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PROTEIN STRUCTURE AND WATER ABSORPTION[1]

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Received August 1, 1937

The capacity shown by all proteins for absorbing water is a familiar fact to all colloid chemists. There are innumerable studies in the literature dealing with the subject. Dry proteins will absorb water from moist air or from water in the fluid state, and protein sols if placed in a dialyzing bag will, under suitable conditions, draw more water into the bag. The protein particles in solution exert an osmotic pressure; if they carry a net positive or negative charge, they cause the establishment of a Donnan equilibrium among the diffusible ions present, which adds an additional factor to the internal osmotic pressure and causes more water to flow into the system.

It is a comparatively simple matter to work out the conditions controlling the reversible intake of water into a protein sol. There is considerable evidence that some of the water is very closely associated with or "bound" to the protein molecule (2), and it has indeed been suggested (11) that this firmly bound water is actually linked to definite positions in the protein molecule by a coördinate link or hydrogen bond, though it may merely be held in a dynamic equilibrium around the charged centers of the protein zwitterion. The rest of the water held in the system is held by the osmotic equilibrium.

The amount of osmotic water present in any system is controlled by the extent to which the system is free to swell. In a structureless system like a sol, osmotic water flows in until it is balanced by the head of pressure in the osmometer. As soon as structure is present, the mechanical hindrance to swelling, due to the structure, begins to have an effect. This begins to show even in systems as apparently homogeneous as gelatin gels.

Figure 1 shows the swelling of a number of gelatin gels set from sols of varying concentration under varying external conditions. It should be noted that these gels have never been dried out. The original concentration at the moment of setting has a striking and consistent influence on swelling under all conditions (3). This has also been shown by Kunitz

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[1] Presented at the Fourteenth Colloid Symposium, held at Minneapolis, Minnesota, June 10–12, 1937.

(12), who found that a 10 per cent gelatin gel forms a stable system which maintains equilibrium with water, while more concentrated gels absorb water and less concentrated gels actually expel water when in contact with water.

If gelatin gels set at different concentrations are dried down before

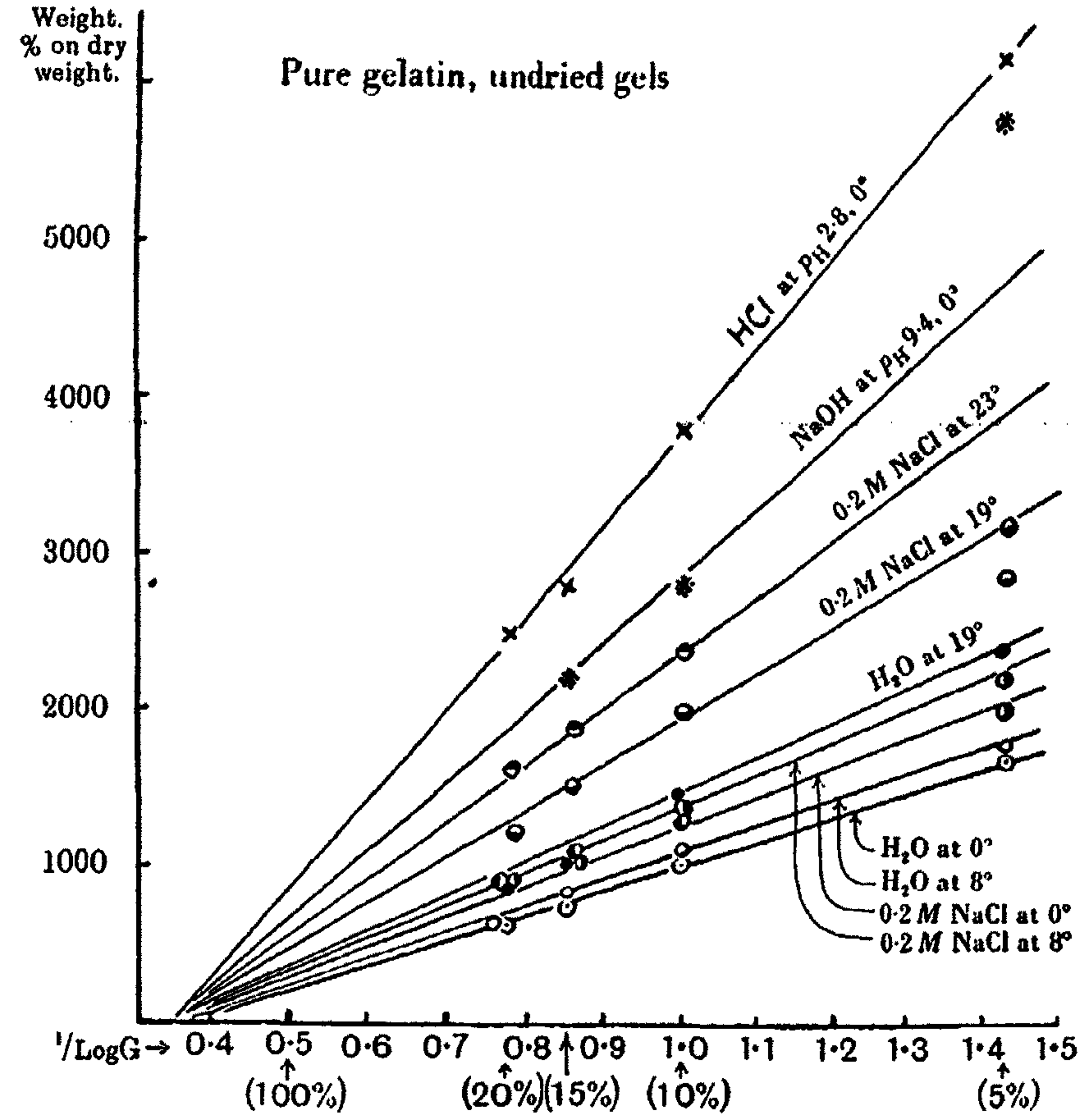

FIG. 1. Swelling of a number of gelatin gels. Ordinate = 1/log G, where G = concentration of gel at setting; abscissa = swollen weight of gel as percentage of dry weight.

being placed under the experimental conditions, the effect of the original concentration still persists, and to this is added an additional factor, due to the drying. It is noticeable that gelatin gels once dried never swell to the same extent as before drying.

For gelatin gels which have never been dried out, swelling measured as a percentage gain in weight on the dry weight of the gelatin is a linear function of 1/log *G*, where *G* is the percentage concentration of gelatin in the original gel. The simplest inference from this is that the molecules of gelatin in the gel form cross links, making a kind of internal scaffolding throughout the gel, and that the more crowded the molecules, the more rigid the scaffolding. Apparently these molecular cross links are not all readily broken, even by acid or alkali, until fairly high concentrations are reached.

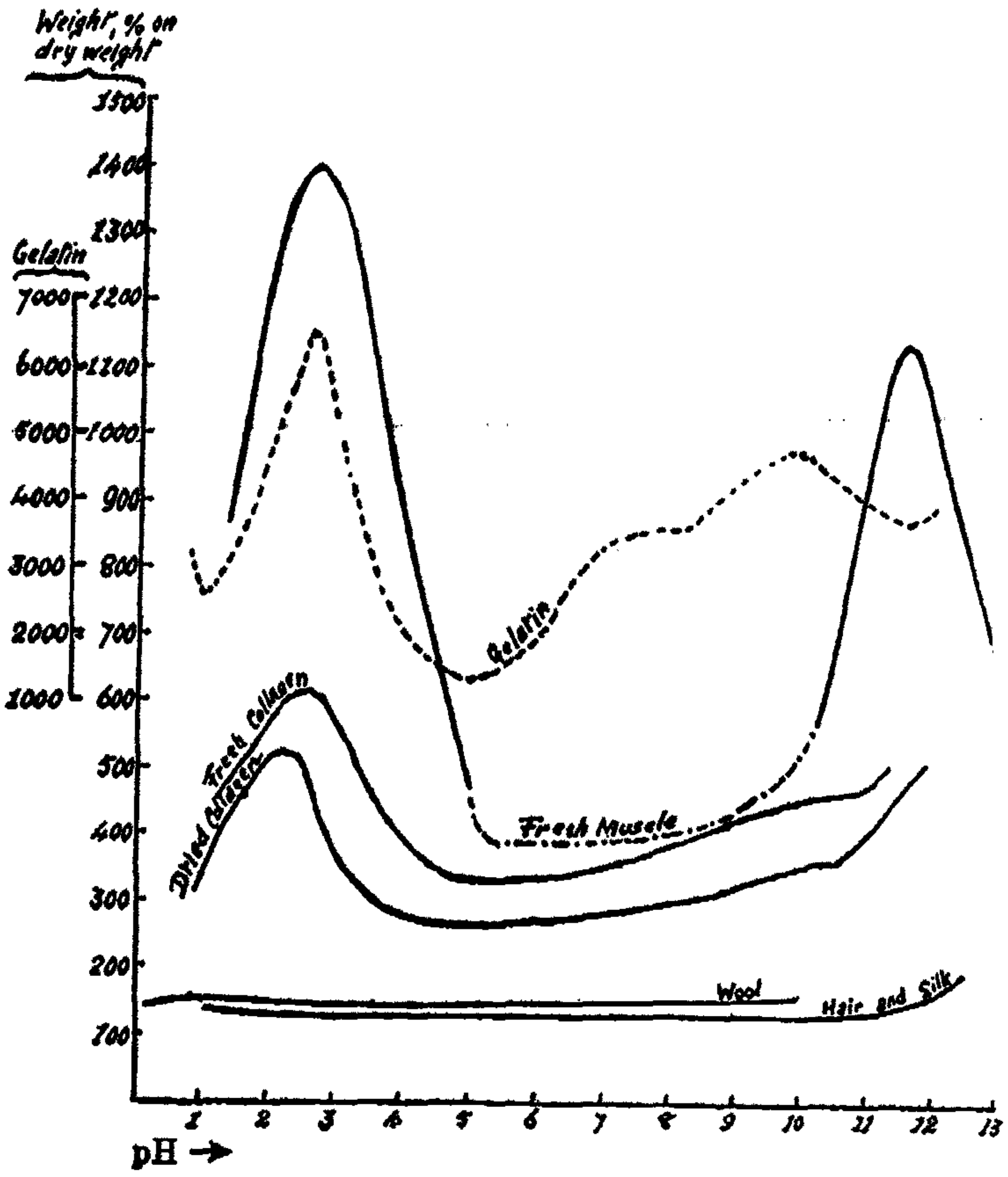

FIG. 2. Comparison of swelling of gelatin with tissues. Note that the gelatin curve is plotted on a reduced ordinate.

The importance of structure in controlling swelling becomes even more obvious when biological systems are considered. These swell much less freely than gelatin gels, the order of swelling for a tissue containing about 10 per cent of dry matter being about equivalent to that for a gelatin gel containing 30 to 50 per cent of dry gelatin.

Figure 2 shows the swelling in hydrochloric acid and sodium hydroxide of a number of tissues of animal origin, with the swelling of dry leaf gelatin plotted on a reduced scale for comparison (5). There are two noteworthy points shown here:—firstly, that the more water the tissue contains under natural conditions, the greater the degree of swelling under artificial conditions. For instance, frog's muscle contains 80 to 85 per cent water; collagen, in the form of small hide pieces, freed from extraneous proteins, 60 to 65 per cent; and the protein fibers about 12 to 15 per cent. It can be seen in table 1 that the original water content of the tissue, which can be taken as an inverse measure of the compactness of the structure, is a better indication of the extent of swelling than the number of acid or basic groups which are given by an analysis of the protein. The second point to be noticed is that while gelatin has a well-marked point of minimum swelling under salt-free conditions, the structured proteins show a more or less extended zone of minimum swelling.

TABLE 1

Percentage of bases and dicarboxylic acids in gelatin and certain tissue proteins, and swelling of gels and tissues expressed as percentage of the swollen weight on the dry weight

Initial concentration of gelatin gel was 12 per cent on setting

PARTS PER 100 PARTS DRY PROTEIN	GELATIN	FROG MUSCLE	COLLAGEN	KERATIN		SILK FIBROIN
				Wool	Horsehair	
Lysine	5.9	7.9	5.9	2.3	1.1	0.2
Histidine	0.9	2.5	0.9	0.7		
Arginine	8.2	6.5	8.2	7.8	7.6	0.7
Total bases	15.0	16.7	15.0	10.8	9	1
Glutamic and aspartic acids	9.2	19.7	9.2	15.2	4.0	?
Water at minimum swelling	1200	300 (approx.)	260	40	28	32
Osmotic water at acid maximum	5200	1100	230	7	0	0
Osmotic water at alkaline maximum	1500	800	120	Osmotic maximum, if any, lost in curve of alkaline solution		

The protein fibers, namely, wool, hair, and silk, are held together by a type of internal molecular scaffolding. Salt linkages between amino and carboxyl groups of the side chains of adjacent polypeptide chains and direct linkage between the carbonyl and amino groups of the polypeptide chains have been suggested (4). Weakening the structure by previous treatment with alkalies leads to an increase of swelling at all reactions. With silk fibers there is a uniform increase of swelling over a wide range of pH values, but hairs, which are characterized by a higher content of dibasic or diacidic residues, show definite maxima in both acid and alkaline regions, after alkaline pretreatment (7, 8).

In considering biological systems, it must not be forgotten that the system may consist of more than one component. Gelatin gels, threads of silk fibroin, and possibly hairs, may be regarded as structures built up of a single protein, and held together by internal linkages. Other systems may be more complicated. Collagen fibers, for instance, never consist simply of bundles of collagen molecules in parallel alignment, but have, in addition, a fine investing tissue of reticulin which forms a sheath around the fibers and fiber bundles, possibly even around the fine fibrils. The reticular network investing the fibers is to a certain degree extensible, but tears under sufficient mechanical strain. It is weakened by the action of acid at about normal concentration. The full allowance of reticular tissue seems to be laid down at an early stage of an animal's growth, so

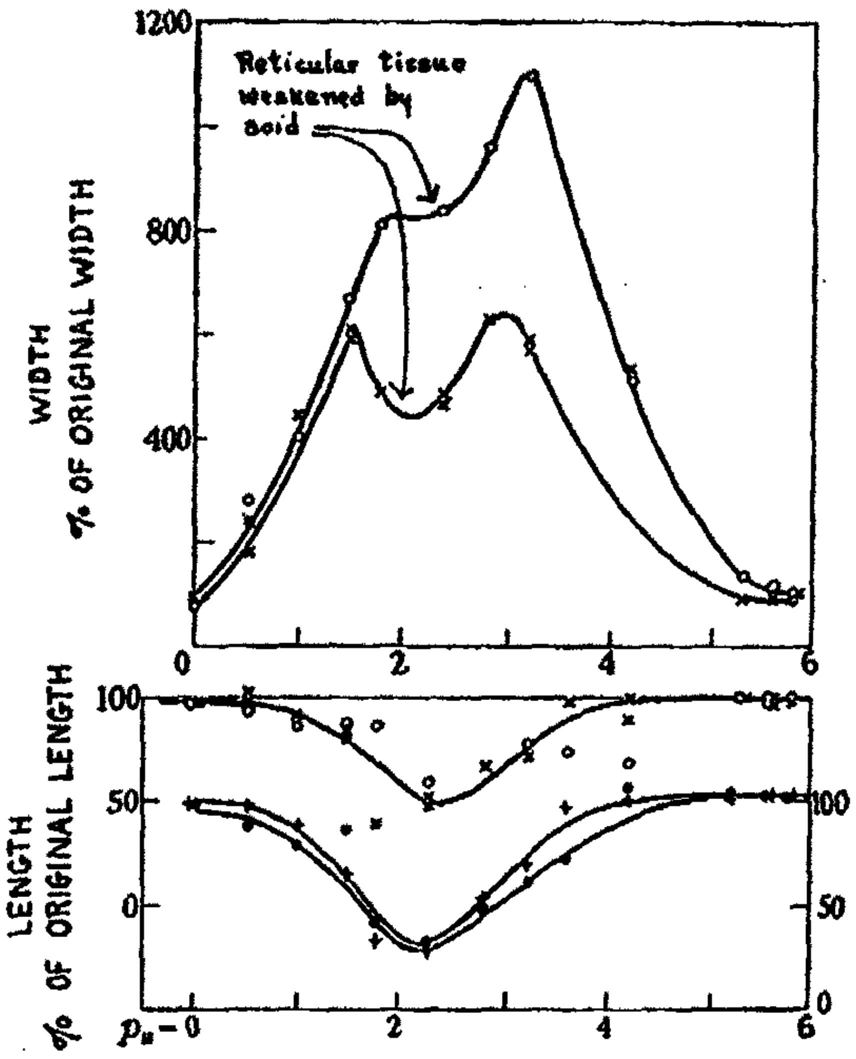

FIG. 3. Swelling of tendons from young (six-weeks old) and old (five-months old) rats in hydrochloric acid solutions. Note that swelling is shown by a contraction in length and an increase in width. ○ and ● = old tendons; × and + = young tendons.

that in half-grown animals the proportion of reticulin to collagen is higher than in fully grown animals (14). Figure 3 shows the swelling at varying pH values in the acid range of tendons from the tails of half-grown and fully grown rats (9). Both curves show a point of maximum swelling near pH 3, and the point at which the acid weakens the reticular tissue is indicated in the figure. The curve for the young tendons is especially interesting, and might lead to some strange calculations did not a microscopical examination reveal the true reason for its shape. In the more dilute acid solutions, swelling is restrained by the reticular tissue; in the more concentrated, the latter is weakened and gives way. Hence, in dilute acids, adult tendons swell more than young; in more concentrated acids, both swell to the same extent. This is illustrated in figure 4.

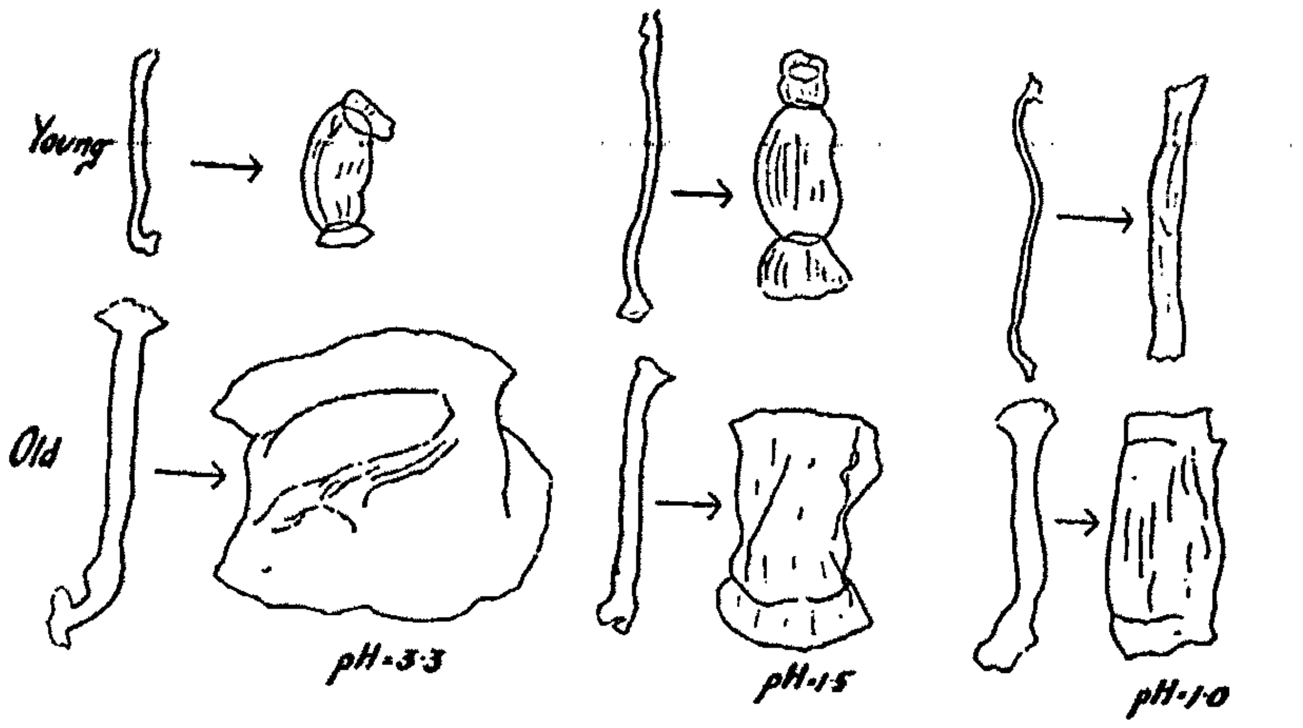

FIG. 4. Swelling of tendons of young (six-weeks old) and old (five-months old) rats in hydrochloric acid solutions. Note complete rupture of reticular tissue in old tendons at pH 3.3.

Another important influence which structure has is on the geometry of swelling. Freshly set gelatin gels appear to swell equally in all directions; dried gels which have been dried under strain, as in the usual method of drying leaf gelatin on nets, expand in all three dimensions, but more freely along the axis where there has been no strain. With the appearance of histological structure, expansion no longer takes place in three dimensions. Silk fibers and hairs expand in diameter only, the length remaining constant, except in a few special circumstances, where marked contraction, or, in the case of hairs, elongation may occur. Collagen fibers swelling in water or salt solutions increase in diameter but not in length, and the increase in diameter occurs evenly all up the fiber. Collagen fibers swelling in acid or alkali shorten in length and increase unevenly in width, showing bulges and constrictions, where the reticular sheath has or has not given way under the internal osmotic pressure. Figure 4 shows the swellings and constrictions fairly well. Osmotic swelling can be prevented by loading the fiber. If swelling has already taken place, the original length can be restored and the absorbed water can be largely, though never completely, driven out by loading the fiber (10). Under these conditions, however, even a load sufficient to break the fiber does not bring back the original width. Since swelling has been achieved by tearing the reticular sheaths, loading the fiber will obviously not restore these to their places.

The swelling of structured tissue is therefore of two types: the first is due to the drawing in of water by osmotic or other forces against the restraining forces of structure; the second is due to a weakening of the structure, allowing water to pass in simply from its own diffusion pressure. These two types are easy to recognize in practice: the former leads with collagen fibers to a shortening of the swollen fiber, a turgid condition, and a glassy appearance; the latter leads to an increase in diameter only, a flaccid condition, and an opaque appearance, due to the separation of the fibrils in the fiber from each other.

It is not proposed in this paper to enter into a full discussion of the theory of swelling, only to point out that structural features must always be taken into consideration, and that the order of size of the structures concerned may vary from a cross link between one protein molecule and another to the appearance of a second tissue formed from a different protein with characteristic properties.

Imbibition or swelling in water appears to be due to the binding of water at certain localities in the molecule, and in closely packed structures the centers of hydration in two molecules may be linked to each other with the reduction of the amount of water which can be held in this way.

The action of salts, which always promote swelling in the isoelectric region, is probably a solvent action and due to the influence of the salt ions on the multipolar molecule of the proteins leading to a rearrangement of the interionic forces of the system. Salts will not weaken a direct carbonyl-imino linkage between the backbones of adjacent molecules.

Acids and alkalies form salt linkages with the protein zwitterion and lead to the setting up of a Donnan equilibrium. Where the structure is very closely packed, salt formation does not start until a certain potential of hydrogen or hydroxyl ions is reached (1, 6, 15). Thus, in structured systems, minimum swelling occurs over a more or less extended zone. At higher concentrations acids and more especially alkalies weaken protein structures. Possibly the outstanding and universal effect of moderately concentrated strong alkalies in promoting swelling under all conditions lies in the fact that they can break all types of links between protein molecules, namely, a salt linkage, a carbonyl-imino linkage, and even a disulfide bridge.

With structured tissues such as collagen fibers, the action of sodium hydroxide in promoting swelling through the weakening of the structure can be readily demonstrated. Figure 5 shows the swelling curves of the tendons from rats' tails over a pH range of 9 to 14. In the young tendons (six-weeks old rats) the reticular tissue is sufficiently strong to resist the tearing forces due to the internal osmotic pressures set up in the sodium hydroxide solutions. The swelling curve of these tendons for varying pH values therefore shows a typical point of maximum swelling such as must occur if swelling is due to a Donnan equilibrium. With the tendons from the "medium" (three-months old) rats, which have practically at-

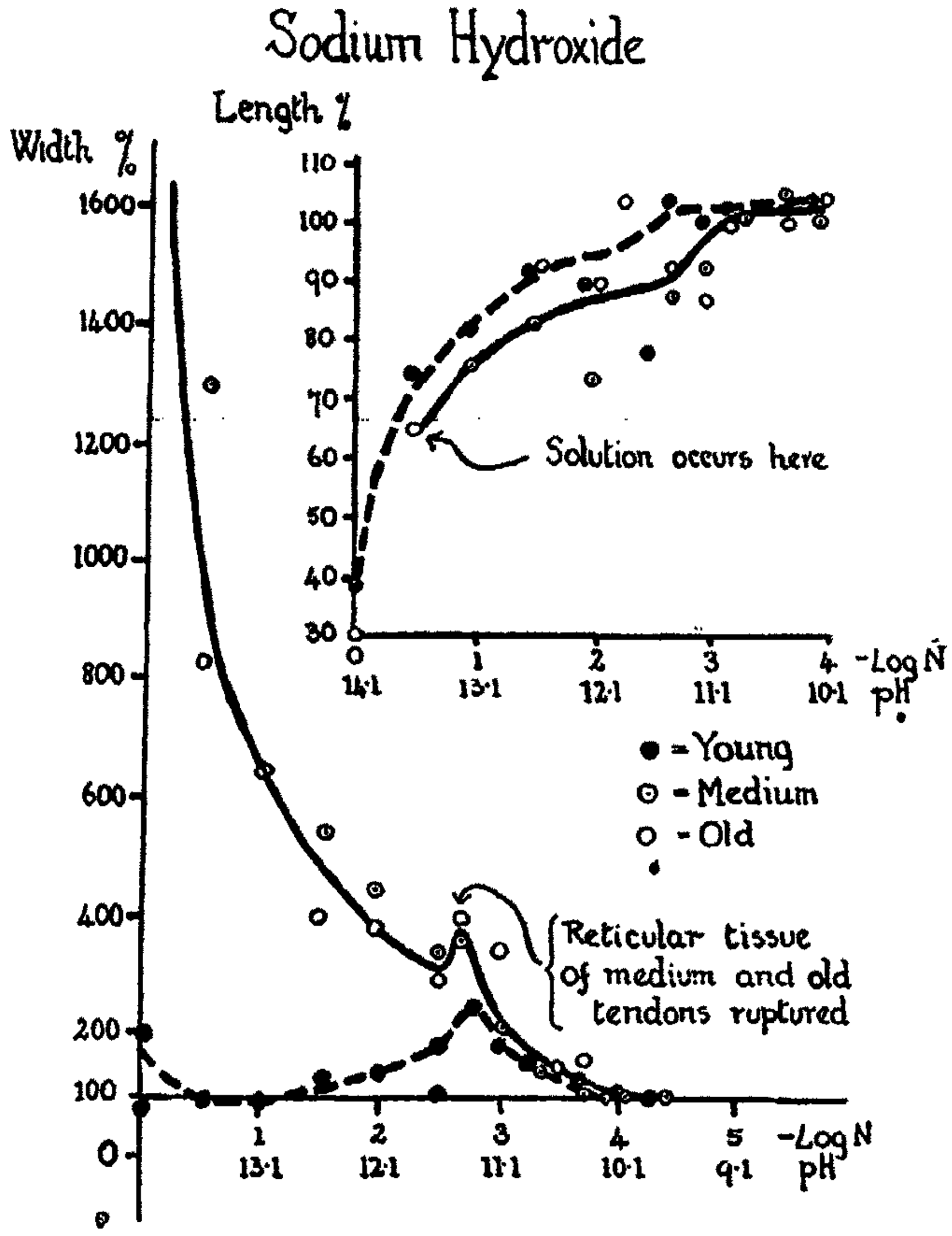

FIG. 5. Swelling of tendons from young (six-weeks old), medium (three-months old), and old (five-months old) rats in sodium hydroxide solutions. Note that swelling is shown by a contraction in length and an increase in width.

tained adult dimensions, and also with those from the "old" (five-months old) rats, which are fully grown, the story is somewhat different. The reticular sheaths of these full-sized tendons are not so strong as those of the small ones, and near the point of maximum swelling the reticular tissue gives way, partly as a direct consequence of the internal osmotic pressure and partly because it itself is progressively weakened as a result of the action of the alkali. This is illustrated in figure 6, which shows the behavior of the tendons from the "medium" or three-months old rats. It can be seen that in $N/2000$ sodium hydroxide (pH 10.8) there is some swelling, but no rupture of the reticular tissue; moreover, swelling is complete in forty-eight hours. In $N/1000$ sodium hydroxide (pH 11.1)

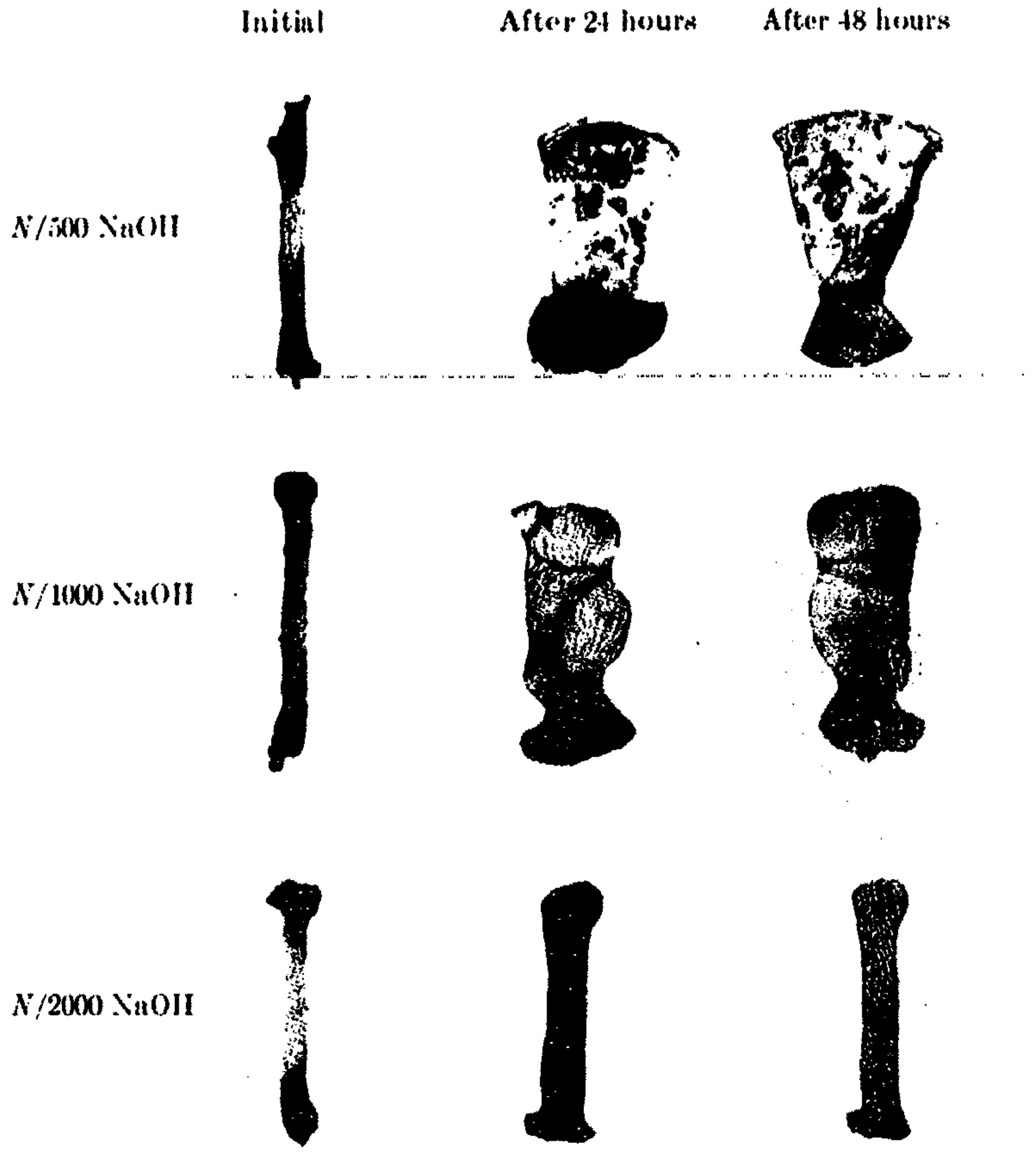

FIG. 6. Swelling of tendons of medium (three-months old) rats in sodium hydroxide solutions. Note mechanical rupture at $N/1000$ and progressive weakening at $N/500$.

the reticular tissue tears under the internal osmotic pressure, but is not progressively weakened by the alkali, since here again swelling is complete within twenty-four hours. In $N/500$ sodium hydroxide (pH 11.4) the reticular tissue itself is weakened by the action of the alkali. This can be seen by comparing the condition of the tendon after twenty-four and forty-eight hours, respectively. In sodium hydroxide solutions of pH > 11.4, swelling is progressive with time and leads ultimately to solution.

SUMMARY

The effect of structure on the water absorption of proteins is shown even in such apparently simple systems as gelatin gels. The extent of swelling of these under all conditions is a function of the original concentration at the moment of setting.

The relation between swelling and concentration in freshly made gels can be expressed as $S = f\,1/\log G$ where S equals the swollen weight and G the concentration of the gelatin. Gels which have been dried down also show the effect of the original concentration. Dried gels never swell as freely as fresh gels.

Protein fibers and other tissues show a much lower degree of swelling than gels. They also show an extended range of pH values over which *no change in weight occurs for a change of* pH. Protein tissues swell under varying conditions in proportion to their original water content.

Protein fibers give evidence that swelling is restrained through the presence of a type of internal scaffolding formed by cross links between adjacent protein molecules. In some tissues there is also a type of external scaffolding,—tendons, for instance, have the parallel bundles of collagen molecules sheathed in a fine investing tissue,—and unless the swelling pressure is sufficient to tear this, little swelling occurs.

On account of their complex structure, tissues give more complicated swelling curves than gels.

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THE STUDY OF COLLOIDAL DIMENSIONS, THERMODYNAMIC ACTIVITY, AND THE MEAN MOLECULAR WEIGHT OF THE MIXED PROTEINS IN BLOOD SERUM[1]

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Received August 1, 1937

Estimates as to the molecular weights of blood serum albumin and globulin by the osmotic method (Adair (1, 2, 3, 4, 15)) and by the ultracentrifuge method (Svedberg) are in reasonably close agreement. Serum albumin has a molecular weight of about 70,000, as compared with about 170,000 for globulin. Other things being equal, these values would indicate that at equal concentrations (in units of mass) albumin would have 2.4 times the osmotic activity of globulin.

In biological systems the proteins occur as mixtures, and the relation between the total colloid osmotic activity and the several components in such mixtures is of importance. This is particularly true of blood serum, in which it is generally believed that the osmotic activity of the colloids (almost entirely proteins) is a primary force involved in the preservation of the fluid balance between blood and tissue. In the literature on this subject there are a number of discrepancies,—disagreements with theoretical requirements as well as in the detailed numerical results.

Previous investigators have sought, empirically, to formulate an equation which will describe the relation between colloid osmotic pressure and the concentration of the proteins in blood serum (cf., e.g., 6, 8, 17). In blood serum the proteins are albumin and globulin (plus an insignificant amount of fibrinogen), and, if we may accept the application of Dalton's law of partial pressures to this system (cf. Adair (1)), the relation must be of the form:

$$\text{Colloid osmotic pressure} = f'\text{A} + f''\text{G} \qquad (1)$$

i.e., the C. O. P. will be the sum of a function of the albumin concentration and a function of the globulin concentration. The simplest form these

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[1] Presented at the Fourteenth Colloid Symposium, held at Minneapolis and Rochester, Minnesota, June 10-12, 1937.

functions could take would be as coefficients, i.e., constants for multiplication:

$$\text{C. O. P.} = k'\text{A} + k''\text{G} \tag{2}$$

Values for k' and k'' have been obtained for human blood serum by Govaerts (8) and von Farkas (6):

$$\text{C. O. P. (mm. H}_2\text{O)} = 75.4\text{A} + 19.5\text{G (Govaerts)} \tag{3}$$

$$\text{C. O. P. (mm. H}_2\text{O)} = 68\text{A} + 25.1\text{G (von Farkas)} \tag{4}$$

where the concentrations of albumin and globulin are in grams per 100 cc. and the temperature is about 20°C.

Recently, Wells, Youmans, and Miller (17) have proposed the formula:

$$\text{C. O. P.} = \text{Total protein } (21.4 + 5.9\text{A}) \tag{5}$$

Curiously enough, these authors stress the point that their formula omits globulin, and they argue that globulin is without any important effect. It would seem, however, that their formula (5) should be written:

$$\text{C. O. P.} = (\text{A} + \text{G})(21.4 + 5.9\text{A}) \tag{6}$$

or

$$\text{C. O. P.} = 5.9\text{A}^2 + 21.4\text{A} + 5.9\text{AG} + 21.4\text{G} \tag{7}$$

The data of Wells and his colleagues may be fitted to equation 2 above by the method of least squares[2]. When this is done we have:

$$\text{C. O. P.} = 71.5\text{A} + 8.5\text{G} \tag{8}$$

as the best fit for these data.

In this laboratory we have studied the C. O. P., albumin and globulin, in serums from fourteen subjects, with at least two experiments on each; eight of these subjects were normal, while six were patients with cirrhosis of the liver. Colloid osmotic pressure measurements were made in duplicate at 0°C. by the classical equilibration method as applied by Adair. Proteins were estimated by the Kjeldahl method, using the factor 6.25 to convert nitrogen to protein concentration; separation of albumin and

[2] The least squares equations for the general type equation,

$$\text{C. O. P.} = k'A + k''\text{G}$$

are:

$$\Sigma\text{A(C. O. P.)} = k'\Sigma\text{A}^2 + k''\Sigma\text{AG} \tag{1}$$

$$\Sigma\text{G(C. O. P.)} = k'\Sigma\text{AG} + k''\Sigma\text{G}^2 \tag{2}$$

globulin was made by the method of Howe (10). These data were fitted to equation 2 (above) by the method of least squares with the result:

$$\text{C. O. P. (mm. } H_2O) = 45.2A + 18.8G \qquad (9)$$

The numerical values for k' and k'' in the equations given above (3, 4, 8, and 9) cannot be compared directly, for reasons which will be discussed below, but the ratios of the osmotic activity in serum of albumin to globulin, k'/k'', may be compared. This is done in table 1.

The colloid osmotic pressure measured in all these studies, as well as the effective force in the living animal, is the sum of the simple osmotic pressure of the proteins as particles and the Gibbs-Donnan effect which arises from the fact that we have to deal with protein ions. The calculation of k'/k'' from molecular weights would be complicated if it could be shown, first, that the Gibbs-Donnan effect is of greatly different magnitude with albumin than what it is with globulin, and, second, that the Gibbs-Donnan effect is a large part of the total gross colloid osmotic pressure as measured in all these studies. It is easy to show that these factors are not of sufficient magnitude to affect the simple calculation of k'/k'' appreciably.

TABLE 1

Ratio of the osmotic activity of albumin as compared with globulin in human blood serum

k'/k''	AUTHORITY
3.9	Govaerts (8)
2.7	von Farkas (6)
8.4	Wells, Youmans, and Miller (17)
2.4	Present results
2.4	Simple theory

Van Slyke, Hastings, Hiller, and Sendroy (16) have shown that at pH = 7.35 the base-combining power of albumin is about 1.4 times as great as that of globulin; in other words, the Gibbs-Donnan effect will be greater with albumin than with globulin. In blood serum in the physiological range of pH the Gibbs-Donnan effect is of the order of 20 per cent of the total colloid osmotic pressure when the A/G ratio is about 1.8. Under the same conditions of salt concentration and pH, the Gibbs-Donnan effect would be of the order of 16.5 per cent of the total C. O. P. in a pure globulin solution and slightly less than 22 per cent in a pure albumin solution. Accordingly, the maximum error from the neglect of the difference in Gibbs-Donnan effect in albumin and in globulin solutions would be less than 5.5 per cent. In the living organism, even under pathological conditions, the variation in A/G is restricted, so that the greatest error that could arise from this source would still be less than 5 per cent of the total colloid osmotic pressure.

