of a marked scattering. In some cases, the usual direction of the recoil track does not coincide with the direction of flight of the α particle, but this is no doubt due to a large deflection of the recoil atom by a collision with an atom near its point of origin. The marked ionisation of the recoil atom per unit path is clearly shown by the density of the initial part of its track. Dee has examined the recoil tracks from actinon and actinium A in an electric field in a Wilson expansion chamber and determined the charge and mobility of the recoiling atoms," p. 155.

"When strong sources of radium C, thorium C, or polonium deposited on a small flat plate are viewed in a dark room with a rested eye, the source is seen to be surrounded by a weakly luminous hemispherical zone extending over the range of the α particles. This luminosity excited by the α rays in gases was first studied by the late Sir William and Lady Huggins, who examined the spectrum of the weak light emitted by radium preparations in air and found it to coincide with the band spectrum of nitrogen. This appears to be due to the α ray bombardment of nitrogen occluded in the source. These experiments have been confirmed by a number of observers including Himstedt and Meyer, Walter, Pohl, and Bosch. The spectrum of luminous radium bromide is in part continuous, due to the fluorescence of the crystal. In an atmosphere of helium, a few helium lines were noted but no lines were observed in hydrogen, carbon monoxide and carbon dioxide. The luminosity excited in gases can be best studied by using a source of polonium which emits only α rays, and screening the photographic plate from the direct α radiation. There seems to be no doubt that the spectrum of the weak luminosity produced by α rays is in general similar to that produced by the electron discharge under special conditions in gases at low pressure. Such an effect is to be expected, since the α rays cause the same general type of ionisation and molecular dissociation produced in a vacuum tube by cathode rays and positive rays. The luminosity produced by α rays, however, under ordinary experimental conditions is exceedingly feeble compared with that produced in a discharge tube. . . .

Plates of mica are rapidly coloured brown or black by α rays, the rapidity of coloration depending on the composition of the mica. Geologists long regarded with curiosity small coloured areas in certain kinds of mica, for example, in biotite, cordierite, and muscovite. The sections of these coloured areas are usually circular in shape, and exhibit the property of pleochroism under polarised light, and for this reason were called 'pleochroic haloes.' The centres of these areas usually contain a minute crystal of foreign matter. Joly first pointed out that these haloes were of radioactive origin, and were due to the coloration of the mica by the α rays expelled from a nucleus which contains radioactive matter. This subject has been investigated in detail by Joly and his pupils, by Mügge and many others. In homogeneous material, the haloes are spherical with a radioactive inclusion in the centre and often show a well-marked structure consisting of a number of rings. The radii of these rings are closely connected with the ranges in mica of the different groups of α rays expelled from the active material. In the complete uranium halo, the outer ring marks the range of the α particle from radium C′ (7 cm. in air), and in the thorium halo the range of the α particles from thorium C′ (8.6 cm. in air)" p. 179. Poole concludes that the colour changes in mica are due to chemical decomposition of water molecules by the alpha rays and oxidation of the iron in the mica," p. 183.

"We have seen in the foregoing sections that all the elements from boron to potassium can be disintegrated by the bombardment of α particles, with the two exceptions of carbon and oxygen. The result of the disintegration is in every case the emission of a hydrogen nucleus or proton. No evidence has been obtained of the ejection of particles of any other type. So far as has been ascertained, only one proton is emitted from the disintegrating nucleus; this appears most clearly from the experiments in the expansion chamber.

"While in some cases, e.g. aluminium, the kinetic energy of the particles after disintegration may be greater than the kinetic energy of the incident α particle, in other cases, e.g. nitrogen, it is less. Thus some disintegrations take place with liberation of energy, others with an absorption of kinetic energy. The probability of producing a disintegration with an α particle of given energy varies from one element to another. While the information so far obtained on both these points is meagre and indefinite, yet there emerges from the results a distinct difference in behaviour between the elements of odd atomic number and those of even atomic number. In general the protons emitted by the odd-numbered elements are faster and more numerous than those from the even-numbered elements. It will be recalled that the early experiments were successful in showing the disintegration of the odd elements as far as phosphorus, while the disintegration of the even elements was only observed later.

"This difference between elements of odd and even number manifests itself in other ways. Harkins has shown that elements of even number are on the average much more abundant in the earth's crust than those of odd number. Aston has found that odd elements may have at most two isotopes differing in mass by two units, while even elements may have a large number with a considerable range in mass. The conclusion seems to be that the even elements are more firmly built than the odd elements. In the case of the lighter elements the difference between odd and even has been shown by Aston to extend to the masses of the nuclei. Aston's measurements of the masses of the lighter elements are sufficiently accurate to give some indication of the relative stabilities of nuclei. It is generally assumed that the nuclei of all elements are built up from two units, the proton and the electron. The mass of a nucleus is not given by the sum of the masses of the protons and electrons contained in it, as measured in free space, for inside the nucleus the protons and electrons are packed so closely together that their electromagnetic fields interfere and a fraction of their combined mass is destroyed. The mass destroyed appears as a release of energy in the formation of the nucleus, the greater the loss of mass the more firmly are the charged particles bound together and the more stable is the nucleus so formed. The atomic number and the mass number of the element give the numbers of protons and electrons in the nucleus, and an accurate measurement of the mass of the nucleus will give the loss of mass or release of energy in its formation. Aston expressed his measurements of the masses of the elements in terms of the 'packing fraction,' the divergence of the mass of the atom from the whole number rule divided by its mass number. The packing fraction is therefore 'the mean gain or loss of mass per proton when the nuclear packing is changed from that of oxygen to that of the atom in question.' A high packing fraction indicates looseness of packing of the proton and electron, and, therefore, low stability. We are here concerned not so much with the actual value of the packing fraction as in the change of the packing fraction from one element to the next. If we assume that the disintegration of an element consists solely in the ejection of a proton from the nuclear structure, the residual nucleus will be the next lower in the scale. If, as seems very probable from Blackett's experiments, some disintegrations consist in the binding of the α particle and the emission of a proton, the newly formed nucleus will be the next higher in the scale of elements. In either case an element of odd number will change into one of even number. Now Aston's results show that the light elements of odd number have in general a much higher "packing fraction" than those of even number. Thus when an element of odd number changes into one of even number there will be in general a disappearance of mass. This mass may appear as kinetic energy associated with the emitted proton. Thus Aston's measurements afford a general explanation of the high speeds associated with the protons emitted in the disintegration of the odd-numbered elements," p. 304.

"A claim that lead could be transmuted to mercury and thallium in an arc was made by Smits, but after further experiment withdrawn. Reports of transmutations of even more remarkable type were made by Wendt and Irion, who stated that tungsten was decomposed and partly transmuted into helium when, in the form of a fine wire, it was electrically deflagrated; by Riding and Baly, who claimed that helium and neon were formed from nitrogen subjected to cathode ray bombardment; and by Paneth and Peters, who stated that small quantities of helium could be synthesised from hydrogen by dissolving the latter in palladium. The experiments of Wendt and Irion were repeated very carefully by Allison and Harkins, but no evidence of the production of helium was found. The claim of Paneth and Peters was soon withdrawn and the appearance of helium in the experiments received a more prosaic explanation. It was found that a glass surface which has been completely freed from helium by prolonged heating in hydrogen is able to absorb a detectable amount of helium, almost free from neon, from the atmosphere during only a single day's contact with the air; and also that glass (and asbestos) surfaces which do not give off detectable quantities of helium when heated in a vacuum or in oxygen release quantities of the order of 10^{-8} c.c. when heated in hydrogen. In later experiments precautions were taken to exclude the escape of helium absorbed in the glass surfaces, or the diffusion of helium from the air through hot glass, and the possibility was examined of the formation of helium from certain substances under the action of various agents. Under these conditions the results were entirely negative, and no quantity of helium larger than 10^{-10} c.c. was obtained.