The effect of pH must also be considered. The pH of different samples of serum will vary slightly and the conditions of measurement of the C. O. P. may accentuate this variation. Since the isoelectric points of albumin and globulin are nearly the same (cf. Van Slyke and others (16)), there can be no significant differential effect on albumin as opposed to globulin and again it must be concluded that the constancy of the ratio k'/k'' will be almost entirely unaffected.

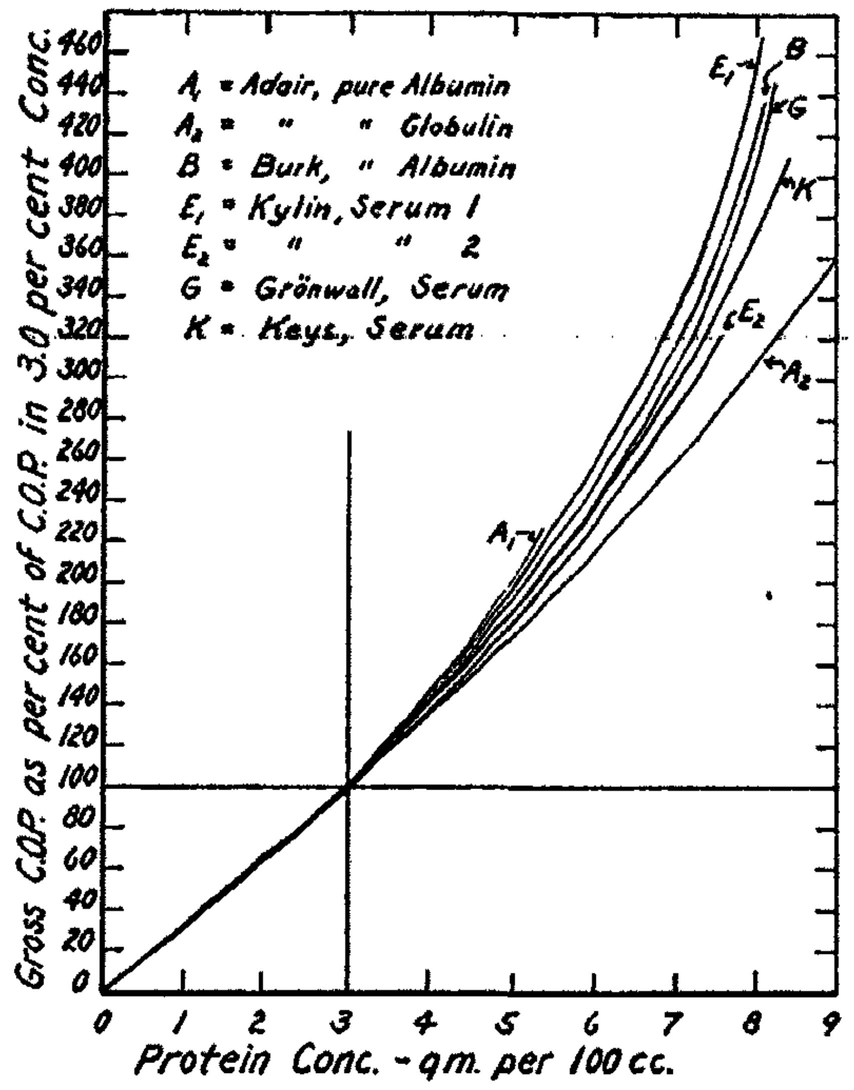

FIG. 1. The effect of protein concentration on the relative gross colloid osmotic pressure. Temperatures in separate series from 0° to 22°C.

Marrack and Hewitt (14) found that variations in pH have a definite effect on the C. O. P., but this is so small that, over the range pH 6.7 to 7.7, even the absolute magnitudes of k' and k'' will change no more than 4 to 8 per cent.

It has long been known that when the concentration of a protein solution is increased the colloid osmotic pressure increases more than in simple linear proportion. In other words, the values of k' and k'' in equation 2 are not independent of the total protein concentration. This in itself is sufficient to account for some of the apparent discrepancies in the osmotic coefficients reported in the literature. The correction for this effect in blood serum would be relatively simple if it could be shown that the effect of protein concentration on the C. O. P. is not dissimilar in different mixtures of albumin and globulin. Figure 1 shows that this is indeed the fact at protein concentrations below 6 per cent. Even at 8 per cent concentration it is probable that differences in the effect of concentration on the osmotic activity of albumin as compared with globulin are relatively insignificant.

It is clear that equation 2 may now be extended to cover more than a fixed level of total protein concentration:

$$\text{C. O. P.} = f_c(k'\text{A} + k''\text{G}) \qquad (10)$$

For measurements at 0°C., we may use the data of the experiments reported in this paper:

$$\text{Gross C. O. P. (mm. } H_2O) = f_c\,(45.2\text{A} + 18.8\text{G}) \qquad (11)$$

Values for f_c for various concentrations of total protein are listed in table 2.

TABLE 2

Values of f_c *in the equation:* C. O. P. $= f_c(k'\text{A} + k''\text{G})$

General relation between f_c and protein taken from averages of data given in figure 1. Absolute numerical values calculated from results with twenty-eight samples of blood serum with average protein concentrations, including experiments with dilutions, of 3.49 g. per 100 cc.

PROTEIN	f_c	PROTEIN	f_c	PROTEIN	f_c
grams/100 cc.		*grams/100 cc.*		*grams/100 cc.*	
1.0	0.88	3.5	1.00	6.0	1.17
1.5	0.90	4.0	1.03	6.5	1.22
2.0	0.92	4.5	1.06	7.0	1.28
2.5	0.95	5.0	1.09	7.5	1.35
3.0	0.98	5.5	1.12	8.0	1.45

So far we have attempted to provide a relation between serum albumin and globulin concentration and C. O. P. and have extended this to cover variations in total protein concentration from 1 to 8 g. per 100 cc. The numerical values of the coefficients, however, are based on constant temperature (0°C.), constant pH (7.2 to 7.4), and constant salt concentration. Variations in these factors must now be considered.

The effect on the C. O. P. of variation in the salt concentration is illustrated in figure 2. The pathological extremes in salt concentration are less than ± 10 per cent of the normal salt concentration of the serum; this range corresponds to less than ± 1 per cent of the gross C. O. P. It must be concluded that variations in the salt concentration in all natural serums are too slight to have any appreciable effect.

The extreme range, compatible with life, for the pH of the serum in man is perhaps 6.6 to 7.8, but the range which may be endured for more than an hour or so is probably no greater than from pH 6.9 to 7.6. Differences in pH of this amount will affect the C. O. P. by less than 6 per cent of the total pressure (Marrack and Hewitt (14); cf. above). Obviously the effect of variations in pH may be neglected as a first approximation, unless the pH of the serum is altered experimentally *in vitro*.

The effect of temperature on the colloid osmotic pressure of serum or serum proteins has been little studied. From the simple van't Hoff equation, $p' = cRT$, it might be expected that the C. O. P. would vary in direct proportion to the absolute temperature. Some comparisons of the C. O. P. measured in human blood serum by the method of Krogh and Nakazawa (12) at 22°C. and by the method of Keys and Taylor (11) at 0°C. indicate that this is approximately the case for a limited range of temperature, and we may write, tentatively:

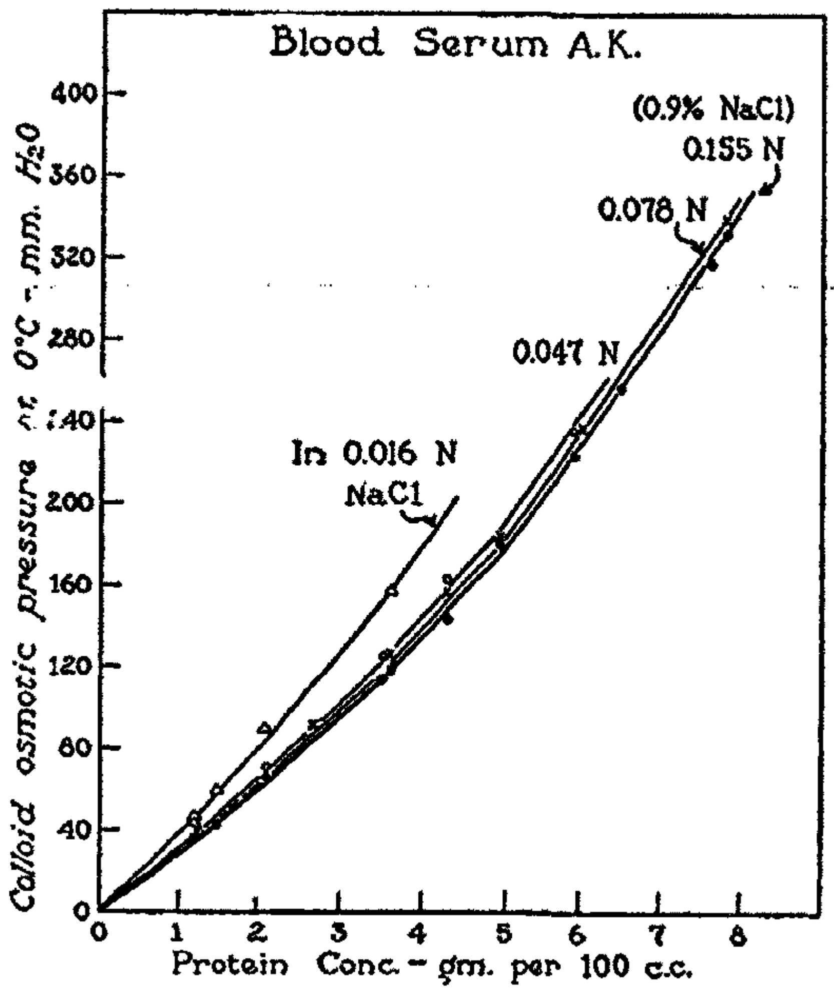

FIG. 2. Relations between gross colloid osmotic pressure, protein concentration, and salt concentration in various dilutions of normal human serum. All values at pH = 7.4 and $T = 0$°C.

$$\text{C. O. P.} = f_c(45.2A + 18.8G) \times \frac{T(^\circ\text{Absolute})}{273} \qquad (12)$$

So far in this paper the main concern has been to provide a reasonable basis for mathematical description and comparison of measurements of the gross colloid osmotic pressure in mixtures of albumin and globulin such as blood serum. It must be recognized at the outset that the sharp division of plasma proteins into discrete entities labelled "albumin" and "globulin" is largely a matter of convenience. There is no reason to doubt that there are distinct species of proteins in blood plasma which correspond, at least roughly, to what we refer to as albumin and globulin, but it is much less certain that these protein types are quantitatively separable, with unvarying precision, by any present-day methods. This does not, however, invalidate the use of these terms in a *mathematical* formulation of the relations between the amounts of these types and the osmotic effects of mixtures of them. Such a formulation is a preliminary step toward the practical application of the classical laws of thermodynamics to a complex system such as blood plasma. Some outlines of the further analysis of the system, in terms amenable to experimental attack, may be given here.

Consider the equilibrium of a system when blood plasma or serum is separated from a protein-free transudate by a crystalloid-permeable, colloid-impermeable membrane (such as the capillary membrane in man). The essential variables may be represented, for the physiological range pH 6.5 to 8.0:

I	II
SUBSTANCE	SUBSTANCE
P = Protein	
P^- = Proteinate	
BP^+ = Base bound by protein	
B^+ = Free base	Total base = B^+
H^+	H^+
Cl^-	Cl^-
A^- = All other anions	All other anions = A^-

We shall denote the Gibbs chemical potential by $\llbracket\ \rrbracket$, where $\llbracket\ \rrbracket = \alpha[\ ]$, where α is an osmotic coefficient and the square brackets denote equivalent concentrations. Subscripts 1 and 2 will be used to distinguish the serum and the transudate phases respectively. As a first approximation we may assume that all ions except proteinate are univalent; this can create no very great error in natural biological systems where, in fact, less than 5 per cent of the free ions are multivalent.

Applying Dalton's law of partial pressures we have (13):

$$\text{C. O. P.} = RT\{\llbracket P\rrbracket + \llbracket P^-\rrbracket\} + RT\{\llbracket A^-\rrbracket_1 + \llbracket Cl^-\rrbracket_1 + \llbracket BP^+\rrbracket + \llbracket B^+\rrbracket_1 - \llbracket B^+\rrbracket_2 - \llbracket Cl^-\rrbracket_2 - \llbracket A^-\rrbracket_2\}^*$$

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* Note that H^+ is omitted; the number of hydrogen ions present is so small as to be negligible in summing up all ions or molecules.

From the application of Gibbs–Donnan equilibria, we have:

$$\frac{\llbracket \mathrm{Cl}^- \rrbracket_1}{\llbracket \mathrm{Cl}^- \rrbracket_2} = \frac{\llbracket \mathrm{A}^- \rrbracket_1}{\llbracket \mathrm{A}^- \rrbracket_2} = \frac{\llbracket \mathrm{H}^+ \rrbracket_2}{\llbracket \mathrm{H}^+ \rrbracket_1} \tag{14}$$

and also:

$$E = \frac{RT}{F} \ln \frac{1}{\lambda} \tag{15}$$

where E is the membrane potential and λ is the ion ratio (in activities) for the distribution of any diffusible ion between the two phases. In another form we may write the equation for the Gibbs-Donnan equilibrium:

$$\llbracket B^+ \rrbracket_2 \{\llbracket \mathrm{Cl}^- \rrbracket_2 + \llbracket \mathrm{A}^- \rrbracket_2\} = \{\llbracket \mathrm{Cl}^- \rrbracket_1 + \llbracket \mathrm{A}^- \rrbracket_1\} \{\llbracket \mathrm{A}^+ \rrbracket_1 + \llbracket \mathrm{B}^+ \rrbracket_1\} \tag{16}$$

From the principle of electrical neutrality, we have:

$$[\mathrm{A}^-]_2 = [\mathrm{B}^+]_2 - [\mathrm{Cl}^-]_2 \tag{17}$$

and

$$[\mathrm{BP}^-]_1 = [\mathrm{P}^-]_1 + [\mathrm{A}^-]_1 + [\mathrm{Cl}^-]_1 - [\mathrm{B}^+]_1 \tag{18}$$

Finally, we have, for the true colloid osmotic pressure of the protein alone:

$$\begin{aligned}(\text{C. O. P.})_0 = \text{C. O. P.}' - RT\{&\llbracket \mathrm{BP}^+ \rrbracket_1 + \llbracket \mathrm{B}^+ \rrbracket_1 + \llbracket \mathrm{Cl}^- \rrbracket_1 + \\ &\llbracket \mathrm{A}^- \rrbracket_1 - \llbracket \mathrm{B}^+ \rrbracket_2 - \llbracket \mathrm{Cl}^- \rrbracket_2 - \llbracket \mathrm{A}^- \rrbracket_2\}\end{aligned} \tag{19}$$

and, following van't Hoff:

$$(\text{C. O. P.})_0 = \frac{\frac{(\text{Tot. prot.})}{(\text{Mol. wt.})}}{V} RT \tag{20}$$

where (Tot. prot.) represents the mass of the proteins, and V the solvent volume.

The equations given here are presented as a guide to the further study of natural solutions of proteins. It should be obvious that, in the last equation (20), the separation of total protein into albumin and globulin may be done by the utilization of the arguments and equations (2 through 9) presented in the first part of this paper, and that this need not involve, necessarily, a precise laboratory method for the quantitative separation of the two chief varieties of protein.

For a preliminary application of the arguments given here, the necessary measurements, in a membrane system separating serum from a protein-free transudate at equilibrium, are: (*1*) (Tot. prot.); (*2*) $[\mathrm{Cl}^-]_1$ and $[\mathrm{Cl}^-]_2$; (*3*) $[\![\mathrm{H}^+]\!]_1$ and $[\![\mathrm{H}^+]\!]_2$; (*4*) $[\text{Tot. base}]_1$ and $[\text{Tot. base}]_2$; (*5*) E (the membrane potential); (*6*) C. O. P. (the gross colloid osmotic pressure); (*7*) temperature (T); and (*8*) V (the solvent volume). Simultaneous measurement of all these variables is technically feasible, and from them, by use of the foregoing equations, it should be possible to arrive at satisfactory values in this complex system for: $\alpha_{\mathrm{Cl}-}$, $\alpha_{\mathrm{prot.}}$, $[\![\mathrm{BP}^+]\!]$, and the mean molecular weight of the mixed proteins. In addition, there are sufficient cross checks so that any gross deviation from theory should be readily apparent.

Preliminary experiments indicate that, in fact, there do not appear to be any important factors not yet considered in the foregoing tentative analysis. Detailed results will be presented at another time.

SUMMARY

Discrepancies in the literature between the molecular weights of serum albumin and serum globulin and their reported osmotic effects in the mixtures occurring in blood serum are principally the result of the limitations of methods for the quantitative estimation of these proteins in the presence of each other. By the use of a variety of precautions an agreement is reached between analytical results and simple theory.

Serum albumin has about 2.4 times the osmotic activity, per gram, exhibited by globulin. It is shown that this relation is not seriously disturbed by variations in pH over the range 6.7 to 7.7, nor by variations in the total protein concentration up to 6 per cent and, with less certainty, up to 8 per cent of the total concentration.

The effect of total protein concentration on the relative colloid osmotic pressure per gram of protein concentration was studied, from which it was concluded that albumin and globulin, and various mixtures of these proteins, exhibit nearly the same effect, quantitatively, up to around 8 per cent concentration. A table of conversion factors is given, as well as numerical constants for the osmotic activities of the two proteins.

Equations are presented which describe the relations of the activity coefficients of the proteins and of chloride in the presence of the proteins, the protein concentration, the molecular weight of the proteins, the membrane potential, and the gross colloid osmotic pressure. The analysis provides a reasonable preliminary guide to the further thermodynamic study of the complex system of blood serum and a transudate.

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OSMOMETRIC STUDY OF GUM ACACIA SOLUTIONS USED FOR INTRAVENOUS INJECTION[1]

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Intravenous injections of gum acacia solutions are widely used, clinically, to increase the colloid osmotic pressure (C. O. P.) of the blood plasma. In addition to the lack of available data on the effects of such injections on the total C. O. P. of the blood plasma, there is a discrepancy in the reported C. O. P. values, or mean particle size, in simple gum acacia solution itself. This is probably the result of several factors, among which importance may be given to variations in individual samples of gum acacia, especially with regard to particle size and sodium and calcium content.

The basic structure of gum acacia is a galactoso-glucuronic acid (3, 8). Primarily it is a mixture of polymerized anhydrides of galactose and arabinose in varying proportions. In the crude state the calcium, potassium, and magnesium salts of arabic acid predominate. It has been repeatedly demonstrated that the sodium salt of gum acacia gives higher C. O. P. values than the calcium salt (2, 7). Perhaps these two factors alone account for part of the discrepancy in the reported values (table 1). However, a variability in the C. O. P. from 8 to 275 mm. of mercury in a single concentration of gum acacia seems large, even if we assume different particle size and salt concentrations. All of these authors, as far as we are aware, assumed that a protein-tight membrane was also impermeable to gum acacia particles. In no instance is there mention that the membranes used were "acacia-tight" or that the outer medium was tested for the presence of gum acacia.

In this investigation we first attempted to measure the C. O. P. of 6 per cent gum acacia, using tested protein-tight collodion sacs suspended in a suitable medium at 0°C. Regardless of the outer medium (phosphate buffer, physiologic saline solution, or distilled water) the C. O. P. value continued to fall during a period of at least twelve days. Qualitative tests showed that gum acacia entered the outer medium in each instance. When phosphate buffer (pH = 7.4) was the outer medium it was noticed

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[1] Presented at the Fourteenth Colloid Symposium, held at Minneapolis and Rochester, Minnesota, June 10–12, 1937.

that small, grayish-white crystals collected on the outside of the collodion sacs and a few crystals settled out in the bottom of the tube containing the buffer. These were assumed to be, without direct evidence, crystals of calcium phosphate. The membranes employed possessed a permeability to distilled water varying between 0.005 to 0.014 cu. mm. per minute per square centimeter per 1 cm. of water pressure.

The properties of gum acacia sol are greatly changed by the presence of proteins. When 6 per cent gum acacia is added to human blood serum, a stable equilibrium is quickly reached in collodion sac osmometers and there is no evidence of leakage of the acacia through the membrane. There is a rise in the C. O. P. of the serum approximately in proportion to the amount of acacia added (table 2). In the presence of relatively large amounts of protein, the change in C. O. P. attributable to the gum acacia is such as to indicate a mean particle size of the order of 100,000.

TABLE 1

Measurements of the colloid osmotic pressure of 6 per cent solutions of acacia

SALT CONTENT OF MEDIUM	pH	COLLOID OSMOTIC PRESSURE	AUTHOR
		mm. Hg.	
0		246–275	Pfeffer, 1877
0		134	Moore and Roaf, 1907
Na salt	CO_2-free	274	Gasser, Erlanger, and Meek, 1919
Na salt	CO_2-saturated	83	Gasser, Erlanger, and Meek, 1919
0.9 per cent NaCl		16	Krogh and Nakazawa, 1927
0.65 per cent NaCl		18.6	Drinker, 1927
Locke, slightly modified	7.3	57.5	Went, 1929
0	4.5	56–58	Dodds and Haines, 1934
0.9 per cent NaCl	4.2	8.8	Dodds and Haines, 1934
0.9 per cent NaCl		11	Onozaki and Sanada, 1935
0.9 per cent NaCl	4.292	18	Butt and Keys, 1937

Experimentally, Drinker (6) has observed that when a sufficient amount of horse serum is added to an acacia solution, the capillary membrane in contact with the mixture retains its normal semipermeability but does not display the free leakage which appears when acacia alone is used.

Obviously the true C. O. P. of simple gum acacia solutions cannot be obtained by the use of ordinary protein-tight membranes. Membranes of less permeability were prepared by incorporating a water-soluble, non-volatile swelling agent (glycol) in anhydrous ether-alcohol collodion as described by Pierce (14). These membranes had a permeability to distilled water varying from 0.003 to 0.004 cu. mm. per minute per square centimeter per 1 cm. of water pressure. Some of these membranes were "acacia-tight" and with them equilibration was attained usually within forty-eight hours. The values obtained indicate that a 6 per cent gum acacia solution has a C. O. P. that approximates that of the normal human blood plasma (table 3).

The second phase of the investigation was concerned with the results of intravenous injection of gum acacia solution in humans. Determinations were made of the C. O. P., the serum proteins (albumin and globulin),

TABLE 2

The effect of acacia on the colloid osmotic pressure of normal serum in vitro

DILUTIONS OF HUMAN SERUM WITH BUFFER AND ACACIA	C.O.P. IN MM. OF WATER PER GRAM OF PROTEIN NITROGEN PER 100 CC. OF SERUM	MEMBRANE PERMEABILITY PER CUBIC MILLIMETER PER MINUTE, PER SQUARE CENTIMETER, PER 1 CM. OF WATER PRESSURE
5 cc. of serum 5 cc. of buffer	215	0.005
5 cc. of serum 4.5 cc. of buffer 0.5 cc. of 6 per cent acacia	256	0.003
5 cc. of serum 5 cc. of buffer 0.5 cc. of 6 per cent acacia	255	0.002
5 cc. of serum 4 cc. of buffer 1 cc. of 6 per cent acacia	281	0.011

TABLE 3

Colloid osmotic pressure determinations of gum acacia

SOLUTION	pH	C.O.P. IN MM. OF MERCURY
12 per cent arabic acid	7.227	33+
6 per cent arabic acid	7.227	13
6 per cent gum acacia (Na salt)	4.292	18
4 per cent gum acacia (Na salt)	4.292	5.2

and the fate of the injected acacia in three cases of cirrhosis of the liver and in one of subacute toxic degeneration of the liver.

The gum acacia employed in each case was a 6 per cent (with 0.9*N* sodium chloride) solution sterilized in the autoclave. Mention is made that these solutions were autoclaved, because this process supposedly increases the C. O. P. of the solution (5). Following the intravenous injection of a solution of 6 per cent gum acacia the C. O. P. of the blood

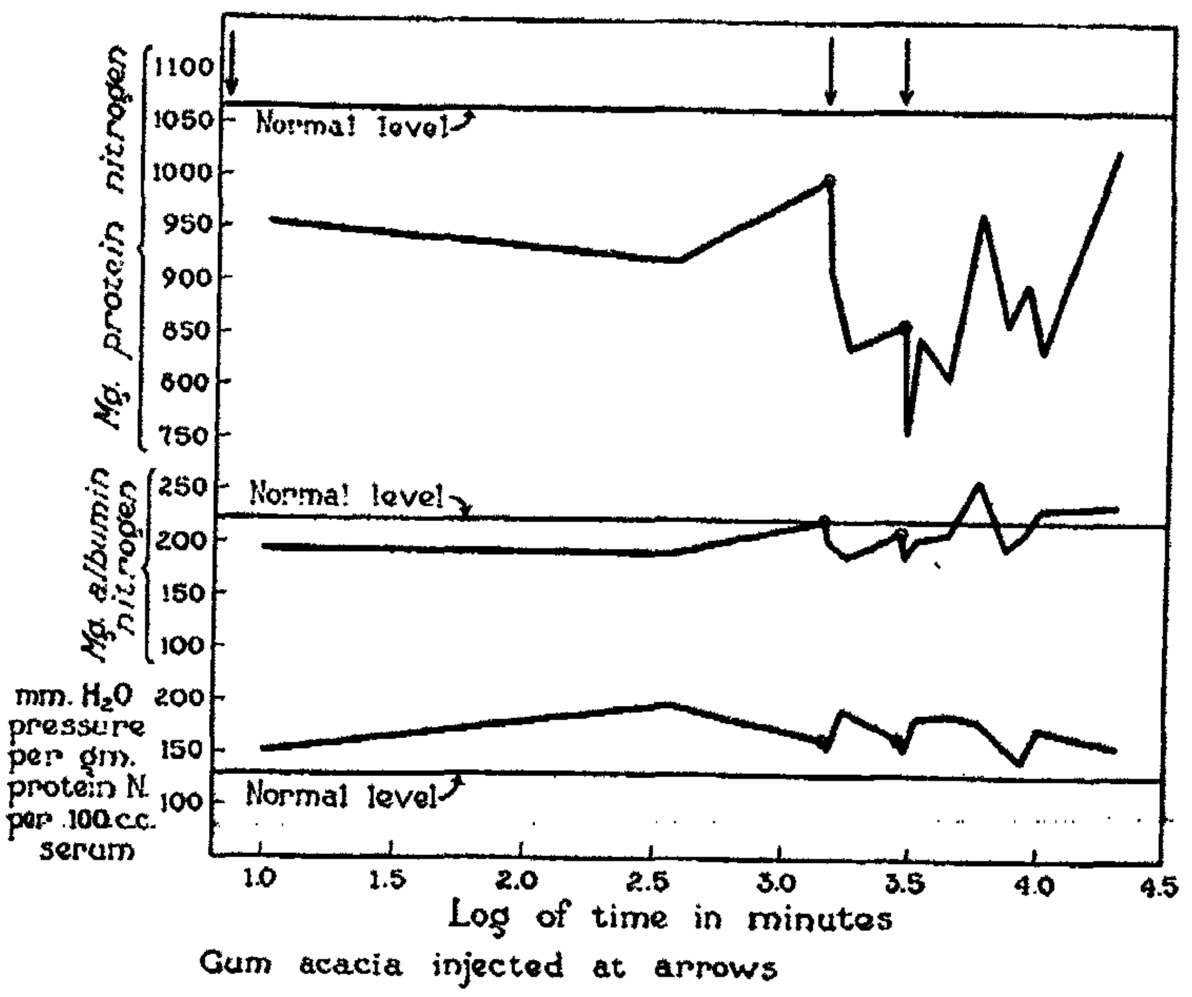


FIG. 1. The effect of the intravenous injection of gum acacia solution in an individual with cirrhosis of the liver.

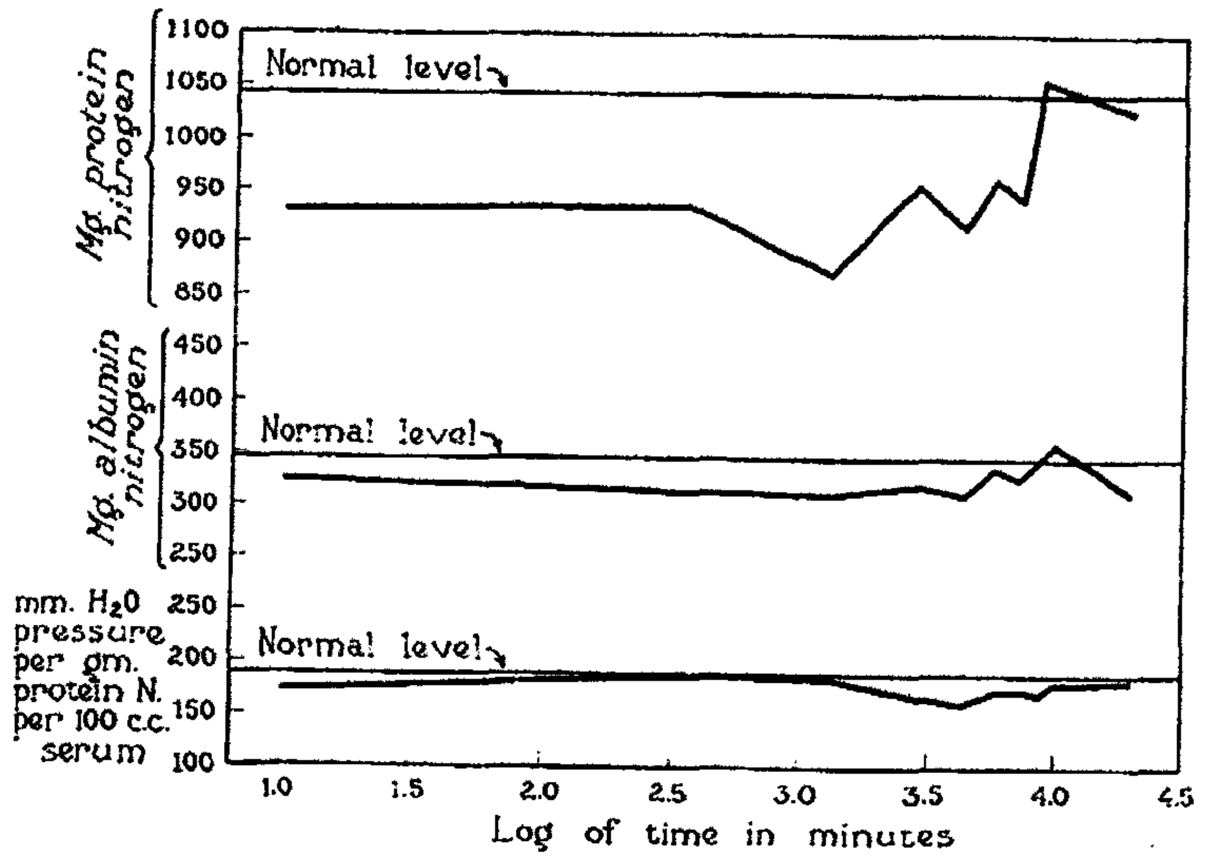
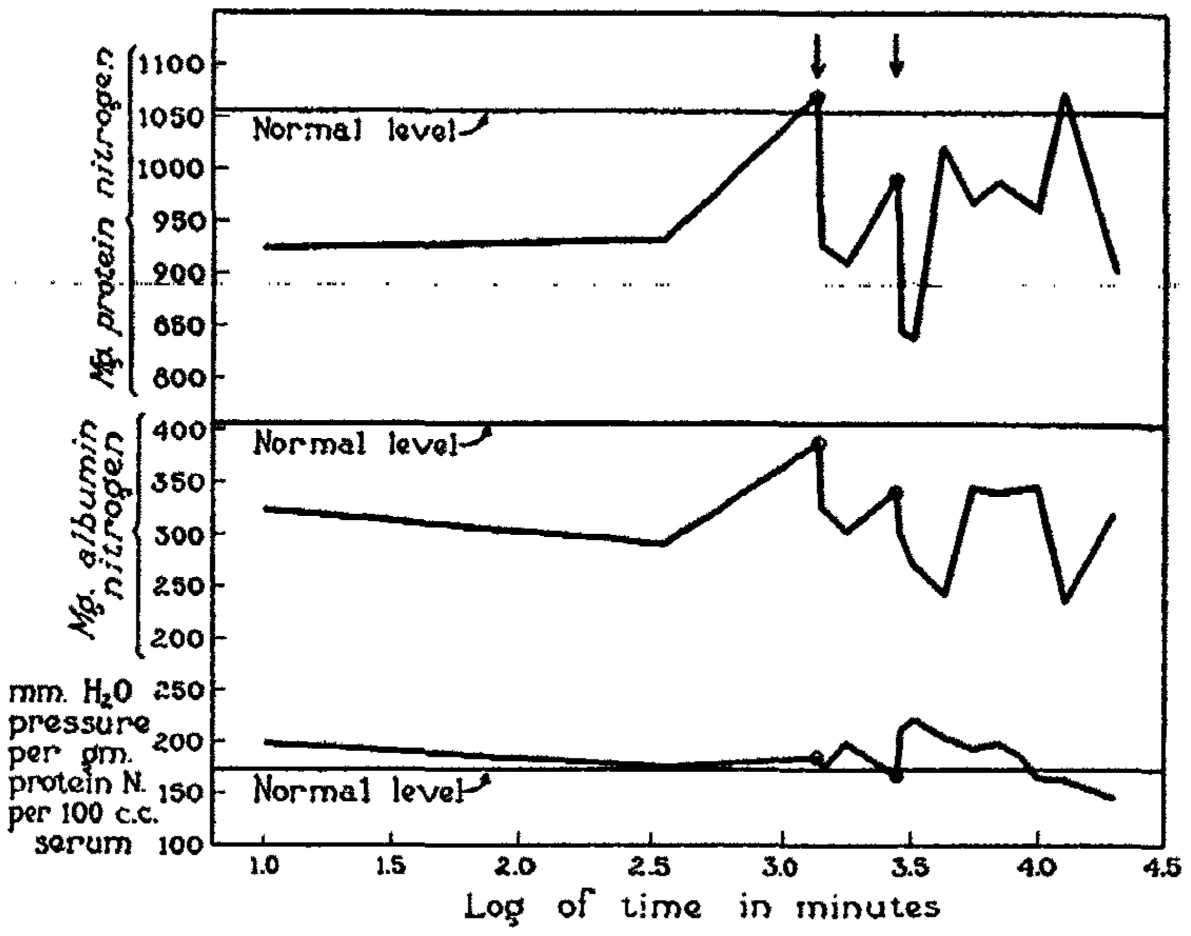


FIG. 2. The effect of injection of 500 cc. of 6 per cent gum acacia in an individual with cirrhosis of the liver.

serum is assumed usually to be elevated only for a period of forty-eight hours (1). However, it will be seen in figure 1 that the C. O. P. of the blood serum remained above the patient's basal level, following the third 500-cc. injection of gum acacia, for a period of four days.

In the case summarized in figure 2 there was only one 500-cc. injection of gum acacia. The C. O. P. of the blood serum in this instance was maintained above or at the basal level for only twenty-four hours.

It is frequently stated in the literature that the serum proteins, particularly the albumin fraction, fall to a low concentration in man and animals following the intravenous injection of gum acacia solution (4). Only in the case summarized in figure 3 was the albumin concentration decreased appreciably following this procedure, and at no time was this reduction of the magnitude reported in the literature.



Gum acacia injected at arrows

FIG. 3. A case of cirrhosis of the liver showing the occasional reduction of concentration of albumin following the injection of gum acacia solution.

DISCUSSION

It seems that the failure to consider the variability of individual gum samples in regard to particle size and salt content, together with the employment of protein-tight rather than acacia-tight membranes, probably accounts for most of the errors in the reported C. O. P. determinations of gum acacia. It is significant that the divergent values reported in the literature are not supported by any acceptable criteria of equilibrium and are in sharp disagreement with the results of cryoscopic measurements.

It appears that the disperse phase in simple gum acacia sols is composed of particles of variable size, with molecular weights ranging perhaps from less than 2000 up to several hundred thousand or more; the observed colloid osmotic pressure of such sols will depend partly on the method of preparation, but more particularly on the permeability of the membrane used.

It is difficult to explain why gum acacia when added to human serum will not leak through a collodion sac from which it previously would escape. Drinker observed increased permeability, dilatation, and edema when a frog's leg was perfused with a buffered 3 per cent gum-saline solution, but these increases disappeared upon the addition of horse serum in amounts greater than 15 per cent to the perfusion medium. His conclusion that serum is necessary for the maintenance of normal capillary tone does not help the understanding of the mechanics of the phenomenon.

In dogs with intact circulations, Stanbury, Warweg, and Amberson (15) have replaced the plasma proteins with gum acacia in saline solution so that the plasma protein level was maintained below 0.2 per cent. These animals were maintained in normal health for months without any symptoms of edema or shock. It appears that some of the functions of the plasma colloids can be replaced, in the experimental animal, by gum acacia solutions sufficiently purified and properly buffered, and in which at least 20 per cent of erythrocytes are suspended. This, however, does not explain why, at the isolated capillary membrane, gum acacia freely leaks through when not mixed with serum. It has been suggested (10) that the value of gum acacia in maintaining blood volume may be the result of its adsorption on the capillary walls, whereby the exit of fluid from the vessel is impeded. However, Amberson and his coworkers have demonstrated that gum acacia alone is not effective in maintaining blood volume if there is an oxygen lack.

SUMMARY

In the concentration usually employed for clinical use (6 per cent), gum acacia behaves as a typical lyophilic colloid that is highly aggregated. It exerts a C. O. P. (18 mm. of mercury) that is nearly equivalent to that of the normal colloids of the plasma.

Gum acacia particles readily leak through ordinary protein-tight membranes but are restrained by membranes of less permeability. The effect of human serum on the permeability of membranes to gum acacia has been discussed.

In four human cases with liver injury the injection of gum acacia was followed by a rise in the C. O. P. of the blood serum with no significant change in the concentration of the albumin or globulin fractions. The C. O. P. of the serum remains markedly elevated for some hours after injections of gum acacia, but this effect disappears in a few days.

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THE INFLUENCE OF GELATIN AND ELECTROLYTE CONCENTRATION ON THE RATIO OF ELECTROÖSMOTIC TO ELECTROPHORETIC MOBILITY[1]

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While it has been repeatedly shown that in salt solutions of concentration greater than 1×10^{-2} molar the ratio of electroösmotic to electrophoretic velocity at a gelatin–aqueous interface is unity, White, Monaghan, and Urban (8) presented evidence that this holds true only for electrolyte concentrations above the range 10^{-3} to 10^{-2} molar. At concentrations below this range the ratio of the velocities departs from unity, becoming as high as 2.0. Bull (2) and Moyer and Abramson (7), however, state that with protein surfaces the ratio is unity, even in very dilute salt solutions (conductivities corresponding to 1 to 4×10^{-5} M potassium chloride). The present communication is a partial repetition and an extension of the experiments of White, Monaghan, and Urban and of Moyer and Abramson to investigate the reason for the apparent discrepancy. The present report presents evidence that the observations both of White, Monaghan, and Urban and of Moyer and Abramson are correct, but are not comparable, owing to the influence of the concentration of gelatin employed.

METHODS

A cylindrical Pyrex Mattson-type cell was used. The gelatin was adsorbed on powdered Pyrex particles 1 to 3 micra in diameter. The cell was always allowed to stand at least a half hour, usually an hour or more, filled with the experimental solution, or with this slowly passing through it.

The preparations of gelatin used were as follows: Eastman Purified, ash content 0.03 per cent; Coignet "Silver Lable"; Afga "Lichtfilter" (Ucopoco 6415 "with low ash content"), ash 1.10 per cent. The filtered 1 or 2 per cent stock solutions were kept in the ice box when not in use, and were used within two days or so of preparation.

Observations of the time to traverse a given distance were made and recorded by the same observer. The average was taken of five traverse times in each direction. The mean velocity for a given depth was cal-

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[1] Presented at the Fourteenth Colloid Symposium, held at Minneapolis, Minnesota, June 10-12, 1937.

culated from the mean velocities in the two directions. Drift was usually small; in one experiment for which the deviations of the times in each direction were calculated, the deviation was 4.2 per cent.

Readings were taken at a number of levels in the cell, as recommended by Moyer and Abramson. It can be shown that the equation

$$y = b\ (x - x^2) + c \tag{1}$$

used by them for the flat cell describes the observed velocity at any level in the round cell as well[2]; y is the observed velocity at any fraction, x, of the diameter from the top; b is the slope of the resulting straight line, and c is the intercept at $x = 0$, i.e., the velocity at the wall. For any given solution, b and c should be constants. Since at the wall $y_0 = c$, c is the difference between the electroösmotic and electrophoretic velocities. In the round cell the ratio is

$$R = \frac{u}{v} = \frac{y_{0.5} - y_{0.147}}{y_{0.147}} = \frac{y_{0.147} - y_0}{y_{0.147}} \tag{2}$$

where the subscripts refer to the fraction of the diameter from the top at which the velocity was observed, and u is the electroösmotic, v the electrophoretic velocity. The values of c, R, u, and v, given in tables 1 and 2 arise not from any single pair of observations but from an application of equation 1 to points obtained throughout the upper half of the cell. In every case the values of $y_{0.5}$, $y_{0.147}$, or y_0 used to determine R according to equation 2 are obtained graphically from the straight-line plots of equation 1, as is illustrated in figures 2 and 3. The values of $y_{0.147}$ and $y_{0.5}$ so obtained agree closely with the values directly observed at these levels. The conclusion that R was unity where there was no observable movement near the wall was confirmed graphically.

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[2] Mattson (J. Phys. Chem. **37**, 223 (1933)) gives the equation

$$V = c\left(r^2 - \frac{a^2}{2}\right)$$

for the velocity, V, of the liquid at any radius, r, from the center in a tube of radius a, c being a constant. The fraction of the diameter measured downwards from the top is

$$x = \frac{a - r}{2a}$$

The observed velocity, y, of a particle is the sum of v, its electrophoretic velocity, and V. In terms of x we have

$$y = V + v = -4ca^2\ (x - x^2) + \tfrac{1}{2}ca^2 + v$$

which is of the same form as equation 1 of the text, in which b is $-4ca^2$ and c is $\tfrac{1}{2}ca^2 + v$.

EXPERIMENTAL

Tests of completeness of coating of walls and particles

For the present argument it is essential to know that a gelatin concentration of 0.01 per cent produces an effective coating on both glass particles and cell wall. While it has been the universal finding that this concentration is sufficient to ensure adequate coating (1, 4, 6), two types of experiments were carried out to test this point.

First, if the cell is allowed to stand filled with 1 per cent gelatin in distilled water for an hour, then rinsed with 0.01 per cent gelatin in distilled water, the ratio is still well above unity; in one case of three the ratio was not altered by previous cell treatment with 1 per cent gelatin, in two cases it was somewhat lowered, presumably because of adventitious factors. Also, in the case of the experiments with 0.02 per cent Eastman gelatin given in table 2 the cell had stood for an hour before the experiment filled with 1 per cent gelatin, yet the ratio is clearly greater than unity. We confirm earlier findings that equilibrium conditions are established within an hour.

Second, simultaneous determinations of electrophoretic and electroosmotic isoelectric points were carried out. If the cell is incompletely coated while the particles are completely coated there will be electroösmotic movement with no electrophoretic movement. A series of 0.01 per cent solutions of Eastman's gelatin was prepared from the same stock solution. All were $2 \times 10^{-4} M$ in added chloride, with various proportions of hydrochloric acid and potassium chloride to vary the pH, which was determined with the glass electrode. The results are shown in figure 1. Plotting u, electroösmotic velocity, and v, electrophoretic velocity, against pH gives smooth curves, both of which cross the axis of zero mobility at pH 4.75.

The objection might be raised that even though a concentration of 0.01 per cent gelatin coats the cell wall sufficiently to make the wall behave as a gelatin surface when at its isoelectric point, the coating may still not be adequate to make the wall behave as a gelatin surface when zeta is other than zero, while the broken particle surfaces would be adequately coated. That is, the advocates of the view that the ratio is always unity, given identical surfaces, might say that our findings are due merely to incompleteness of the cell wall coating as compared with the particle coating. A further reason, however, for believing that the cell wall is in fact completely coated in 0.01 per cent gelatin is the finding of Dummett and Bowden and of ourselves that electroösmotic velocity at constant pH falls as gelatin concentration is increased from zero and becomes constant at a concentration between 0.001 and 0.01 per cent, i.e., the electroösmotic velocity changes from that of bare glass to that of gelatin, the latter being attained at between 0.001 and 0.01 per cent gelatin. The argument must be confined to completeness of coating of the *cell wall*; it cannot be maintained that the particles are less completely coated than the cell wall, for in that case electrophoretic velocity would be greater than electroosmotic. Monaghan and White (5) found that when one uses microscopic glass particles with fused surfaces the ratio of electroösmotic to electrophoretic velocity is greater than unity in potassium chloride solutions of 10^{-3} *M* or lower concentration. Here we have a case where wall and particle surfaces are known to be identical; the observation has a rather direct bearing on the point under discussion, in that it shows that it is possible to have a greater than unity ratio with identical surfaces, although it does not directly prove the case for gelatin. The matter seems worth discussing, aside from its purely theoretical implications, because of its rôle in the explanation advanced by White and Monaghan (9) of the common observation that the critical potential (as determined by electrophoresis) seen with electrolytes which coagulate on low concentration is lower than that with those which require higher concentrations; the lower apparent critical potential with the polyvalent electrolytes is considered to be an artifact due to the impossibility of calculating the true zeta potential from electrophoretic mobility in dilute solutions.

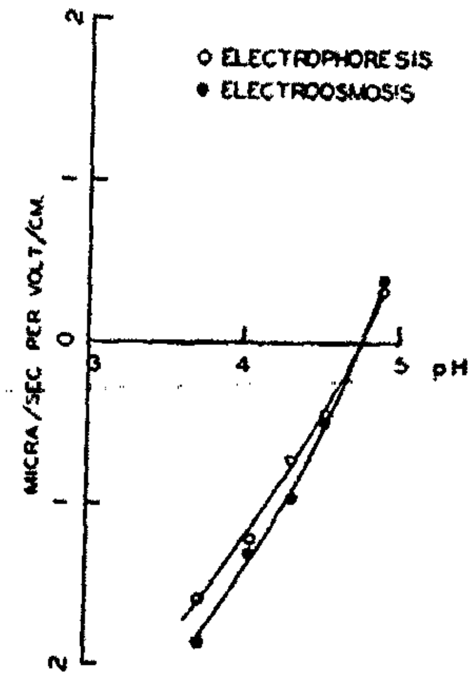

FIG. 1

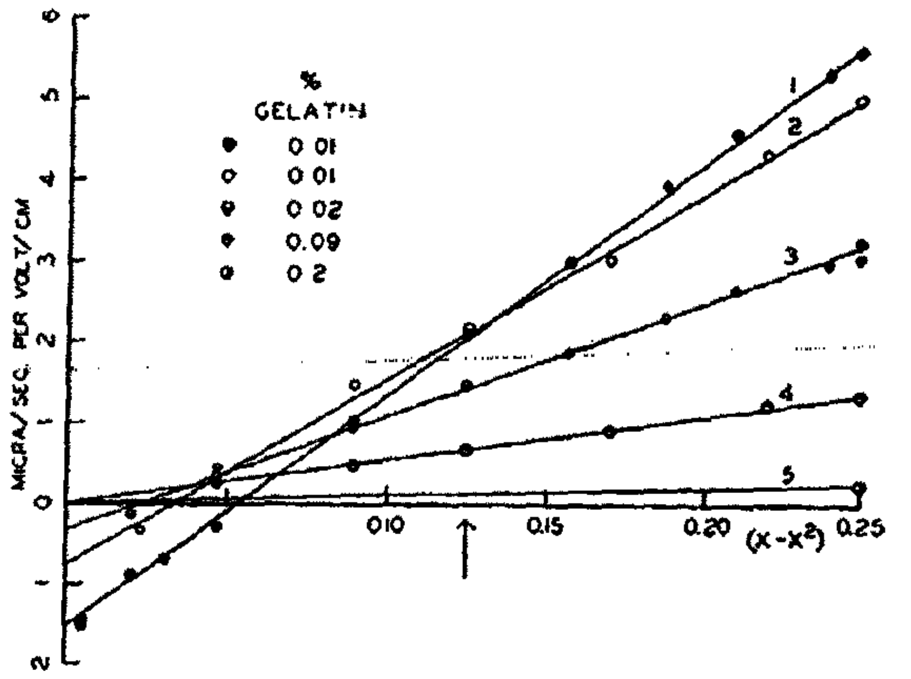

FIG. 2

FIG. 1. pH-mobility curves of electrophoresis and electroösmosis in 0.01 per cent Eastman gelatin, showing identity of isoelectric points.

FIG. 2. Effect of varying gelatin (Eastman) concentration in distilled water on mobilities and ratio of mobilities. The function $(x - x^2)$ of equation 1 is plotted on the horizontal axis. The *y* intercept shows the excess of electroösmotic over electrophoretic mobility. The arrow indicates the level, $x = 0.147$, of true electrophoretic mobility. The mobility at the center of the cell, where $x - x^2 = 0.25$, is the sum of electroösmotic and electrophoretic mobilities. The numbers of the various curves refer to the experiment numbers of table 1.

Effect of gelatin concentration

We find that varying the gelatin concentration, in distilled water solution, has a very marked effect (table 1 and figure 2). In every case, concentrations of 0.08 per cent or more give low mobilities, and ratios of unity. For concentrations of 0.01 to 0.02 per cent gelatin, except Agfa gelatin, the electroösmotic mobility is the larger, the ratio ranging from 1.13 to 1.78. The spread of values at a given concentration (0.01 per cent) in different experiments must be due to the combination of a number of uncontrolled factors, such as the following: protein concentration itself, within small limits; accidental electrolyte contamination; age and history of the gelatin solution; temperature.

TABLE 1

Effect of gelatin concentration in distilled water

EXPT. NO.	GELATIN	c	u	v	R	pH
	grams per 100 cc.	*micra per second per volt per cm.*				
	Eastman					
1	0.01	1.53	3.57	2.04	1.75	6.32
2	0.01	0.78	2.88	2.10	1.37	
3	0.02	0.32	1.73	1.41	1.23	
4	0.09	0	0.68	0.68	1.00	
5	0.2	0	0.135	0.135	1.00	4.87
	Coignet					
6	0.01	1.82	4.29	2.43	1.76	
7	0.01	1.05	3.52	2.48	1.42	
8	0.01	1.73	3.80	2.20	1.77	6.12
9	0.01	0.70	1.98	1.28	1.55	
10	0.02	0.66	2.32	1.64	1.41	5.59
11	0.1	0	0.64	0.64	1.00	
12	0.2	0.02	0.475	0.45	1.06	5.28
	Agfa					
13	0.01	0	0.45	0.45	1.00	6.80
14	0.02	0	0.20	0.20	1.00	
15	0.05	0	0.07	0.07	1.00	
16	0.1	0	0.06	0.06	1.00	
17	0.2	0	Very slow		1.00	6.21

Effect of electrolytes

Table 2 shows that the ratio of the two mobilities is slightly more than unity in 10^{-3} *M* potassium chloride, but is unity in 10^{-2} *M*, confirming the results of White, Monaghan, and Urban (8). Both Coignet and Eastman gelatins, the latter in two concentrations, 0.01 and 0.02 per cent, show this effect. Comparison of the two gelatin concentrations in each concentration of added electrolyte shows a lower velocity for higher gelatin concentration, as did the experiments on gelatin in distilled water. Figure 3 shows straight-line plots of experiments with 0.01 per cent Eastman gelatin.

TABLE 2

Effect of added electrolyte

EXPT. NO.	GELATIN	ADDED KCl	c	u	v	R	pH
	grams per 100 cc.	*molar*	*micra per second per volt per cm.*				
	Eastman						
1A	0.01	0	1.60	3.65	2.05	1.78	
1B	0.01	10^{-4}	0.93	2.25	1.32	1.70	
1C	0.01	10^{-3}	0.20	0.99	0.79	1.25	
1D	0.01	10^{-2}	0	0.49	0.49	1.00	
3A	0.02	0	0.32	1.73	1.41	1.23	
3B	0.02	10^{-4}	0.40	1.40	1.00	1.40	5.15
3C	0.02	10^{-3}	0.17	0.77	0.60	1.28	5.00
3D	0.02	10^{-2}	±	0.32	0.36	0.92	4.86
	Coignet						
7A	0.01	0	1.05	3.52	2.48	1.42	
7B	0.01	10^{-4}	0.90	3.18	2.28	1.39	
7C	0.01	10^{-3}	−0.43	1.43	1.85	0.77	
7D	0.01	10^{-2}	0	0.72	0.72	1.00	
9A	0.01	0	0.70	1.98	1.28	1.55	
9B	0.01	2×10^{-4}	0.34	1.40	1.06	1.32	
9C	0.01	10^{-3}	0.09	0.74	0.64	1.16	

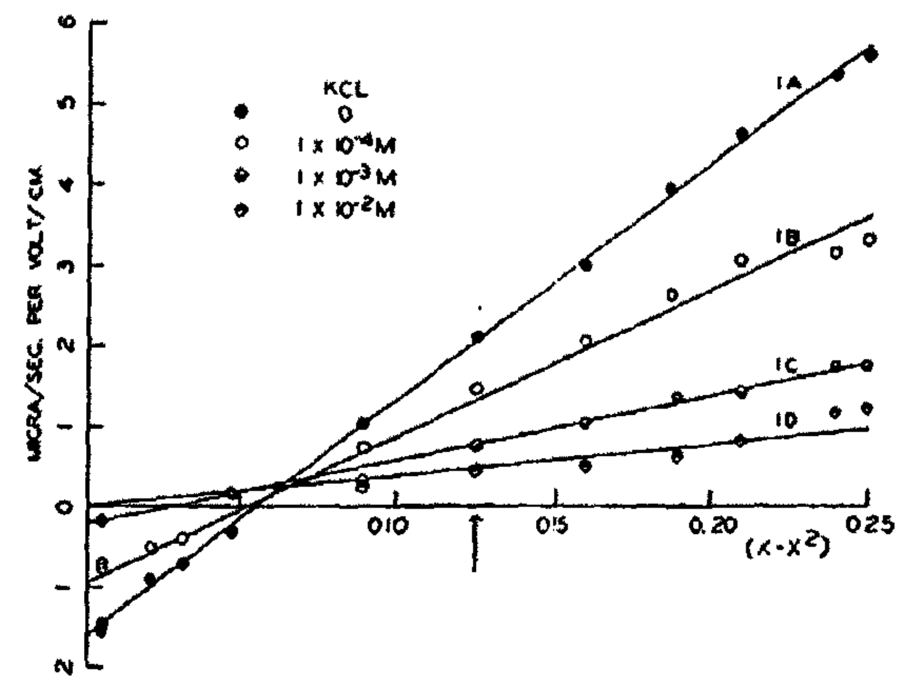

FIG. 3. Effect of varying concentration of added electrolyte on mobilities and ratio of mobilities of 0.01 per cent Eastman gelatin. The numbers of the curves refer to the experiment numbers of table 2.

Differences in the gelatins

Since we did not dialyze any of these preparations, some differences due to the ash content may be expected. The specific conductances of 0.1 per cent solutions of these gelatins were measured in a separate set of experiments, and were found to be 7.67, 30.6, and 36.2 × 10^{-5} mhos for Eastman, Coignet, and Agfa gelatin, respectively. Neither the makers' stated ash content nor the determined conductivity suffices to account for the low mobility of our sample of Agfa gelatin; it must be attributed to the intrinsic properties of this particular protein.

DISCUSSION

Four of the six experiments on gelatin reported by Moyer and Abramson were done with gelatin concentration of 0.2 per cent, one with 0.05 per cent gelatin, and one with 0.02 per cent gelatin, the last showing the highest value of the ratio found by them, 1.11. Bull's experiments were done with gelatin concentrations ranging from 0.158 to 0.219 per cent, and were all in 3 to 8 × 10^{-4} M hydrochloric acid. Since White, Monaghan, and Urban used a gelatin concentration of 0.01 per cent (Eastman purified gelatin, no dialysis) the present series of experiments shows that there is no incompatibility in the results of the various workers.[3] Moyer and Abramson's velocities are expressed only in relative units, and so do not permit a quantitative comparison.

That the reversal near the wall is not due to any specific wall effects, as suggested by Moyer and Abramson to account for their occasional observation of this same phenomenon, is seen from the fact that the value of c at the wall is determined not solely by points taken near the wall, but is consistent with mobilities at depths all the way down to the center. The nearest approach to the wall which it is feasible to make is a matter of 0.01 to 0.02 mm., the cell diameter being 2.420 mm.

The present experiments confirm the previous work of White, Monaghan,

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[3] Since this paper was written Moyer, working in Abramson's laboratory, informs us that he finds that with 0.01 per cent and even with 0.001 per cent gelatin the ratio is usually unity, provided that the particles are first treated with a stronger gelatin solution, and sometimes even without such pretreatment His interpretation is that when adequate measures are taken to insure complete coating of both surfaces the ratio is unity. We find, on the other hand, the ratio greater than unity with 0.01 per cent gelatin even though both cell and powder have first been treated with 1 per cent gelatin and then allowed to come to equilibrium with 0.01 per cent. It seems to us most probable that differences in the nature or previous treatment of the gelatins must be responsible for the discrepancies of observation; it will be noted that our Agfa gelatin always showed unity ratio even with 0.01 per cent concentration in distilled water. The fundamental question of whether a ratio greater than unity, when it is observed, is due to a real difference in the electrokinetics of electrophoresis and of electroösmosis, respectively, or merely to a lack of identity of surfaces is still not answered to the satisfaction of all concerned.

and Urban in showing the electrophoretic velocity to be lower than the electroösmotic in low gelatin and electrolyte concentrations; they also confirm the work of Bull and of Moyer and Abramson, in finding the velocities the same with higher gelatin but unchanged electrolyte concentration. The essential difference between the two sets of experiments seems to lie in the concentration of gelatin. No satisfactory explanation of the reason for this effect of gelatin concentration is apparent; however, its similarity to that of added inorganic electrolyte suggests that the gelatin, by virtue of its ionization as zwitter ions, is itself the equivalent of added electrolyte. The zwitter-ion electrolyte, although often stated to have the properties of a strong electrolyte, would not be revealed by the conductivity measurements which have usually served as criteria for freedom from electrolytes. The suggestion may be given a rough quantitative test. According to the compilation of Czarnetsky and Schmidt (3), the total acid-binding capacity of gelatin is 89 × 10^{-5} moles per gram; the total base-binding capacity is 64 × 10^{-5} moles per gram, averaged from conductimetric and potentiometric determinations. These experimentally determined values agree roughly with those calculated by them from the known amino acid composition. On this basis, at the isoelectric point there are present 64 × 10^{-5} moles of zwitter ions per gram of gelatin, and a 0.1 per cent solution is 6.4 × 10^{-4} molar in zwitter-ions, at a maximum. Since the concentration of potassium chloride required to bring the ratio of the two velocities to unity falls between 10^{-3} and 10^{-2} molar, it is evident that if the gelatin is acting as a zwitter-ion electrolyte, it is either about twice as effective as is potassium chloride, or it has an additional effect of some other nature.

TABLE 3

Effect of added zwitter ions

0.01 per cent Eastman gelatin in 1 × 10^{-4} *M* acetate buffer

ADDED GLYCINE	pH	SPECIFIC CONDUCTIVITY AT 25°C.	u	v	R
molar		*mhos × 10^5*	*micra per second per volt per cm.*		
0	5.39	1.57	1.97	1.13	1.74
5 × 10^{-5}	5.45	1.39	2.19	1.30	1.68
5 × 10^{-4}	5.35	1.34	2.10	1.50	1.40
5 × 10^{-3}	5.44	1.40	1.91	1.66	1.15
1 × 10^{-2}	5.21		1.25	1.05	1.19
5 × 10^{-2}	5.50		1.65	1.65	1.00
2 × 10^{-1}		1.15			

In order to test experimentally the concept that zwitter ions may affect electrophoretic mobility, the influence of added glycine in various concentrations on the ratio of electroösmotic to electrophoretic mobility of

0.01 per cent Eastman gelatin was determined. The values of u and v in this series were determined by observations at the 50 and 14.7 per cent cell diameter levels. The findings are shown in table 3. It is evident that added glycine, although it has no significant effect on conductivity of the solutions employed, acts as does added potassium chloride in lowering the ratio to unity. The supposition is thus strengthened that the unity ratio seen in high gelatin concentrations, as 0.1 or 0.2 per cent, is due to the same mechanism.

SUMMARY

Evidence is presented that 0.01 per cent gelatin is sufficient to coat completely the suspended particles and cell wall, giving characteristic protein surfaces; our former finding is confirmed that here the ratio is greater than unity in potassium chloride solutions of concentration $10^{-3}\,M$ or lower.

Evidence is presented that the ratio of electroösmotic to electrophoretic mobility is dependent on the concentration of gelatin as well as of added electrolyte.

The effect of added gelatin is qualitatively the same as that of added electrolyte and is apparently due to its zwitter-ion concentration.

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THE INTERACTION BETWEEN PROTEINS AND FATTY ACIDS ON THE SURFACE OF AQUEOUS SOLUTIONS[1,2]

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The problem of the interaction between proteins and lyophobic substances seems to be of interest in regard to the structure of proteins, since it bears upon the function of the lyophilic and lyophobic groups as well as on the structure of certain biological systems which consist mainly of proteins and such lyophobic materials as fats and lipids. The membranes of the living cells are examples of such systems, and their structure and function depend not only on the chemical composition but to a large extent also on the orientation of the individual compounds on the surface. A relatively easy way of studying such systems is provided by the method of spreading in surface films, inasmuch as proteins in the cell membranes as well as on the surface of aqueous solutions are probably present in the surface-denatured state (6). Such studies have been carried out recently by Hughes (7) and by Schulman and Hughes (10). Their investigations differ essentially, however, from those described in this paper, in that they studied the phenomenon of "film penetration" by injecting the protein underneath a film of fatty acids and similar materials, whereas in these experiments proteins and the lyophobic material were spread simultaneously in order to ascertain complete spreading. In order to deal with relatively simple and well-defined systems, instead of fats and lipids, fatty acids such as stearic acid, palmitic acid, or myristic acid were chosen for these studies. Of these acids only myristic acid gave satisfactory results under the conditions of spreading used.

The experiments reported below are to be regarded as preliminary; publication at the present stage seemed desirable, however, as many data have been accumulated and a partial analysis of the problem accomplished.

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[1] Presented at the Fourteenth Colloid Symposium, held at Minneapolis, Minnesota, June 10–12, 1937.

[2] The experimental part of this paper was carried out in 1934–35 at the University College, London, England. The author is greatly indebted to Professor F. G. Donnan, F.R.S., for his hospitality and for his interest in these investigations.

[3] George Fisher Baker Research Fellow.

EXPERIMENTAL

A. Preparation of solutions

Ovalbumin solutions were prepared in exactly the same manner as described in the previous paper (8), i.e., by separating the yolk of fresh hens' eggs from the white, diluting the latter with distilled water, and filtering off the precipitated globulins. The filtrate was electrodialyzed in Pauli's apparatus (9) for several days, the voltage being gradually increased from 5 to 220 volts. After seven days the conductivity had reached its minimal value of $81 \cdot 0^{-5}$ mhos with 2 per cent protein solution (pH 4.80).

Aqueous solutions of fatty acid were prepared by dissolving the acid first in a minimal volume of 96 per cent ethyl alcohol and adding to this solution dilute potassium hydroxide until a water-clear solution resulted. This soap solution was spread on $N/10$ hydrochloric acid, thus forming a film of the free fatty acid on the surface. When using palmitic acid it was found that homogeneous films of the fatty acids could not be obtained under any circumstances, the area per molecule yielding values of 12 to 13 sq. A. U. instead of the theoretical value of 20.5 sq. A. U. at zero compression. Likewise, when using the choline salt of palmitic acid, which is more soluble in water than the potassium salt, the area per molecule of fatty acid was reduced to 18 sq. A. U.

When using the potassium salt of myristic acid it was found that the area per molecule of fatty acid depended, as in the former case, on the amount of potassium hydroxide added to the alcoholic solution of the myristic acid. In all instances the myristic acid was dissolved in 5 cc. of ethyl alcohol and diluted with potassium hydroxide to 100 cc. With a mole ratio of potassium hydroxide to myristic acid of 4:1 the area per molecule of fatty acid amounted to 38 to 42 sq. A. U. at zero compression. A mole ratio of 2:1 yielded an area of 41.5 to 47 sq. A. U., and a mole ratio of 1.2:1 an area of 51 to 52 sq. A. U., in good agreement with the theoretical value. The transition from the expanded to the condensed state occurred at an area of 31.5 sq. A. U., which is 0.5 sq. A. U. smaller than the theoretical value. All results refer to 18.0°C.

Mixtures of protein and fatty acid were prepared by adding to the solution of potassium myristate which contained 5 per cent alcohol (mole ratio of potassium hydroxide to myristic acid = 1.2:1) varying amounts of ovalbumin solution. The total volume of the mixture was always 5 cc. The concentration of ovalbumin and potassium myristate was adjusted in such a way that about 0.05 to 0.08 cc. of the solution when spread yielded a film which almost covered the free surface of the trough.

B. Measurements

The apparatus of Adam and Jessop (3) was used. The films were frequently examined by the dark-ground illumination introduced by Zocher and Stiebel (11) and with the simplification used by Adam (1). A brass trough was used, and the temperature regulated by an electrical heater below the trough. The technique was essentially the same as described in the previous paper (8). The solutions were spread from an Agla micrometer syringe, capable of being read to 0.0001 cc. Complete spreading was attained 15 min. after the material had been put on the surface of a solution of $N/10$ hydrochloric acid. All measurements quoted below are the mean of seven to ten readings.

RESULTS

Experiments on the spreading of isoelectric ovalbumin on $N/10$ hydrochloric acid showed that the properties of the films deviated only slightly from those of previous investigations. The area per molecule at zero compression was 5600 sq. A. U., whereas it amounted to 5000 sq. A. U. when the protein was spread on $N/20$ acetate buffer (pH 4.8). Collapsing started at a pressure of 15 dynes per centimeter, 3 dynes lower than when spread on acetate buffer. The slope of the straight part of the pressure-area curve was 72 sq. A. U. per dyne or 1.29 per cent of the area at zero compression, as compared with 70.5 sq. A. U. per dyne or 1.41 per cent of the area at zero compression when spread on acetate buffer.

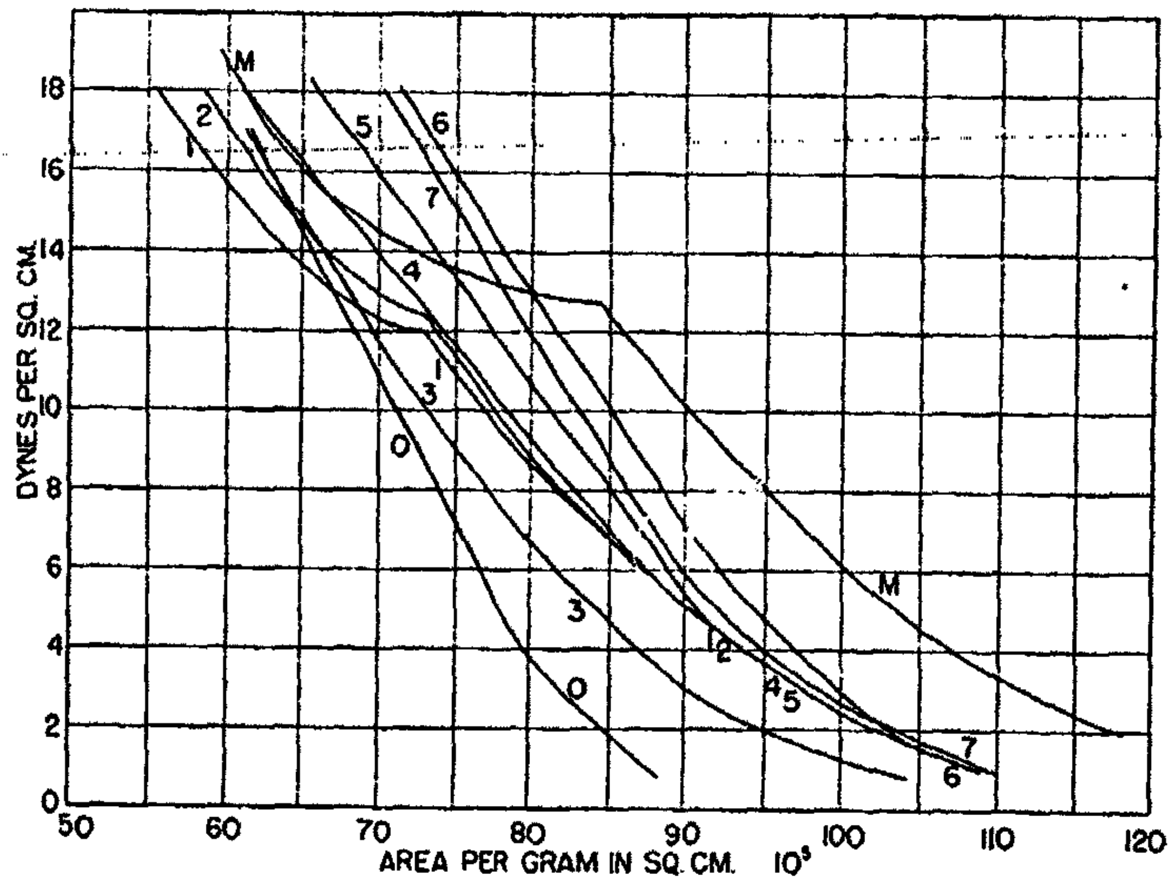

FIG. 1. Spreading of potassium myristate, ovalbumin, and mixtures of both on $N/10$ hydrochloric acid. Curve O, ovalbumin; curve M, potassium myristate; curve 1, mole ratio of potassium myristate to ovalbumin 393; curve 2, mole ratio 247; curve 3, mole ratio 97.5; curve 4, mole ratio 67.5; curve 5, mole ratio 30.7; curve 6, mole ratio 17.8; curve 7, mole ratio 9.

Figure 1 shows the pressure-area curves of pure myristic acid, of pure ovalbumin, and of mixtures of both. Plotted as ordinates are the surface pressures in dynes per centimeter and as abscissae the surface areas per gram of solute in square centimeters $\times 10^{-5}$. Table 1 illustrates the composition and the properties of the films.

There appear two distinct changes in the properties of the films as the relative amount of myristic acid in the mixtures decreases. The inflection point, which in the case of pure myristic acid marks the transition from the liquid-expanded to the condensed state, disappears, and whereas at high relative concentrations of myristic acid the films are in the liquid state throughout the whole pressure range, with decreasing relative amount of fatty acid they assume gradually the solid type which is characteristic for the pure protein film.

TABLE 1

Mixed films of myristic acid and ovalbumin

CURVE NO.	PER CENT OF MYRISTIC ACID PER GRAM OF MIXTURE	MOLE RATIO OF MYRISTIC ACID TO OVALBUMIN	TOTAL AREA PER GRAM OF MIXTURE IN CM.^{2} $\times 10^{-5}$			INFLECTION POINT AT DYNES	PROPERTIES OF FILMS
			2 dynes	5 dynes	10 dynes		
M.....	100		118	103.5	90	12.6	Liquid
1......	72.2	393	102.5	91	77.6	12	Liquid
2......	43.6	247	102.5	90.5	77.7	12.3	Liquid
3......	39.3	97.5	95	84.3	73.2	17.4	Liquid
4......	30.9	67.5	103	91	78.5	No inflection point	Slightly elastic, rigid
5......	16.9	30.7	102	91.1	81.5	No inflection point	Elastic and solid above 5 dynes
6......	10.5	17.8	103.5	95	85	No inflection point	Elastic and solid above 5 dynes
7......	5.6	9	104	92	83	No inflection point	Elastic and solid above 5 dynes
0......	0	0	84.5	73	71	No inflection point	Elastic and solid above 4 dynes

DISCUSSION

Whereas a plot as illustrated in figure 1 does not reveal any regularity of the behavior of the individual compounds, a deeper insight into the mechanism of the mutual interaction between the two compounds can be gained when it is assumed that the surface of either one of the compounds remains unaltered by the addition of the other.

Figure 2 illustrates the extrapolated pressure-area curves of myristic acid, calculated on the basis that the area of ovalbumin was unchanged by the addition of the fatty acid. From each curve of figure 1 the values of the total area per gram were read off at about twenty different pressures and the area per molecule of myristic acid calculated, taking into account the change of the area of ovalbumin with pressure. *Vice versa*, the area per molecule of protein was computed in the same manner, assuming that the surface area of the fatty acid remained unchanged by the addition of the protein. This is illustrated by figure 3.

Figure 3 reveals a marked decrease of the area of the protein upon addition of a large excess of fatty acid. Such a decrease seems rather improbable, since the molecule cannot occupy less area than it does in the condensed film of the pure substance. Assuming that in the condensed state the lyophobic groups of the polypeptide chain are oriented perpendicular to the surface, which is in keeping with the results of x-ray analysis (5), an increase of the surface area of the protein would be conceivable only either by tilting of the molecule about the polypeptide chain or by decreased lateral adhesion between neighboring molecules. The curves of figure 3 reveal also a sharp break, which is preceded by a flattening out and followed by a sharp *increase* of the area with increasing pressure. Such a shape of pressure-area curves seems rather improbable and is without precedent in the literature.

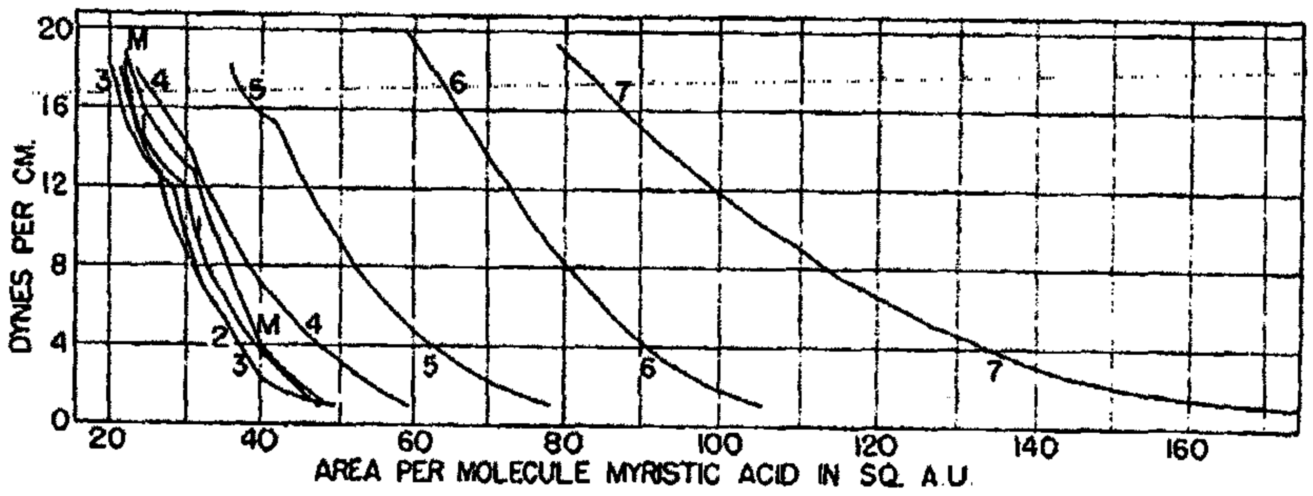

FIG. 2. Extrapolated curves of area per molecule of myristic acid, based on the assumption that the area of the protein remains unchanged by the addition of the fatty acid. Curve M, myristic acid without addition of ovalbumin; curve 1, mole ratio of myristic acid to protein 393; curve 2, mole ratio 247; curve 3, mole ratio 97.5; curve 4, mole ratio 67.5; curve 5, mole ratio 30.7; curve 6, mole ratio 17.8; curve 7, mole ratio 9.

There is, on the other hand, strong evidence for the assumption that the molecules of the fatty acid will be influenced by the large and rather compact molecules of the protein film. Figure 2 shows that with mole ratios of fatty acid to protein of 393, 247, and 97.5, respectively, the area per molecule of myristic acid is somewhat decreased. This decrease is probably due to a condensing effect, which has been observed by Adam and Jessop (4) for mixtures of cholesterol and myristic acid and which has been ascribed to a prevention of the spreading of myristic acid by the large and rather inert molecules of cholesterol. In our case this condensing effect is very small and indicates the absence of any special attraction between the molecules of the protein and of the fatty acid at these concentrations. The change from the solid state when the protein is spread alone, to the liquid state when the acid is present is noteworthy and probably due to slight changes of the lateral adhesion between neighboring molecules.

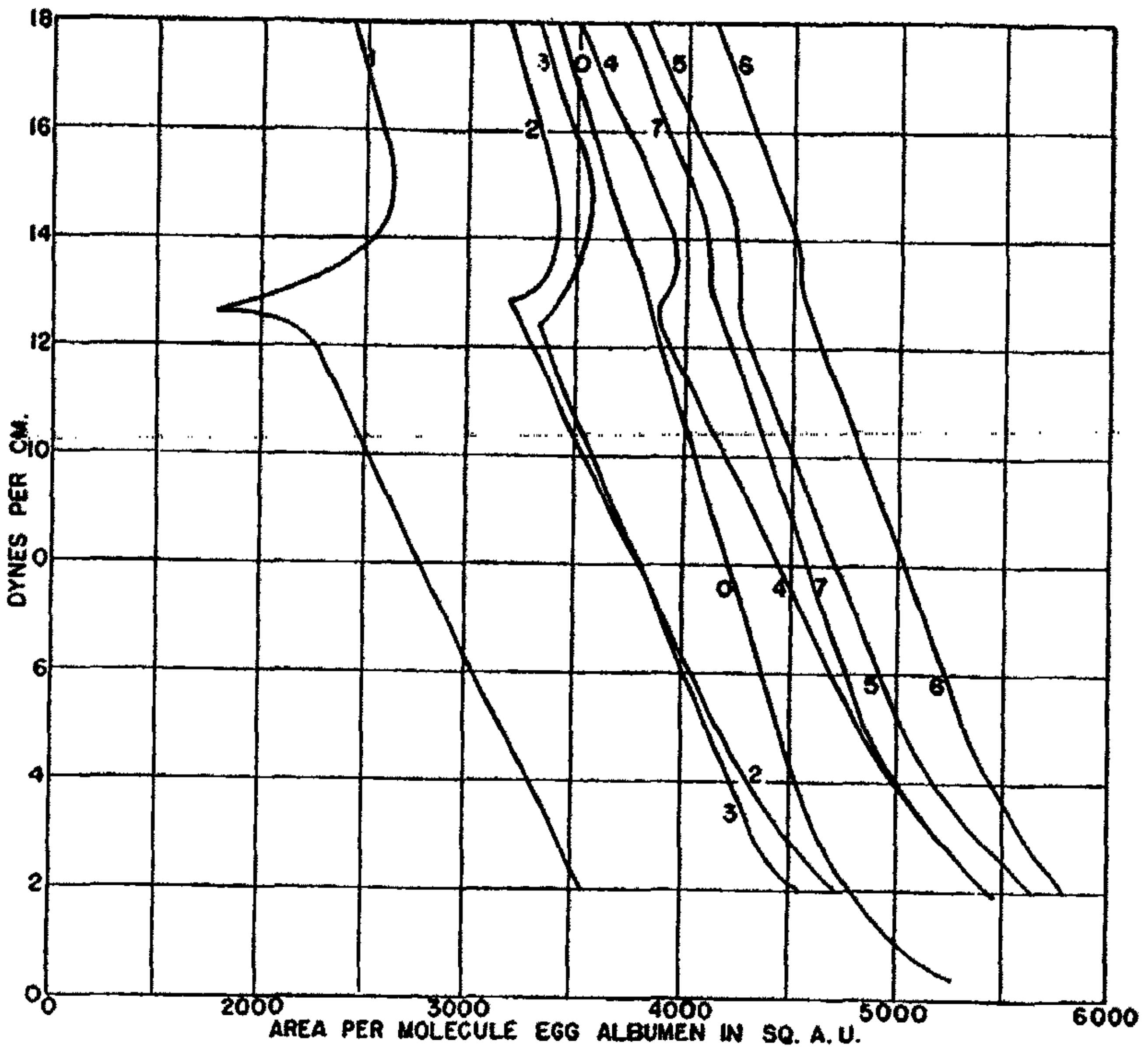

Fig. 3. Extrapolated curves of area per molecule of ovalbumin, based on the assumption that the area of the fatty acid remains unchanged by the addition of the protein. Curve O, ovalbumin without addition of myristic acid; curve 1, mole ratio of myristic acid to ovalbumin 393; curve 2, mole ratio 247; curve 3, mole ratio 97.5; curve 4, mole ratio 67.5; curve 5, mole ratio 30.7; curve 6, mole ratio 17.8; curve 7, mole ratio 9.