"There can be little doubt that the claims which have so far been made of the transmutation of elements by the use of agents other than swift α particles are untrustworthy. In all the cases reported the presence of an element has been mistaken for its creation. On the present views of atomic structure the nucleus of an atom is extremely small and the forces binding together its component parts are of great intensity, corresponding to several million volts. It seems unlikely that the transmutation of elements on a chemical scale, as opposed to the radioactive scale, will be possible until such potentials are also available in the laboratory," p. 316.

"It may be repeated that the collisions to which this result [of ionisation by β particles] refers are those in which the energy loss is of the order of 50 volts. In connection with the straggling of β particles where the important energy transfers are of the order of 1000 volts, it was found that again classical theory predicted a probability of energy transfer about half that found, although in this case the dependence on velocity appeared to be correct. Williams and Terroux have also investigated the probability of energy transfers of amount 5000 to 10,000 volts by observing the frequency of branch tracks. Here also the actual probability of transfer of energy is greater than that calculated on the classical theory and the dependence on velocity is also in disagreement. Since we have seen that to within about 20 per cent. the total loss of energy is given correctly by the classical theory, it is clear that there must be a divergence from theory in the opposite direction for non-ionising collisions. It appears that the energy actually lost in non-ionising collisions is less than one-seventh of that calculated on classical theory," p. 450.

"The study of the penetrating radiation had its origin in the observations of Elster and Geitel and of C. T. R. Wilson that there was always a small amount of residual ionisation in an electroscope. They found that there was a definite transport of charge to the insulated system even after all possible precautions had been taken to reduce electrical leakage over the insulators. The order of magnitude of this residual ionisation corresponded to the production of about twenty pairs of ions per second per cubic centimetre. McLennan and Burton and Rutherford and Cooke found that the ionisation could be considerably reduced by surrounding the electroscope with a thick layer of some material, and they concluded that part of the ionisation must be due to an external penetrating radiation. That the greater part of this effect was due to radioactive material in the ground was shown by McLennan, Wulf, Gockel, Wright and others, who found that the ionisation was reduced when the apparatus was set up over a deep lake. Bergwitz and Gockel attempted to pursue this further by making observations in balloons. If the radiation came entirely from the earth the effect should decrease with height, due both to the increased distance and to the absorption of the air. Hess was the first to obtain definite results by this method, and showed that, while the ionisation decreased slightly up to a distance of 1000 metres, above 2000 metres it began again to increase, and at 5000 metres it was already two or three times the value found at ground-level. This indicated definitely the presence of radiation travelling downwards through the earth's atmosphere, and in view of the possible cosmic origin of the radiation gave a fresh interest and importance to the investigations. These experiments were continued by Kolhörster with improved apparatus and he was able to extend the measurements to a height of 9000 metres. He observed that the absorption coefficient of the radiation increased with altitude up to 7000 metres and then fell sharply. Quite recently he has made other balloon ascents which have confirmed the maximum of the absorption coefficient between 6000 and 7000 metres, but so far no quantitative theoretical explanation has been offered.

"Millikan and Bowen have reported the results obtained from two flights of small pilot balloons carrying recording electroscopes which reached heights of 11.2 and 15.5 kilometres. The average discharge rate above the 5 kilometre level was about three times the rate at the surface. Hess and Kolhörster have pointed out that this rate was less than that to be estimated from their results," p. 485.

"Some remarkable experiments have recently been carried out by Regener in which he was able to detect ionisation at a depth of 231 metres of water below the surface of Lake Constance. He used a steel ionisation vessel of 39 litres capacity filled with carbon dioxide at 30 atmospheres pressure, and the position of the fibre of the electrometer was registered on a photographic plate at hourly intervals. . . . The great extension in our knowledge of the penetrating radiation provided by these experiments will be appreciated from the fact that even the second value at 78.6 metres is beyond the region explored by Millikan and Cameron," p. 488.

"It is extremely unlikely that the very penetrating radiation observed by Regener could be corpuscular in nature, but it is possible that it is true electromagnetic radiation excited in matter by the impact of the high-speed corpuscles which are responsible for the ionisation observed at smaller absorptions. A detailed examination of this view shows that the chief difficulty will be to account satisfactorily for the phenomena in the transition region.

"At present it is not possible to form any definite idea as to the nature of these corpuscles, they might be either electrons or protons. At such high energies as 10^9, volts, electrons and protons have comparable masses and momenta and the chief remaining distinction is the sign of the charge," p. 490.

"The existence of elements representing nearly all nuclear charges between 1 and 92 is a striking and unexpected fact indicating that, whatever the nuclear charge, stable nuclei can be formed between these limits. The remarkable stability of nuclei and particularly even-numbered nuclei is even more emphasized by the existence of a whole series of isotopes over a considerable range of mass. The nucleus appears to survive the introduction of a certain number of additional protons and electrons without any apparent loss of stability. While so far the observed differences of mass between the lightest and heaviest isotope of an element is limited in general to about 10 per cent. or less, it is by no means certain that a more systematic search may or may not reveal the presence of additional isotopes existing in relatively small amount over a still greater range of mass," p. 524.

"The general evidence on nuclei strongly supports the view that the α particle is of primary importance as a unit of the structure of nuclei in general and particularly of the heavier elements. It seems very possible that the greater part of the mass of heavy nuclei is due to α particles which have an independent existence in the nuclear structure," p. 532.

"It has already been mentioned that there are two exceptions to this general conclusion —potassium and rubidium both show a weak β ray activity which is specific to these elements. This fact was discovered by Campbell and Wood in an examination of the activities of the alkali metals. They found that the β ray activity was shown by all potassium salts, whatever their origin, in proportion to their content of potassium. Tests for the presence of an emanation in the substances used gave a negative result, and they concluded that the observed emission of β rays was a property of the potassium atom. The β radiation was more easily absorbed than that from a uranium oxide preparation, giving a value for μ/ρ in tin varying from 27 to 11 as against a value of 10 with uranium. Similarly, the β radiation from rubidium was shown to be a property of the rubidium atom. Rubidium gave, weight for weight, about seven times the effect of potassium, but the radiation was much more easily absorbed. Subsequent investigations by Campbell, Henriot, Biltz and Marcus, Hahn and Rothenbach, Hoffman, and others have confirmed the conclusion that the β radiations of these elements are not due to traces of radioactive impurity but to the elements themselves. All attempts to influence the activity of either element by chemical operations, and thus to prove that the activity is due to radioactive impurity, have been unsuccessful. Biltz and Marcus prepared specimens of K_2SO_4 from potassium minerals of different geological ages; the activity of the specimens per atom of potassium was always the same. Hahn and Rothenbach compared the activities of rubidium sulphate of different ages, 21 years old, 11 years, and new. No difference could be found.

"In both cases the radiation is a β radiation; no α rays have been observed. Campbell showed that the rays from potassium were deflected in an electric field in the same direction as the β rays from a layer of uranium oxide. The deflection in a magnetic field was observed by Henriot and Vavon for the rays from potassium, by Bergwitz for the rays from rubidium," p. 541.

Holmes and Lawson "conclude that the half-value period of rubidium is probably about 10^{11} years, and of potassium 1.5×10^{12} years. These estimates were based on the assumption that all the atoms of the element are similar in their radioactive behaviour. On the other hand, it is known that both potassium and rubidium consist of two isotopes of masses 39 and 41, 85 and 87, respectively, and it may be that only one of these isotopes, or possibly a third unknown isotope, is responsible for the β radiation. In the case of potassium, a partial separation of the isotopes was obtained by Hevesy. The heavy fraction was collected and an atomic weight determination by Hönigschmid gave a value 0.005 unit greater than that of ordinary potassium. The activity of this fraction was measured by Biltz and Ziegert and found to be about 4 per cent. greater than that of common potassium. The results are in good agreement with the assumption that the isotope of mass 41 is mainly if not solely responsible for the β radiation of potassium. Since this isotope forms only one-twentieth of the element, it will have, if entirely responsible for the radioactivity, a half-value period of about 7.5×10^{10} years.