With mole ratios smaller than 97.5 a marked increase of the area of myristic acid sets in which, with a mole ratio of 9, assumes values of more than 180 sq. A. U. at zero compression. This increase is accompanied by a gradual increase of the compressibility of the films as revealed by the flattening out of the curves at low pressures (curves 5, 6, and 7 of figure 2).

Furthermore, within this range of concentration the curves do not show a transition from the expanded to the condensed state and do not tend to a definite limiting area at zero compression. These facts as well as the large areas, which could not be accounted for even if the molecules lie flat on the surface, suggest that with low relative concentrations of myristic acid the films are in the liquid-expanded and vapor-expanded state, respectively.

In general, the extent of lateral adhesion between the molecules determines whether a film is expanded or condensed. For a given chain length of a fatty acid, for instance, the lateral adhesion between the end groups can be enormously decreased when the end groups become ionized. Thus, acids form gaseous films on alkaline solutions, whereas on acid solutions they are in the liquid-expanded and condensed state (Adam (2)).

This decrease of lateral adhesion between the end groups could be brought about not only by electrical repulsion between ionized groups but likewise by attractive forces acting between certain groups of the protein and the unionized groups of the fatty acid, which would tend to pull the latter apart (ion-dipole forces). Since the films are spread on an acid solution it is reasonable to assume that the protein will possess only positively charged groups, which presumably are the centers of attraction for the carboxyl groups of the fatty acid. The resultant effect will, as a first approximation, depend on the amount of lateral adhesion between the hydrocarbon chains of the fatty acid and on the amount of attraction between the positively charged groups of the protein and the carboxyl groups of the fatty acid. If no interaction between the hydrocarbon groups of the fatty acid and those of the protein takes place, the first effect should be independent of the relative amount of fatty acid present. The second effect, however, will increase with decreasing relative amounts of fatty acid since, the number of positively charged groups per molecule protein being limited, only a certain number of fatty acid molecules can react electrostatically with each protein molecule, whereas the rest will be unaffected.

Such an hypothesis concurs with the experimental findings: At high relative concentrations of myristic acid the films are coherent and no considerable interaction takes place. As the relative amount of myristic acid decreases, a competition between the adhesive forces of the hydrocarbon chains of the fatty acid and the attractive forces between the end groups of the latter and the positively charged groups of the protein sets in which, with a large excess of protein, leads to a state where the molecules of the fatty acid are neither upright nor lying flat on the surface but are in a vibratory motion between these two extremes of orientation. The total effect would be a gradual change from the liquid-expanded to the vapor-expanded or gaseous state. The fact that with low concentrations of the fatty acid the films are solid would not necessarily contradict this view; it would be conceivable that the vapor-expanded or gaseous film of the fatty acid is imbedded in the rigid structure of the protein film. This hypothesis is, of course, only suggestive, and its proof has to await further work along this line.

SUMMARY

As a preliminary study of the problem of the interaction between proteins and lyophobic substances, the behavior of ovalbumin and fatty acids on the surface of aqueous solutions has been studied.

Mixed films of ovalbumin and myristic acid have been prepared by spreading a solution of potassium myristate and ovalbumin on the surface of $N/10$ hydrochloric acid. If it is assumed that the protein occupies the same area as in the pure film of that substance, no appreciable interaction between the two compounds could be found with films containing between about 400 and 100 molecules of myristic acid per molecule of protein. With films containing less than 100 molecules of myristic acid, a marked increase of the area per molecule of fatty acid sets in which, with a mole ratio of 9, reaches a value of more than 180 sq. A. U. The hypothesis has been advanced that within this range of concentration the films are in the vapor-expanded or gaseous state, owing to a sharp decrease of the lateral adhesion between the molecules of the fatty acid. This decrease of the lateral adhesion is presumably brought about by attractive forces acting between the carboxyl groups of the fatty acid and the positively charged groups of the protein film.

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THE EFFECT OF ROENTGEN RAYS ON THE COLLOIDAL PROPERTIES OF ERYTHROCYTES[1]

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INTRODUCTION

In a recent address Failla (2) advanced a theory of the action of penetrating radiation on living material. The theory is based on the observation that both the cells of irradiated tissue and their nuclei swell following exposure to Roentgen rays or to the alpha, beta, or gamma rays of radium. It is known that radiation of these types ionizes matter, producing "radio ions." These are "atoms, molecules, or aggregates which either have lost or have acquired electrons." They are distinct from ordinary chemical ions, and usually recombine rapidly by exchange of an electron. They may, however, regroup themselves with the formation of new chemical substances. If this latter process takes place inside a living cell, and if the new substances have a smaller molecular weight than the parent substances, the osmotic pressure inside the cell will increase. If the intercellular fluid, such as blood or lymph, is affected to a less extent than the cell contents, or if it is replaced with unchanged fluid by the circulation, the cells will swell. Direct injury to the cell membrane would intensify this effect by weakening the resistance of the membrane to the increased internal pressure.

It is difficult to test this theory with cells imbedded in a slowly permeable stroma, such as those in the intact organism or in tissue culture. Of isolated cells the most readily available are mammalian erythrocytes. These are undesirable because of their well-known high radioresistance. On the other hand, since they are non-nucleated, they are free from the complications which might be introduced by the presence of a second osmotic system within the first. Accordingly, suspensions of washed sheep erythrocytes were chosen for the present study.

Since it was found that hemolysis played an important part in the phenomena observed, it will be convenient here to review the mechanism of this process. When erythrocytes are placed in hypotonic solutions they swell in accordance with osmotic laws (4, 7). There is at first no

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[1] Presented at the Fourteenth Colloid Symposium, held at Minneapolis, Minnesota, June 10-12, 1937.

change in the permeability or electrical properties of the membrane (3). When the membrane has been stretched to a critical degree, however, it suddenly becomes completely permeable to hemoglobin, about 90 per cent of which then escapes into the surrounding medium in less than 1 sec. (9). The electrical properties of the membrane change at the moment of hemolysis, but the membrane persists unruptured as a "ghost." If the hemolyzed ghosts are then placed in hypertonic solutions they shrink like normal erythrocytes and regain most of their former osmotic and electrical resistance (9). The permeability of the membrane in hypotonic hemolysis is nearly constant regardless of the tonicity of the solution used to bring about the hemolysis (9).

When hemolysis is brought about by a lysin such as saponin, instead of by exposure to hypotonic solutions, the primary effect is on the membrane rather than on the contents of the cell. As in hypotonic hemolysis, the cell hemolyzes completely or not at all. However, after hemolysis by saponin the cell membrane is irreparably damaged, does not recover its former properties, and may disappear altogether (3).

Although the hemolysis of the individual erythrocyte is an "all or none" process, the hemolysis of any given sample of blood is not, because the red cell population is a heterogeneous one showing all degrees of resistance. Hence it is possible by appropriate treatment to hemolyze any fraction of a sample of cells from zero to 100 per cent. Since hemoglobin solutions obey Beer's law (1), the per cent of hemolysis is readily determined by means of photoelectric readings on the supernatant liquid obtained by centrifuging a partly hemolyzed suspension.

METHOD

Preliminary work was done on heparinized blood in order to avoid possible osmotic effects from a small molecule anticoagulant such as oxalate. Heparin did not prove a satisfactory anticoagulant for large volumes, however, so, as no difference was detected in the behavior of washed cells from oxalated and heparinized samples, oxalated blood was used in most of the work. Sheep blood containing 2 mg. of potassium oxalate per cubic centimeter was obtained in 300-cc. lots fresh from the slaughter house. It was centrifuged at once, the plasma pipetted off, and the cells decanted from the potassium oxalate precipitate and washed three times with 0.9 per cent sodium chloride solution. The cells were then suspended in such a quantity of 0.9 per cent sodium chloride solution that, when packed, they would occupy about 50 per cent of the volume of the suspension. The suspension was kept in the ice box until used.

Before being irradiated the suspension was placed in 1-cc. hematocrit tubes closed with vaccine stoppers and centrifuged at a force of 1000 × gravity. Forty-five minutes was required for the packed cells to come to constant volume at this centrifugal force. The sodium chloride solution was then removed, the tubes re-stoppered, placed in a cardboard box, and irradiated. Sodium chloride solution of the desired concentration was then added, the cells redispersed by shaking, and the tubes kept in a horizontal position in the ice box for seventeen to twenty hours. They were then re-centrifuged, and the cell volume read with a precision of about ±0.5 per cent.

The per cent hemolysis was determined by photoelectric readings on the supernatant liquid in the hematocrit tubes. Reference values for 100 per cent hemolysis were obtained by centrifuging tubes of stock suspension, removing the saline, and adding distilled water. Owing to the high opacity of the completely hemolyzed preparations there was a possible error of 10 per cent in these photoelectric readings. The error in reading the partially hemolyzed preparations was proportionately less, so that, although all the determinations in a given experiment were subject to the possible error in the 100 per cent value, they were consistent among themselves to a higher precision than that of the 100 per cent standard. As Roentgen irradiation colors the glass of the hematocrit tubes, blank readings were always made on tubes of the same color as the experimental ones.

Several investigators (5, 6) have shown that hemolysis is profoundly influenced by temperature. It was impossible in the present work to maintain a constant temperature throughout the course of an experiment. Hence great care was exercised to avoid temperature differences between irradiated and control tubes during manipulation.

The Roentgen rays were obtained from a mechanically rectified machine with water-cooled tube having glass walls 4 mm. thick. It was operated at 200 kv. and 30 ma.; distance from target to hematocrit = 40 cm.; filter = 1 mm. glass + 1 mm. cardboard; intensity = 270 r. per minute; dose = 16,200 roentgens. This dose is much greater than any which would be tolerated by the intact organism, but previous experience by the author and many others has shown that material irradiated *in vitro* is usually highly radioresistant.

RESULTS

Preliminary work indicated that, when whole sheep blood was irradiated, or when centrifuged cells were irradiated alone and unirradiated plasma added, the irradiated cells swelled slightly. This is in accord with Failla's theory. When plasma was irradiated and then added to unirradiated cells, no significant change in the volume of the cells was found. This may indicate either that there is a differential effect on the cell proteins or that changes produced by irradiation in the less concentrated plasma proteins are too small to produce osmotic effects greater than the experimental error. It was apparent at once, however, that much larger effects could be produced by equilibrating the irradiated cells with sodium chloride solutions. This is to be expected from the Donnan relations. Hence most of the work was done with cells equilibrated with salt solutions.

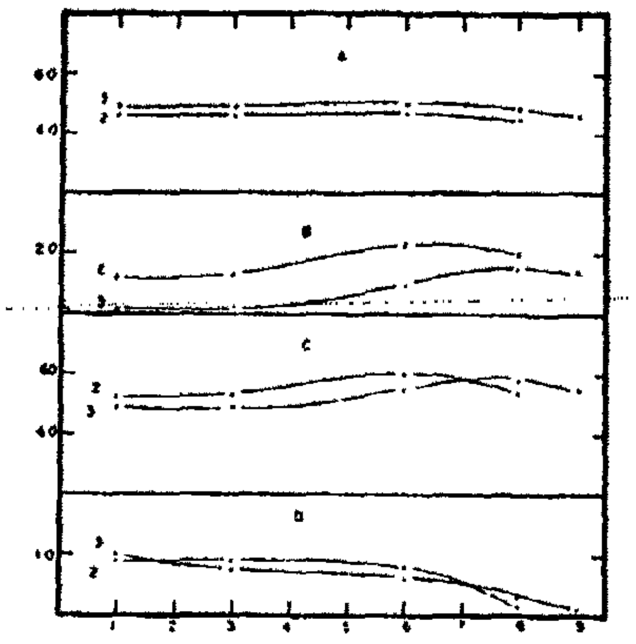

Fig. 1

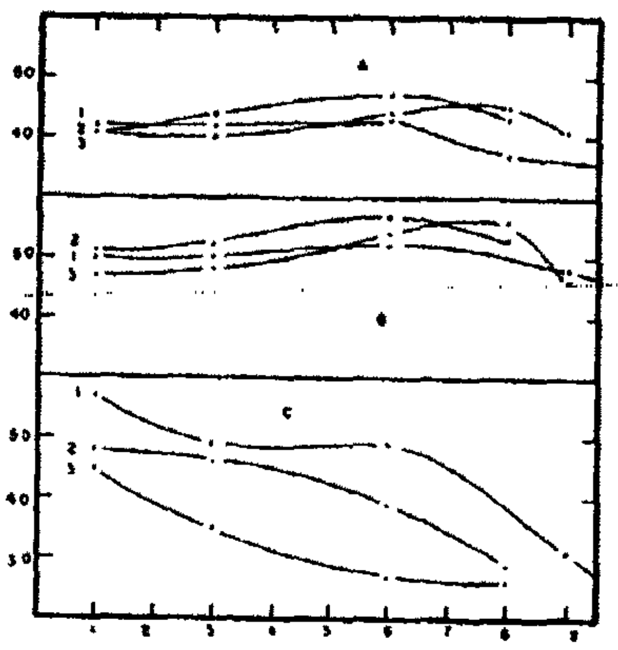

Fig. 2

Fig. 1. Changes in stock suspensions with time. Abscissae = age in days. Ordinates: A = absolute cell volume from hematocrit readings; B = per cent hemolysis; C = specific cell volume; D = photoelectric readings on completely hemolyzed samples.

Fig. 2. Changes with time in the absolute cell volume of unirradiated cells equilibrated with fresh sodium chloride solutions. Abscissae = age in days of cells when fresh solutions were added. Ordinates = absolute cell volume from hematocrit readings. Curves in A, cells in 1.8 per cent sodium chloride; curves in B, cells in 0.9 per cent sodium chloride; curves in C, cells in 0.6 per cent sodium chloride.

As the effects of irradiation on fresh and aged blood differed markedly, the changes which took place in the control suspensions with time will first be outlined. Figure 1 shows changes taking place in two stock suspensions of washed cells which were kept in 0.9 per cent sodium chloride solution in the ice box. The volume of the cells as shown by the hematocrit readings remains approximately constant over a period of several days. The degree of hemolysis, on the other hand, increases rather suddenly after a variable period of time which, for the samples shown, was about six days. If the specific cell volume is calculated by the formula,

$$\text{specific cell volume} = \frac{\text{absolute cell volume}}{100 - \text{per cent hemolysis}}$$

it is seen that the volume of the remaining intact cells increases. At the same time the light absorption of the hemoglobin in samples completely hemolyzed by the addition of distilled water increases, as is shown by the drop in the curves for the photoelectric cell readings. The dotted portions of the curves indicate regions in which the photoelectric readings on the completely hemolyzed samples were so small that calculations of per cent hemolysis were subject to large errors. These changes suggest that a spontaneous change takes place in the cell contents which results in an increased intracellular osmotic pressure. This causes the cells to swell, and brings about the hemolysis of those in which the process is most pronounced. In the samples illustrated, the relative rates of swelling and hemolysis were such that the total volume of the unhemolyzed cells remained approximately constant until near the end of the period of observation.

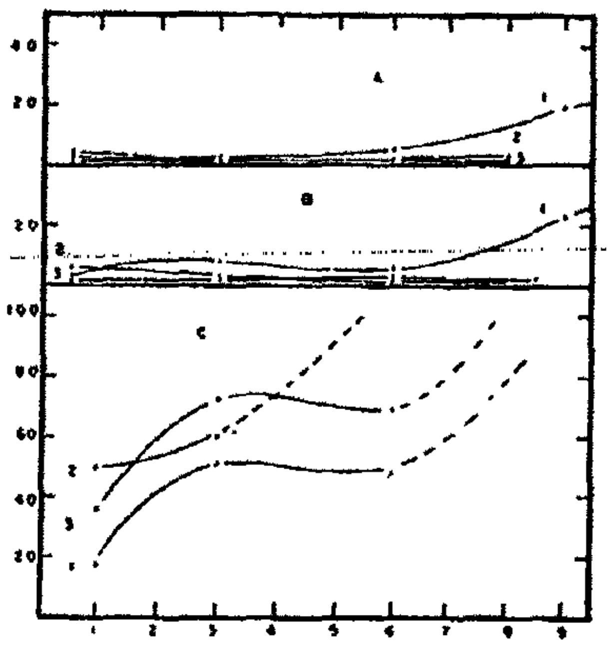

FIG. 3

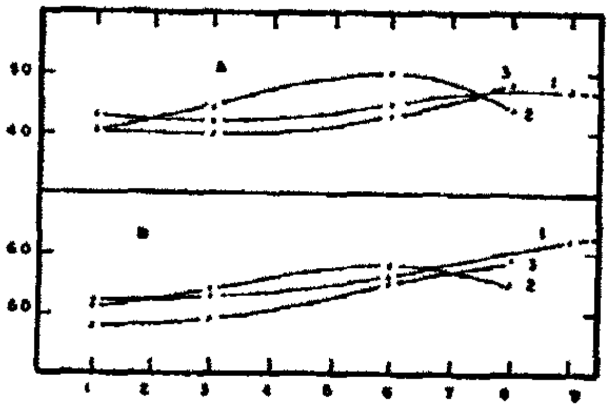

FIG. 4

FIG. 3. Changes with time in the per cent hemolysis of unirradiated cells equilibrated with fresh sodium chloride solutions. Abscissae = age in days of cells when fresh solutions were added. Ordinates = per cent hemolysis. Curves in A, cells in 1.8 per cent sodium chloride; curves in B, cells in 0.9 per cent sodium chloride; curves in C, cells in 0.6 per cent sodium chloride.

FIG. 4. Changes with time in the specific cell volume of unirradiated cells equilibrated with fresh sodium chloride solutions. Abscissae = age in days of cells when fresh solutions were added. Ordinates = specific cell volume. Curves in A, cells in 1.8 per cent cent sodium chloride; curves in B, cells in 0.9 per cent sodium chloride.

When samples of such suspensions are removed from time to time, centrifuged, the old saline removed, and the cells equilibrated for eighteen hours in the ice box with hypertonic, isotonic, and hypotonic sodium chloride solutions, curves like those in figures 2, 3, and 4 are obtained. The absolute cell volume, per cent hemolysis, and specific cell volume are plotted against days of age of the cells when placed in fresh saline. Curves No. 2 and 3 are for the same suspensions as those illustrated in figure 1, and the cell volumes are corrected for losses from hemolysis in the stock suspension. Data were not complete on the hemolysis, which was small, in the stock suspension for curve No. 1, and the cell volumes for this preparation are uncorrected. In these preparations the cells which were shown by calculation of the specific cell volume in the stock suspension to be somewhat swollen were unable to withstand the further swelling caused by hypotonic solutions, and hemolyzed so extensively that the absolute volume of the intact cells fell rapidly. The specific volume of the cells in hypotonic saline was found to rise very rapidly with increasing age of the cells, but the experimental error of both hematocrit and photoelectric readings is so large in this range that calculations of specific cell volume are without quantitative significance, and are not shown in the chart. On the other hand, if cells of the same lot were placed in isotonic saline, they underwent some additional increase in volume, but this was not sufficient to cause much hemolysis. Cells placed in hypertonic saline, while they shrank somewhat less than they did when fresh, nevertheless diminished somewhat in volume and hemolyzed only very slightly. If the preparations were observed still longer, a marked increase in the light absorption of hemoglobin was found to take place in sodium chloride solutions of all concentrations, the absolute cell volume decreased, and hemolysis finally became complete. Numerous other samples of erythrocytes were found to behave in the same way as those illustrated, although the changes outlined took place at different ages in the different samples.

If the changes induced by irradiation are due to a change in the state of aggregation of the cell contents, it is to be expected that the effect of irradiation of fresh and old cells will be different. This is found to be the case, as is shown in figures 5, 6, and 7. The percentage change in absolute and specific cell volumes and the absolute change in per cent hemolysis are plotted against age of blood sample at the time of irradiation. It is seen that, when *fresh* cells are irradiated and then equilibrated with sodium chloride solutions of different concentrations, the hemolysis undergone by the irradiated cells is always greater than that of the controls. Because of the pronounced hemolysis of irradiated cells suspended in hypotonic saline the absolute volume of the remaining cells is less than that of the controls, while that of the less hemolyzed irradiated cells in isotonic saline undergoes little change, and that of irradiated cells in hypertonic saline remains greater than that of the controls. The specific volume of all the cells irradiated when fresh is greater than that of the controls. As the cells age, however, these relationships change, so that in the oldest preparations the hemolysis of the irradiated cells is less than that of the controls. This reversal of radiosensitivity takes place at approximately the same age as the most marked increase in the light absorption of the hemoglobin.

It appears therefore that irradiation of fresh packed sheep erythrocytes results in the splitting of the hemoglobin to compounds of smaller molecular weight. This causes the cells to swell relatively to the controls when subsequently placed in sodium chloride solutions, and to hemolyze when the swelling is great enough. This is in accord with the theory of Failla. As the cells age, however, a spontaneous change takes place in the cell contents which causes the cells to swell. Irradiation of these swollen cells reduces their volume, probably through coagulation of the altered hemoglobin. No evidence is at hand at present as to the nature of the

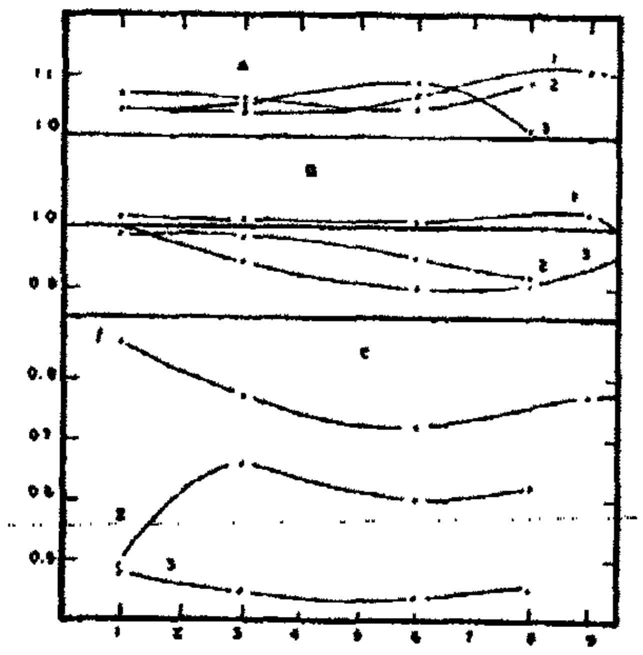

FIG. 5

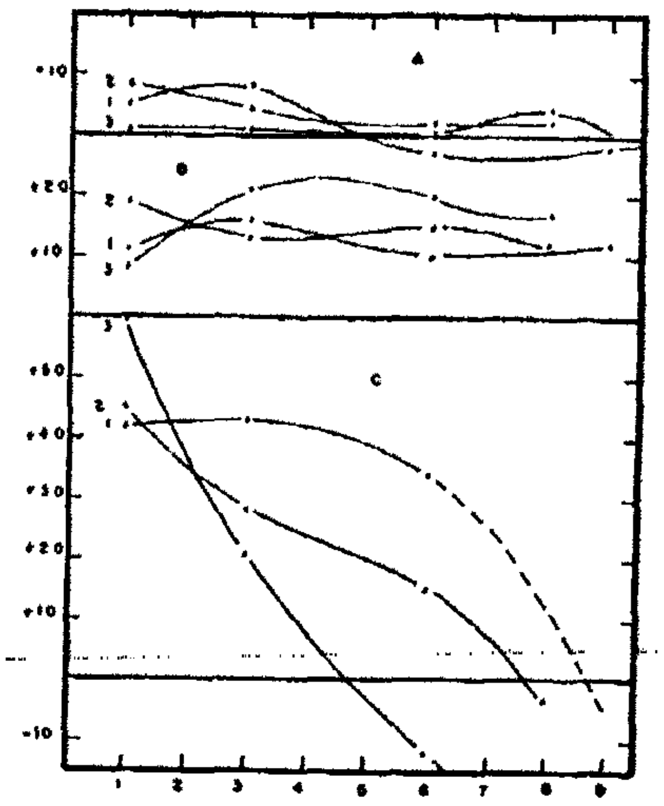

FIG. 6

FIG. 5. Changes in radiosensitivity with time. Abscissae = age in days of cells when irradiated. Ordinates = absolute volume of irradiated cells/absolute volume of control cells. Curves in A, cells in 1.8 per cent sodium chloride; curves in B, cells in 0.9 per cent sodium chloride; curves in C, cells in 0.6 per cent sodium chloride.

FIG. 6. Changes in radiosensitivity with time. Abscissae = age in days of cells when irradiated. Ordinates = per cent hemolysis of irradiated cells minus per cent hemolysis of control cells. Curves in A, cells in 1.8 per cent sodium chloride; curves in B, cells in 0.9 per cent sodium chloride; curves in C, cells in 0.6 per cent sodium chloride.

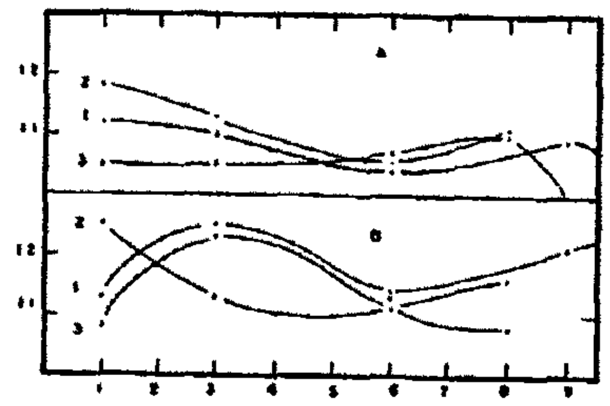

FIG. 7. Changes in radiosensitivity with time. Abscissae = age in days of cells when irradiated. Ordinates = specific volume of irradiated cells/specific volume of control cells. Curves in A, cells in 1.8 per cent sodium chloride; curves in B, cells in 0.9 per cent sodium chloride.

spontaneous change in the hemoglobin which results in a reversal of the radiation effect. Preliminary work in which the catalase of the cells was inactivated with sodium chlorate indicates that methemoglobin formation may play a part.

No mention has been made of the possible effect of radiation on the cell membrane. The data are more in harmony with the theory that the major portion of the irradiation effect is on the cell contents. It is hoped that direct evidence on this question may be obtained by a study of the radiosensitivity of cells whose membranes have been weakened by a lysin.

Since the sensitivity of cells which have been irradiated while packed and almost free from saline and then suspended in saline of different concentrations is the same within the experimental error as the sensitivity of these cells when they have been suspended in the corresponding saline solutions just prior to irradiation, it is obvious that the effect of the radiation is on the cells themselves rather than on the medium.

SUMMARY

The effect of 200 kv. Roentgen radiation on the osmotic properties of sheep erythrocytes has been studied.

The volume and the susceptibility to hemolysis of erythrocytes which were irradiated when fresh was increased by irradiation. This effect was reversed when the cells were irradiated after they had been kept in physiological saline for several days at low temperatures.

This is interpreted as meaning that the hemoglobin of fresh cells is split to compounds of smaller molecules by Roentgen radiation, while that of aged cells is coagulated.

The author wishes to express her thanks to Dr. G. Failla for suggesting the problem, and to Mr. John Sachs for technical assistance.

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VIRUS PROTEINS—A NEW GROUP OF MACROMOLECULES[1]

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INTRODUCTION

Although observations of preparations that were undoubtedly colloidal solutions were recorded over a hundred years ago, it is generally regarded today that colloidal chemistry came into being in 1861 when Graham (15) attempted to divide substances into two classes which he called crystalloids and colloids, respectively. Graham's crystalloids were substances which tended to form crystals on coming out of solution and which diffused readily through a membrane, while his colloids were substances which tended to separate out as amorphous masses and which would not diffuse through a membrane. The crystalloids were generally regarded as molecules and the colloids as particles consisting of aggregates of molecules. The molecules have ranged from fractions of a millimicron up to about 1 or 2 mμ in diameter and the colloids from several hundred millimicrons down to about 2 mμ in diameter. Because of the lack of knowledge of macromolecules, colloid chemistry has been built chiefly around work on small particles of gold, silver, mastic, etc., each particle consisting of a great number of molecules. Probably for this reason the idea gradually developed that solutions of such particles were quite different from solutions of molecules and hence that colloidal solutions were different from "true" solutions. However, in 1905 Einstein (11) pointed out that according to the kinetic theory there should be no difference between a suspended particle and a molecule of the same size and that the laws based on the kinetic theory should apply to colloidal solutions in much the same way that they apply to "true" solutions. He considered that colloidal solutions should exhibit such phenomena as osmotic pressure and diffusion and that an equilibrium between the force of gravity and diffusion might be expected. These theoretical considerations were immediately put to experimental test, first by Perrin (30) in 1908 and later by Svedberg (43), Westgren (49), Zsigmondy (55), and others. These workers used colloidal solutions of gold, silver, platinum, selenium, gam-

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[1] Presented at the Fourteenth Colloid Symposium, held at Minneapolis, Minnesota, June 10-12, 1937.

boge, and mastic, and were able to get particles having diameters as small as about 2 mμ. They determined experimentally the sedimentation equilibrium, osmotic pressure, diffusion, and Avogadro's number, and found that laws based on the kinetic theory did hold for these colloidal solutions. Since then a tremendous amount of experimentation has been done with such colloidal solutions. Despite the fact that these artificially produced colloids have been found to be polydisperse (44) and that certain minor discrepancies have been noticed (17), it is still generally acknowledged that the laws governing ideal gases tend to apply to most colloidal solutions, that is, solutions of particles having diameters ranging upwards from about 2 mμ. Nevertheless, Graham's ideas have persisted and there has been a tendency to segregate solutions into colloidal solutions and "true" solutions. The abundance of substances such as gold, silver, mastic, etc. which could be obtained in the form of small particles and the relative lack of macromolecules probably fostered this situation.

The rise of protein chemistry, as evidenced by the work of Sorenson (34) and Osborne (29), the chemical studies of Loeb (22), Northrop's studies on enzymes (26) and other proteins (27), the solubility studies of Cohn (9), and especially the ultracentrifugal studies of Svedberg (45, 14), has not only supplied the colloid chemist with a great group of macromolecules, but has forced down practically all barriers between colloidal solutions and "true" solutions. This group of proteins includes those having sedimentation constants[2] of from 2 to 130, corresponding to molecular weights of from about 18,000 to 10,000,000, and on the basis of spherical molecules to diameters of from about 1 to 25 mμ. The work of the investigators just mentioned has demonstrated that, although the molecules of these proteins are of colloidal size, they nevertheless possess many of the properties of ordinary molecules and their solutions may be considered "true" solutions. The protein molecules already described have thus not only bridged the gap between ordinary molecules and colloidal particles, but with respect to size have actually trespassed into the realm of colloidal gold and silver particles. However, the artificially produced colloids have remained as the sole representatives of particle sizes ranging upward from about 25 mμ, for the hemocyanin protein molecules with diameters ranging from about 8 to 25 mμ have been the largest hitherto reported (14). The purpose of the present paper is to describe the isolation and properties of a new group of macromolecules, the virus proteins (35), the molecules of which are larger than those of any protein previously described. The smaller virus proteins have sedimentation constants of the same order as those of the largest hemocyanins and the largest virus proteins may prove to have sedimentation constants of the order of a few thousand. Despite their tremendous size, the virus pro-

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[2] The sedimentation constants are expressed in units of 10^{-13}.

teins have many of the properties of ordinary molecules. Although it is possible that further work may reveal such confusing dissociation phenomena as that exhibited by hemoglobin (42) and by some of the hemocyanins (14), all of the data available at present indicate that the virus proteins fulfill the accepted chemical definition of a molecule as the smallest weight which cannot be subdivided without a complete change in the properties. This new group of macromolecules bridges the last gap between particles visible under the microscope and molecules, hence the colloid chemist now has at his disposal molecules ranging in diameter from that of the very small hydrogen molecule up to that of the largest virus protein, which may prove to be of the order of 200 mμ.

THE NATURE OF VIRUSES (8, 31)

Viruses are submicroscopic infectious entities which are capable of causing disease in man, animals, plants, insects, and bacteria. Such diseases as the various types of encephalitis, poliomyelitis, measles, yellow fever, certain types of tumorous growths, the common cold, rabies, dog distemper, foot-and-mouth disease, and the several mosaic and yellows diseases of plants are considered to belong in the group of diseases caused by viruses. In the past, viruses have been characterized by their invisibility, by their ability to pass filters capable of holding back ordinary bacteria, and by their inability to multiply in the absence of living cells. However, even these general characteristics have not been completely acceptable, for there have been reports that some viruses have been seen, others held back by filters, and still others cultivated in the absence of living cells. The confused state of knowledge concerning even the simple basic properties of viruses has led to an even greater confusion regarding the nature of these agents. They have been regarded variously as protozoa, as invisible forms of ordinary bacteria, as a new kind of invisible living organism, as unusual products of cellular metabolism, as enzymes, and as different kinds of inanimate chemical substances. However, because viruses may multiply or reproduce, because they are specific in that certain ones occur or cause disease only in certain hosts, because they may change or mutate and adapt themselves to new conditions, and because of the lasting immunity which follows most virus diseases, the majority of the workers in the virus field have chosen to regard viruses as invisible living organisms. It is obvious that the arguments for the living nature of viruses are very strong, for the properties just enumerated are characteristic of living things. However, certain other properties, such as their small size and their inability to grow on lifeless media, suggested that they might differ somewhat, and they have been placed, therefore, in a group apart from ordinary living organisms and have been called viruses.

EXPERIMENTAL

The isolation of virus proteins

The virus selected for initial study was tobacco mosaic, the first of all viruses to be discovered (16). It was selected because of its unusual stability, its high infectivity, and its ready availability. After several years of preliminary experimentation, much of which was based on the earlier work of Vinson (48) and others, it was found possible to isolate from mosaic-diseased Turkish tobacco plants a crystalline protein (35, 37). This protein was unusual in that its molecules were found to possess the properties of the virus and to be considerably larger than those of any other known protein, for the molecular weight was found to be 17,000-000 (13). This work was immediately extended to include the study of other viruses. Crystalline tobacco mosaic virus protein was first isolated early in 1935 by chemical means. The same methods were successfully used in the isolation of several different strains of tobacco mosaic virus, but difficulty was encountered when they were applied to certain of the less stable viruses. In the meantime, it had been found (54) that crystalline tobacco mosaic virus protein could be readily obtained by centrifuging the extracts of diseased plants by means of the newly developed air-driven quantity centrifuge (1, 7, 50, 51). The very rapid and effective centrifugal method was used, therefore, for the less stable viruses and found to be very successful (41). Turkish tobacco plants diseased with latent mosaic of potato (X-virus) were examined and a high molecular weight crystalline protein with a sedimentation constant of about 113 and possessing the properties of this virus was isolated. From Turkish tobacco plants diseased with ring spot virus a crystalline protein having a sedimentation constant of about 115 was isolated. A protein having a sedimentation constant of about 180 was isolated from plants diseased with severe etch virus. This study has recently been extended to include viruses affecting animals, and Beard and Wyckoff (3), using the air-driven quantity centrifuge, were able to isolate from virus-induced rabbit papillomas a protein having a sedimentation constant of about 250 and having the properties of the virus. Bacteriophage may be regarded as a virus disease of bacteria, and in this connection it is interesting to note that Northrop (28) has isolated a high molecular weight protein from bacteriophage-infected staphylococcus cultures, and Schlesinger (32) has obtained a protein-containing material having a particle size of about 100 mμ from coli-phage infected colon bacillus cultures. The largest of the viruses, such as those causing the pock diseases, are thought to be about 200 mμ in diameter (6, 12). Although, with the sole exception of size, these large viruses appear to be similar to the small viruses, insufficient experimental evidence is available at present to justify the definite conclusion that they either are or are not protein molecules. In view of the results with some of the smaller viruses, there should be no objection to using, as a working hypothesis, the idea that the largest viruses are also macromolecules.

The question of identity of protein with virus activity

Although the question as to whether or not the virus activity is a specific property of these macromolecules is probably of greatest interest to pathologists and bacteriologists, it is deemed of sufficient interest to colloid chemists to warrant a brief review at this place of some of the experimental data. Since tobacco mosaic virus protein has been subjected to the most extensive investigation, most of the data to be presented will refer to this virus protein (see reference 37 for recent bibliography).

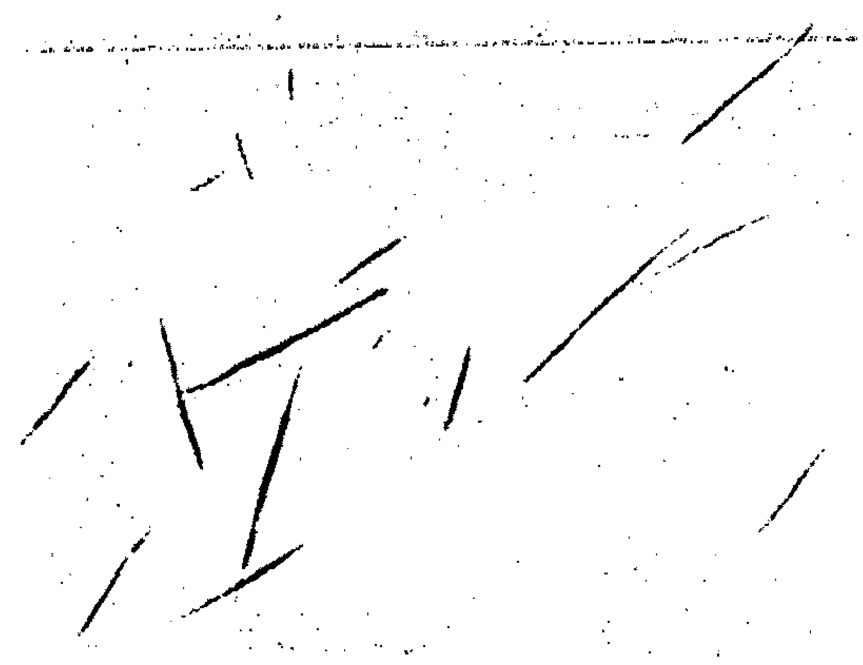

FIG. 1. Crystalline tobacco mosaic virus protein. × 675. (Photograph by J. A. Carlile)

Figure 1 is a reproduction of some of the crystals of tobacco mosaic virus protein which were prepared by Dr. Loring. These crystals are actually quite small, for they are only about 0.02 to 0.03 mm. in length. It is possible to vary their size by a factor of about 10 by changing the conditions of crystallization. It seems likely that their form is different from that of the material reported by Best (4), for vigorous shaking does not cause these crystals to break up into invisible units. They are true crystals, since they are doubly refractive and give a regular crystalline pattern on x-ray analysis (53). A typical elementary analysis is given in table 1. A typical dilution curve showing the virus activity of the protein as tested on *Phaseolus vulgaris* plants is given in figure 2. This dilution series was prepared by mixing 1 cc. of a solution containing 10 mg. of virus protein per cubic centimeter with 9 cc. of 0.1 M phosphate buffer at pH 7, then mixing 1 cc. of this solution with 9 cc. of phosphate buffer, etc. The pipets and glassware used were chemically clean and had not been specially treated. The virus activity of the protein may be determined by rubbing, by means of a small bandage gauze pad, a solution containing a known amount of the protein over the upper surfaces of the leaves of certain plants. About forty-eight hours later there will appear on the leaves many spots or lesions if there was much virus protein in the solution and but a few spots or lesions if there was but little virus protein in the solution. Thus the number of lesions obtained serves as a rough index of the amount of virus. The activity of one solution may be compared with that of another by applying one to the right or left halves of all of the leaves and the other to the remaining halves of all the leaves. This method suitably standardized is used to measure virus concentration, and it is sufficiently accurate so that differences in virus concentration greater than about 10 per cent may be detected without difficulty using only about forty to fifty leaves (23).

TABLE 1

Elementary analysis and optical activity of crystalline tobacco mosaic virus protein

	C	H	N (DUMAS)	P	ASH
Per cent of dry weight	50.74	7.56	16.56	0.51	0.53
Optical activity $[\alpha]_D^{20^\circ}$ per milligram of nitrogen					0.42 0.44

Samples in dilute sodium hydroxide at pH 11.2 ± 0.1

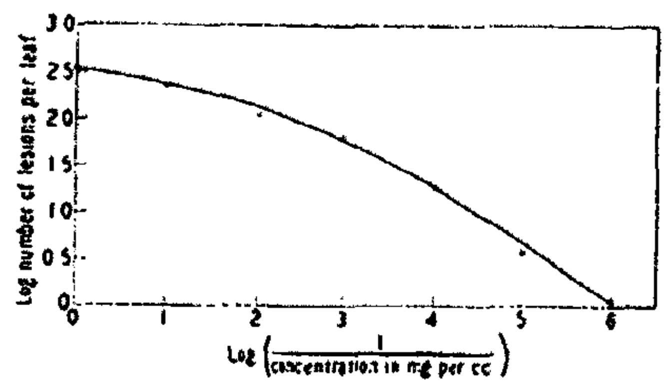

FIG. 2

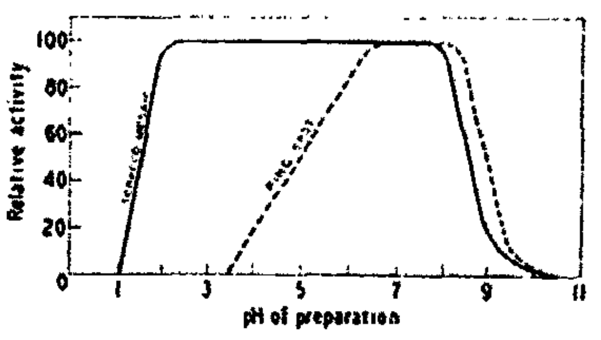

FIG. 3

FIG. 2. Dilution curve of tobacco mosaic virus protein in 0.1 *M* phosphate buffer at pH 7

FIG. 3. The activity, as measured by the lesions obtained with test solutions expressed as a percentage of those obtained with controls, of tobacco mosaic virus protein and of tobacco ring spot virus protein after one day at various pH values and readjustment to pH 7.

In table 2 data from recent work (24) are reproduced in which the activity of once-crystallized protein is compared with that of fifteen-times-crystallized protein. It may be seen that in experiment No. 1, test No. 1, a solution containing 10^{-5} g. of once-crystallized protein per cubic centimeter, on inoculation to the halves of forty-two bean leaves, gave an average of 66.6 lesions per half-leaf, whereas a solution containing 10^{-5} g. of fifteen-times-crystallized protein per cubic centimeter, on inoculation to the other halves of the same forty-two bean leaves, gave an average of 68.4 lesions per half-leaf. The odds are less than 20 to 1 that the activity of these two solutions is different, hence it is concluded that there is no difference in their virus activity. Examination of the results reveals the

TABLE 2

Relative infectivity of tobacco mosaic virus protein after one crystallization and after fifteen crystallizations

EXPERIMENT	TEST	PREPARATION	CONCENTRATION IN GRAMS OF PROTEIN PER CC.	
			10^{-5}	5×10^{-6}
1‡	1	Crystallized once	66.6*	43.3
		Crystallized fifteen times	68.4	49.0
		Number of half-leaves	42	42
		M.D./S.D.†	0.44	1.4
	2	Crystallized once	38.6	34.5
		Crystallized fifteen times	35.5	32.9
		Number of half-leaves	44	44
		M.D./S.D.	1.05	0.47
2‡	1	Crystallized once	79.8	38.4
		Crystallized fifteen times	72.5	47.0
		Number of half-leaves	44	44
		M.D./S.D.	1.59	2.57
	2	Crystallized once	51.1	42.4
		Crystallized fifteen times	55.3	41.9
		Number of half-leaves	34	36
		M.D./S.D.	0.98	0.12

[*] Numbers opposite a particular preparation represent the average number of necrotic lesions per half-leaf obtained on *Phaseolus vulgaris* on inoculation with the designated preparation and concentration. A given preparation was administered to the right halves of half of the leaves and to the left halves of the remaining leaves in each test.

[†] To show a significant difference between the mean number of lesions in any one experiment, the ratio of the difference of the mean (M.D.) to the standard deviation of the difference (S.D.) should be not less than 2.1.

[‡] In experiment No. 1, 30 per cent, and in No. 2, 81 per cent of the original amount of virus protein was lost in the mother liquor during recrystallization.

fact that the tobacco mosaic virus protein may be crystallized fifteen successive times without changing its virus activity, and that it may be fractionally crystallized so that only 19 per cent of the original amount of protein remains without any change in the specific virus activity. The crystalline protein obtained from many different lots of plants diseased with the same virus strain has the same chemical composition, isoelectric point, optical rotation, x-ray diffraction pattern, sedimentation constant, and biological activity. The absorption spectrum of the virus protein was found to agree essentially with the destruction spectrum of the virus activity (21). The same protein was isolated from many different species of plants diseased with the same virus strain, whereas somewhat similar although different proteins were isolated from the same species of plant diseased with different strains of a given virus and markedly different proteins were isolated from the same species of plant diseased with different viruses. For example, the same protein was isolated from Turkish and Burley tobacco, tomato, phlox, and spinach plants diseased with ordinary tobacco mosaic virus, whereas four somewhat similar proteins differing in certain respects were isolated from four groups of Turkish tobacco plants diseased with four different strains of tobacco mosaic virus, and three completely different proteins were isolated from three groups of Turkish tobacco plants diseased respectively with latent mosaic, tobacco ring spot, and severe etch viruses. The different virus proteins may be characterized by their sedimentation constants, pH stability range, solubility, isoelectric point, heat coagulation point, x-ray diffraction pattern, immunological reactions, and biological activity. For example, the sera of animals injected with a solution of tobacco mosaic virus protein give a precipitin test when mixed with solutions containing but 10^{-6} g. per cubic centimeter of tobacco mosaic virus protein or protein of closely related strains and fail to give a precipitate when mixed with solutions of latent mosaic or ring spot virus proteins. Likewise, antisera to ring spot virus protein fail to react with tobacco mosaic or latent mosaic virus protein. Treatment of tobacco mosaic virus protein with hydrogen peroxide, formaldehyde, nitrous acid, or ultra-violet light produces inactive native proteins that, although slightly altered chemically, retain certain chemical and serological properties characteristic of the virus protein (36). The sera of animals injected with a solution of inactive protein have a neutralizing effect *in vitro* on virus activity not possessed by normal sera. This point may prove of importance, for it is a demonstration that a virus can be inactivated without seriously changing its immunological properties.

The x-ray diffraction patterns of tobacco mosaic, latent mosaic, and ring spot virus proteins have been determined and found to be different. The pH stability ranges of the activity of tobacco mosaic virus protein

(5, 38) and of tobacco ring spot virus protein (40) have been determined and are given in figure 3. Ring spot and latent mosaic virus proteins are much less stable towards acid and slightly more stable towards alkali than tobacco mosaic virus protein. The virus proteins lose their virus activity when they are denatured by acid, by alkali, or by heating. Tobacco mosaic virus protein coagulates on heating to about 75°C., whereas ring spot virus protein coagulates at 64°C. The isoelectric point of the former is at pH 3.5 and of the latter at pH 4.7. A marked Tyndall cone is shown when a beam of light is passed through solutions of virus proteins. The amounts of the different virus proteins occurring in the same species of host have been found to vary widely. In Turkish tobacco plants tobacco mosaic virus protein reaches a concentration of from 2 to 4 mg. per cubic centimeter of extract, latent mosiac virus protein a concentration of about 0.2 mg. per cubic centimeter of extract, and ring spot virus protein a concentration of about 0.02 mg. per cubic centimeter of extract. In accordance with this, tobacco mosaic virus protein was found to be about 500 times, latent mosaic virus protein about 5000 times, and ring spot virus protein about 50,000 times more active than the starting material. Beard and Wyckoff (3) were able to isolate about 1 part per 4000 of the rabbit papilloma tissue in the form of a homogeneous protein having a sedimentation constant of about 250. They found the activity of the virus protein to be several thousand times that of the starting material. The papilloma virus protein was found to coagulate on heating to 66–67°C., and Shope (33) has reported that the virus activity of papilloma extracts begins to diminish at 67°C. and is completely destroyed at 70°C.

The fact that the virus proteins behave as macromolecules makes possible a new and different method of approaching the question concerning the identity of activity and protein, for their tremendous size makes it possible to centrifuge the protein molecules from solution under a variety of conditions. If the virus activity is a specific property of the high molecular weight protein, then, following centrifugation of different amounts of protein from solutions at different hydrogen-ion concentrations or from solutions containing other proteins, the virus activity of the upper portions of the centrifuged solutions should be diminished and be proportional to the amount of high molecular weight virus protein that they contain. Such experiments have been carried out with tobacco mosaic virus protein, and in every instance the virus activity of the various samples was found to be proportional to the amount of high molecular weight virus protein present (39). Representative results obtained on centrifuging tobacco mosaic virus protein on either side of the isoelectric point are given in table 3. This protein is insoluble at the isoelectric point and when centrifuged gives a protein-free and inactive supernatant.

Sedimentation constants

The very high molecular weights of the virus proteins make it quite difficult to determine molecular weights by ordinary methods or even by means of diffusion or osmotic pressure measurements. For example, in the case of tobacco mosaic virus protein, although it was possible by means of the diffusion and osmotic pressure to determine that the molecular weight was of the order of several million (35), it was found impossible to secure satisfactory duplication of the results. The ultracentrifugal method for the determination of molecular weights (45), however, is especially suited for such macromolecules. Dr. Svedberg was supplied with a sample of crystalline tobacco mosaic virus protein, and the first sedimentation constant determinations of a virus protein were made in

TABLE 3

Correlation of virus activity and protein on centrifugation of tobacco mosaic virus protein at pH 2.4, 6.7, and 9.4[*]

pH DURING CENTRIFUGATION	PROTEIN CONCENTRATION AFTER CENTRIFUGATION IN MG. PER CC.	PORTION OF CENTRIFUGED SAMPLE USED	PROTEIN CONCENTRATION USED FOR TESTS IN GRAMS PER CC.	
			10^{-4}	10^{-5}
2.4	1.2	Upper portion	57.9†	25.3
	28.3	Lower portion	62.1	30.4
		Number of half-leaves	52	52
		M.D./S.D.‡	0.96	2.34
6.7	1.2	Upper portion	145.0	74.8
	16.8	Lower portion	161.2	82.8
		Number of half-leaves	56	56
		M.D./S.D.	2.02	1.89
9.4	2.1	Upper portion	128.6	67.6
	16.7	Lower portion	142.1	74.5
		Number of half-leaves	56	56
		M.D./S.D.	2.09	1.91

[*] Tests following dilution of lower portions to same protein concentration as in the corresponding upper portions of centrifuged samples. All dilutions were made with 0.1 *M* phosphate buffer at pH 7. *Phaseolus vulgaris* was used as the test plant.

[†] Numbers opposite a given preparation represent the average number of lesions per half-leaf obtained on inoculation with the designated preparation and concentration. A given preparation was administered to the right halves of half of the leaves and to the left halves of the remaining leaves in each test.

[‡] To show a significant difference between the mean number of lesions in any one experiment, the ratio of the difference of the mean (M.D.) to the standard deviation of the difference (S.D.) should be not less than 2.1.

his laboratory at Upsala (13). This sample of virus protein proved to have a sedimentation constant of about 200 and to be inhomogeneous with respect to molecular weight. The protein was found to be completely homogeneous with respect to isoelectric point. At pH 9.8 the protein was found to have formed two components having sedimentation constants of 185 and 125, respectively, and at pH 11.7 it was found to have been split into low molecular weight components having constants of 8.1 and 3.8, respectively. Since tobacco ring spot virus protein becomes largely inactivated on standing at room temperature for twenty-four hours, and since even the supposedly very stable tobacco mosaic virus protein has been found to change somewhat on merely standing for several days, it has been found preferable to carry out the determinations as soon as possible after the isolation of the protein. The recent ultracentrifugal studies have been performed, therefore, by Dr. Wyckoff at the Princeton laboratories of The Rockefeller Institute. The previously determined sedimentation constants for tobacco mosaic virus protein have been confirmed (54), virus protein completely homogeneous with respect to molecular weight has been obtained, and the work has been extended to include a study of the pH stability range of the different virus proteins (52).

Shape of molecule

Svedberg (13) found that the molecular weight of the tobacco mosaic virus protein obtained from sedimentation equilibrium determinations was of the same order of magnitude as that calculated from the sedimentation constant on the assumption of a dissymmetry constant $f/f_0 = 1.3$, a value found for other high molecular weight proteins. This result, although somewhat uncertain, owing to the low diffusion of the protein, nevertheless indicates that the molecules depart somewhat from a spherical shape. Takahashi (46) in 1933 noticed that the clarified juice from mosaic-diseased Turkish tobacco plants exhibited double refraction of flow. Solutions of crystalline tobacco mosaic virus protein have recently been examined and have also been found to show double refraction of flow (47); it was concluded that the virus protein is composed of rod-shaped particles. Other workers (2), on the basis of x-ray data, have also concluded that the molecules of this virus are rod-shaped and have a minimum length not less than ten times the width.

If the dissymmetry is of an extreme nature so that the molecules more nearly resemble threads than elongated ellipsoids, it seems likely that their solutions should be unusually viscous. For example, the viscosity of muscle globulin, which is supposed to be comprised of rod-shaped molecules, is quite high. The relative viscosities of solutions of tobacco mosaic virus protein, of the high molecular weight *Limulus polyphemus* hemocyanin,[3] and of egg albumin[3] have been determined and compared with that of muscle globulin as recorded by Edsall (10) and with that of gelatin as determined by Kunitz (18). It may be seen from the results, which are given in figure 4, that the viscosity of the virus protein is considerably smaller than that of muscle globulin and lies between that of gelatin and of egg albumin and hemocyanin. This may be regarded as indicating that the dissymmetry is not of an extreme nature. The viscosity of the virus protein at various hydrogen-ion concentrations is given in figure 5. It may be seen that the relative viscosity becomes greater

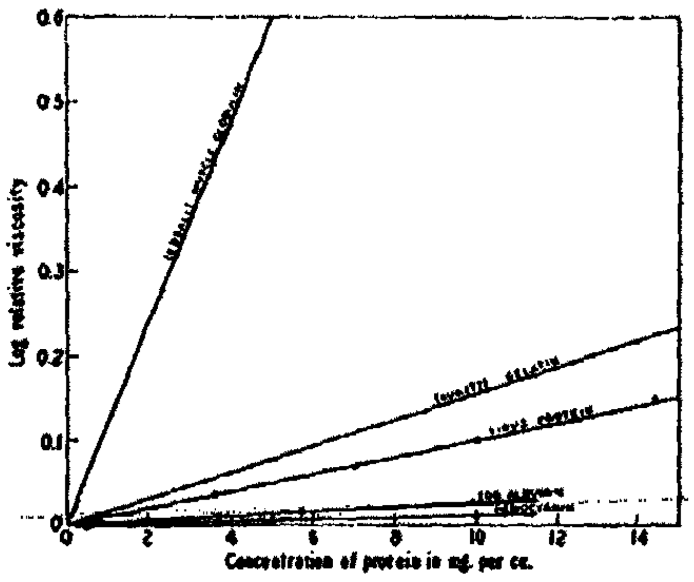

FIG. 4

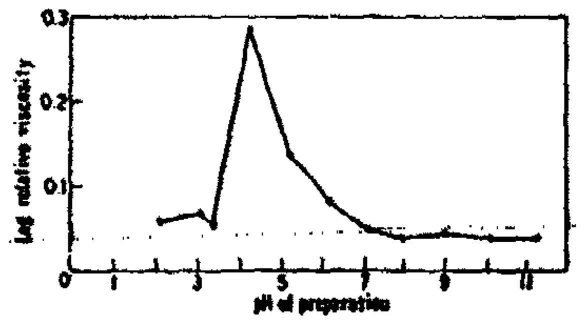

FIG. 5

FIG. 4. Viscosity-concentration curves for tobacco mosaic virus protein at 25.6°C. ± 0.2° in 0.1 *M* phosphate buffer at pH 7 and for other proteins.

FIG. 5. The viscosity at different hydrogen-ion concentrations of a solution containing 5.5 mg. of tobacco mosaic virus protein per cubic centimeter in 0.075 *M* buffer.

TABLE 4

Hydration of tobacco mosaic virus protein as determined from viscosity in 0.1 M phosphate buffer at pH 7 and 25.6°C. ± 0.2°

CONCENTRATION OF PROTEIN IN MG. PER CC.	RELATIVE VISCOSITY	CALCULATED VOLUME OF HYDRATED PROTEIN IN CC. PER 100 CC. OF SOLUTION	VOLUME IN CC. OF HYDRATED PROTEIN PER GRAM OF DRY PROTEIN	VOLUME IN CC. OF WATER OF HYDRATION PER GRAM OF DRY PROTEIN
1.0	1.025	0.6	6.0	5.2
3.6	1.094	2.1	5.8	5.0
10.0	1.270	5.3	5.3	4.5
14.5	1.417	7.6	5.3	4.5
28.7	2.140	15.9	5.5	4.7
47.7	3.630	25.2	5.3	4.5

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[3] The writer is indebted to Dr. C. V. Seastone for this sample of hemocyanin and to Dr. M. Kunitz for a supply of crystalline egg albumin.

as the isoelectric point is approached from the alkaline side and then falls off rapidly as the protein crystallizes from solution. The solution of the protein at pH 2 has about the same viscosity as have solutions at hydrogen-ion concentrations between pH 7 and 11. The specific volume of the protein was determined pycnometrically using toluene and butyl alcohol; the value found was 0.77. This is somewhat higher than that previously reported (13). The water of hydration per gram of dry protein has been calculated from the density and from the viscosity data, using Kunitz's empirical equation (18); the results are given in table 4. The value obtained is considerably larger than that found for hemoglobin and trypsin (19) and is of the same order as that of gelatin (18). As a whole, the ultracentrifugal results, the orientation phenomenon, and the x-ray and viscosity data may be considered to be in harmony with the idea that the length of the tobacco mosaic virus protein molecule may be of the order of ten times the width. Similar data are not now available with respect to other virus proteins. However, the obvious orientation phenomenon has not been observed in the case of the tobacco ring spot virus proteins. It is possible, therefore, that the proteins of tobacco mosaic virus and its strains may differ somewhat from those of other viruses with respect to shape.

THEORETICAL CONSIDERATIONS

The virus proteins not only bridge the gap between molecules and artificially prepared colloidal particles, but they also bridge the gap between molecules and living organisms. The smaller virus proteins (latent mosaic virus protein, $S_{20} = 113$) are of the same order of size as the largest hemocyanin molecules (*Busycon canaliculatum* hemocyanin, $S_{20} = 130$ (14)), whereas the largest viruses (vaccine virus, diameter = about 175 mμ (12)) are of the same order of size as admittedly living organisms (bovine pleuro-pneumonia, diameter = about 150 mμ (12); sewage organism, diameter = about 200 mμ (20)). Shall the virus proteins be classified as molecules or as living organisms? Since they have been shown to possess the ordinary chemical properties which are characteristic of molecules and to react as molecules, the chemist would be inclined to regard them as molecules. However, in addition to the chemical properties which they possess as molecules, they also possess virus activity. In a test tube or when applied to a non-susceptible host, virus proteins appear as inanimate matter, devoid of special activity. Yet, when a few molecules of a virus protein are administered to the living cells of a susceptible host, they immediately bring about the production of millions of molecules of the same kind. In living cells and only in the living cells of a susceptible host have they been found to reproduce or multiply, and this production of new virus protein results in what we call disease. Because of this reproductive power, they have been called autocatalysts (35). Although this is technically incorrect in that the reaction is very probably not that of true autocatalysis, the term was used because the net result is somewhat similar to that of an autocatalytic reaction. However, the mechanism by means of which a molecule in a specific living cell is able to cause the production of identical or similar molecules is unknown. It may be similar to the mechanism which the geneticists postulate for the production of genes (25). The virus protein molecule may be able to cause smaller molecules already present in the cell, or smaller molecules produced by the cell as a result of the presence of the virus molecule, to organize and combine to form a new virus molecule. It is an amazing fact that living cells are able at a moment's notice to produce millions of molecules of any one of a number of different virus proteins depending upon the exact molecule introduced, and yet be entirely unaffected by still other virus proteins. Another amazing phenomenon is that, although a cell exhibits a remarkable tendency to produce only exact duplicates of the virus protein molecule introduced, there is a slight but distinct tendency to produce a few slightly differing molecules. The reproduction of such slightly different molecules and their subsequent separation and isolation give rise to new strains of the virus. This phenomenon, in which the virus protein becomes changed and gives rise to a new strain causing a new disease, has been called mutation.

Because viruses may reproduce and mutate, and because of their specificity and the lasting immunity they usually induce, pathologists and bacteriologists have for years regarded them as submicroscopic living organisms. Since the virus protein molecules possess such properties, many workers today choose to regard these macromolecules as living organisms. It is obvious that as molecules they possess properties which differ somewhat from the ordinary properties of molecules and that as organisms they possess properties which differ somewhat from the ordinary properties of organisms. In this paper the properties of viruses as macromolecules have been stressed. This has been done because the advances in virus research which have been made in the past few years have resulted largely from the consideration of viruses as chemical entities and the virus proteins as macromolecules. Further attempts to classify viruses more exactly as either molecules or as organisms should await more experimental data.

SUMMARY

Colloid chemistry originally evolved from knowledge of particles rather than of molecules, and for years colloidal solutions of particles consisting of aggregates of molecules were supposed to differ from solutions of mole-

cules. It was shown on theoretical grounds and later proven experimentally that the laws based on the kinetic theory applied to colloidal solutions as well as to solutions of molecules. The tendency to segregate colloidal solutions remained until several workers demonstrated that solutions of proteins having molecular weights ranging up to about ten million were solutions of molecules, despite the fact that they exhibited many of the properties of colloidal solutions. The discovery that many of the viruses, which as a group range in size from about 5 to 200 mμ, are protein molecules thus makes available a new group of macromolecules. The virus protein of tobacco mosaic, an infectious disease of certain plants, has been subjected to extensive investigation. It has been obtained in crystalline form and has been found to be homogeneous with respect to size and isoelectric point and under specified conditions to possess constant properties such as composition, isoelectric point, optical rotation, x-ray diffraction pattern, sedimentation constant, absorption spectrum, immunological reactions, solubility, pH stability range, heat coagulation point, and biological activity. Despite its tremendous size, tobacco mosaic virus protein has many of the ordinary properties of molecules. In addition, however, it possesses virus properties which include the ability to reproduce and to mutate, specificity of action with respect to host, and the ability to induce immunity. Several virus proteins, some from other plant diseases and some from animal and bacterial diseases, some larger and some smaller than tobacco mosaic virus protein, have been isolated and are now under investigation in various laboratories. The virus proteins thus represent a new group of macromolecules which are considerably larger than those of any group of proteins hitherto described. Because of this tremendous size, the air-driven quantity centrifuge and the ultracentrifuge are peculiarly adapted to the isolation and study of the virus proteins. Since the virus proteins possess virus activity and certain properties characteristic of organisms, as well as the properties of molecules, any attempt at this time to classify them definitely as molecules or as organisms should be one solely of convenience. However, their characterization as molecules is providing a new experimental approach to the general problem of the nature of viruses.

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ELECTROKINETIC ASPECTS OF SURFACE CHEMISTRY. I

THE ELECTROPHORESIS OF ADSORBED EGG ALBUMIN[1]

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The properties of protein surfaces have become of increasing importance, especially in biological systems. In view of their complexity, it seems desirable to examine in some detail the characteristics of adsorbed surface films of proteins and of protein particles, and the influence of the adsorption process on the electrical properties of the surface. The data extant are difficult to interpret because of differences in method. Thus, the small discrepancy noted between the electric mobility of dissolved egg albumin investigated with the moving-boundary method of Tiselius (31) and that of adsorbed egg albumin studied by Abramson (4) and Smith (26, 27) emphasizes the need for a special investigation of this protein surface in an attempt to determine the cause of the differences observed. Since the work of Ramsden (23), it has been realized that egg albumin denatures when at an air-water interface. In any investigation of this character one must distinguish carefully between surfaces of normal and surface-denatured egg albumin. Furthermore, the possibility of polymolecular films consisting of a surface-denatured layer coated with partially denatured or oriented layers, together with the possible effect of the underlying surface, must be kept in mind.

Tiselius, using egg albumin crystallized from solutions of ammonium sulfate by the method of Sørensen (29) and electrodialyzed, concluded that the isoelectric point lies at pH 4.55 in $M/50$ sodium acetate buffer at 20°C. More recently Annetts (6), working in the same laboratory, has reported a single mobility value at pH 5.0 which agrees closely with Tiselius' curve. The concentration used by Annetts was 2 per cent albumin, whereas Tiselius usually used about 0.3 per cent.

A number of "inert" surfaces have been shown by Abramson and others (2, 4, 21) to be identical in behavior in the electric field when coated with any one of several proteins if the concentration is high enough to insure a complete film. It has also been shown by Abramson (2) that the mo-

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bility curve of purified egg albumin (Sørensen) adsorbed on quartz is nearly parallel but not identical with that of dissolved albumin. The position of the isoelectric point was found to be dependent on the ionic strength, shifting to lower pH values as the sodium acetate concentration is increased (3). The influence of ionic strength on the isoelectric point has been specially investigated by Smith (26). She found that the isoelectric point of quartz and collodion particles suspended in egg albumin is at pH 4.82–4.83 in $M/50$ sodium acetate buffer. In a later paper, the same author (27) has demonstrated that the nature of the crystallizing salt, ammonium sulfate (Sørensen) or sodium sulfate (Kekwick and Cannan (13)), produces very little or no effect on the isoelectric point ($<$ 0.01 pH at $M/50$ acetate). The pH of the isoelectric point in acetates was found to be linearly related to the ionic strength, being increased by divalent and trivalent cations and decreased by univalent cations. Of all these salts, lithium acetate had least effect. Extrapolation to zero ionic strength for each cation gave a common isoelectric point of pH 4.86 ± 0.02, a value in close agreement with the isoionic point in the absence of salt at pH 4.88 deduced by Sørensen, Linderstrøm-Lang, and Lund (30). In their excellent work on the titration curve, Kekwick and Cannan (13) likewise found no significant difference in titration curve between samples of egg albumin prepared by the two methods mentioned.

These different values for the isoelectric point can scarcely be ascribed to differences in the electrophoretic techniques employed by the investigators cited, for it has been shown that measurements in U-tubes agree completely with those made in vertical and horizontal microelectrophoresis cells (5). In any case, the position of the isoelectric point should be nearly independent of the construction and calibration of the electrophoresis instrument, since no motion of liquid or particles occurs in a cell with the surface of both the particles and wall at the isoelectric pH (4, 21).[3]

It is our purpose in this communication to present careful measurements of electric mobilities of highly purified normal and surface-denatured egg albumin adsorbed on a variety of surfaces, in an endeavor to throw light on the nature of adsorbed protein films, which, it is now realized, are of so much importance in biology and medicine (4, 5, 17, 20).

MATERIALS AND METHODS

Electrophoretic measurements

Measurements of electrophoresis were made with two horizontal Abramson microelectrophoresis instruments (4), using methods described in detail elsewhere (19). Human erythrocytes were used to check the

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[3] Measurements of the isoelectric point in the center of the cell are valid only if $R = 1$.

calibration of these instruments, for it has been shown that the surface of the red blood cell is extremely constant in behavior (4, 5). Both instruments gave a value of 1.30μ per second for the electric mobility of red cells in $M/15$ phosphate buffer at pH 7.4; this is within 1 per cent of the best data available (4).

It is not generally realized that for systems where the surface of the wall of the chamber and the surface of the particle are identical (i.e., the ratio R of electroösmosis to electrophoresis is 1.0) the theories of Smoluchowski and Komagata permit measurements to be made at the middle of the cell where the velocity gradient is zero. This practice is of advantage for suspensions near the isoelectric point, where it is desirable to time particles moving with as great a velocity as possible.

When the cell is wide and the equation of Smoluchowski applies (4),

$$V = 2/3\ V_{0.5} \tag{1}$$

where V is the true velocity and $V_{0.5}$ the velocity at the center of the cell.

In general, the parabola,

$$V_{\text{obs.}} = b(x - x^2) + c \tag{2}$$

(where x is the fraction of the total depth at which the observed velocity $V_{\text{obs.}}$ is obtained; b and c are constants) can be used to describe the $V_{\text{obs.}}$-depth curve (21). Komagata (14) has presented measurements in cells whose ratio of width to depth, k, is as small as 6, yet even in these cases equation 2 can be fitted to his data. Here, let $c = 0$ (since electroösmosis = electrophoresis) and let the true mobility be that obtained at the depth $x = a$. Then,

$$V = 4V_{0.5}\,(a - a^2) \tag{3}$$

Transforming Komagata's equation for flat closed cells into terms of fractional depth measured from the top of the cell, we have

$$a = \frac{1}{2} \pm \sqrt{\frac{1}{12} + \frac{32}{\pi^5 k}} \tag{4}$$

On substitution of this expression in equation 3, it is found that

$$V = \left(\frac{2}{3} - \frac{128}{\pi^5 k}\right) V_{0.5} \tag{5}$$

Table 1 shows a comparison between experiment and theory. Komagata's data were reduced to $c = 0$ by subtracting the intercept on the $V_{\text{obs.}}$ axis from $V_{\text{obs.}}$. The observed values for V were interpolated from smooth curves. The cells used in our work had values of $k > 20$.

Smith and Lisse (28) have recently described a new double-tube cylindrical cell in which measurements are made at the axis of the smaller tube where the velocity gradient is zero. It will be seen that the flat cell also possesses these advantages when $R = 1.0$.

In the present experiments, particles were measured at the usual stationary levels (equation 4) except in certain cases when it was clear that $R = 1.0$ (21) and the particles were moving too slowly to be easily timed at the 0.2 and 0.8 levels.

Protein preparations

Five distinct preparations of egg albumin were prepared from fresh hen's eggs (< 1 day old) by crystallizing four times from sodium sulfate by the method of Kekwick and Cannan (13). Two preparations were crystallized at 25°C., the rest at 32°C. One preparation was dried while in the crystalline state (13). The crystallizing salt was added very cautiously, as directed, until microscopic examination revealed well-formed albumin crystals. Precipitates formed when the salt was added too rapidly adsorbed impurities and made purification difficult. The resultant preparations were dialyzed until the specific conductance was of the order of 1×10^{-4} mho. They were kept covered with a mixture of washed mineral oil and toluene and stored in a refrigerator. One preparation, which showed a trace of opalescence, gave abnormal values (see below); on filtration through No. 40 Whatman filter paper, values were identical with data secured from unfiltered preparations which had clarified by slow settling. No differences were ever found between preparations if suitable care was taken. All preparations were absolutely water-clear. Preliminary preparations with only traces of color gave anomalous results. Concentrations were determined by drying a weighed sample at 110°C.

TABLE 1

Comparison of velocities calculated from measurements at the center of the cell with those observed at the stationary level in cases when $R = 1.0$

OBSERVER	k	V (OBSERVED)	V (CALCULATED FROM EQUATION 5)	V (CALCULATED FROM EQUATION 1)	ERROR FROM USE OF EQUATION 1
					per cent
Komagata	6.0	5.3	5.4	6.3	14
Komagata	12.0	6.9	6.9	7.3	6
Moyer	20.6	1.29	1.28	1.34	5

Schulz and Zsigmondy (25) have proposed the use of the gold number in testing the purity of egg albumin. A high gold number indicates purity, i.e., a low protective action. They state that pure crystalline egg albumin should give gold numbers between 2 and 8; traces of ovomucoids or other proteins reduce these values to 0.03–0.05. Gold numbers were obtained with three of our preparations; each was greater than 7. As a further check on the purity, a quantitative estimation of the amount of heat-denaturable albumin in one preparation showed that it was 100 per cent denaturable (within 0.5 per cent).

Buffer mixtures

Unless otherwise mentioned, mobility determinations were carried out in $M/50$ sodium acetate buffers of constant ionic strength. These were prepared from standard acid and alkali. Hydrogen-ion activity was usually measured by the quinhydrone electrode and checked by the Clark rocking hydrogen electrode over the range of pH investigated. In one series the glass electrode was used.[3] Values of pH are referred to the pH of an equimolar mixture of $M/100$ sodium acetate–acetic acid, $pK' = 4.70$. This mixture gives values in agreement with $N/10$ hydrochloric acid, pH 1.08, with the added advantage of less variability in liquid junction potential.[4] No corrections were needed because of the low protein and salt concentrations.

Preparation of particles

Quartz particles were carefully cleaned and fractionally sedimented by the method of Abramson (1). Pyrex glass particles were prepared by grinding clean Pyrex glass in a mortar and sifting to get particles passing 300 mesh. Decolorizing carbon and mineral oil were of usual laboratory grade. Collodion particles were prepared by the method of Loeb (15) and washed thoroughly by centrifugation. The silica gel (Patrick) was purified by the method of Reyerson and Clark (24).[5] It was electrodialyzed, finely ground, and placed in water overnight before using. Aluminum oxide which had been carefully purified and ground in an agate mortar was obtained through the courtesy of Professor R. A. Gortner. The various particles were suspended by shaking in water and adding a suitable small amount to a concentrated protein solution. Under the microscope only three or four particles could be seen in each field. After several minutes the salt was added, then the acid, and lastly water to the volume desired. Unless specified, the final protein concentration was 0.5 per cent. Measurements were carried out using higher concentrations with each type of particle, but no differences could be noted. A tempera-

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[3] Thanks are due to Dr. Ivon R. Taylor and Mr. Julius C. Abels for carrying out the pH determinations with this electrode.

[4] Personal communication from Dr. Theodore Shedlovsky.

[5] Thanks are due to these workers for a supply of this substance.

ture coefficient of 2 per cent per degree was used to bring all values of mobility to 20°C. Room temperatures were usually 22°C.

EXPERIMENTAL

The small open circles in figure 1 are the data of Tiselius for the electric mobility of dissolved egg albumin in $M/50$ acetate buffers at 20°C.

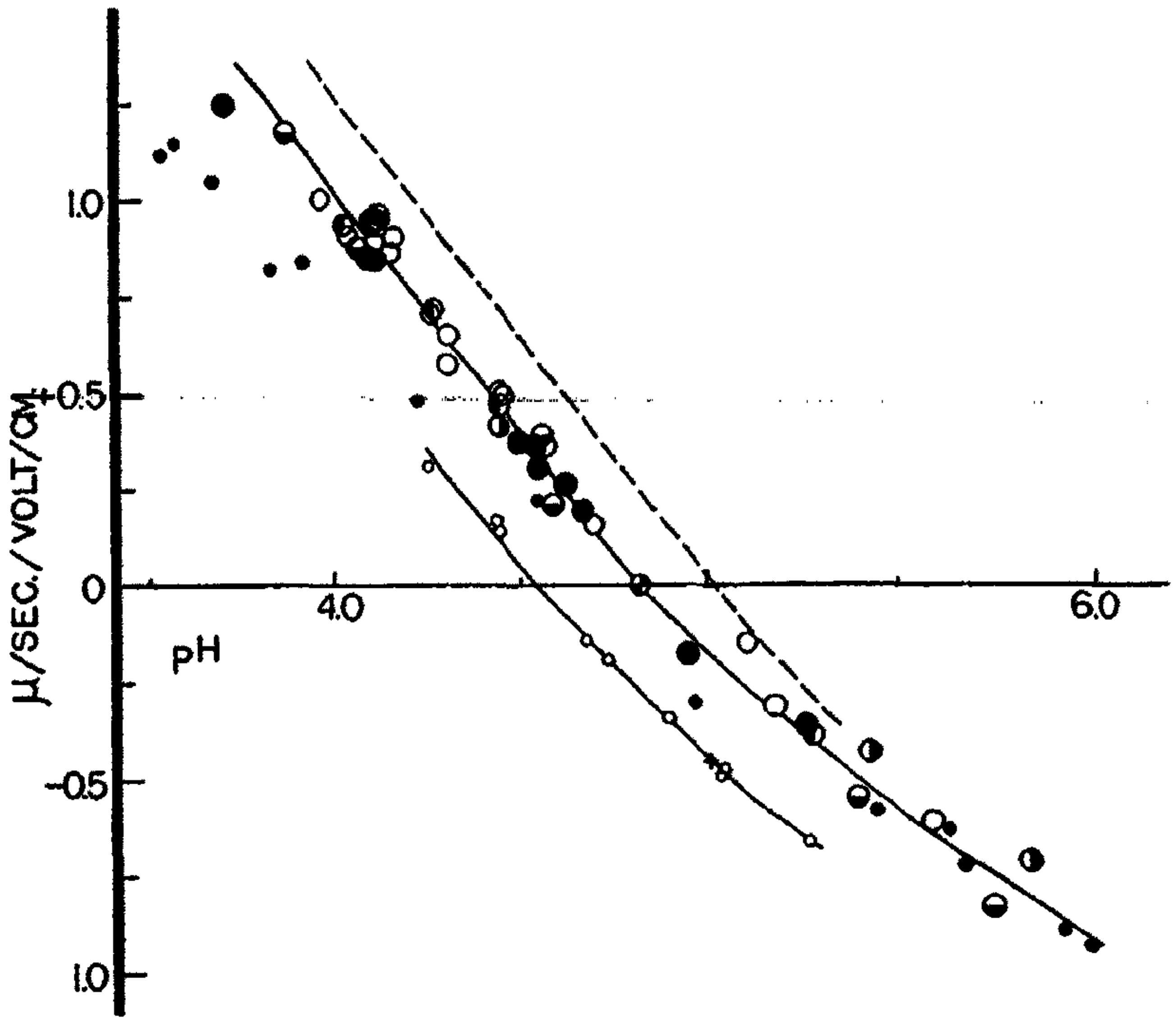

Fig. 1. The small open circles are data of Tiselius for the electric mobility of *dissolved* egg albumin. The cross is the single point measured under the same conditions by Annetts. Abramson's data for egg albumin adsorbed on quartz particles are plotted as small closed circles. The large open and half-closed circles are similar data of our own obtained with glass, collodion, quartz, mineral oil, and carbon surfaces coated with four preparations of egg albumin (each type of circle represents a separate preparation of egg albumin) in $M/50$ acetate buffers. The large closed circles are results obtained with another preparation coated on quartz in $M/50$ sodium chloride–hydrochloric acid solutions. The dashed line is the smoothed curve for surface-denatured material.