"No transformation products either of potassium or of rubidium have so far been detected. Since the emission of a β particle raises the nuclear charge by one unit, potassium should change into calcium and rubidium into strontium. If in potassium only the isotope 41 is radioactive, the product will be a calcium isotope of mass 41; at present only two calcium isotopes are known, of masses 40 and 44. Using the above period for potassium 41, it can be calculated that, since the consolidation of the earth's crust, about 2 per cent. of this isotope will have disintegrated. The maximum amount of calcium 41 which has accumulated in potassium minerals during all geological time will amount therefore to about 0.1 per cent. of their potassium content. Even if a potassium mineral could be found which contained only a trace of calcium, it would be exceedingly difficult to detect the difference in atomic weight between the calcium of the mineral and calcium of other origin. In the case of rubidium, the chemical difficulties in the way of establishing the difference in atomic weight between strontium produced by the decay of rubidium and ordinary strontium would not be so great. On the other hand, there is no real rubidium mineral; this element is widely disseminated over the earth's crust but always in small amounts," p. 543.

Wilder D. Bancroft

The Physical Properties of the Soil. *By Bernard A. Keen. 22 × 14 cm; pp. vii + 380. New York and London: Longmans, Green and Company, 1931. Price: $8.00; 21 shillings.* The chapters are entitled: historical introduction; mechanical analysis; distribution and movement of water in the soil; soil properties at low moisture contents—the field range; soil and clay pastes and their behavior; the properties of soil and clay suspensions; soil constants and equilibrium points; physical properties of soil under field conditions—cultivation and cultivation implements; soil temperature; the soil atmosphere.

"Although numerous histories of agriculture have been written, a wealth of untouched material still remains. In particular, no attempt has hitherto been made to trace the relations between the growth of ideas on the physical properties of soil and the development of cultivation implements. An endeavour to do this is made below, attention being confined primarily to British conditions," p. 1.

"In 1523 Fitzherbert's 'Boke of Husbandry' appeared. The book will always remain famous as the earliest work in the English language dealing expressly with practical agriculture, but it deserves to be also remembered for the acuteness of many of the observations on soil cultivation. Fitzherbert possessed a keenly observant mind, and his facts are given with surprising accuracy, although centuries were to pass before the full explanations could be given," p. 3.

"Although Fitzherbert's main concern was to give detailed technical instructions in adjusting and using the implements for the best advantage, he was, at the same time, forming ideas on the physical properties of soil. He recognized the beneficial effect of frost, and alternations of wet and fine weather on heavy soil laid up in ridges. He was fully aware of the danger of freshly ploughed strong land running down to a hard crust under heavy rain. He stressed the value of keeping a rough, lumpy surface over the winter wheat, for not only did this keep the land warmer, but it prevented weed growth, and in the spring the lumps of soil broke down into finer mould, to the benefit of the corn. The distinction between soil and subsoil was not explicitly mentioned, but he drew attention to certain places in Cornwall and Devon where, if the husbandman ploughed deep, he would 'passe the good grounde and have but lyttel corn,' even though the inevitable mattock was used for breaking down the clods. This type of soil, in Fitzherbert's opinion, was more suitable for grazing than for arable farming," p. 5.

"Further trials showed that draught was very little affected by speed. Pusey was very much interested in this result and discussed its practical application at some length. It explained what had much puzzled him in his tests: the invariably higher draught given on all types of soil by the Scottish plough. This plough had a high reputation, based on the greater area ploughed in a day by the Scottish ploughmen as compared with that done in England. Pusey's tests showed that this merit was not due to the design of the plough, which was inferior to the best English patterns, but to the superior adaptation of the brisk Clydesdale horses used to draw it. Although the plough draught was greater than expected, it did not, of course, increase with speed, and was, in addition, well within the power of the animals, whose greater pace enabled them to plough more in a given time than the English horses," p. 21.

"Since the supreme advantages of steam power were the extra depth of working, and speed of work, was it not right to utilise the second one as well as the first and, by substituting cultivators for ploughs, further increase the effective speed of working by combining into one the two operations of deep ploughing and subsequent cultivation? The query was a legitimate one, especially as the actual operation of cultivation had assumed much more importance with the new husbandry; and besides this, there was some evidence that it might obviate the necessity for drainage operations. The key to the matter lay in the ground itself. In general, deep cultivation would answer so long as the soil was not weedy; in this case the plough was preferable, as it would bury any such growth. In other cases the soil needed the weathering effect of winter on the ploughed furrows to be kept in good tilth," p. 26.

"It was stated in the introduction to this chapter that the promise of an accurate specification of size distribution held out by the elegant experimental methods of Odén and others could not be substantiated, owing to the existence of an inherent source of error in every method so far devised. This error was first clearly brought to light by Coutts and Crowther during the experiments at Rothamsted while the Odén-Keen balance was under construction. They were employing a silt suspension of known concentration, whose particles settled completely in a reasonably short time. Knowing the dimensions of the cylindrical sedimentation vessel, the pan, and its depth below the surface of the liquid, the weight of particles that should have been caught by the pan was easily calculable. In many cases surprising differences were obtained between this weight and that actually measured. Examination by transmitted light of the condition in the neighborhood of the pan disclosed the cause of the error. The particles originally underneath the pan subside, and leave clear liquid behind them, since the pan itself intercepts those particles that would enter the clear liquid. On the other hand, in the annular region surrounding the pan, no such interception occurs. In consequence, there is a constant tendency for the suspension density in this annular region at the level of the pan to be greater than that immediately under the pan. Interchange of suspension between the two regions inevitably occurs, and complicated currents are set up in the fluid which interfere seriously with the free vertical fall of the particles, thus contravening the fundamental assumption on which the whole of the mathematical analysis is based," p. 66.

"The factors causing aggregations of soil particles are the cementation by calcium carbonate, a loose aggregation by organic matter, cohesion between particles, and aggregation analogous to the flocculation of weak suspensions. Preliminary treatment with HCl will remove the first, vigorous mechanical pestling or brushing in water the third, while the fourth is dealt with by adding a deflocculating agent, *e.g.* ammonia, in the International method. The effect of organic matter was studied by Robinson, who suspected that the mechanical analysis of certain Welsh soils by the older British method (p. 46) gave unduly low figures for clay when the field behavior of these soils was considered. He found that a preliminary treatment with hydrogen peroxide decomposed or rendered soluble the non-structural organic matter, thus releasing the fine mineral particles held by it, and the percentage of clay was appreciably increased in the subsequent mechanical analysis. This preliminary treatment is included in the International method," p. 74.

"The Odén-Keen automatic recording balance was developed at Rothamsted to provide a continuous graphical record of the change of weight with time, of a pan suspended in a sedimenting soil suspension. It has been found exceedingly useful for other work—*e.g.* evaporation studies, in which single experiments may extend over a considerable period.

"In the original Odén form, weights were automatically dropped into one pan at the instant that the increasing weight in the other pan caused the balance to tilt. The improvements introduced at Rothamsted consisted in the addition of electromagnetic control for the intervals between successive additions of these weights, and the provision of a device giving graphical record of the changes in current. It was found possible to adapt the well-known Callendar Recorder to serve both these purposes," p. 82.

"The feature of the two preceding sections is the demonstration that water movement and distribution are intimately connected with the geometry of the soil framework. Hence, in order to picture the configuration of the pore space, attention should be devoted primarily to the solid part of the soil, *i.e.* to the soil framework. The irregular shapes and sizes of actual soil particles necessitate recourse to some regular and uniform material for the purposes of theoretical development. We therefore consider the so-called "ideal" soil, consisting of spheres all of the same radius, packed together in a systematic manner," p. 109.

"The salient features of the moisture relations are the quantum-like movements of water associated with the filling and evacuation of cells and the fact that different moisture contents can be associated with a given pressure deficiency, the actual value of the moisture content depending on the manner in which that value is approached. These features and the corresponding pressure deficiencies have been verified experimentally by Haines both for 'ideal' and 'natural' soils in a series of simple and ingenious experiments," p. 121.

"The papers of Tempany and Hardy contain exhaustive accounts, based on measurements of the linear shrinkage of soil blocks from which the volume shrinkage was inferred. Tempany concluded that the space between the mineral particles was wholly occupied by a water-saturated gel-skeleton, whose contraction, when water was lost by evaporation, was manifested by shrinkage of the block. Hardy showed that, apart from the doubtful general nature of this hypothesis, it failed to explain the slight shrinkage of some laterite soils from Barbados. Hardy adopted Wilsdon's view that the colloid material possessed a reticulate or minutely porous structure, and contained water in two phases, one adsorbed in the walls of the gel and the other filling the vesicles of the gel, and concluded that shrinkage was due solely to the loss of vesicular water," p. 137.

"In the field, soils are not normally in the plastic condition described in the preceding section, but have a looser structure. Nevertheless, marked shrinkage effects are shown by heavy clay soils on drying. Deep cracks up to an inch in width at the surface are common even in English clay soils during drought, and much mechanical damage to root systems may result. In clay soils under tropical and sub-tropical conditions larger cracks may develop, several inches in width and several feet in depth. In the older 'basin' system of irrigation in Egypt, the soil, after the winter crop of wheat or berseem, remained from May to August, when the Nile flood waters again became available. The extent of the cracking during the 'sheraqi,' or summer fallow, on a typical square metre of the surface can be seen from Fig. 37. Only the larger cracks are shown; there are numerous smaller ones ramifying in all directions. The work of Mosseri shows that this shrinkage not only improves the tractability of the heavy clay deposits in the Nile valley, but as the soil dries out, the deleterious salts concentrate on the outside of the lumps and are thus washed down by the subsequent irrigation of flood water. Mosseri has stated that this effect has been largely responsible for the past freedom of the Nile valley from alkali troubles," p. 143.

"At the time when the so-called 'adsorption isotherm' was receiving much attention in colloid science, attempts were made to estimate indirectly the amount of colloidal material in soil. Ashley used the adsorption of a dye (malachite green) and Mitscherlich and Floess worked with water vapour. The hypothesis on which these methods were based was soon abandoned, but the methods themselves were revived by American workers in connection with their studies of the 'ultra-clay' extracted from soil suspensions by a high-speed centrifuge. They concluded that the relative absorptions of a dye, ammonia, water vapour, or the heat of wetting, shown by the whole soil and by the colloidal material extracted from it, gave a fair measure of the total colloidal content.

"Joseph has criticised the assumption because these methods often give values for the colloid content exceeding the clay content. This would imply that some of the silt fraction was colloidal, which is unlikely. The explanation suggested is that silt possesses some of the properties (*e.g.* base exchange, heat of wetting) chosen for estimation of the colloidal material, and is thus erroneously included in the latter. Joseph further suggested that the clay content as determined by mechanical analysis should be regarded as the colloidal content also. This view was supported by his observation that with repeated passage of a clay suspension through the supercentrifuge used for collecting colloidal clay, the whole of the clay could be obtained in the colloidal form," p. 170.

"Although the colloidal material is essentially a crystalline bentonite, it is not composed of finely divided unaltered crystals of the original clay mineral, but has suffered change in chemical composition by weathering. Kelley demonstrated this by grinding very finely in a ball-mill actual rock materials, calcium-saturated bentonite, and clay colloids, and determining the exchangeable bases before and after the operation. He found that the other replaceable bases, particularly magnesium, were increased in the case of bentonites and clay colloids, but not in the ground rock material, and concluded that these bases were caught in the meshes of the clay crystals, which were ruptured by grinding, thereby exposing the replaceable loss to base exchange. This difference between the original rock and clays was taken to be a consequence of the weathering processes in soil formation . . . .

"The physical and physico-chemical properties of clay suspensions have been the subject of a great number of experiments in recent years, and a connected account would be a difficult matter even if investigators had come to a general measure of agreement. But the literature abounds in anomalies and contradictions, and there is every sign that this will continue for some time to come. The reason is twofold: the experimental methods of colloid science have, with few exceptions, not yet reached the desired stage of refinement; and, compared with the majority of systems studied in colloid science, the clay particle is exceedingly complex. Apparently unimportant small differences in experimental conditions—often unrecognised, and, more often, not recorded—may profoundly affect the measurements, and, in turn, the conclusions. Perhaps the greatest difficulty, apart from that of preparing clay for experiment in some definite and reproducible state, is that chemical decomposition of the clay complex and base exchange phenomena frequently occur, in addition to the particular effect that the investigator is ostensibly studying. In consequence, phenomena ascribed to the original clay material may really belong to a different complex, and one, moreover, which has probably been changing continuously during the experiment," p. 175.

"The idea that the soil moisture could be regarded as distributed in a thin continuous film over and around the soil particles was generally held at the end of the last century; in 1897 Briggs gave it a definite physical form, and treated the films from the standpoint of the surface tension over their curved surfaces, using the ideal soil as his model. The films were convex outwards over the surfaces of the particles, and concave outwards at the points of contact of the particles. Moisture gradients produced by evaporation or percolation were thus analogous to changes in film curvature, or, what amounted to the same thing, changes in the thickness of the films. Movement of soil moisture from regions of high to low water content, and its equilibrium distribution under any given conditions, could therefore be treated as a matter of the resultant force of surface tension oversurfaces of varying curvatures, and of gravity. The treatment, in fact, was closely modelled on the classical work of Reinold and Rücker on soap bubbles, which is familiar to all physicists.

"Owing to the omission of one step in his chain of reasoning—apparently minor but, in reality, vital—Briggs missed the really important consequence of his hypothesis, and thirty years were to elapse before Haines gave the correct version (Chapter III, Section C). As developed by Haines, the geometry of the ideal soil was used to define the characteristics of the pore space, and this, in turn, served to specify the configuration of the water films. Briggs omitted the intermediate step, and referred the water film directly to the soil particles," p. 203.

"Alway and Shull made further criticisms with special reference to the wilting-coefficient. The former showed that if the atmospheric conditions were modified, plants would not wilt until the soil moisture was reduced nearly to the hydroscopic coefficient. Shull's work showed that the plant wilted although the amount of soil moisture and the osmotic pressure gradient from soil to root were in its favour; the explanation of the wilting was that evaporation continued from the leaves largely independent of conditions in the soil. The work of these two investigators demonstrated that the wilting-coefficient depended on the physiological behavior of the plant and the atmospheric conditions, as well as on the soil-water relationships," p. 208.

"In preparing soil for shrinkage determinations, the mass is kneaded with successive additions of water until it shows signs of becoming sticky or fluid. The point at which the mass is just not sticky or adhesive to the fingers is well defined and can be determined accurately after a little practice. It can be regarded as the moisture content at which the attractive power of the soil for water is just satisfied, and is now generally referred to as the 'sticky-point.' The determination was advocated by Hardy, who considered that it measured the maximum imbibitional capacity of the soil colloidal material for water," p. 220.