The value given by Annetts has been plotted as a cross on Tiselius' curve. The small closed circles are the data of Abramson for egg albumin-coated quartz particles under these conditions. The other large points are values for the electric mobility of particles of Pyrex glass, mineral oil, carbon, collodion, and quartz when coated with egg albumin and suspended in

M/50 acetate buffer at 20°C. The different kinds of circles indicate the five preparations of egg albumin. No differences could be noted between the behavior of these various types of particles in contact with any of the different egg albumin preparations over the range of pH investigated, nor could any differences be found between the different preparations of the protein when coated on any one of these particle types; this was tested in each case. Although space does not permit any indication of the various underlying surfaces in figure 1, measurements were distributed fairly evenly over the five particle types. Data for the construction of the smoothed curves in figures 1 and 2 are presented in table 2. It will be noted that the points follow a nearly linear course from pH 3.8 to pH 4.82, the isoelectric point.[6] From here the curve remains parallel to that of

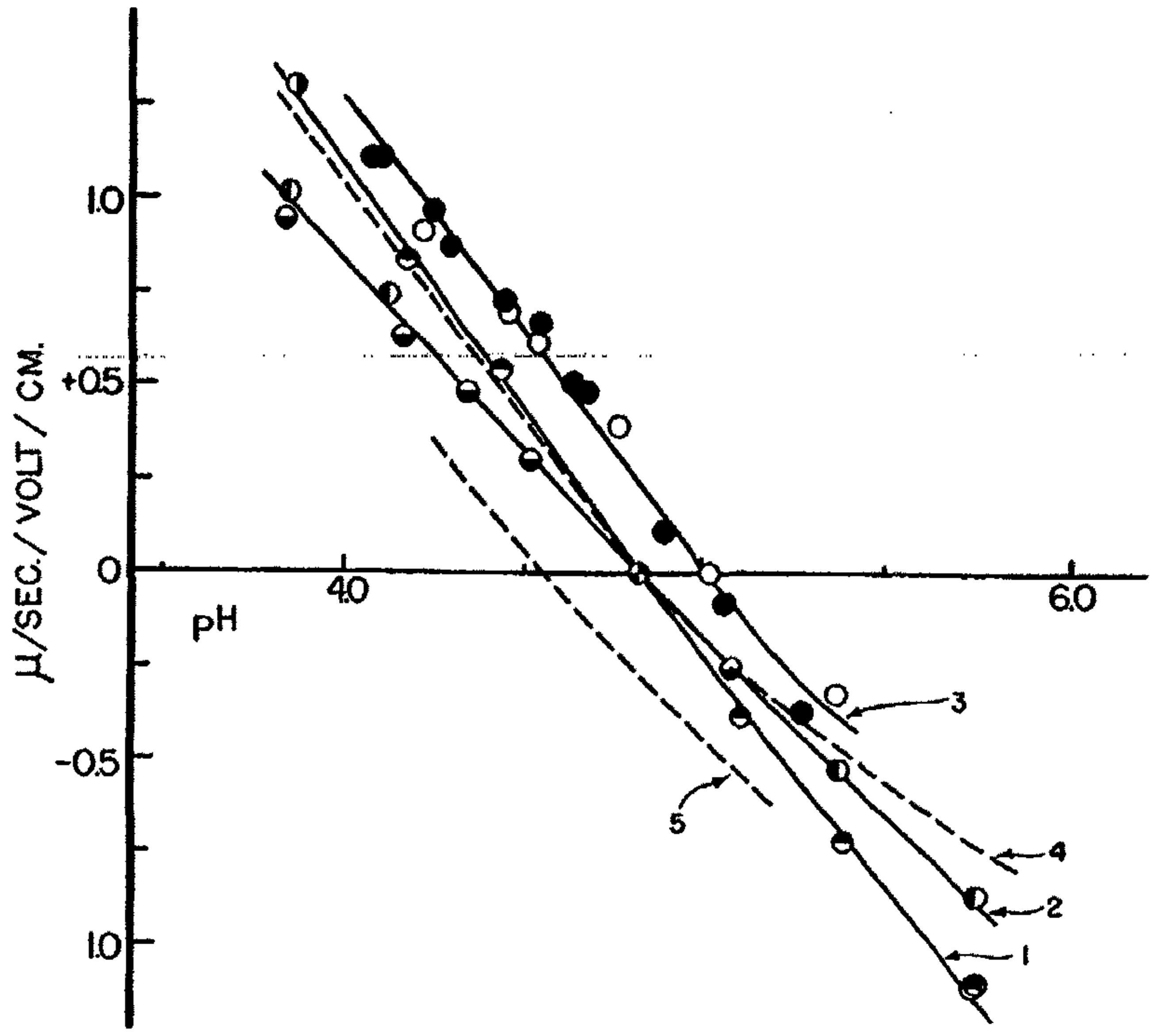

FIG. 2. Curve 1, aluminum oxide particles coated with two preparations of egg albumin; curve 2, the same preparations on silica gel; curve 3, surface-denatured egg albumin,—open circles, freely suspended, closed circles, adsorbed on quartz; curve 4, egg albumin on "inert" surfaces (from figure 1); curve 5, smoothed curve of Tiselius' data.

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[6] The positions of the isoelectric points discussed in this paper were determined in all cases by finding the pH of least motion and also by interpolation of the mobility curve. No differences between these two methods were ever noted.

Tiselius by bending slightly toward the base line. A separate series of observations was carried out with completely different apparatus, using quartz coated by an additional preparation of egg albumin (0.76 per cent) and suspended in sodium chloride-hydrochloric acid solutions likewise at a constant ionic strength of 0.02. In this case, pH was measured by the glass electrode. These data are plotted as large closed circles (figure 1). The agreement is excellent, emphasizing the importance of ionic strength rather than total buffer molarity in influencing the mobility. The position of the isoelectric point was identical, within the limits of error, with the data in the acetate buffer.

The behavior of albumin-coated silica gel is shown in curve 2 of figure 2. It will be noted that the mobilities are significantly affected by the underlying surface. Silica gel is not only extremely hydrophilic but also possesses an ionogenic surface. Another surface of this type but positive in charge is aluminum oxide (Al_2O_3). Aluminum oxide when coated with egg albumin yielded the same isoelectric point as the other surfaces (curves 2 and 4). As in the case of silica gel, the curve is composed of two straight lines radiating from the isoelectric point (curve 1, figure 2). The position of the curve, while close to that of curve 4 on the acid side of the isoelectric point, was markedly divergent at higher pH values.

TABLE 2

Data for the construction of smoothed curves in figures 1 and 2

NORMAL EGG ALBUMIN*				EGG ALBUMIN ON SILICA GEL		EGG ALBUMIN ON Al_2O_3		SURFACE-DENATURED EGG ALBUMIN	
pH	v†	pH	v	pH	v	pH	v	pH	v
4.00	+1.02	5.40	0.50	4.00	+0.83	4.00	+1.08	4.00	+1.27
4.82	0	5.60	0.65	4.82	0	4.82	0	5.02	0
5.00	−0.17	5.80	0.79	5.80	−0.93	5.80	−1.20	5.20	−0.22
5.20	0.34	6.00	0.92					5.40	0.40

* Adsorbed on glass, quartz, collodion, mineral oil, and carbon.

† In μ per second per volt per centimeter.

It has been mentioned that one preparation which had become opalescent had a high gold number but behaved anomalously from the other preparations. Quartz particles placed in buffers containing this preparation (0.5 per cent protein) were isoelectric at pH 5.02, although the mobility curve was parallel to that of the other preparations on its acid side (large closed circles, curve 3, figure 2). Upon filtration all traces of this exceptional behavior disappeared. Dilute egg albumin from another preparation which had not required filtration was shaken to produce surface-denatured egg albumin. Particles of this denatured material suspended in buffers (without additional particles) yielded the data plotted as large open circles in curve 3 of figure 2. These too were isoelectric at pH 5.02. As usual, particles moved independently of size and shape. It appears probable that the opalescent solution contained traces of surface-denatured protein; these, being strongly surface-active (7), were selectively adsorbed. The data indicate that normal albumin does not coat surface-denatured albumin which has been formed at an air-water interface and subsequently dispersed by shaking, or if it does, it in turn is denatured. This hypothesis is borne out by the fact that the one set of data was obtained with quartz in 0.5 per cent albumin, whereas the undenatured albumin in the final dilutions of purposely denatured material could not have been higher than 0.008 per cent if none had been denatured, yet both curves are the same. The presence of undenatured protein in the surface-denatured sample was demonstrated by filtering off the coagulated material and heat-denaturing the clear filtrate.

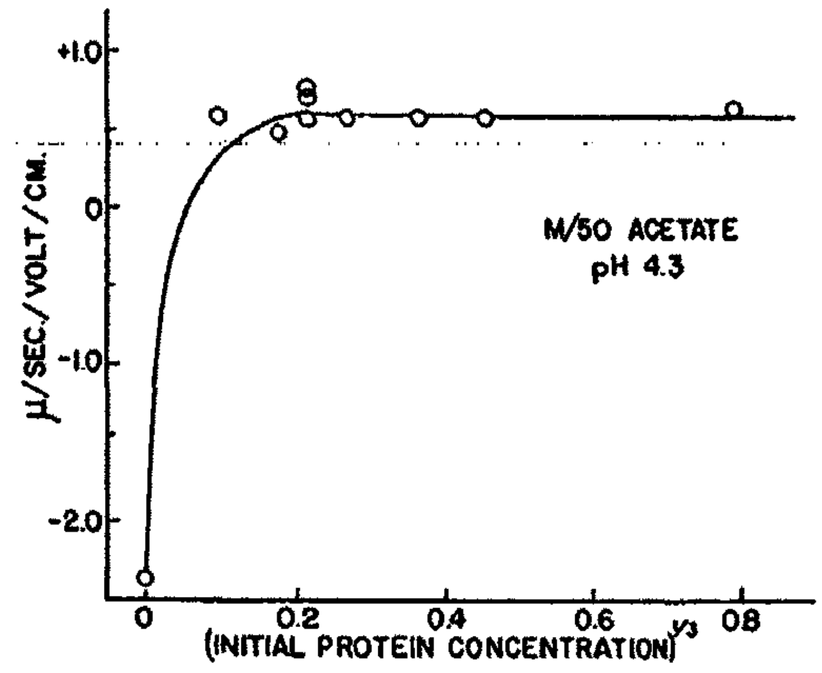

Fig. 3. Electric mobility of glass plotted against cube root of initial protein concentration in per cent.

The change in mobility with concentration of the initial protein solution is shown in figure 3. This experiment was performed in a cell which had first been filled with strong protein solution, then rinsed with water. As will be noted, the curve is perfectly regular and smooth, showing no exceptional behavior at low concentrations beyond a tendency for higher variation between mobilities at concentrations where the coating is presumably incomplete. This is similar to the curves of Freundlich and Abramson (9) for crude egg albumin.

Neurath (22) has pointed out that egg albumin spread in a surface trough requires up to seven minutes to become surface-denatured. Special observations to test this point, made within a minute after adding glass particles to the protein solution (pH 4.2), showed no progressive changes in mobility with time. The order of adding the reagents was found to have no effect. Evidently the protein coating is at equilibrium with the medium very soon after its formation.

DISCUSSION

The isoelectric point

Our value for the isoelectric point of egg albumin is identical with that found by Smith at the same ionic strength, yet the mobility curve is shifted 0.27 pH unit from Tiselius' curve for dissolved protein. Although Tiselius' value for the isoelectric point is pH 4.55, his value for the isoionic point is pH 4.76. Smith, however, found complete agreement (within 0.01 pH) between the isoionic and isoelectric points over a wide range of salt and protein concentrations. This makes it possible that a reinvestigation of the subject, using both macro- and micro-electrophoresis techniques on the same highly purified sample, would yield results more in agreement. If, however, Tiselius' data are correct, it is rather remarkable that the same shift in isoelectric point is produced for all the adsorbing surfaces. A simple explanation for this shift based on electrical adsorption is not available, as two of the surfaces were positive (carbon and aluminum oxide) and the rest negative, yet all have the same isoelectric point when coated with egg albumin.

On the basic side of the isoelectric point, the agreement between our results with quartz and those of Abramson is excellent. Barring a few of his points at low mobilities where measurements cannot be carried out with the same accuracy, his curve could be considered as having the same isoelectric point as ours but diverging in slope on the acid side. The results of Abramson were carried out with quartz particles which had been specially cleaned by long boiling with concentrated hydrochloric acid and which had been in contact with water for several years.[7] As this material was no longer available, quartz was treated with hydrochloric acid and washed, but no change in protein behavior was observed. Since Abramson's results were based on two samples of egg albumin (crystallized four times and water-clear[7]), it is altogether possible that long soaking had hydrated the surface of his quartz similar to silica gel. Indeed, our silica gel curve (figure 2, curve 2) is within the limits of error of Abramson's points (10 per cent[7]) so that the difference cannot be considered significant.

Nature of the surface film

Hitchcock (12) has shown that egg albumin is adsorbed as a film of polymolecular thickness on porous collodion membranes by demonstrating

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[7] Personal communication from Dr. Abramson.

that a weighable amount, far in excess of that needed for a monomolecular layer, is present. It is therefore not surprising that the underlying surface has so little effect on the mobility. It should be mentioned that the theoretical possibility of the underlying surface affecting electric mobilities of proteins was pointed out by Halpern (10).[8,9] The difference between the effect of the "inert" surfaces on one hand and silica gel or aluminum oxide on the other can scarcely be explained by chemical union of amino or carboxyl groups with the surface, for the isoelectric point is unchanged; moreover, aluminum oxide is basic and silica gel acidic.

Consideration of the modified Debye approximation (2, 4),

$$\pm v = \frac{\pm Q}{C\eta r(\kappa r + 1)} \tag{6}$$

where v = electric mobility, Q = net charge, C = proportionality constant, r = radius, η = coefficient of viscosity, $\kappa = f$ (ionic strength), shows that addition of a constant charge to Q (equivalent to removal or addition of electrons by electrical adsorption) would shift the isoelectric point but leave the curves parallel if the radius remained constant. A change in the effective radius (here probably that of the protein molecule (2, 4, 21)) would rotate the curve on its axis, leaving the isoelectric point unchanged.[10] We are inclined to look for an alteration of this kind as an explanation of the effect of silica gel and aluminum oxide.

It was discovered by Loeb (16) that after collodion particles had been placed in a strong solution of egg albumin, a few drops of the suspension added to a large volume of salt solution showed properties greatly altered from those of dissolved protein. The collodion was precipitated at concentrations far below those needed to precipitate dissolved egg albumin. Loeb concluded that these experiments indicated that egg albumin adsorbed on quartz was surface-denatured. If this were so, it might be expected that the innermost layer would be different in charge density from the outer coating, if surface denaturation at a solid surface produces a film oriented in the same direction as at an air-water interface. Yet figure 3 shows no changes in mobility with increasing protein concentration once the surface is coated. Particles of glass treated as in Loeb's experiments gave exceedingly variable mobilities in buffer solutions,

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[8] Dummett and Bowden (8) have maintained that hemoglobin likewise shows the influence of the underlying surface. See, however, references 4, 19, and 32.

[9] Gelatin apparently is not so easily affected by positive and negative ionogenic surfaces, for Hazel and King (11) find that the mobility curves of gelatin-coated manganese dioxide and ferric oxide are identical.

[10] Under our conditions, the value of C is probably near 6π (2, 4). A slight change in r would probably produce a change in C of secondary order of magnitude.

indicating that under these conditions the surface film is no longer complete.

Evidently the isoelectric point (pH 5.02) or the curve shape of surface-denatured albumin when suspended in buffer is not affected by its adsorption nor does it tend to adsorb egg albumin in an unaltered state. The possibility exists that such a surface may progressively denature new layers as they are adsorbed. The presumptive shift of isoelectric point from pH 4.55 to pH 4.82 on adsorption on "inert" surfaces indicates that only about two polar groups per molecule are lost by this process. Moreover, if denatured, the egg albumin surfaces which are isoelectric at pH 4.82 are not identical with egg albumin denatured at an air-water interface.

The shift of isoelectric point to higher pH values by this type of denaturation was to have been expected from the results of Bull and Neurath (7), who found that between pH 4 and pH 6 the pH of a solution of egg albumin increases 0.6 pH unit incidental to surface denaturation. This would indicate a binding of acid or a release of base corresponding to a shift in charge, as discussed in connection with equation 6. It is, however, probable that the protein molecule spreads out during denaturation (7, 18, 22) so that equation 6, derived for a sphere, would no longer apply. The results also agree with the concept of Mirsky and Pauling (18) that, on spreading out, a protein releases paired carboxyl and amino groups by breaking hydrogen bonds. As they suggest, this would shift the isoelectric point upward on the pH scale.

SUMMARY

1. A combination of Komagata's expression for the position of the stationary level in flat closed electrophoresis cells with the theory of Smoluchowski permits the true mobility to be calculated from measurements at the center of the cell, providing that the cell wall and particle surfaces are the same in composition.

2. Highly purified solutions of egg albumin adsorbed on "inert" surfaces such as quartz, glass, mineral oil, carbon, and collodion, exhibit the same isoelectric point at pH 4.82 in $M/50$ acetate or sodium chloride–hydrochloric acid solutions. This isoelectric point confirms the results of Smith.

3. The electrophoretic mobility-pH curve is identical for all of these surfaces when coated with any of five preparations of egg albumin and suspended in $M/50$ acetate or sodium chloride–hydrochloric acid solutions of constant ionic strength.

4. When egg albumin is adsorbed on silica gel or aluminum oxide particles, its isoelectric point remains at pH 4.82 but each curve is influenced by the nature of the underlying surface.

5. Surface-denatured egg albumin freely dispersed or adsorbed on

quartz is isoelectric at pH 5.02 in $M/50$ acetate buffers. The electric mobility curve is correspondingly displaced, but is parallel to that for native egg albumin on "inert" surfaces.

6. The nature of the surface film of egg albumin is discussed in the light of these results.

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STUDIES ON SILICIC ACID GELS. VIII

THE TIME OF SET OF GELS CONTAINING STRONG ACIDS

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INTRODUCTION

The time required for the setting of a sol of hydrated silica, giving what we call a silicic acid gel, has been found to depend primarily upon the concentration of silica, the temperature, and the hydrogen-ion concentration. A careful study of the relation between time of set, as we have defined it, and the temperature on the one hand and the hydrogen-ion concentration on the other, for gels produced from solutions of sodium silicate and acetic acid, has already been reported from this laboratory in previous papers of this series (3, 4, 5). In addition, the same study, extended to other weak acids,—citric, succinic, and tartaric,—was reported by Hurd (1).

We have suspected that the weak acids, because of the buffering effect of the sodium salts formed during the reaction with the sodium silicate, give a practically constant hydrogen-ion concentration. Hence the reaction of setting, whose rate manifestly depends upon the hydrogen-ion concentration should, and does, proceed at a more uniform rate than it would in a solution whose hydrogen-ion concentration was not so constant. In order to investigate this phenomenon, we have made a study of the time of set of gel mixtures produced by mixing solutions of sodium silicate with solutions of the strong acids, nitric, hydrochloric, and sulfuric. The effect of temperature and of hydrogen-ion concentration upon the time of set of such mixtures is reported in this paper.

EXPERIMENTAL

The gel mixtures were produced in the same way as those reported in the former papers of this series. A large volume of sodium silicate solution was made by dilution of "E" brand silicate, produced by the Philadelphia Quartz Company, with recently boiled, distilled water. The large amount ensured uniform concentration throughout this investigation. This solution titrated 1.255 N, as equivalent in sodium hydroxide against standard sulfuric acid using methyl orange. Standard 2.0 *N* solutions of nitric, hydrochloric, and sulfuric acids were prepared.

During the studies on gels containing acetic acid, a considerable variation in the concentration of acetic acid was made. This was necessary in order to make a suitable variation in the hydrogen-ion concentration, owing to the buffering effect of the sodium acetate formed. Here, however, in mixtures of solutions of a strong acid and sodium silicate, the hydrogen-ion concentration changes very rapidly near the neutral point, just as occurs during the neutralization of a strong acid with a strong base. This rapid change in hydrogen-ion concentration made it impossible to measure out two different mixtures which would have the same hydrogen-ion concentration. Accordingly, double mixtures were made in each case, one half of which was used to measure pH and the other half to measure the time of set. By attempting to measure the same amount of acid and of silicate for each trial, we secured a sufficient variation of pH; in fact, some mixtures came on the alkaline side and were discarded, since this study was confined to acid gel mixtures. For the mixtures with lowest pH a little more acid was used. These mixtures could be made up by measure to within a few tenths of a pH unit.

The amount of the acid solution, nitric, hydrochloric, or sulfuric, required to neutralize 50 cc. of the 1.255 *N* silicate solution was determined by a titration. This would be almost the same for each acid. The mixtures were made by placing this amount of acid solution, measured from a special pipet or from a buret, in a beaker and adding enough distilled water to give exactly 110 cc. In another beaker was placed 50 cc. of the silicate. The two beakers and contents were placed in a thermostat whose temperature was just far enough below the temperature of the thermostat used for determining the time of set so that the temperature of the mixture would rise to exactly the correct temperature. This heat is provided by the immediate ionic reaction. It varies a little, but is approximately 1.4°C. When the acid and the silicate solutions had attained the temperature of this temporarily used thermostat, they were mixed, the procedure always being to pour the silicate into the acid and then to pour the mixture back and forth several times. Thereupon the mixture was divided, 80 cc. being poured into a 100-cc. Pyrex Griffin beaker, which had been held in the thermostat used for the determination of the time of set. The other 80 cc. was used to determine the pH at 25°C. by the quinhydrone method, using a bright platinum wire. This has been shown to be accurate by Hurd and Griffeth (2).

The time of set was determined by the tilted-rod method, as described by Hurd and Miller (4). It is true, as Prasad and Parmar (8) have remarked, that the tilted-rod method for determination of the time of set gives the time for a certain fraction of the process of gelation to occur.

Nevertheless, we have found from a great many determinations that the method, empirical as it is, gives very reproducible results.

The thermostats have been described in other papers in this series.

THE VARIATION IN THE HYDROGEN-ION CONCENTRATION

With these strong acids the hydrogen-ion concentration of the mixtures was found to show from an appreciable to a considerable change from the time of mixing until the gel had set. The change probably continued in all cases for some time after the gel had set, as was verified by sufficient experiments. The change, after setting had occurred, was very small, however, and naturally could be disregarded, so far as its effect upon the time of set was concerned, since the gel had already set.

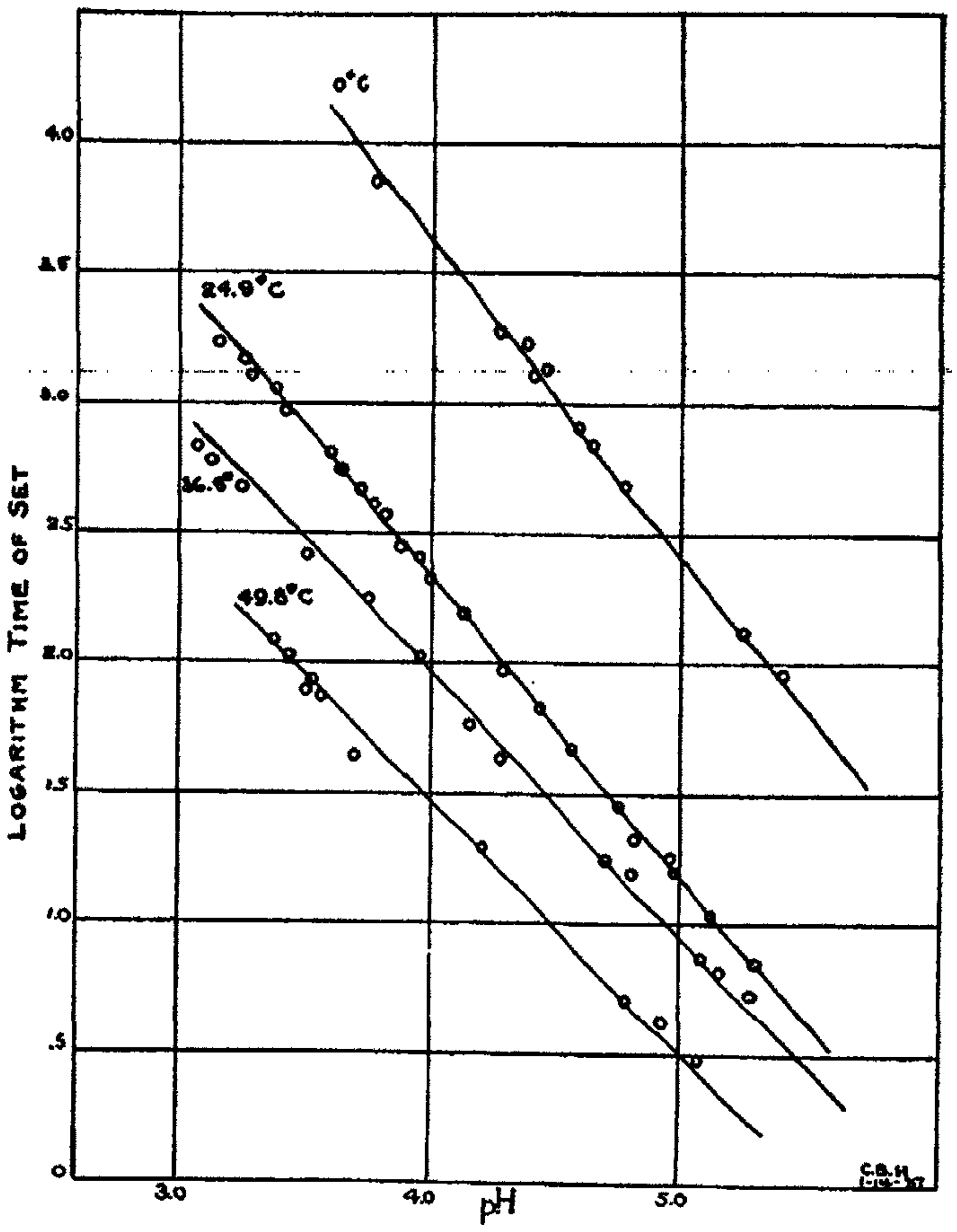

FIG. 1. Relation between logarithm of time of set and pH for gel mixtures using hydrochloric acid

The change was least with the gels of higher hydrogen-ion concentration, as would be expected. Such gels reached a constant pH before setting, but as the pH approached 7 greater changes occurred. These gels set more quickly and in some the pH was not constant until some time after the gel had set. We have measured the pH frequently for each mixture, but record here only the constant value.

This change in the pH has very real significance and will be treated fully later in another paper. As a rough comparison, the pH change at pH = 3.0 would be 0.2 pH unit or less, while for pH = 6.0 a change up to 0.6 pH unit was observed. No great difference was noted in this respect between the three strong acids used.

TABLE 1

Logarithm of times of set in minutes as a function of pH, temperature, and acid used

pH	LOGARITHM OF TIME OF SET IN MINUTES AT				
	0°C.	24.9°C.	35.3°C.	36.5°C.	49.8°C.
Nitric acid gels					
3.0	4.70	3.44	2.92		2.38
3.5	4.09	2.90	2.44		1.92
4.0	3.48	2.36	1.96		1.46
4.5	2.86	1.82	1.49		1.01
5.0	2.26	1.28	1.02		0.56
Hydrochloric acid gels					
3.0	4.89	3.48	2.96	2.39	
3.5	4.26	2.90	2.46	1.98	
4.0	3.64	2.34	1.96	1.46	
4.5	3.03	1.76	1.46	0.99	
5.0	2.41	1.18	0.98	0.51	
Sulfuric acid gels					
3.0	5.40	3.32	2.84		2.16
3.5	4.72	2.82	2.42		1.76
4.0	4.04	2.30	2.00		1.38
4.5	3.36	1.79	1.58		1.00
5.0	2.67	1.28	1.16		0.62

EXPERIMENTAL RESULTS

The many data for the time of set as a function of the pH for each of the three acids at each of four temperatures were plotted on curves such as the one shown by figure 1. For these mixtures the concentrations are, in gram-moles per liter: Na = 0.392, SiO_2 = 0.638, and acid added very slightly more than equivalent to the sodium. This very slight excess

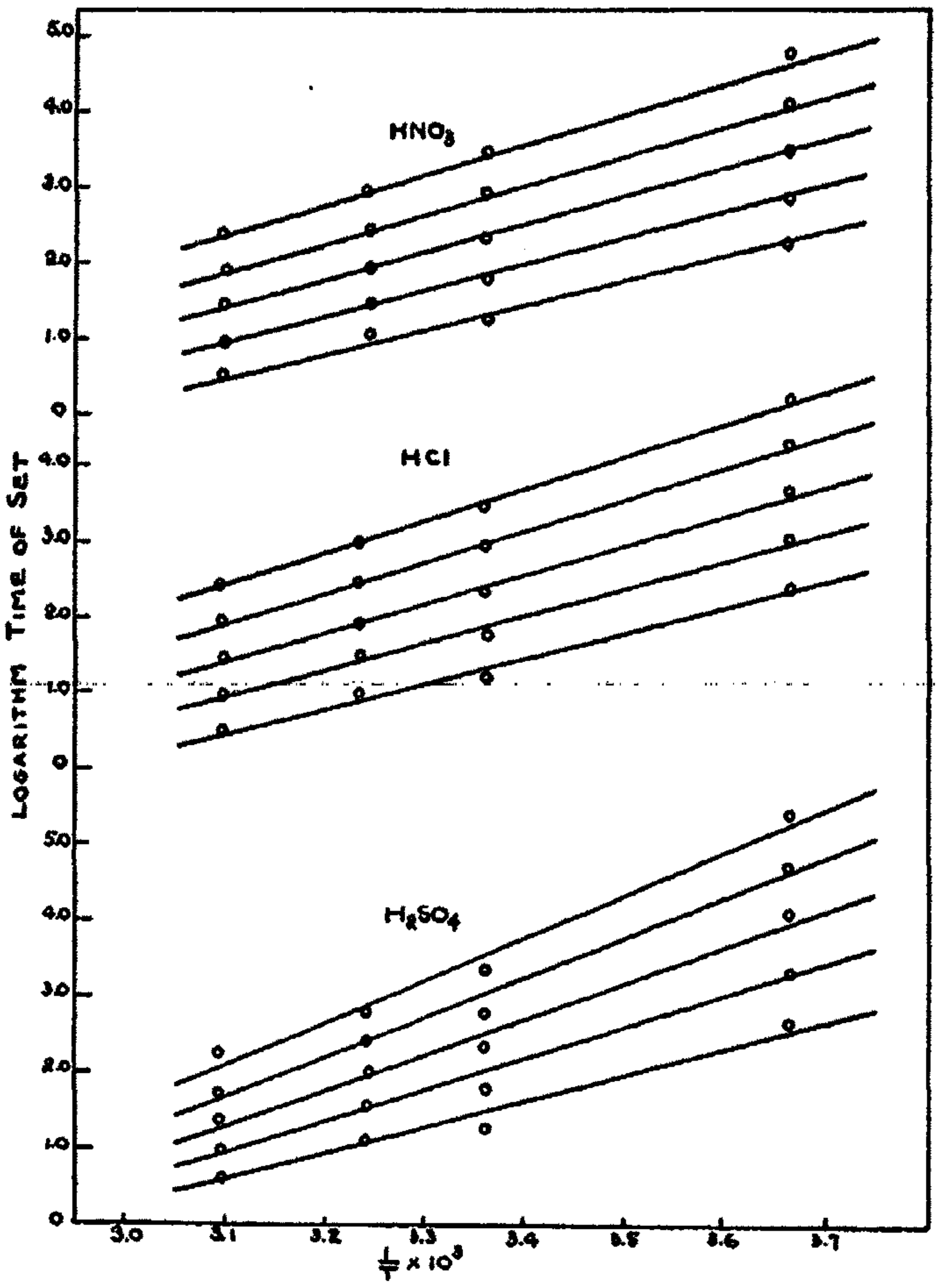

FIG. 2. Relation between logarithm of time of set and reciprocal temperature for gel mixtures which contain the strong acids

TABLE 2

The heat of activation of the setting of silicic acid gels made with strong acids

pH	NITRIC ACID	HYDROCHLORIC ACID	SULFURIC ACID
	Q	*Q*	*Q*
	calories	*calories*	*calories*
3.0	18,200	20,280	26,550
3.5	17,300	18,870	24,130
4.0	16,400	17,630	21,630
4.5	15,380	16,470	19,070
5.0	14,570	15,230	16,510
Mean	16,370	17,700	21,580

gave, as explained before, sufficient variation in the hydrogen-ion concentration. The hydrogen-ion concentration in each is shown by the pH.

From the three curves data were interpolated to give the results shown by table 1. These data show the effect of temperature upon times of set for five series of pH values for each acid, which would have been impossible to obtain by direct mixing, as has been explained.

These data were plotted on large graph paper with the logarithm of time of set as ordinates against reciprocal absolute temperature as abscissae. Figure 2 shows a composite plot.

As previously shown by Hurd and Miller, the slopes of these curves multiplied by 2.30 R give a quantity called the heat of activation. The values obtained for this quantity are given in table 2.

DISCUSSION

In order to explain the data of table 2, it will be necessary to refer briefly to the previous work which has been reported, upon the effect of temperature on the time of set of various silicic acid gel mixtures.

The original investigation, upon the effect of temperature on the time of set of silicic acid gel mixtures produced by mixing solutions of sodium silicate and acetic acid, has been mentioned (4). The data showed that this quantity, which we have called the heat of activation, remained practically constant regardless of the kind of sodium silicate used or of the acidity, so long as the gel mixtures were acid.

The following investigation, which included also the weak acids, citric, succinic, and tartaric, and in which a correction was made for the small initial rise of temperature (about 1.4°C.) showed again that the heat of activation was very nearly constant (1). While the agreement for citric, acetic, and succinic acids fell within the experimental error, the value for tartaric acid was a little larger than could be explained on the basis of experimental error. The average values for acetic, citric, succinic, and tartaric acids were, as reported, 17,140, 16,940, 17,190, and 17,530 calories, respectively.

While we may, therefore, feel considerable confidence in viewing this heat of activation as a very fundamental constant, whether different types of sodium silicate or different weak acids are used, the fact that the strongest acid of the four, tartaric acid, showed a larger value than could be explained, deserved an explanation.

A glance at table 2 shows this more strikingly. There is much more variation in the heat of activation for any one strong acid than was shown by the weak acids. We should note here, also, that a wider range of pH was covered with the strong acids. In addition, the differences between the strong acids are much greater than were shown by the weak acids.

The explanation of this apparent discrepancy between the results shown by the weak and the strong acids lies in the fact, reported in this paper, that during the process of setting the gel mixtures have shown from a measurable to a considerable change in pH. Since, as Hurd, Raymond, and Miller (5) have shown, the velocity of the setting reaction is inversely proportional to the hydrogen-ion concentration, these gel mixtures using strong acids are undergoing a reaction whose velocity varies. This is the more evident, since in mixtures of sodium silicate and a strong acid there is little buffering power, while in the mixtures made from the weak acids, the presence in the mixture of the sodium salt of the weak acid and the excess weak acid gives excellent buffering power.

While it might be possible to add buffering mixtures to these gel mixtures containing the strong acids, in order to obtain a constant pH, such a process would prove undesirable. The systems would be much more complicated than our present mixtures and, as we are aware, simplification rather than complication should be sought in these already complicated solutions.

To proceed in the other direction, the very pure silica sols produced by the oxidation of silane by Kargin and Rabinovich (6) would prove a very interesting field for these temperature-time of set studies. This is impossible, unfortunately, owing to the fact that the formation of the original sol of hydrated silica or silicic acid occupies a considerable time. It is essential that the sol be prepared within a few seconds.

The whole study of the change in the pH of the sols during setting is of the greatest importance and will be reported from this laboratory in a paper to follow. It is possible for us to borrow from the proposed paper sufficient data to show why we may expect the energy of activation to vary in these mixtures involving strong acids. In addition, this variation of the hydrogen-ion concentration bears directly upon our theory of the mechanism of setting.

The present theory for the setting of these gels of silicic acid is derived from the statement of Mylius and Groschuff (7) and others, that in the instantaneous reaction of the acid with the sodium silicate, a simple silicic acid is formed. This is probably a monosilicic acid. Such an acid, according to Treadwell and Wieland (9), shows an appreciable ionization, since the value for its first ionization constant, K, equals $10^{-9.7}$. According to the theory, this simple silicic acid forms long chains of silicic acids by condensation. These acids must become weaker, owing to their increasing molecular weight, and also owing to the fact that the more active hydrogens have been removed during the condensation. It is probable that larger and larger groups condense as the process goes on. Thus the setting appears to take place very suddenly, regardless of whether one is observing the viscosity, tensimeter reading, elasticity, scattering of light, or any one of other characteristic properties, although a relatively long preliminary or induction period has passed. When these groups have become sufficiently large, there is probably little, if any, acidic ionization giving hydrogen ions. Kargin and Rabinovich have reported a pH of 7.0 for their pure silica sols.

The disappearance of this acid and the corresponding decrease in the hydrogen-ion concentration through its effect upon the specific reaction rate undoubtedly is the cause of the variation in these results for the energy of activation. It is doubtful whether we shall be able to measure this quantity in the mixtures containing the strong acids with any greater accuracy. We may say, therefore, that it is our belief that the energy of activation for the setting reaction for silicic acid gels in acid mixtures is very close to 17,100 calories.

It is difficult to give a true idea of the meaning and significance of this energy of activation. If we use it in a purely descriptive sense, we may say that it is a constant by means of which we can calculate the time of set for any given mixture at any reasonable temperature. This constant, naturally, has the dimension of calories.

If we attempt to attach more theoretical significance to this "energy of activation," we must call attention again to the theory that the condensation takes place between two molecules which come into sufficiently close contact so that water may split off. Although at first these molecules are undoubtedly monosilicic acid, as the process continues larger and larger groups must meet and condense. The chances for a condensation resulting from a collision are greater the greater the activity of these supermolecules. It is probable, therefore, that we may apply Arrhenius' idea to this reaction, and that the activity of the groups depends upon the energy of activation.

SUMMARY

The time of set has been determined for a large number of silicic acid gel mixtures, produced by mixing solutions of sodium silicate and either hydrochloric, nitric, or sulfuric acid.

The temperature was varied. The pH was measured in each case.

A variation in the heat of activation of the setting reaction was found, both at different pH values and for the different strong acids.

For these strong acid-gel mixtures, a variation was shown in the pH value as the setting proceeded. This is different from the cases where weak acids have been used.

A discussion is presented of the bearing of these data upon the theory of setting, which assumes that the simple silicic acids condense into polyacids and finally into very complex chains through the splitting out of water. The data substantiate the theory.

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THE SOLUBILITIES AND ACTIVITY COEFFICIENTS OF LANTHANUM IODATE IN CONCENTRATED SALT SOLUTIONS AT 25°C.

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The effect of one salt, in solution, upon the solubility of another salt has long been an accepted method for the study of the properties of solutions, and for the determination of activity coefficients. This field has been well covered in the case of uni-univalent salts at low concentrations, but little work has been done with saturating salts having high valence ions. Almost no work has been done in concentrated solutions.