"There are good reasons for the inclusions of the sticky-point in any scheme of 'single value' measurements for soils. It is a measurement with definite physical significance, and is highly correlated with the ignition loss—in itself a desirable measurement—and it provides a measure of the water held by colloidal material and the interstitial water, the latter having a reasonably constant value for a very wide range of soils," p. 226.

"Meanwhile there arises the fundamental question as to the origin or cause of the variations in soil resistance. What has led to the apparently fortuitous and erratic variations shown in the typical isodyne maps of Figs 57, 60-62? The key is to be found in the observation that they remain constant from season to season. They are almost certainly the resultant of the age-long soil-forming processes. For example, drainage would not proceed uniformly over a field. Small differences in the degree of packing of the particles, minute differences in contour of the surface, would have a cumulative effect on the physico-chemical composition, which would be demonstrated by differences in properties of the kind discussed above. The whole gamut of geological, climatic, and vegetative factors are concerned, and to these must be added the progressive changes brought about by man in his agricultural operations. With the exception of the latter factor, therefore, the isodynes may be ranked with the observations made on soil profiles in the modern system of soil classification," p. 256.

"By destroying weeds cultivation obviously conserves soil moisture. There is also a widespread belief among practical men that the creation of a loose, dry mulch on the soil surface by frequent cultivation prevents loss of water from the underlying moist soil. The effect is ascribed partly to the poor heat conductivity of the dry layer keeping the underlying moist soil at a lower temperature and thus reducing its rate of evaporation, but mainly to the interruption of capillary rise of moisture which, but for the loose dry layer, would reach the surface and evaporate continuously. There is also a third effect, which is not much mentioned in the literature but is of importance on moist, medium, and heavy soils in humid climates. This is the tendency to form a surface cap or crust in a dry spell following heavy rain. It is most noticeable in the spring, and the delicate roots of young plants are often injured when the soil contracts into a crust. Cultivation breaks and loosens the surface layers before they have dried out and thus prevents crust formation," p. 271.

"Veihmeyer's extensive results in large tanks and field plots under a wide range of conditions also showed that no appreciable conservation of moisture was secured by mulching. Rotmistroff reached the same conclusion from his studies at Odessa. On the other hand, King, Hilgard and Loughridge, Cameron and others concluded that upward capillary movement of water to the surface was responsible for considerable losses that could only be prevented by maintaining a dry soil or other mulch at the surface.

"The divergence of opinion can be largely but not wholly resolved. Upward capillary movement of water is now known to be effective over short distances only (p. 93). Hence the conception of a mulch as breaking the capillary channels and thus preventing water from actually reaching the soil surface is invalid, unless a permanent or temporary water table exists within some 6 ft. from the surface. Examination of the experimental conditions used by the above workers shows that in nearly all cases where no benefit resulted from mulching, no water table existed near the surface; conversely, mulching did conserve moisture if such water table existed," p. 273.

"Russell and Appleyard showed that after the soil air was evacuated it was possible to remove a further quantity of gas, consisting largely of CO_2 with some nitrogen. They suggested that this dissolved atmosphere came from the colloidal material in the soil. Winogradsky has shown by a direct microbiological technique that both aerobic and anaerobic conditions exist in soil that is in good physical condition and well aerated. This observation is quite consistent with our picture of the structure of a soil in good tilth, and a rough general idea of the conditions can be attempted.

"The soil particles are aggregated into compound particles or sponge-like crumbs, lying loosely together. The pore spaces between these aggregates are of the same order of dimensions as the compound particles themselves, and this would allow free movement of air and of water. Within the compound particle, however, the dimensions of the pore spaces are in all probability much smaller, as many of the individual particles forming the crumb are very minute. The exterior surface of the compound particle may be regarded as perforated with very small holes communicating with the interior. Owing to the capillary phenomena these minute pores would always tend to be closed with water, and this effect would be aided by such portions of the colloidal material that swell in water. Many of the compound particles therefore could, for a time, develop anaerobic conditions in the interior, although surrounded by fully aerobic conditions," p. 353.

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The Development of Physiological Chemistry in the United States. *By Russell H. Chittenden. 23 × 16 cm; pp. 427. New York: Chemical Catalog Company, 1930. Price: $6.00* In the preface, p. 7, the author says: "In the following pages the attempt has been made to show by explicit statements of actual experimental accomplishments, at different times and in different places, by many workers and groups of workers, something of the progress which has been made in this country during the past half century in the field of physiological chemistry. . . Critical analysis of the accomplishments recorded here has not been attempted; care has been taken to avoid playing the part of a critic of either work or workers."

Some of the sub-heads are: standing of physiological chemistry and physiology in this country in 1870-1880; establishment of the first laboratory of physiological chemistry in the United States; early lines of experimental work; study of proteins; establishment of a department of physiological chemistry at Columbia University; studies at the University of Pennsylvania; chemistry of the brain; chemical study of the tubercle bacillus; specialization in physiological chemistry; physiological chemistry at Yale; vitamines; internal secretions.

The studies of Atwater and Benedict with the "respiration-calorimeter confirmed many of the findings of European physiologists and at the same time gave added data of physiological value for the solving of problems in nutrition. Thus they showed that the heat produced by a man in a given period of time is the same in quantity as that which can be derived from the energy liberated in the oxidation of food materials during the same period; that the energy which a man expends at hard work, is the exact equivalent of the energy liberated by the body metabolism. Their results confirmed the views held by physiologists generally that the energy of muscular work comes mainly not from the oxidation of protein matter, but from the oxidation of carbohydrates and fats, thus affording added proof of the incorrectness of the old theory that protein was the sole source of the energy of muscle work. Especially noteworthy is the fact that these investigations demonstrated for the first time on *man* the application of the principle of the conservation of energy to the human organism," p. 58.

"In contrast to the 14-18 grams of total urinary nitrogen, which must be looked on as normal if the Voit and Atwater dietary standards are followed, Folin pointed to his analyses of normal urines which showed a daily total nitrogen varying from 4.2 to 8.0 grams from a man, perfectly normal, who had for years subsisted on a low nitrogen diet, and 3.8 to 6.5 grams, 3.6 to 6.7 grams and 2.8 to 5.3 grams of urinary nitrogen per day in three other individuals fed on a starch and cream diet. The important matter, however, connected with these figures was the peculiar distribution of the urinary nitrogen. Thus, on a protein-rich diet Folin found 86-89 per cent of the nitrogen was in the form of urea, while on the protein-poor diet the urea-nitrogen had dropped to as low as 62 per cent of the total.

"Again, it was observed that where the protein metabolism was reduced toward the minimum, creatinine-nitrogen was markedly increased, in one case even to 11 per cent of the total nitrogen. These and other facts led Folin to the conclusion as a principle in the chemistry of metabolism, that *the distribution of the nitrogen in urine among urea, and the other nitrogenous constituents depends on the absolute amount of total nitrogen present.* Folin deemed the part played by creatinine as a factor in the relative distribution of the urinary nitrogen the most interesting feature of these investigations and he was led to adopt as "another fixed principle in the chemistry of metabolism" the fact that the *absolute quantity of creatinine eliminated in the urine on a meat-free diet is a constant quantity different for different individuals, but wholly independent of quantitative changes in the total amount of nitrogen eliminated,*" p. 80.

"Intermediate products between proteins and acid-albumin, however, may be produced by the action of acids. Thus, Osborne found that if crystallized edestin was dissolved in the least possible quantity of hydrochloric acid and then precipitated by addition of a small amount of sodium chloride, the precipitate could not be wholly dissolved in a strong solution of the salt. In other words, a portion of the original edestin had been converted into an insoluble form which could not be made soluble again in a neutral salt solution. Further, as it was not soluble in dilute solutions of potassium hydroxide it could not be acid-albumin. Since practically all seed proteins behave in this manner, Osborne has suggested for such insoluble products the general term 'proteans.'"

"Especially interesting was the observation made by Osborne that the acidity of edestan chloride was three times that of edestin chloride; i.e., that the basic property of this altered product was much greater than that of the protein from which it was formed. Toward alkalies the vegetable proteins are more resistant. Thus, Chittenden and Osborne (1891) found that zein, even when exposed to the action of a two per cent solution of potassium hydroxide at 40°C., for twenty-four hours, did not lose its original solubility in alcohol, although it is possible an 'alkali albumin' soluble in alcohol may have been formed," p. 102.

"Again, it is to be remembered that with the exception of man and the anthropoid ape, uric acid is not the main end-product of purine metabolism in the mammalia, the urine containing an oxidation product of uric acid, *viz.*, allantoin. When allantoin is abundant, uric acid is correspondingly diminished. Further, in those animals which excrete relatively large amounts of allantoin certain of the tissues have the power *in vitro* of converting uric acid into allantoin. As a result of these conditions, the oridinary breed of dog, for example, oxidizes the larger portion of the uric acid formed in the metabolic processes, also destroying the greater portion of any uric acid given subcutaneously," p. 138.

"Especially noteworthy were Stanley R. Benedict's results obtained in an investigation of the metabolism of Dalmatian coach dogs, 1916-1917. This breed of dogs proved to have a very peculiar purine metabolism, in that, as Benedict found, they excrete relatively large amounts of uric acid even on a purine-free diet. Thus, with one dog of this breed, weighing about ten kilograms on a diet containing only 2.03 grams of nitrogen there was an excretion of 0.154 gram of uric acid nitrogen and 0.073 gram of allantoin nitrogen, with a total nitrogen output of 5.4 grams. Further Benedict found that the excretion of uric acid showed no gain when the nitrogenous food was increased fourfold, although the output of allantoin increased as the nitrogen intake was augmented," p. 139.

"In searching for a chemical explanation of antiketogenesis, Shaffer made the suggestive discovery that while hydrogen peroxide oxidizes aceto-acetic acid slowly in an alkaline solution, the addition of glucose to the mixture causes the aceto-acetic acid to disappear rapidly, the rate of disappearance increasing with increase in the amounts of glucose and alkali. In strongly alkaline solution at 38° C. with an excess of glucose and hydrogen peroxide the oxidation is complete in a few hours. Glucose was thus shown to possess in alkaline solution *in vitro* a ketolytic action in hastening the oxidation of aceto-acetic acid, which, as Shaffer stated, 'appeared to be analogous to its antiketogenic action in the body.' Glycerol and fructose were also found to be ketolytic, while lactic acid had no such power," p. 188.

"Bloor's investigations of the distribution of lipoids in the blood in various diseases have given interesting results, but only a brief reference can be made here. In acute experimental anemia in rabbits, it was found that of the phosphoric acid compounds of the blood, the lipoid phosphorus was most noticeably affected by the lipemia which resulted. Values as high as five times the normal were observed in the plasma, and twice or over the normal value in the corpuscles. It was also noted that when the lipoid phosphorus was at these levels in either plasma or cospuscles, there was an accompanying increase in inorganic phosphate, which would seemingly imply some relationship between inorganic phosphorus and the lipoid phosphorus," p. 204.

"Apparently all soluble salts of manganese increase liver autolysis, due, as Bradley believed, to an alteration of the normally resistant fraction of the liver proteins, by which they become digestible by the protease. He found that further foreign proteins, such as casein and peptone, as well as the coagulated liver proteins, are digested by the autolytic enzymes of the liver, but this was not true of the crystallized vegetable protein edestin, unless manganous chloride was present. Ovalbumin, on the other hand, could not be digested by the liver except in the presence of hydrochloric acid," p. 208.

"That the reaction, both sensitization and intoxication, must be due to the protein molecule seems perfectly certain, since it is quite inconceivable that any admixture having sufficient potency could be present in the injected protein, where such small amounts are employed, as to produce the effect noted. Again, the experiment with egg albumin affords a good illustration of the well-known fact that both sensitization and intoxication may result from the action of one and the same protein molecule. In such case the question arises as to whether the whole protein molecule is active in accomplishing both sensitization and intoxication, or whether one part of the molecule is responsible for the sensitization while another part causes the intoxication.

"Many attempts to answer this and similar questions have been made without any convincing result. If, as has been claimed by several workers in this field, the intoxication that follows the second injection of protein into animals that have been sensitized by a previous injection is due to a cleavage of the protein molecule with liberation of toxic groups, it is conceivable that the intoxicating effect may be the result of some action on the part of the aromatic radicals of the protein molecule. The work of Wells has brought to light many interesting facts bearing on this question, some quite new, some simply confirmatory of the work of others.

"Thus gelatin, the poorest of all proteins in aromatic radicals, was found to be lacking in the ability to participate in the anaphylaxis reaction, either with itself or with other proteins; animals sensitized to egg whites did not show any symptoms when injected with a solution of gelatin and conversely did not sensitize to egg white. Again, gliadin with its low content of tyrosine and phenylalanine was found to be weak in either intoxicating or sensitizing properties, presumably the former. Pure zein, on the other hand, was actively and specifically toxic to guinea pigs sensitized with zein, although this protein is lacking in both tryptophane and lysine. Plainly, the aromatic radical tryptophane does not take any part in the intoxication produced by proteins, or at least is not an essential factor.

"However important the individual amino-acids may be in contributing to the anaphylactic properties of proteins, it is evident that it is the protein molecule as a whole that is antigenic; when the protein molecule is broken down, the fragments are without antigenic action. Thus, as Wells has found, even such large molecules as the proteoses, peptones, and polypeptides are without the power to either sensitize or intoxicate guinea pigs whether used in conjunction with themselves or with undigested egg white. Likewise, the crystallizable amino-acids were similarly inactive. In other words, as soon as proteins are altered or decomposed to any extent beyond the coagulable form their anaphylactic properties disappear," p. 236.

"Among the proteins of vegetable origin, the so-called proteoses obtained by Osborne from different seeds and grains were found by Wells and Osborne to be distinguishable by their biological reactions as well as by their chemical behavior. They possessed strong anaphylactogenic properties, causing very severe anaphylactic intoxication when injected into sensitized guinea pigs, even in doses of 0.001-0.0005 gram, such doses proving fatal with some of them. Further, their activity was not destroyed by heating at 100° C. for one-half hour. These so-called proteoses are clearly chemically and biologically distinct from the other vegetable proteins so thoroughly studied by Osborne, the anaphylactic intoxication they produce greatly exceeding that induced by the reserve proteins of seeds in general. As stated in an earlier chapter these so-called vegetable proteoses must be quite different from the proteoses formed in pepsin and trypsin proteolysis, since the latter are not possessed of any anaphylactogenic properties whatever.

"The work of Wells and Osborne with isolated pure proteins has strengthened belief in the view 'that the antigenic capacity of a protein depends on the entire large colloidal molecular structure, while its specificity seems to reside in certain of the radicals of the molecule.' The older belief that the immunological specificity manifested by individual proteins must be due to differences, too slight to be detected by any known method, either chemical or physical, has given way to the conviction that 'immunological differences between proteins are usually, and as far as now known always, associated with and presumably dependent upon chemical differences which can be detected by chemical or physical methods.' To this view the work of Osborne and Wells has contributed much, but while admitting that the specificity of the anaphylaxis reaction is connected with the chemical structure of the protein molecule, there remains the question what groups or radicals are concerned in these extremely delicate immunological reactions, where traces of protein almost unbelieveably small are able to produce such startling physiological results," p. 239.