W. D. Harkins and W. T. Pearce (6) have determined the solubility of lanthanum iodate in water and in dilute solutions of several salts. They have interpreted their data on the basis of the stepwise partial dissociation of lanthanum iodate.

La Mer and Goldman (7) have studied the solubility of lanthanum iodate in various aqueous salt solutions by the leaching method. They give two values for the solubility of the iodate in water, neither of which agrees with that of Harkins and Pearce. Their work was done in dilute salt solution, except in the case of potassium chloride where a 2.0 molar concentration was reached. Interpreting their results with reference to the Debye–Hückel limiting law, they find increasing negative deviations with increasing concentration of lanthanum nitrate and potassium chloride. At low concentrations the curves for these salts fuse into that of the limiting law, while with potassium sulfate solutions as solvent, the curves show radical positive deviations with no sign of fusion. This phenomenon was previously observed by Brönsted and Peterson (2), and has since been called the "unsymmetrical valence type effect."

La Mer and Mason (10) find similar positive deviations using cobaltammines as saturating salts, while Peterson and Meyers (12), with copper iodate, find positive deviations with potassium sulfate solvent solutions but not with magnesium sulfate.

The aim of the present work has been to redetermine the solubility of lanthanum iodate in pure water, and to extend the study of the solubility of lanthanum iodate in solutions of typical salts up to concentrations approaching saturation.

MATERIALS

The lanthanum iodate was prepared by precipitation, following the method of La Mer and Goldman (7). The prepared salt was not allowed to dry, but was kept under water until used. Some of the lanthanum iodate used with potassium chloride solutions was subsequently examined under a micrometer microscope. The particles were irregular in shape and microscopically they showed no definite crystalline form. The x-ray pattern, however, showed crystalline structure. The mean dimensions of the smallest particles were 0.0098 mm. x 0.0073 mm., the largest particles being five to eight times this large. The salts used in preparing the solvent solutions were recrystallized at least twice, the last time from conductivity water. Sodium oxalate from the Bureau of Standards was used as the primary standard to which all analytical data were referred.

METHOD

The work of La Mer and Goldman in dilute solutions was done by the leaching method originated by Brönsted and La Mer (1). An attempt was made to use this method for the determination of solubilities in concentrated solutions, but it seemed impossible to obtain consistent results in this case. Accordingly, this method was abandoned and a rotating shaker was used. In determining solubilities with this apparatus, a generous portion of the lanthanum iodate paste was washed several times with portions of the solvent solution and finally transferred to duplicate oil-sample bottles with the bulk of the solution. The bottles were then clamped to the shaker and rotation started.

After a minimum of two weeks' rotation at 25°C. the bottles were removed from the shaker and suspended near the surface of the water in the constant-temperature bath. The suspension was allowed to settle overnight and the clear solution siphoned into similar bottles also held in the bath. After at least three hours more of settling, the supernatant liquid was again transferred, this time to two dry 250-ml. flasks. Completeness of settling was checked on each solution by means of the Tyndall effect from the beam of a small arc lamp. If more than a very slight cone was visible, the solutions were allowed to settle until they were optically clear.

The analyses of the saturated solutions for iodate ion were made in triplicate, by titration with standard sodium thiosulfate solution of the iodine liberated according to the reaction:

$$IO_3^- + 5I^- + 6H_3O^+ \rightleftharpoons 3I_2 + 9H_2O$$

In the analysis, the method of La Mer and Goldman (7) was substantially followed. The best of modern analytical technique was observed at every step. Carefully calibrated pipets and Normax volume burets were used.

Since in the late afternoon the blue color of the sky interfered with correct determination of the starch-iodine end point, all titrations were carried out under artificial light. The light, which struck the solutions from the top and side, was furnished by a 40-watt. frosted bulb, backed by a reflector and covered by a ground glass. By this means it was possible to maintain a precision of two parts per thousand or better in all titrations.

APPARATUS

The rotating shaker, mentioned above, consisted of a 12-inch brass disc fixed to a brass shaft which ran in brass bearings suspended from an angle iron frame. On each side of the disc were eight hinged bands by which sixteen 200-ml. oil-sample bottles could be clamped to the disc. The bottles were arranged with their necks toward the common center. Owing to the slight taper of the bottles, the squeezing effect of the bands tended to force the stoppers against a concentric brass ring which prevented their leaking. The whole assembly was submerged in a specially constructed water bath. This bath was thermostated to 25°C. ± 0.01° by means of a large mercury regulator, supersensitive thermionic relay, and electric heater. The shaker was rotated at 35 R.P.M. by means of a rubber and fabric vee belt running from a countershaft above the water to a large pulley on the shaker shaft. The entire shaker mechanism was hinged so that it could be swung out of the bath for inspection and changing bottles.

THEORY

The phenomenon of solubility may be approached from either of two standpoints. The first is the kinetic viewpoint, from which one strives to explain the observed effects from the individual behavior of the ions and molecules. The second is the thermodynamic approach which systematizes the field.

The discovery by means of x-rays of the ionic structure of crystals has necessitated a rearrangement of the kinetic picture of solubility. A crystal of a salt, such as lanthanum iodate, must be thought of as a space lattice of lanthanum and iodate ions. The pattern of ions in this space lattice has not been worked out to date[1], yet it must be such that the electrical attractions between the oppositely charged ions are satisfied. When such a crystal is placed in a polar solvent, as water, water dipoles are attracted

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[1] Dr. E. S. Gantz of this laboratory has kindly made for the author an x-ray powder diffraction picture of the lanthanum iodate used. This analysis indicates that lanthanum iodate crystals have the ionic type of lattice.

by the unbalanced electrical fields at the crystal boundaries. This orientation of water dipoles around the crystal has a tendency to weaken the attractive forces holding the ions of the crystal together. The result is that the kinetic motion of some of the surface ions is sufficient to free them from the attraction of their neighbors and they escape into the body of the liquid. Once the ions have escaped from the crystal, water dipoles will orient themselves completely around the ions. The external fields of these ions are thus largely satisfied by this water sheath. G. W. Stewart (14) contends that sufficient attractive forces still exist between dissolved ions to give a "structure" to the solution. This "structure" may be considered as a mobile, widely spaced, ion lattice similar perhaps to that in the crystal itself.

The process of solution will continue, following the above mechanism, until the condition which we know as saturation has been reached. In this state a condition of equilibrium exists between the solid and the dissolved solute. Evidently the forces causing the escape of ions from the crystal have been balanced by attractive forces between the ions working in the other direction.

EFFECT OF SALTS

The macroscopic effect of salts upon the solubility of a substance, as experimentally observed, is well known. The presence of salts with a common ion tends to decrease the solubility of a salt in water solution. When no common ion is present, an increase in solubility of the saturating salt is observed. The actual mechanism behind the phenomenon, however, can only be postulated.

According to Butler (3), the ions of salts mutually affect each other in two ways: (1) directly, owing to the forces between their electrical charges, whereby they attract ions of opposite charge and repel ions of like charge; (2) indirectly, through the effect of their electrical fields upon the molecules of the solvent. A suitable theory of solubility must take both of these effects into consideration. The latter effect, i.e., the orientation of water about the salt ions in solution, has already been discussed. It would lower the mole fraction of free solvent water in the solution, and hence have a depressing effect upon the solubility. The increase in solubility, observed in the present case, must obviously be due to the first of these forces mentioned.

In order to account for this "salting-in" effect, let us visualize conditions in a potassium chloride solution saturated with the salt, lanthanum iodate. If we consider both salts to be completely ionized, the following species will be present: La^{+++}, K^+, H_3O^+, IO_3^-, Cl^-, OH^-, H_2O. According to Debye and Hückel (4), a given ion will, at any time, be surrounded by an ionic atmosphere in which ions of opposite charge predominate. Thus, a lanthanum ion will be surrounded by an atmosphere in which iodate, hydroxide, and chloride ions predominate, while an iodate ion will be largely surrounded by potassium, oxonium, and lanthanum ions. In order for a lanthanum iodate crystal to grow, lanthanum and iodate ions must be able to settle out on the crystal lattice. If the ionic atmosphere around the lanthanum ions is composed largely of iodate ions, the chance of lanthanum and iodate ions settling out upon the crystal lattice of some adjacent lanthanum iodate solid will be comparatively great. Equilibrium with the solution tendency of the crystal will obtain at a low concentration, and we say that the salt has a low solubility. On the other hand, if the residual force fields about the chloride ions are greater than those around the iodate ions, the chloride ions will predominate in the ionic atmosphere of the lanthanum ions. The result of this will be that lanthanum and iodate ions will have less opportunity to settle together upon the solid lattice. The equilibrium will thus be displaced, by the presence of chloride ions, in the direction of increased solubility.

If some other negative ions with greater residual force fields than those of the chloride ions are placed in the solution, they will usurp the place of the iodate ions to a still greater extent. Thus, with sulfate ions present, a still greater increase in the solubility of the lanthanum iodate should be observed.

There is, of course, the possibility of lanthanum and chloride ions or lanthanum and sulfate ions forming lattices of their own under these conditions. This does not take place, however, because the tendency toward solubility is too great, owing in part to the fact that these same chloride and sulfate ions, with their large residual force fields, are too highly hydrated.

Glasstone, Dimond, and Jones (5) give the following relative hydration numbers for negative ions on the basis of the iodide ion as zero:

ION	HYDRATION NUMBER	ION	HYDRATION NUMBER
$Fe(CN)_6^{----}$	75	$C_2H_3O_2^-$	13
$C_2O_4^{--}$	31	Cl^-	10
SO_4^{--}	26	ClO_3^-	9
$Fe(CN)_6^{---}$	23	Br^-	5
F^-	17	NO_3^-	2
CrO_4^{--}	14	I^-	0

The values were obtained from a study of the salting-out effect. They consider these values a measure of the strength of the electrostatic fields surrounding the ions. Randall and Faily (13) arrange the negative ions in order of decreasing salting-out effect thus: $OH^- > SO_4^{--} > CO_3^{--} > ClO_3^- > BrO_3^- > Cl^- > Ac^- > IO_3^- > Br^- > I^-$. Although the iodate ion is not mentioned in Glasstone's table, it will probably have no greater value than that of the chlorate ion. It is to be observed in both of these series that the order is $SO_4^{--} > Cl^- > IO_3^-$. It will be shown later that this fact, together with the theory proposed above, easily explains the solubility behavior of these solutions.

There is no doubt a similar effect with reference to the anion of the saturating salt. Experimental evidence, however, points to the fact that in the case of lanthanum iodate, with a high valence cation, the solubility behavior is principally dependent upon the high valence ion. Thus, with a uni-trivalent saturating salt, sulfate solvent salts *have a normal effect* (10).

TABLE 1

The solubilities and activity coefficients of lanthanum iodate in aqueous potassium chloride solutions

MOLALITY OF ADDED SALT	SOLUBILITY OF $La(IO_3)_3$ (BY ANALYSIS)	DENSITY AT 25°C. (EXPTL.)	SOLUBILITY OF $La(IO_3)_3$ (CALCULATED)	μ MOLAL	$\mu^{\frac{1}{2}}$	$\log \frac{S}{S_0}$	$-\log \gamma_{\pm}$	$\gamma_{\pm}$
	moles per liter		*moles per 1000 g.*					
0.0000	0.0006634	0.99749	0.0006653	0.003992	0.06318		0.0953 0.09555	0.8030 0.8025
0.0010	0.000684	0.99750	0.000686	0.005116	0.07153	0.01347	0.10902	0.7780
0.005	0.000737	0.99776	0.000739	0.009434	0.09713	0.04555	0.14110	0.7226
0.010	0.000786	0.99801	0.000789	0.014734	0.12138	0.07402	0.16957	0.6767
0.050	0.001014	1.00000	0.001019	0.056114	0.23688	0.18508	0.28063	0.5216
0.100	0.001195	1.00243	0.001202	0.107212	0.32743	0.25675	0.35230	0.4443
0.500	0.001919	1.02090	0.001952	0.511712	0.71533	0.46744	0.56299	0.2735
1.000	0.002452	1.04277	0.002531	1.015186	1.00757	0.58021	0.67576	0.2110
2.000	0.003167	1.08268	0.003368	2.020208	1.4213	0.70437	0.79992	0.1585
3.500	0.003898	1.13787	0.004329	3.525974	1.8778	0.81336	0.90891	0.1233

Note: Each of the values given above is the mean of the results from at least two experiments.

DISCUSSION OF DATA

In the present research, the work of La Mer and Goldman (7) on the solubility of lanthanum iodate in potassium chloride and potassium sulfate solutions has been repeated on a molal basis, and carried into a region of higher concentrations. In addition, solubility data have been obtained in the presence of the bi-univalent and bi-bivalent salt types. The solvent salt solutions were made upon a molal basis. The solubilities were first determined on a molar basis, the densities were determined, and the molal solubilities then calculated from these data.

Tables 1, 2, 3, and 4 give the solubilities and activity coefficients of lanthanum iodate in potassium chloride, potassium sulfate, magnesium chloride, and magnesium sulfate salt solutions, respectively. The solubility of the salt in conductivity water is also given. It is believed that the column headings are self-explanatory.

TABLE 2

The solubilities and activity coefficients of lanthanum iodate in aqueous potassium sulfate solutions

MOLALITY OF ADDED SALT	SOLUBILITY OF $La(IO_3)_3$ (BY ANALYSIS)	DENSITY AT 25°C. (EXPTL.)	SOLUBILITY OF $La(IO_3)_3$ (CALCULATED)	μ MOLAL	$\mu^{\frac{1}{2}}$	$\log \frac{S}{S_0}$	$-\log \gamma_\pm$	$\gamma_\pm$
	moles per liter		*moles per 1000 g.*					
0.0000	0.0006634	0.99749	0.0006653	0.003992	0.06318		0.09555	0.8025
0.0010	0.000824	0.99790	0.000826	0.007962	0.08923	0.09421	0.18976	0.6460
0.005	0.001215	0.99847	0.001219	0.022314	0.14936	0.26300	0.35855	0.4380
0.010	0.001488	0.99952	0.001493	0.038958	0.19738	0.35096	0.44651	0.3577
0.050	0.002568	1.00554	0.002581	0.165480	0.40679	0.58873	0.68428	0.2069

Note: Each of the values given above is the mean of the results from at least two experiments.

TABLE 3

The solubilities and activity coefficients of lanthanum iodate in aqueous magnesium chloride solutions

MOLALITY OF ADDED SALT	SOLUBILITY OF $La(IO_3)_3$ (BY ANALYSIS)	DENSITY AT 25°C. (EXPTL.)	SOLUBILITY OF $La(IO_3)_3$ (CALCULATED)	μ MOLAL	$\mu^{\frac{1}{2}}$	$\log \frac{S}{S_0}$	$-\log \gamma_\pm$	$\gamma_\pm$
	moles per liter		*moles per 1000 g.*					
0.0000	0.0006634	0.99749	0.0006653	0.003992	0.06318		0.0953 0.09555	0.8030 0.8025
0.0010	0.000702	0.99757	0.000704	0.007226	0.08503	0.02478	0.12033	0.7580
0.005	0.000817	0.99798	0.000820	0.019919	0.14113	0.09072	0.18627	0.6512
0.010	0.000908	0.99841	0.000911	0.035466	0.18833	0.13634	0.23189	0.5863
0.050	0.001306	1.00180	0.001311	0.157866	0.39732	0.29466	0.39021	0.4072
0.100	0.001601	1.00589	0.001608	0.309648	0.55645	0.38338	0.47893	0.3319
0.500	0.002782	1.03666	0.002817	1.516902	1.2316	0.62669	0.72224	0.1896
1.000	0.003508	1.07255	0.003590	3.021540	1.7382	0.73200	0.82755	0.1487
2.000	0.004209	1.13805	0.004413	6.026478	2.4549	0.82171	0.91726	0.1210
3.000	0.004639	1.19716	0.004995	9.029970	3.0050	0.87550	0.97105	0.1069

Note: Each of the values given above is the mean of the results from at least two experiments.

In figure 1 the molal solubilities of lanthanum iodate in each of the four solvents are plotted against the cube root of the molality of solvent salt. The cube root plot was resorted to in order that the points representing low concentrations would be spread more evenly upon the curve. It is believed that the inflection points observed at high concentrations in the sulfate curves have no especial significance and are occasioned only by the method of plotting. Simple solubility versus molality curves do not exhibit these inflection points.

TABLE 4

The solubilities and activity coefficients of lanthanum iodate in aqueous magnesium sulfate solutions

MOLALITY OF ADDED SALT	SOLUBILITY OF $La(IO_3)_3$ (BY ANALYSIS)	DENSITY AT 25°C. (EXPTL.)	SOLUBILITY OF $La(IO_3)_3$ (CALCULATED)	μ MOLAL	$\mu^{\frac{1}{2}}$	$\log \frac{S}{S_0}$	$-\log \gamma_{\pm}$	$\gamma_{\pm}$
	moles per liter		*moles per 1000 g.*					
0.0000	0.0006634	0.99749	0.0006653	0.003992	0.06318		0.09555	0.8025
0.0010	0.000846	0.99766	0.000848	0.009088	0.09533	0.10551	0.20106	0.6294
0.005	0.001209	0.99839	0.001213	0.027278	0.16497	0.26078	0.35633	0.4402
0.010	0.001448	0.99921	0.001452	0.048712	0.22071	0.33899	0.43454	0.3677
0.050	0.002384	1.00496	0.002390	0.214310	0.46293	0.55540	0.65095	0.2234
0.100	0.003021	1.01167	0.003028	0.418168	0.64665	0.65813	0.75368	0.1763
0.500	0.005863	1.06116	0.005879	2.035274	1.4266	0.94627	1.04182	0.0908
1.000	0.008198	1.12180	0.008227	4.049362	2.0123	1.09222	1.18777	0.0649
1.500	0.009690	1.17865	0.009759	6.058554	2.4614	1.16635	1.26190	0.0547
2.000	0.010558	1.23098	0.010702	8.064212	2.8397	1.20644	1.30199	0.0499

Note: Each of the values given above is the mean of the results from at least two experiments.

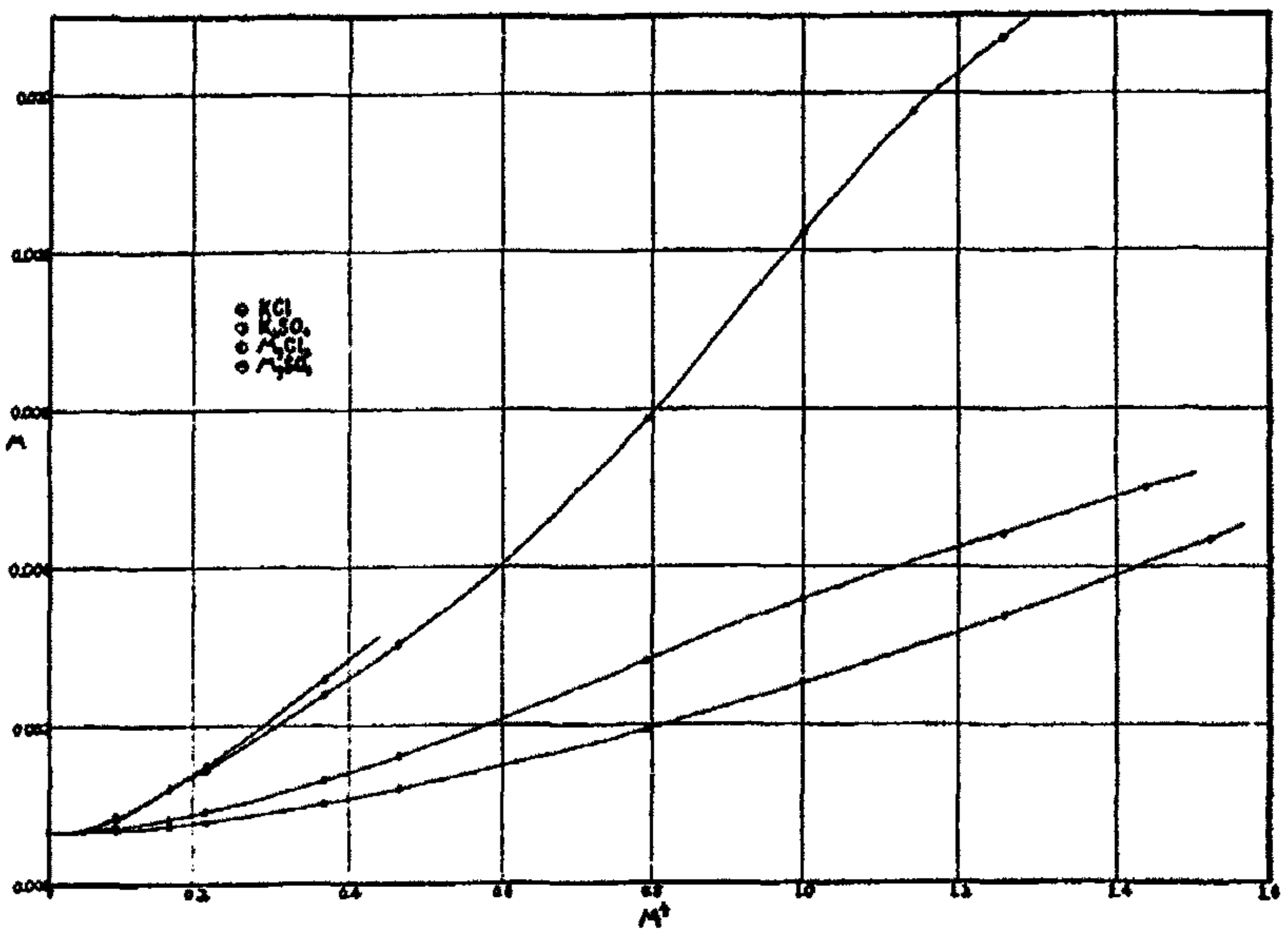

FIG. 1. Plot of molal solubilities of lanthanum iodate in salt solutions against the cube root of the molality of the solvent salt.

The relative positions of the curves are important. It will be noticed that lanthanum iodate is least soluble in potassium chloride, slightly more soluble in magnesium chloride, much more soluble in magnesium sulfate, and most soluble in potassium sulfate solutions. The high solubility observed in the sulfate solutions is accounted for in the section on theory. The relative positions of the magnesium and potassium salt curves are more difficult to explain. In the section on theory it was postulated that the solubility behavior of salts depends upon the antagonistic action of two forces. One of these is the salting-*out* effect due to hydration. The other is the salting-*in* effect due to a shift in the composition of the ion atmosphere. Two chloride ions, as in magnesium chloride, should have a greater effect in increasing the solubility than the single chloride ion of potassium chloride. This is true in spite of evidence that the magnesium ion has a greater salting-out effect than the potassium ion[2]. The solubility should therefore be greater in magnesium chloride than in potassium chloride solutions, which agrees with experiment.

If the salting-out tendency of one magnesium and two potassium ions were the same, we should expect lanthanum iodate to have the same solubility in the two chloride salts of these elements at the same chloride-ion activity. It is actually found that the solubility in 1 *M* magnesium chloride is only 4 per cent less than that in 2 *M* potassium chloride, so that this expectation is almost realized.

Conversely, where we have two salts which have the same anion, the salting-in effect upon a saturating salt with a high valence cation will be practically the same. The greater hydrating power and salting-out tendency of the magnesium ion over that of even two potassium ions reduces the solubility of the saturating salt in magnesium sulfate to below that in potassium sulfate solution.

ACTIVITY COEFFICIENTS

Referring again to the tables, in the seventh columns are found the common logarithms of the solubility ratios. The solubility ratio is the molal solubility of the lanthanum iodate in the salt solutions divided by the molal solubility in pure water. It gives the relative increase in solubility produced by the addition of the solvent salt. In the final two

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[2] While authorities differ on the exact values of the effective radii of ions, all agree that the magnesium ion is much smaller than the potassium ion. Eldridge (The Physical Basis of Things, p. 247. McGraw-Hill Book Co., New York (1934)), states that if the ion is considered as a charged sphere, its potential is proportional to the charge, and inversely proportional to the radius. A small ion will therefore have a greater charge density than a large ion of the same valence. The charge density of an ion will determine its extent of hydration, and hence its salting-out effect. See also Clark: The Electronic Structure and Properties of Matter, John Wiley and Sons, New York (1934).

columns are found the negative logarithms of the mean molal activity coefficients, and the mean molal activity coefficients of the lanthanum and iodate ions as defined by Lewis and Randall (11).

Experimentally, the mean molal activity coefficient, $\gamma_{\pm}$, is obtained from the relation,

$$\frac{S_0}{S} = \frac{\gamma_{\pm}}{\gamma_{\pm_0}}$$

from which, by taking the common logarithm of both sides, we obtain the expression:

$$-\log_{10}\gamma_{\pm} = \log_{10}\frac{S}{S_0} - \log_{10}\gamma_{\pm_0}$$

The constant value, $-\log\gamma_{\pm_0}$, is the logarithm of the mean activity coefficient of the saturating salt ions in the pure solvent and can be obtained in several ways. Two independent methods were used in the present investigation. The first method involved the plotting of the values of $\log\frac{S}{S_0}$ at low concentrations against $\sqrt{\mu}$ on a large scale and extrapolating the curve to zero ionic strength. A series of extrapolations was carried out independently by six different persons on the potassium chloride and magnesium chloride curves. A mean of all readings on the two curves gave a value of $-\log_{10}\gamma_0 = 0.0953$. The second method involved the calculation of $-\log_{10}\gamma_0$ from the Debye-Hückel limiting law (4):

$$-\log_{10}\gamma_{\pm_0} = -\frac{1.814 \times 10^6}{(D_0T)^{3/2}} Z_1Z_2\sqrt{\mu_0}$$

Here Z_1 and Z_2 are the valences (3, -1) of the ions of the saturating salt; $D_0 = 78.77$, Drude's value of the dielectric constant of water at $T = 298.1°A$. Calculated from this expression $-\log_{10}\gamma_{\pm_0} = 0.0955$, which is in excellent agreement with the experimental value.

Figure 2 shows the values of $\log\frac{S}{S_0}$ plotted against the values of the square root of the total ionic strength of the solution. If the linear relation above holds, this plot should give a straight line. The line corresponding to the limiting law given above is also shown. The curves for lanthanum iodate in potassium chloride and magnesium chloride solutions fuse into that of the limiting law at low concentrations. Those for the salt in potassium sulfate and magnesium sulfate solutions show the characteristic "hump", or positive deviation from the limiting law observed by other investigators (2, 7, 9, 10, 12). Instead of fusing into the limiting law line at low concentrations, these curves cross the line at an ionic strength of about 0.0056 and finally join each other if continued a short distance below the axis.

The relative positions and shapes of the curves resulting from the present investigation are in agreement with the work of Brönsted and La Mer (1), La Mer, King, and Mason (9), and La Mer and Mason (10), using cobaltammines as saturating salts, and with that of La Mer and Goldman (7) using lanthanum iodate. The results of Peterson and Meyers (12) are not entirely confirmed in that, while they find similar curves for copper iodate in potassium sulfate and potassium chloride solvents, their curves for this salt in *both* magnesium sulfate and magnesium chloride solutions fall below that for the salt in potassium chloride. This behavior of their magnesium sulfate curve cannot be explained on the basis of the theory postulated (see page 97), even though copper iodate has a lower valence cation and would hence be less affected by shifts in the ion atmosphere.

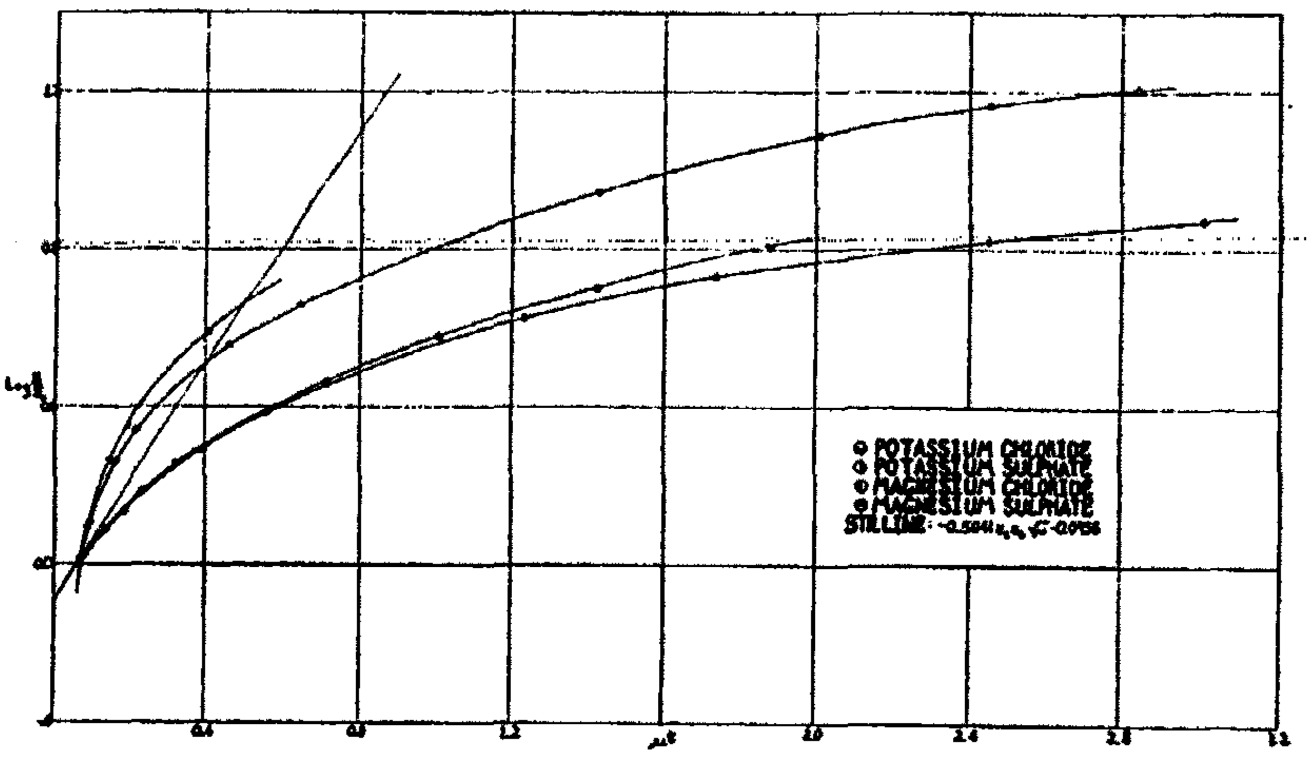

FIG. 2. Values of log $\frac{S}{S_0}$ plotted against the values of the square root of the total ionic strength of the solution.

Numerous attempts have been made to develop mathematical relations in harmony with the experimental behavior of saturating salts of unsymmetrical valence type in ion solvents. Up to the present time most of these have been only partially successful. It is probable that the Debye-Hückel extension of La Mer, Gronwall, and Greiff (8) comes as near as any to a satisfactory solution.

SUMMARY

The solubility behavior of lanthanum iodate at 25°C. has been investigated in solutions of potassium chloride, potassium sulfate, magnesium chloride, and magnesium sulfate from 0.001 molal up to concentrations approaching saturation.

The solubility of lanthanum iodate is increased by the presence of added salts. The effect of the different salt types is in the order $KCl < MgCl_2 <<< MgSO_4 < K_2SO_4$, which agrees with the work of earlier investigators.

A modern theory of solubility has been postulated to explain the effects observed.

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THE CATALYTIC ACTIVITY OF COBALT MIXED WITH CERTAIN METALS FOR THE GAS-PHASE REDUCTION OF NITROBENZENE TO ANILINE[1]

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Received April 24, 1937

Many data are available which prove clearly that cobalt is an excellent catalyst for complete hydrogenations. The present experiments have been made in an endeavor to prepare an active cobalt catalyst capable of effecting partial rather than complete hydrogenations. The activity of the various catalyst preparations was judged by the completeness with which nitrobenzene could be converted into aniline.

EXPERIMENTAL METHODS AND RESULTS

The apparatus used, the technique employed to control all factors of the experiment, the method of purification of materials, and the analysis of the products have been described in a previous paper (*1*).

Catalyst A. A pure cobalt catalyst

Twenty-seven and five-tenths grams of C. P. cobalt nitrate hexahydrate was dissolved in 300 ml. of water and added to a solution of sodium hydroxide containing 8.35 g. of sodium hydroxide. The precipitated hydroxide was collected on a filter, thoroughly washed, dried at 105°C. for twenty-four hours, and ignited in a muffle furnace for one hour at 280°C. to remove "bound water". The latter temperature was measured by a thermometer. The data secured over this catalyst are in table 1.

Catalyst B. A pure cobalt catalyst supported on asbestos

This catalyst was prepared exactly as catalyst A, except that before mixing the solutions the asbestos was thoroughly saturated with sodium hydroxide. The data for the catalyst are shown in table 2. This yield shows that the yield of a supported catalyst is comparable to one non-supported.

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[1] Presented before the Division of Inorganic and Physical Chemistry at the Ninety-third Meeting of the American Chemical Society, Chapel Hill, North Carolina, April 14, 1937.

Catalyst C. A cobalt-manganese catalyst

The preparation followed the plan given by M. Salinger (3) for making cobalt permanganate by use of cobalt nitrate, potassium permanganate, and an excess of hydrogen peroxide in the presence of some sodium carbonate to reduce acidity. The material was dried at 105°C. for twenty-four hours and ignited in the muffle furnace for two hours at 285°C. This catalyst was divided into two batches as C1 and C2. Data from this catalyst are in table 3, one case showing the effect of making the second temperature used higher than the first and the other showing the effect of making the second temperature lower than the first.

TABLE 1

The effect of temperature on the activity of a pure cobalt catalyst

Weight of catalyst A, 6.5 g.; temperature of reduction, 215°C.; rate of flow of hydrogen, 10 liters per hour; rate of flow of nitrobenzene, 2.3745 g. per hour

TEMPERATURE	YIELD OF ANILINE IN PER CENT OF THEORY
°C.	*per cent*
215	36.2*
260	5.0
250	
243	24.4
243	27.7†
235	32.2†

* All figures represent rough averages, since excellent checks for low yields are not common.

† The nitrobenzene rate was 4.7509 g. per hour.

TABLE 2

The activity of a cobalt catalyst supported on asbestos

Weight of catalyst B, 5.5 g., including the support; temperature of reduction of oxide, 252°C.; rate of flow of hydrogen, 10 liters per hour; rate of nitrobenzene flow, 4.7508 g. per hour

TEMPERATURE	YIELD OF ANILINE IN PER CENT OF THEORY
°C.	*per cent*
252	8.05

These data show the great sensitivity of cobalt-bearing catalysts to small temperature changes. The usual rule seems to be that after a catalyst has operated at a lower temperature it will suffer a severe hysteresis effect, so that it will not give good yields later. Notice the effect of operating at 223°C. in the case of catalyst C1.

Catalyst D. A cobalt-manganese catalyst prepared like catalyst C and supported on purified asbestos

The data with this catalyst were taken over a wide range of temperatures, all of which gave reasonably good yields except one at 235°C. (See table 4.) All of the factors, exclusive of temperature, were the same as those given in table 3. Attention should be given to the fact that, for some reason that is not yet known, a good yield was obtained at 268°C. following the trial at 235°C.

TABLE 3

The effect of temperature on the aniline yield over a cobalt-manganese catalyst

Temperature of reduction, 260°C.; weight of catalyst C1 and C2, 5.25 g.; rate of flow of nitrobenzene, 2.3754 g. per hour; rate of flow of hydrogen, 10 liters per hour

CATALYST	TEMPERATURE	YIELD OF ANILINE IN PER CENT OF THEORY
	°C.	*per cent*
C1	260	86.9
	223	36.9
	250	54.8
	272	44.5
	290	16.2
	325	
C2	260	99.2
	268	93.6
	255	88.8
	262	87.9

TABLE 4

The effect of temperature on the aniline yield over catalyst D

TEMPERATURE	YIELD OF ANILINE IN PER CENT OF THEORY	TEMPERATURE	YIELD OF ANILINE IN PER CENT OF THEORY
°C.	*per cent*	*°C.*	*per cent*
260	55.6	270	78.9
250	70.3	288	77.4
245	86.9	255	85.7
242	88.2	252	73.3
235	16.2	265	72.8
268	93.4	270	73.3

Catalyst E. A cobalt-molybdenum catalyst

The catalyst used in this case was secured by means of cobalt molybdate made by the method given by Markwald (2). Equivalent quantities of cobalt nitrate and sodium molybdate were mixed in solution. The purple to lavender colored precipitate was collected, filtered, washed, dried twenty-four hours at 105°C., and heated in a muffle furnace for two hours at 330°C. Data are shown in table 5. The outstanding feature of these data indicates that such a combination has to operate at a temperature higher than that of most such catalysts.

TABLE 5

To show the nature of a mixed cobalt-molybdenum catalyst

Weight of catalyst E, 7 g.; catalyst reduced at 255°C., oxidized with air, and reduced again at 260°C.; rate of flow of hydrogen, 10 liters per hour; rate of flow of nitrobenzene, 4.7509 g. per hour

TEMPERATURE	YIELD OF ANILINE IN PER CENT OF THEORY
°C.	*per cent*
260	
290	7.6
312	23.1
320	89.3
332	85.4
310	82.9

TABLE 6

Summary for cobalt-chromium catalysts

COMPOSITION IN MOLE PER CENT OF COBALT AND CHROMIUM	TEMPERATURE OF IGNITION	TEMPERATURE OF REDUCTION	WEIGHT OF CATALYST	RATE OF FLOW OF HYDROGEN	RATE OF FLOW OF NITROBENZENE	TEMPERATURE OF OPERATION	PER CENT YIELD OF ANILINE
	°C.	*°C.*	*grams*	*liters per hour*	*grams per hour*	*°C.*	*per cent*
50:50	300	260	6	10	4.7508	270	89.4
						280	64.3
98:2	320	262	8	10	4.7508	264	74.4
						281	79.0
98.5:1.5	310	265	7	10	4.7508	280	63.4 (average of several)
99.0:1.0	300	265	6.5	10	4.7508	265	25.0 (average)

Catalyst F. Cobalt-chromium mixtures

Three cobalt–chromium bearing catalysts were prepared from solutions of cobalt nitrate and sodium chromate. They were prepared so that they contained cobalt and chromium in the following molecular ratios: 50:50, 98:2, 98.5:1.5, and 99:1. The general treatments of washing, drying, etc. were similar to those previously given. A summary of results is shown in table 6. In many ways these data are interesting and instructive. In the first place it appears possible that an optimum composition might be found that would be an excellent catalyst. It is also to be noted that the used catalyst is green, indicating oxidation to an oxide. Furthermore the catalyst seems to get less effective on successive runs. Finally, the results over these chromium-containing catalysts present a contrast with certain others that contain chromium, e.g., those used in methanol production. Excellent hydrogenation is secured by the latter, whereas the cobalt-chromium oxide catalysts tried were not satisfactory for the reduction to aniline.

SUMMARY

1. Cobalt is too active to hydrogenate nitrobenzene to aniline.

2. A cobalt-manganese mixture, while very sensitive to temperature, will give excellent aniline yields.

3. Cobalt molybdate, operating at a much higher temperature, is fairly efficient.

4. Various proportions of cobalt and chromium were studied, none of which was an excellent catalyst.

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THE RATE OF REACTION OF AMALGAMS WITH ACIDS. I

LITHIUM AMALGAMS[1]

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Received July 6, 1937

In a study of the rate of solution of magnesium in acids (4) evidence for the general kinetic equation for this reaction

$$v = k_1C_{H_2O} + k_2C_{H_3O^+} + k_3C_A \ldots\ldots \text{ etc.} \tag{1}$$

where A represents an acid other than hydrogen ion (H_3O^+) was presented. Whether the measured rates are controlled by diffusion or by the chemical process the logical interpretation of the results is from the point of view of the extended theory of acids. Preliminary experiments with alkali metal amalgams (3) partially confirmed equation 1, and the work of Brönsted and Kane (1) with dilute sodium amalgams offered evidence that the dissolution of sodium amalgam is due to the reaction of the metal with the acid molecule. Brönsted and Kane worked with dilute amalgams and an excess of weak acid. They found that sodium as amalgam dissolved with a velocity which was directly proportional to the square root of the sodium concentration in the amalgam.