"In the latter study [by Mann, Wilhelmj and Bollman] it was found that when glycocoll and alanine were introduced intravenously into normal dogs, a definite specific dynamic action was produced with the usual change in the excretion of nitrogen through the urine, such as ordinarily follows the injection of amino-acids; but when the liver was removed, glycocoll and alanine failed to produce this effect.

"In their study of glycogen, it was observed that in dehepatized dogs the glycogen of the muscles decreased proportionally to the decrease of blood sugar; that when glycogen was introduced intravenously it was converted into glucose and utilized by the hypoglycemic animal. 'The symptoms which appear with a definite hypoglycemic level (0.035 to 0.025 per cent) bear no relation to the absolute amount of glycogen in the muscles and appear while there is still sufficient glucogen to bring the blood sugar to normal if it were released.' In other words, the glycogen of the muscles cannot be drawn upon rapidly to sustain the normal level of sugar in the blood. Hence, it follows that the liver must be the main source of glucose in the blood and that the muscles of the body are of very little, if any, help in the maintenance of the normal content of blood sugar," p. 285.

"The evolution of physiological chemistry, as in the development of most branches of science, has naturally been attended by more or less specialization, resulting in a tendency towards limitation of one person's activities to some particular branch or section of the science. In the earlier years a worker might range from one field to another with reasonable success; he might indeed become proficient in the entire domain of physiological chemistry. Today, however, all this has changed with the rapid development of the past thirty years, and the individual worker must of necessity limit his activities to some special field in which he may hope eventually to become especially proficient and perhaps a recognized authority," p. 287. "Truly hyperspecialization in many directions is a necessary concomitant of progress today in physiological chemistry," p. 289. The reviewer wonders whether this is necessarily true.

"Though the student and practitioner of medicine today must of necessity be fairly well trained in chemistry, indeed must depend upon chemistry for much knowledge of which he stands in need, yet no one in this generation would think, of advocating the establishment of chairs of chemistry in a medical school. Such a procedure would truly be archaic. Wherein is physiological chemistry in any different position? It is true that physiological chemistry, or biochemistry if that term is preferred, is giving first aid in the solving of many problems of great physiological and pathological importance, but so too are chemistry and physics. It may be said that many problems of a chemical nature present themselves which only the well-trained medical man can appreciate the bearings of, but if such problems are to be solved accurately the one undertaking the investigation must be equally well trained in chemistry, otherwise failure is bound to result. It is certainly as practical for the well-trained physiological chemist to cope with such problems, through study of the special medical aspects of the case, as for the medical man to acquire the necessary knowledge of and experience in the use of the chemical procedures called for," p. 323.

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Infra-Red Analysis of Molecular Structure. *By F. I. G. Rawlins and A. M. Taylor. 22 × 14 cm; pp. xv + 176. Cambridge and New York: The University Press; The Macmillan Company, 1929. Price: $3.50.* In the preface the authors say: "It is noticeable that no book in English exists which deals with the application of infra-red spectroscopy to the analysis of molecular structure. This fact made itself evident to us a few years ago at the outset of work in this region of the spectrum, and it is for this reason that we offer our book —with all its failings—to others who may undertake investigations upon molecular physics, and who approach the subject from the point of view either of the mathematician or of the physical chemist.

"The theme is that of the interchange of energy between matter—gaseous, liquid and solid—and infra-red radiation. With the properties of such an energy flux we are but little concerned, and this serves to explain the omission of much that is interesting in the verification of different radiation formulae, and in the ramifications of pyrometry. Actual laboratory procedure for the circumscribed purpose in view claims a chapter to itself, whilst a selection of the most important mathematical conceptions—again strictly limited to the immediate aim—forms an appendix," p. v.

"Since the infra-red radiation consists of electromagnetic oscillations of a frequency which is slow compared with the normal rate of motion of electrons in atomic orbits, emission and absorption will only occur for charged masses moving at speeds which are some hundred times slower than electron velocities. These masses consist in general of charged ions. Thus the utility of the infra-red radiation lies in the fact that it gives a method by which the presence of rotating or vibrating doublets can be detected," p. x.

"In an important paper Czerny, using a modification of Rubens' original method, was able for the first time to observe the pure rotation spectrum of a diatomic molecule (HCl).

He used a diffraction grating and found no less than seven bands between 42μ and 100μ, which show almost constant differences of wave-number," p. 12.

"Schaefer and Philipps have investigated carbon dioxide gas within the range of frequencies accessible with prisms of quartz, fluorite, and rock salt. Bands of high intensity are found at 2.72μ, 4.25μ, 14.87μ, and it is probable that these are due to fundamental modes of vibration. Now a triangular form, if isosceles, has three characteristic oscillations, and hence the supposition is that CO_2 is a very thin isosceles triangle. . . . Eucken brings forward, from chemical and thermodynamical quarters, evidence which suggests that Schaefer and Philipps' results are compatible with a linear form," p. 22.

"The three gases NH_3, PH_3, AsH_3 have formed the subject of an extensive research by Robertson, Fox and Hiscocks. Their results for NH_3 agree in the main with those of Schierkolk, though the detail was carried to a greater degree of refinement. If the view propounded by Hund be accepted, that NH_3 is a tetrahedral molecule with N at the summit, it is impossible to bring the observed bands into line with his scheme of fundamentals and overtones. That the three gases possess very similar structures is shown by the remarkably constant ratios which persist between the positions of corresponding bands (see page 26)," p. 25.

Allibone has done some work "on the so-called 'many-lines' spectrum of hydrogen. It will be remembered that this peculiar spectrum is really the band spectrum of the hydrogen molecule. The reason for its unusual characteristics is that the moment of inertia is so small as to mask the ordinary appearance," p. 37.

"In explosions of coal gas and air, as much as 25% of the energy of the flame and explosion is liberated in the form of infra-red radiation, the partition of which among the scale of wave-lengths is a function of temperature. Absorption of infra-red radiation in front of the flame is not a dominant factor. In a mixture of hydrogen and oxygen, for example, emission (flame) bands are found to which no absorption bands are known to correspond. It may however be otherwise in some cases. When CO and O_2 are exploded, some 30-50% of the total radiation from the explosion lies in the 4.4-4.5μ band. Now Coblentz found that a thickness of 5.7 cm. of CO at atmospheric pressure absorbs about 40% of incident radiation for this band, from which it may be inferred that some pre-heating is present in advance of the CO flame. This might be considered as almost auto-catalytic in effect. David has produced evidence of pre-activation by infra-red radiation from a study of CO-air and CH_4-air reactions. According to his researches, the speeds of explosion are accelerated if immediately before explosion the gaseous mixtures are insolated by infra-red radiation corresponding to the absorption band of the gas. This acceleration takes place towards the end of the explosion, when a compressional wave has set in advance of the flame. A 'duration of life' of several seconds is suggested for molecules of CO and CH_4 under these conditions, which is in agreement with the energy distribution in flame and explosion spectra.

"A number of recent observations by Garner, Johnson and Saunders upon catalytic effects in CO and O_2 explosions (moist and dry) and infra-red emission spectra may be mentioned. Water and other positive catalysts greatly reduce the emission at 4.4μ and 2μ to 8μ; whilst up to the present no contrary effect of increase of infra-red emission has been observed. The authors however remark that the possibility must not be overlooked that catalysis in the flame and explosion is always of this type," p. 38.

"There is a great prevalence of absorption bands of liquids in the visible spectrum, a number of which are probably connected in some way with those of the infra-red. It is hardly likely tha Haber's rule will apply, since this really amounts to the assumption of simple harmonic motion. Victor Henri expresses the opinion that the infra-red and ultraviolet frequencies of a liquid are connected by integral relationships, and that this simple character is maintained when a number of bands are present in either region. This amounts in effect to a general acceptance of Haber's square-root rule, or some similar formula," p. 46.

"Collins, using two spectrometers to obtain high dispersion, has worked between 0° and 95°C. in order to find out the nature of the shift with temperature. He establishes a displacement towards shorter wave-length with increasing temperature, and a marked increase of the intensity of absorption for the bands at 0.77μ, 0.98μ, 1.21μ. This latter effect is described as due to the presence of varying amounts of the polymers $(H_2O)_2$ and $(H_2O)_3$ at different temperatures.

"In a recent contribution Tammann reports the outcome of some extensive researches on the 'water' band at 4.7μ. He finds that this band is very strong in ice, lacking in water-vapour, present but weak in water and much reduced in a concentrated solution of NH_4Cl. The cause is ascribed to changing quantities of the species $(H_2O)n$, as in Collins' examination," p. 48.

"A common microscope cover-slip of thickness 0.09 mm. showed absorptions at 5.5μ and 6.52μ which correspond fairly closely with well-known bands of SiO_2. A specimen of glass only 0.001 mm. in thickness showed a transparency of 90% up to 8μ. This affords an interesting comparison with the behaviour of glass of 'ordinary' thickness, i.e. that of electric lamp bulbs, which is usually opaque to infra-red radiations well on the shorter wave-length side of 3μ. With the very thin piece, Coblentz examined the reflection spectrum, and found a number of considerable maxima near 9μ. When the composition of the melt was altered the intensity varied a good deal, but little effect was recorded upon the positions of the bands. This appears to be in general agreement with what is found for ordinary liquid solutions, in which concentration seems to have little influence on band displacement," p. 59.

"What exactly the relation of the water groups to the radicle groups may be is an interesting though obscure question, but Schaefer has pointed out that this water of crystallization possesses a kind of mimicry, in the sense that it becomes uni-axial in uni-axial crystals, and bi-axial in bi-axial ones: in other words it appears to assume the optical character of its surroundings. A detail which has not up to the present been settled is the relationship of the intensity of these water bands to the number of molecules of water of crystallization present. An interesting case for research would be that of copper sulphate, which at different temperatures holds different numbers of molecules of water of crystallization," p. 62.

"Lindeman has suggested a means by which the frequency may be determined at the temperature of melting. If the atoms in a space lattice are vibrating, then the amplitude can never exceed the lattice spacing, and the attainment of this limiting condition is then characteristic of the melting temperature," p. 82.

"It may be as well to notice here the bearing of the ionic or non-ionic nature of the groups upon the type of infra-red spectra obtained. In the case of polar salts where the units are unquestionably ionic, such as NaCl, KBr, etc., the forces are so related to the masses that the vibration is a slow one lying far out in the infra-red spectrum. In the case of groups like CO_3, NO_3, SO_4, etc., where the charges borne by the central atom can be quite large, the infra-red spectrum always shows the presence of comparatively rapid vibrations, usually corresponding to wave-lengths from 6μ to 15μ or 20μ. This undoubtedly indicates that even though the central atom may exert very great polarizing power upon the external atoms of the group, thereby largely modifying the forces of cohesion and consequently the periods of characteristic vibration, yet the atoms are fully ionized and act upon one another with the ordinary coulomb forces, which are sufficiently strong to account for the rapidity of the fundamental or characteristic oscillation.

"Thus the type of infra-red spectrum may be made a valuable criterion of the nature of the forces within the complex radicles, and consequently of the state of ionization of the component parts. Such an argument may even be extended to a non-metallic compound such as silicon carbide, where intense reflection bands are found in the short infra-red region, which may thus be taken as indicative of the ionic nature of the units Si and C, one having a negative charge the other a positive charge, in spite of the family resemblance between the two atoms. In the following paragraph evidence is mentioned for supposing a similar behaviour even among the atoms of the element sulphur," p. 104.

"Within the last few years it has become increasingly clear that Newtonian mechanics, even assisted when necessary with relativistic refinements, are incapable of describing the states of molecular and atomic systems. In other words, the quantum theory needed a new mechanics suitable for systems of the order of magnitude met with in modern physical research.

"The first attempt in this direction was due to Heisenberg, and resulted (the mathematical machinery being in part due to Born and Jordan) in the matrix mechanics. The basic idea was that only directly observable quantities such as intensity and frequency should find place in a rational theoretical physics, and thus the possibility of knowing the history of an electron in a stationary state (i.e. where it does not radiate) was frankly abandoned," p. 147.

"Thus, in the same way that it becomes unjustifiable to apply the methods of geometrical optics when obstacles and apertures become comparable in their dimensions with the wave-length, Schrödinger considers the breakdown of particle mechanics for distances of the order of molecular or atomic dimensions. This view ascribes the failure of the cruder treatment in both cases to the fact that both light and matter originate in wave motions (compare equation $g = v$ above)," p. 149.

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The Colloid Chemistry of Rubber. *By Paul Stamberger. 25 × 16 cm; ii + 80. London: Oxford University Press, 1929. Price: $2.00.* This book contains the subject-matter of the Gow Lectures given at University College in November 1928. The subjects of the five lectures were: colloid chemistry and colloids; the colloidal properties of rubber—rubber latex and its industrial applications; lyophile colloids (gels)—crude rubber and its solvation; compounding—compounding ingredients—rubber substitutes—synthesis of rubber; vulcanization—devulcanization—recent views on the structure of rubber.

This is a disappointing book because the author does not say anything definite. On p. 18 we read that "in the natural latex we find that the particles vary in size, mostly from 0.1 to 2 μ." There is nothing to show that this is not a haphazard variation, that it depends on the species, and that the latex with the small particles cannot be precipitated readily by centrifuging.

In one paragraph on p. 24 the author has the latex coagulating at pH 4.8 and in the next paragraph at pH 6.6. There is a good deal of question nowadays whether the rubber in the latex is liquid or not. On p. 36 the author says: "In the case of swelling the solvation action of the solvent on the jelly is not sufficiently strong to disintegrate the whole solid, and it combines with it at first, by penetrating between the particles of the solid, separating them from each other to a certain extent and thus increasing the volume.

"In this manner the jelly imbibes solvents. The nature of forces between jelly and liquid has not yet been fully investigated. Katz suggests that in both cases the same forces are present, and does not see much difference between the swelling of a jelly and the solution of a crystal. Other workers, such as Zsigmondy and Kruyt, put forward the hypothesis of adsorption. With the experimental data available at present it is hardly possible to decide which of the theories is correct. It is not impossible that in some cases both phenomena occur, in others one of them only," p. 36.

On p. 40 the author cites von Schröder's experiments with gelatine to show that a gelatine jelly swollen to its maximum, when taken from the liquid and placed in a closed space containing the saturated vapor of the solvent, loses a part of its liquid. He is distinctly supercilious about the apparently contradicting observations by Wolff and Buchner. On p. 44 the author assumes that a solution of killed rubber is a true solution.

"With regard to the colloidal properties of vulcanized rubber, the first question is whether the vulcanized rubber is a two-phase system or not. The possibility of the existence of such a sulphur-rubber dispersion or a rubber-compound rubber dispersion has been mentioned. The vulcanization has been followed under the microscope by E. A. Hauser and Hünemörder; but it is not possible to draw any definite conclusions from this investigation," p. 66.

"The author thinks that the existence of long-chain molecules is the main factor responsible for the behaviour of rubber, which behaviour may be due to a particular aggregation of them. Since crude rubber is in a metastable condition, the circumstances under which it exists will govern the details of its behaviour," p. 76.

The book cannot be recommended.

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