Most of the work described in the literature has been concerned with sodium or potassium amalgams. Lithium amalgam was chosen in the hope that the study could be extended to non-aqueous solutions.

EXPERIMENTAL PROCEDURE

A. Preparation of amalgams

The lithium amalgams used in this work were prepared by the electrolysis of lithium hydroxide solutions, using a platinum anode and a mercury cathode.

All mercury used was purified by running it five times through a four-foot column of dilute nitric acid. In the first part of the work the mercury

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[1] This article is abstracted from the dissertation of Frank A. Fletcher, which was presented to the Faculty of the Graduate School of the University of Pennsylvania in partial fulfillment of the requirements for the degree of Doctor of Philosophy, December 1, 1935.

was next treated by the method of Brummer and St. von Náray-Szabó (2), which consisted in oxidizing the impurities in the mercury anodically in a slowly rotating anode. This anode is dipped into a solution of mercurous nitrate and nitric acid. The cathode consists of mercury. The next step in the purification was the washing, drying, and distillation of the metal under vacuum. It was found unnecessary to use the method of Brummer and St. von Náray-Szabó, and consequently that part of the procedure was omitted. No difference was noted between amalgams made with the mercury treated by their method and then distilled and those made with mercury which was distilled only.

The amalgam, itself, was prepared by the electrolysis of lithium hydroxide solution, using a platinum anode and a mercury cathode. The apparatus consisted of four main parts: the electrolysis chamber, A; the drying chamber, H; the filtration system, L; and the receiver, M.

The electrolysis chamber consisted of a glass tube, 4 cm. inside diameter and 21 cm. long. One end was closed by a large rubber stopper (with holes for electrodes and stirrer), and the other end by a stopcock B. The cathode leads C consisted of copper wires soldered to platinum wires, which were sealed into glass tubing making connection with the mercury D. The anode, E, consisted of a piece of platinum sheet 2.5 cm. by 2.5 cm. The stirrer, F, consisted of a small glass rod immersed in the mercury and used for stirring the amalgam.

After filling the electrolysis chamber about half full of mercury, the two sealed electrodes were immersed, the chamber was filled with approximately 5 molar lithium hydroxide solution, and the electrical circuit was connected. Current was passed through the solution until the amalgam was judged to be of the proper strength (not greater than about 1 molar to remain fluid).

During the electrolysis a large amount of oxygen was evolved at the anode and a considerable amount of hydrogen was evolved at the mercury surface. It was found necessary to stir the mercury occasionally to distribute the amalgam. There was a tendency to crust formation on the mercury surface, which is presumably due to formation of some solid amalgam. After the electrolysis about one-half of the amalgam was run into some previously purified mercury already in the drying chamber.

The drying chamber, H, consisted of a tube 4 cm. in diameter and 12 cm. long. It was closed at both ends by stopcocks, G and B. A capillary T-tube was sealed to the drying chamber at K. This T-tube had two stopcocks sealed to it for admission of nitrogen and for connection to the vacuum line. The advantage of dropping the amalgam into mercury was (*1*) that it helped to cool the amalgam, and (*2*) that it helped to dilute the amalgam. Since the current efficiency of the electrolysis could not be known with accuracy, it was largely a matter of experience to determine the length of time needed to prepare a batch of amalgam. If the electrolysis was continued for too long a time, the amalgam would turn pasty on cooling in the drying chamber, unless it was mixed with fresh mercury. Before being used, the drying chamber was carefully cleaned, dried, and filled with dry nitrogen gas. As soon as all of the amalgam had been run into the drying chamber, the vacuum line was attached to the proper stopcock and small amounts of moisture sucked out.

After drying, the amalgam was admitted to the filtration chamber, L, which consisted of a small Jena tube containing a sintered glass plate.

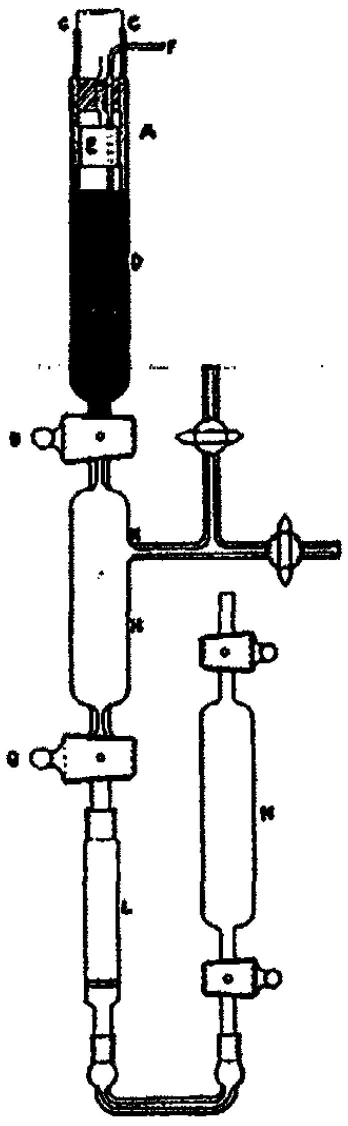

Fig. 1

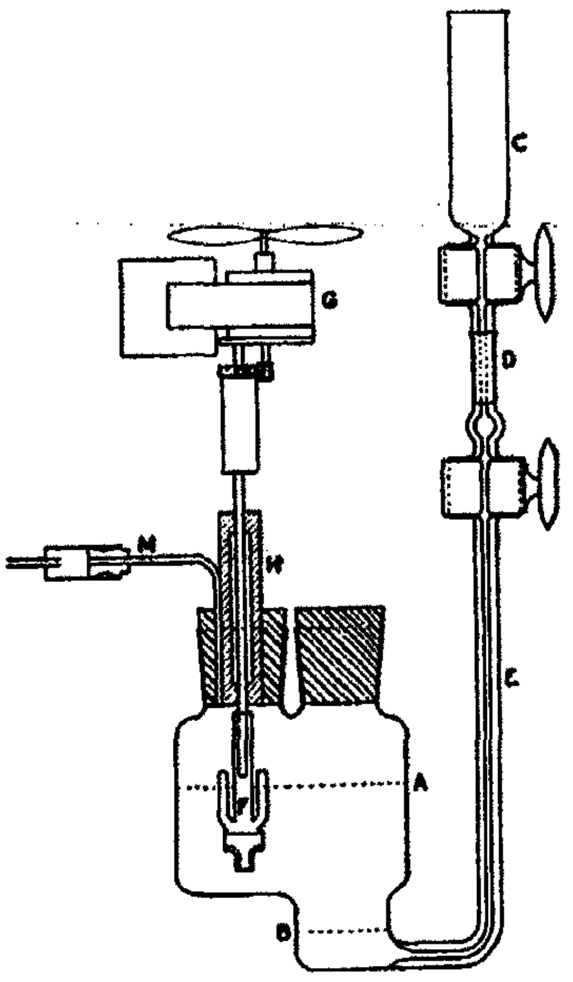

Fig. 2

Fig. 1. Apparatus for preparing amalgam
Fig. 2. Reaction vessel

The tube was attached to the drying chamber by means of a ground-glass joint, and to the U-tube below it by similar means.

This U-tube was joined to a 125-cc. Pyrex gas pipet by means of a third ground-glass joint. The end of the pipet, M, was ground to fit the joint in this apparatus. A joint in a similar U-tube (with a stopcock at one end) was used for transferring the amalgam from the reservoir to the funnel in the reaction vessel as needed.

When a vacuum was applied at the top of the pipet, the amalgam was sucked out through the filtering chamber, through the U-tube into the gas pipet. If the amalgam was too concentrated in any case, crystals collected on the filter plate and filtration ceased.

B. Reaction apparatus

The reaction apparatus consisted of a solution chamber, A, of about 250-cc. capacity, sealed to an amalgam chamber, B, of about 20-cc. capacity. Amalgam was delivered to the amalgam chamber by the funnel, C, through the ground-glass joint, D, and capillary tube, E, approximately 15 cm. long. The solution was stirred by means of a stirrer, F, operated in most of the experiments by a synchronous motor, G, through a mercury-sealed shaft, H, of the type shown in detail by Kilpatrick and Rushton (4). The hydrogen was conducted from the apparatus by means of tube M to the gas collection apparatus, consisting of two 100-cc. water-jacketed gas burets and a leveling tube.

In a study of the water reaction of lithium amalgam the hydrogen was not collected. An indicator was added to the water and acid added from a microburet as fast as lithium hydroxide was formed in solution, as described by Kilpatrick and Rushton (4).

C. Details of procedure

Experiments for the measurement of the acid reaction rate constant were carried out as follows: A known volume (usually 150 cc.) of acid or buffer was added by pipet to the reaction apparatus. Dry nitrogen gas was bubbled through the apparatus to remove oxygen partially. Then the gas collection apparatus was connected to the system, amalgam run from the funnel, C, into the amalgam reservoir, B, the synchronous motor started, and the gas measurements made each minute. The gas temperature was taken as that of the water in the jacket about the gas burets. The barometric pressure was noted. After the reaction was completed, the solution in the reaction vessel was analyzed for acidic or basic content, and the mercury was weighed. By calculating the volume of hydrogen equivalent to the acid used, and subtracting from this the individual readings, a series of figures was obtained which were proportional to the acid concentration. If the logarithm of this series was plotted against time and the slope of the resultant line calculated, it was possible to determine the reaction rate constant for the acid in question.

In the case of the water reactions, the procedure was somewhat similar. The quantity of standard acid added at any time was equivalent to the lithium in the amalgam which reacted. The concentration of the lithium in the amalgam was then equivalent to the difference between the original lithium in the amalgam and the lithium that had reacted. Following Brönsted and Kane, we found that the rate constant could be calculated from the square-root equation. A synchronous motor was used only in the acid rate experiments. A direct current, rheostat-controlled motor was used in the water reaction experiments. The speed was kept as constant as possible by observing a tachometer connected to the motor and adjusting the rheostat accordingly.

EXPERIMENTAL RESULTS

Hydrochloric acid reactions

Hydrochloric acid solutions were used in the measurement of the reaction rate of H_3O^+ with lithium amalgam. In such a reaction the rate is equal to that of the water reaction plus that for the H_3O^+ reaction, since both processes go on simultaneously. In experiments with acids it was necessary to operate within a narrow concentration range to avoid, first, the experimental difficulty of too fast a reaction if the acid concentration chosen was too high (above 0.045 M), and second, the difficulty of determining the reaction velocity constant from the data if the acid concentration chosen was too low (less than 0.015 M), owing to the fact that the water reaction rate became an appreciable portion of the whole rate, and owing to the presence of an induction period. The equation used to calculate the velocity constant of the acid reactions is:

$$k = \frac{2.303\,V}{St} \log \frac{a}{a - x} \tag{2}$$

where k is the reaction velocity constant, V is the volume of acid solution in cm.³, S is the area of the mercury surface in cm.², t is the time in minutes, a is the initial acid concentration in moles per liter, and $(a - x)$ is the acid concentration at time t. The units for k in the above equation are cm. $\times$ minutes^{-1}. All values of k for hydrochloric acid, perchloric acid, formic acid, cyanoacetic acid, and acetic acid reactions are so expressed. If $\log (a - x)$ is plotted against the time, the slope of the line is equal to $\frac{-kS}{2.303V}$.

Table 1 gives the results with the hydrochloric and perchloric acids. From this table it is evident that the rate of reaction is independent of the concentration of the lithium in mercury and proportional to the acid concentration. The slightly higher values of the velocity constant at higher concentration may be attributed to the higher concentration of salt in the aqueous solution. The velocity constants for the perchloric acid solutions are somewhat less than those for the hydrochloric acid. An unusually high velocity constant was found in two experiments. Both of these results were obtained after cleaning the apparatus with hot chromic acid. This treatment was followed by rinsing ten times with water. One explanation is that chromic acid or some component of the cleaning solution is strongly absorbed on the glass surface and that the presence of this material or an activation at the glass-mercury interface causes a more rapid reaction.

The effect of temperature on the rate of reaction is given in table 2. The effect of temperature is small.

The effect of stirring is shown in table 3. The effect of stirring at a liquid-liquid interface when the reaction is followed by gas evolution is a difficult problem. In the first place the aqueous solution must be sufficiently agitated to prevent supersaturation in that phase. On the other hand, the stirring should not change the surface at the interface. In

TABLE 1

Reaction of lithium amalgam with the acid H_3O^+

Surface, 9.63 cm.^{2}; R.P.M., 975; volume, 150 cc.; temperature, 25°C.

ACID	INITIAL CONCENTRATION OF ACID	INITIAL CONCENTRATION OF AMALGAM	VELOCITY CONSTANT k	REMARKS
	moles per liter	*moles per liter*		
HCl	0.0195	0.39	1.09	Average of 2 experiments
	0.0249	0.39	1.07	Average of 7 experiments
	0.0327	0.39	0.98	Average of 4 experiments
	0.0326	0.68	1.24	Average of 2 experiments
	0.0332	0.41	1.06	0.10 *M* LiCl
$HClO_4$	0.0240	0.41	0.97	Average of 4 experiments
	0.0355	0.41	0.90	Average of 2 experiments
	0.0340	0.77	1.14	0.26 *M* $LiClO_4$
	0.0444	0.77	1.04	
	0.0444	0.41	0.94	Average of 3 experiments

TABLE 2

Variation of k with temperature

Surface, 9.63 cm.^{2}; R.P.M., 975; volume, 150 cc.

TEMPERATURE	HYDROCHLORIC ACID	AMALGAM	k	REMARKS
°C.	*moles per liter*	*moles per liter*		
20	0.0249	0.39	0.90	Average of 2 experiments
25	0.0249	0.39	1.07	Average of 7 experiments
30	0.253	0.39	1.30	Average of 3 experiments

TABLE 3

Effect of stirring speed on velocity constant

Surface, 9.63 cm.^{2}; volume, 150 cc.; temperature, 25°C.

R. P. M.	HYDROCHLORIC ACID	AMALGAM	k
	moles per liter		
520	0.0253	0.39	0.89
975	0.0249	0.39	1.07
2450	0.0253	0.39	2.10

addition, the stirring is dependent on the shape of the vessel and the position of the stirrer.

Reactions with weak acids

For this portion of our study we used acetic acid, formic acid, cyanoacetic acid, and *o*-chlorophenol. Buffer solutions prepared from stock solutions of lithium hydroxide and the acid were used. It will be shown in the next section that the presence of sodium or potassium salt in the buffer solution introduces that element into the amalgam in place of some of the lithium. This seems to have been overlooked by others (1). In all cases preliminary experiments were carried out to see that the volume of gas evolved corresponded to the amount of lithium that reacted. The amount of metal that reacted was calculated from the weight of the amalgam taken and the analysis of the amalgam. We were not able to use a buffer of chloroacetic acid, since either the acid or its anion was reduced. In the case of all weak acids except the *o*-chlorophenol the experimental procedure and method of calculation of the velocity constants were the same as for the experiments with the strong acids.

On examination of table 4 it will be noted that the concentration range is rather limited. This is due to the fact that the reaction is too rapid to measure above the initial concentration indicated, if lithium amalgam is used.

The velocity constants are practically the same in the cases of the three acids used. It is evident that diffusion in the aqueous solution may be the controlling process. Since we have reduced the hydrogen-ion concentration to a very low value, the important diffusion processes in the aqueous solution are the diffusion of the acid molecule to the interface and the movement of the reaction products from the surface.

Experiments with o-chlorophenol

In this case we found that the rate was proportional to the square root of the lithium concentration in the amalgam. The rate constants were calculated from the equation:

$$Sk = \frac{2(\sqrt{C_m^0} - \sqrt{C_m})}{t} \qquad (3)$$

where C_m^0 and C_m are the molar concentrations of the lithium in the amalgam at the beginning of the reaction and at time t, respectively. Time is expressed in minutes. No reduction of the *o*-chlorophenol was found.

The velocity constant k also includes the water reaction. It is, however, about three or four times greater than the constant for the water reaction, which, as shown in the next section, also follows the square-root law. Our

TABLE 4

Reaction of lithium amalgam with weak acids

Surface, 9.63 cm.^{2}; R.P.M., 975; volume, 150 cc.; temperature, 25°C.; initial amalgam concentration, 0.41 molar

ACID	INITIAL CONCENTRATION OF ACID	INITIAL ANION CONCENTRATION	k
	moles per liter	*moles per liter*	
Acetic acid	0.0657	0.0657	0.575
	0.0473	0.0473	0.517
	0.0394	0.0394	0.508
	0.0394*	0.0400	0.488
	0.0329	0.0329	0.575
	0.0295†	0.0300	0.550
	0.0262	0.0262	0.473
			Av. = 0.523
Formic acid	0.0488	0.0488	0.565
	0.0390	0.0390	0.557
	0.0325	0.0325	0.545
	0.0325	0.0325	0.560
	0.0293	0.0293	0.564
			Av. = 0.558
Cyanoacetic acid	0.0305	0.0953	0.540
	0.0305	0.0953	0.541
	0.0305	0.0953	0.547
	0.0305	0.0953	0.549
	0.0305	0.0953	0.549
	0.0283	0.0953	0.630
	0.0283	0.0953	0.616
			Av. = 0.567

* Also 0.01 molar in LiCl.

† Also 0.02 molar in LiCl.

TABLE 5

Experiments with o-chlorophenol

Surface, 9.63 cm.^{2}; R.P.M., 975; volume, 150 cc.; temperature, 25°C.; initial amalgam concentration, 0.41 molar

INITIAL CONCENTRATION OF ACID	INITIAL ANION CONCENTRATION	$k \times 10^3$
moles per liter	*moles per liter*	
0.1164	0.1	4.14
0.145	0.1	5.14
0.1129	0.1	4.42
0.1129	0.1	4.43
0.1129	0.1	4.54
Average		4.53

results indicate that for stronger acids the reaction follows the monomolecular law and that for very weak acids and water the square-root law is obeyed. It may be that between these two limits there will be some acid where a combination of the two laws must be taken into account.

The water reaction

Equation 1 contains a term to take the water reaction into account. In order to determine the order of magnitude of this reaction, we carried out a large number of experiments involving the rate of reaction of lithium amalgam with water and with certain salt solutions.

The procedure was as follows: Water (or salt solution) and an indicator were added to the reaction vessel. A 5-cc. microburet, containing standard hydrochloric acid, was arranged over the vessel, and amalgam was admitted. The vessel was open to the air. As the reaction took place, the standard acid was added at a rate great enough to keep the hydrogen-ion concentration approximately constant. Time and buret readings were recorded. This is the method used by Kilpatrick and Rushton (4).

TABLE 6

Effect of hydrogen-ion concentration

R.P.M. = 900

INDICATOR	HYDROGEN-ION CONCENTRATION	$k_w \times 10^4$
	moles per liter	
Thymol blue	4×10^{-10}	0.54
Phenolphthalein	1×10^{-9}	0.93
Bromothymol blue	1×10^{-7}	0.89
Methyl red	1×10^{-6}	1.36
Bromocresol green	2×10^{-5}	0.69
Bromophenol blue	1×10^{-4}	1.27

Our results, given in table 6, confirm the results of Brönsted and Kane (1) that the rate of dissolution of an amalgam is proportional to the square root of the amalgam concentration. All of the above values of k were calculated by equation 3. The concentration units are moles per liter and the time unit is the minute. All constants are based on an interfacial area of 1 cm.^{2}

The results indicate that the velocity constant is independent of the hydrogen-ion concentration between 1×10^{-4} and 1×10^{-10}, although the experiments are not very reproducible. The effect of temperature between 16°C. and 26°C. on these experiments was within the experimental error. The result for each indicator in the table is the average of a large number of measurements.

A number of interesting experiments were carried out using salt solutions in place of water (see table 7). All experiments were comparable with one another. When 1 molar sodium chloride was used the rate constant was much closer to that of sodium amalgam reacting with water than that of lithium amalgam. With lithium amalgam and 1 molar potassium chloride the rate was below that for lithium amalgam and water. These phenomena may be explained by assuming the reaction:

$$\text{lithium amalgam} + \text{sodium chloride} \rightleftarrows \text{sodium amalgam} + \text{lithium chloride}$$

TABLE 7

Reactions of lithium amalgam with aqueous salt solutions

Surface, 9.63 cm.²; volume, 150 cc.; R.P.M., 900; T, 25°C.

SALT USED	MOLAR CONCENTRATION OF SALT	MOLAR CONCENTRATION OF AMALGAM	$k \times 10^3$
NaCl	1.0	0.391	0.28
NaCl	2.0	0.391	0.18
NaCl	0.5	0.391	0.29
LiCl	1.0	0.391	2.81
KCl	1.0	0.391	0.69
NH_4Cl	1.0	0.391	1.76
$MgCl_2$	0.33	0.391	4.19
NaCl	1.0	0.047	0.50
$SrCl_2$	0.33	0.047	0.33
$BaCl_2$	0.33	0.047	0.34
KCl	1.0	0.047	0.42
$CaCl_2$	0.33	0.047	1.04
$MgCl_2$	0.33	0.047	1.65
$CaCl_2$	1.0	0.0235	1.19
$BaCl_2$	0.33	0.0235	0.75
$SrCl_2$	0.33	0.0235	0.56
KCl	1.0	0.0235	0.66
$CaCl_2$	0.33	0.0235	1.18
NaCl	1.0	0.0235	0.67
LiCl	1.0	0.0235	2.73

This reaction may not be complete, but our results indicate that it takes place to a considerable extent. It must also be a rather rapid reaction. It is of interest to know that the constant for the reaction with magnesium chloride was about twice that of the water reaction. These results are in accord with the work of Smith (7). Lewis and Macdonald also noticed the rapid displacement of lithium in the amalgam by sodium (5).

The lack of reproducibility of these experiments may be due in part to the formation of hydrogen peroxide by the reduction of oxygen. To show the effect of hydrogen peroxide on the reaction a few experiments were carried out in dilute hydrogen peroxide solutions. The results are given in table 8.

One interpretation of these results is that the reaction of lithium with water is increased by the presence of an oxidizing agent, due to the removal of a hydrogen film. If this alone were the case, an excess of hydrogen peroxide should not show such an increase in the velocity constant. This process seems to involve an additional reaction, the capture of electrons by the oxidizing agent (6). If we make the assumption that oxygen reacts with lithium amalgam with a velocity constant comparable to that attributable to hydrogen peroxide, we might expect a 10 per cent increase in the water reaction constant due to the presence of oxygen. The lack of reproducibility of the water reaction cannot be attributed to the reaction with oxygen, as experiments (1) have shown the same lack of reproducibility in cases when the oxygen concentration would certainly be small. This problem will be discussed further in a later paper.

Returning to our equation 1 and considering a reaction with (*1*) H_2O, (*2*) H_3O^+, (*3*) HA, a fairly weak acid, and (*4*) a very weak acid, we would have for the total rate of formation of Li^+ ion in the aqueous solution, $\frac{dx}{dt}$, in gram-ions formed per minute:

TABLE 8

Effect of hydrogen peroxide on the reaction

Hydrogen-ion concentration, 1×10^{-9}; initial amalgam concentration, 0.15; R.P.M., 1000; temperature, 25°C.

INITIAL CONCENTRATION OF H_2O_2 IN MOLES PER LITER	10^3k	$\frac{10^3(k-k_w)}{C_{H_2O_2}}$
0	0.81	
0.026	1.38	21
0.052	2.72	37
0.072	4.25	48

For the water reaction:

$$\frac{dx_0}{dt} = \frac{k_w \bar{V} S}{1000} \sqrt{C_m}$$

where $\bar{V}$ is the volume of amalgam in cubic centimeters.

For the hydrogen-ion reaction:

$$\frac{dx_1}{dt} = k_1 S C_A = k_{H_3O^+} S C_{H_3O^+}$$

For HA

$$\frac{dx_2}{dt} = k_2 S C_A = k_{HA} S C_{HA}$$

For HB

$$\frac{dx_3}{dt} = \frac{\bar{V} S}{1000} k_3 C_A \sqrt{C_m} = \frac{\bar{V} S}{1000} k_{HB} C_{HB} \sqrt{C_m}$$

whence

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{\mathrm{d}(x_0 + x_1 + x_2 + x_3)}{\mathrm{d}t} = \frac{VS}{1000}(k_w + k_{\mathrm{HB}}C_{\mathrm{HB}})\sqrt{C_m}$$

$$+ S(k_{\mathrm{H_3O^+}}C_{\mathrm{H_3O^+}} + k_{\mathrm{HA}}C_{\mathrm{HA}}) \quad (4)$$

From the data

$$k_w = 1.19 \times 10^{-3} \qquad k_{\mathrm{H_3O^+}} = 1.07 \times 10^{-3}$$

$$k_{\mathrm{CH_3COOH}} = 0.52 \times 10^{-3} \qquad k_{\mathrm{CH_2CNCOOH}} = 0.57 \times 10^{-3}$$

$$k_{\mathrm{HCOOH}} = 0.56 \times 10^{-3} \text{ and } k_{o\text{-}\mathrm{ClC_6H_4OH}} = 0.027$$

Computations from the above equation indicate that for reactions with the strong acids the water reaction comes in to as much as 20 per cent in some cases. In the case of cyanoacetic acid the H_3O^+ reaction comes in to approximately 10 per cent, while for the other acids the H_3O^+ reaction is negligible. In the case of *o*-chlorophenol the water reaction comes in to 30 per cent but can be directly subtracted from the overall *k*, as both rates are proportional to the square root of the lithium concentration. Equation 4 gives the complete equation corresponding to equation 1. The case of amalgams is considerably more complicated than that of magnesium dissolving in acids. A further discussion of the results will be given in a paper presenting the data on sodium amalgams.

SUMMARY

1. The rates of reaction of lithium amalgams with aqueous solutions of strong and weak acids have been measured.
2. A general rate equation has been derived which expresses the rate of reaction in various buffer solutions.
3. The rate of reaction of lithium amalgams with water is proportional to the square root of the lithium concentration. This rate law also applies to the reaction with *o*-chlorophenol.
4. For the other acids studied the rate is independent of the lithium concentration.
5. An explanation has been offered for the rate of reaction of amalgams with salt solutions.

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THE CODEPOSITION OF METALS OF UNLIKE VALENCE IN ACID SOLUTIONS

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INTRODUCTION

The codeposition of metals in which the two metals plating were of different valence has been investigated. The following systems were included: lead–thallium, silver–copper, nickel–thallium, zinc–thallium, and copper–thallium. The cathode potential method previously described (3) was employed at different current densities at room temperature, in solutions of pH 5. The variation of codeposition with the valence of the metals involved has been determined. From the data obtained a general empirical equation has been derived for such codeposition where mono- and bi-valent metals are involved. It is shown that the valence of the metals has an effect on codeposition not taken into account by the equivalent weights of the two metals plating. Glasstone (2) has made a somewhat similar study on the cathode potential of alloys of zinc, nickel, chromium, and iron. This work will be treated in a separate paper to appear shortly.

EXPERIMENTAL

The variation of the limit of codeposition with the current density was determined for the systems copper–thallium, lead–thallium, silver–copper, and nickel–thallium by the method previously described (3). The system zinc–thallium has already been reported upon (3). The nitrates of the metals were used in solutions of a pH of 5 at room temperature. The data obtained are given in table 1 and are shown graphically in figures 1 to 4, inclusive.

In the figures the cathode potential is plotted against the per cent of the cation having the lower cathode potential in solution. An approximate value of the limit of codeposition may be obtained by selecting the final point of inflection in the composition–E.M.F. curve. This point may

TABLE 1

Data obtained upon codeposition of metals of unlike valence

SYSTEM	2.4 MILLIAMP. PER CM.^{2}		4.4 MILLIAMP. PER CM.^{2}		7.0 MILLIAMP. PER CM.^{2}		10.2 MILLIAMP. PER CM.^{2}	
	Cathode potential	Per cent Cu	Cathode potential	Per cent Cu	Cathode potential	Per cent Cu	Cathode potential	Per cent Cu
Thallium-copper (figure 1)..........	0.656	0.00	0.671	0.00	0.698	0.00	0.714	0.00
	0.648	0.42	0.658	0.63	0.677	0.63	0.667	1.27
	0.645	0.63	0.644	0.85	0.664	0.85	0.383	1.69
	0.356	0.85	0.255	1.27	0.627	1.27	0.245	2.53
	0.039	1.06	0.055	1.69	0.238	1.69	0.200	3.40
	0.016	1.27	0.032	2.11	0.138	2.11		
	0.015	1.69	0.021	2.53	0.102	2.53		
			0.010	3.40	0.078	3.40		

SYSTEM	2 MILLIAMP. PER CM.^{2}		4 MILLIAMP. PER CM.^{2}		8 MILLIAMP. PER CM.^{2}	
	Cathode potential	Per cent Tl	Cathode potential	Per cent Tl	Cathode potential	Per cent Tl
Nickel-thallium (figure 2)..............	0.904	0.54	0.921	0.54	0.975	0.54
	0.861	1.09	0.910	1.09	0.952	1.09
	0.774	1.62	0.868	1.62	0.925	1.62
	0.755	2.17	0.847	2.17	0.885	2.17
	0.750	2.71	0.801	2.71	0.849	2.71
	0.747	3.20	0.780	3.20	0.825	3.20
	0.718	7.18	0.760	4.21	0.801	3.74
			0.745	5.43	0.771	5.01
			0.726	7.50	0.750	6.58
			0.722	8.60	0.745	7.18

SYSTEM	1 MILLIAMP. PER CM.^{2}		2 MILLIAMP. PER CM.^{2}		3 MILLIAMP. PER CM.^{2}	
	Cathode potential	Per cent Ag	Cathode potential	Per cent Ag	Cathode potential	Per cent Ag
Copper-silver (figure 3)..............	0.063	0.00	0.058	0.00	0.040	0.00
	0.115	0.18	0.070	0.18	0.076	1.09
	0.180	0.37	0.096	0.37	0.138	1.49
	0.270	0.46	0.125	0.57	0.278	1.88
	0.305	0.57	0.210	0.77	0.323	2.55
	0.339	0.74	0.271	0.92	0.341	3.70
	0.355	0.91	0.310	1.09		
	0.375	1.29	0.326	1.29		
	0.385	2.55	0.362	1.64		
			0.382	2.55		

TABLE 1—*Concluded*

SYSTEM	1.5 MILLIAMP. PER CM.^{2}		2 MILLIAMP. PER CM.^{2}		3 MILLIAMP. PER CM.^{2}	
	Cathode potential	Per cent Pb	Cathode potential	Per cent Pb	Cathode potential	Per cent Pb
Lead-thallium (figure 4)	0.657	0.00	0.700	0.00	0.729	0.00
	0.655	0.55	0.693	1.11	0.720	1.11
	0.571	1.66	0.626	2.22	0.706	2.22
	0.485	2.77	0.535	3.32	0.680	3.32
	0.475	3.91	0.505	4.43	0.630	4.43
	0.457	11.10	0.499	5.55	0.557	5.55
			0.486	11.10	0.520	8.22
					0.513	11.10

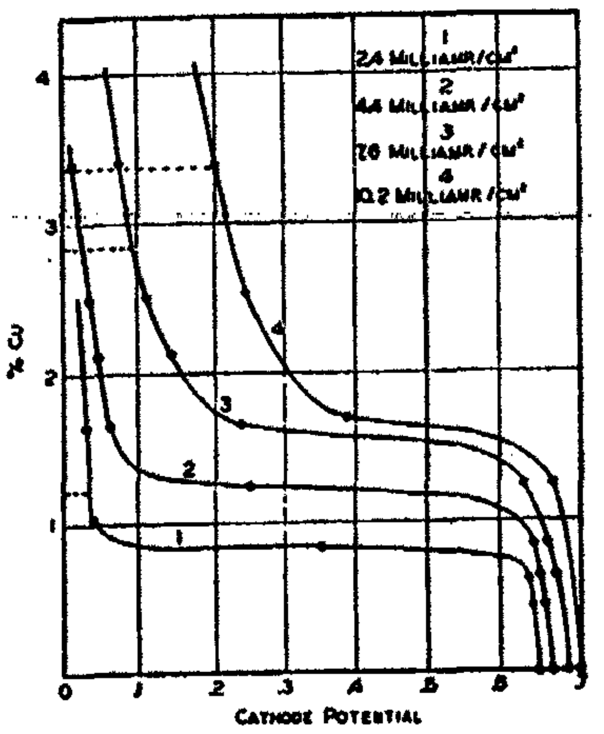

FIG. 1. The system thallium-copper

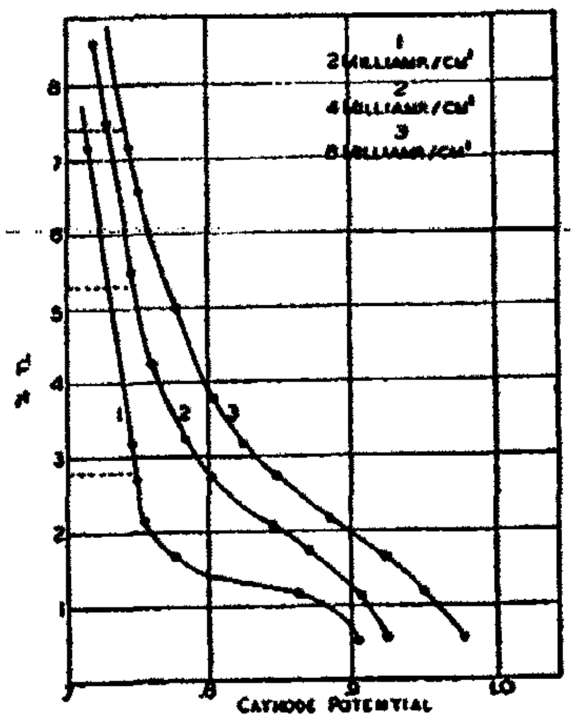

FIG. 2. The system nickel-thallium

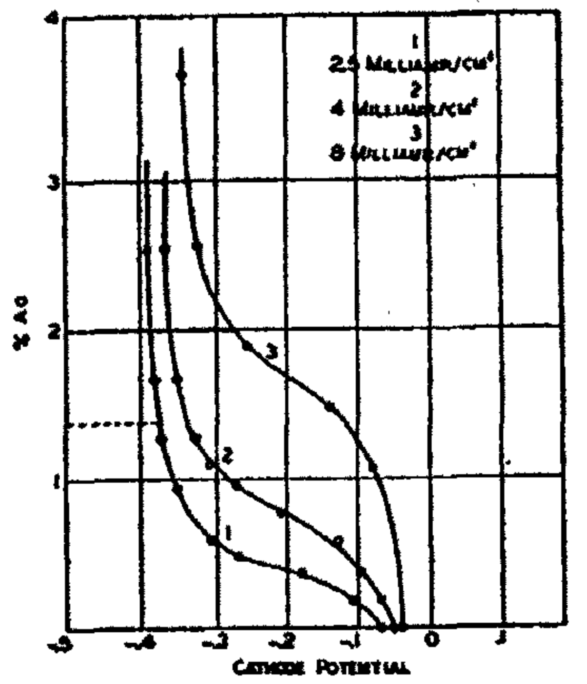

FIG. 3. The system copper-silver

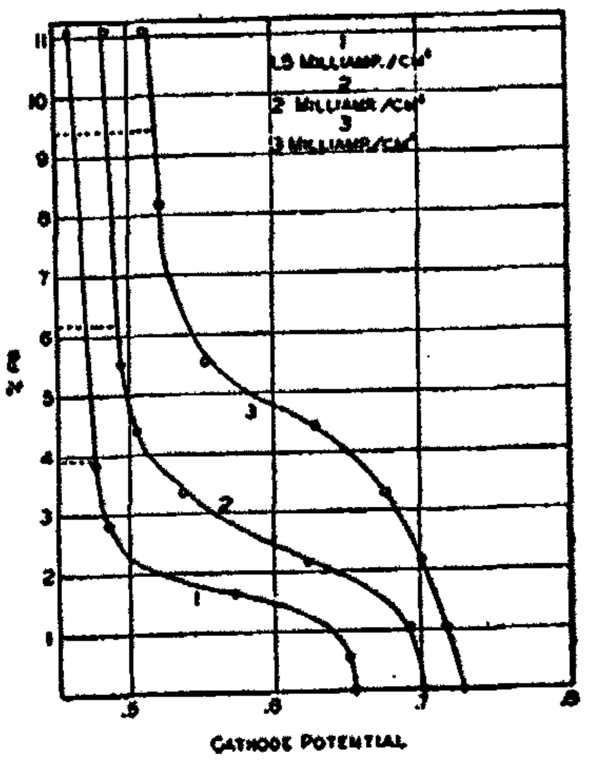

FIG. 4. The system lead-thallium

be determined by analysis or by the crystalline characteristics of the plate. All three methods were employed by the authors, depending upon which seemed best in a particular case. A difference of as large as 0.5 per cent in the value will have very little effect on the following discussion, excepting as to the values of empirical constants which might be varied a small amount. These limits of codeposition are indicated by the broken lines on the curves. As has been previously explained (4), it is nearly impossible to duplicate results involving nickel at high concentrations. This accounts for the absence of the lower portion of the curves in figure 2.

DISCUSSION

It has been pointed out by the authors that in plotting the limiting percentage composition of the solution against the logarithm of the current density, the curve will not be correct for the cases of large limit. However, if the ratio C_1/C_2 is employed, where C_1 is the concentration of the cation of lower cathode potential and C_2 the concentration of the higher, the discrepancy no longer exists. This function will give correct values in the limiting case, and also satisfy the experimental data. The letter l will be used to designate the limit expressed in this manner. In figure 5, l is plotted against the logarithm of the current density. The points fall on a straight line well within the experimental error.

If $\frac{lE_{\mathrm{H}}}{E_{\mathrm{L}}}$ is plotted against $\frac{1}{N}$ at constant current density the curves in figure 6 are obtained. E_{H} is the equivalent weight of the metal of higher cathode potential, E_{L} the equivalent weight of the metal of lower cathode potential, and N is the difference in cathode potential of the two ions involved. Curve I of figure 6 represents the values obtained for the case where the metals plating were both of the same valence. The values for l were calculated from previous data (2). Curve II shows the values obtained for the case where the cation of lower cathode potential is univalent and the cation of higher potential is bivalent. It will be noticed that nickel–thallium falls into this class. Nickel lies below thallium in the E.M.F. series. This shows in an excellent manner the shift of nickel in the series when current is passed through the reversible electrode making it irreversible (5). Curve III gives the values when the cation of lower cathode potential is bivalent and the one of higher potential is univalent. Inasmuch as all of these curves take into account the valence of the metals in the factor $E_{\mathrm{H}}/E_{\mathrm{L}}$, it is to be expected that they may be correlated by some simple function.

The curves are parabolic in form and give the following equations, where current density is expressed in milliamperes per square centimeter.

The constant in each case will be a function of the valence of the metals involved.

$$\text{I.}\qquad l = 0.0524\sqrt{\frac{1}{N}}\cdot\frac{E_L}{E_H}\log C.D.$$

$$\text{II.}\qquad l = 0.00720\sqrt{\frac{1}{N}}\cdot\frac{E_L}{E_H}\log C.D.$$

$$\text{III.}\qquad l = 0.205\sqrt{\frac{1}{N}}\cdot\frac{E_L}{E_H}\log C.D.$$

In the above equation $\frac{lE_H}{E_L}$ represents the ratio of charges carried by the cations at the limit of codeposition. If each charge was neutralized with equal facility, or if the ease of neutralization was only dependent upon the difference in cathode potential and the strength of the current density, then the ratio of the charges carried by the ions at the limit should be constant for any given difference in cathode potential at constant current density regardless of the valence of the metals involved.

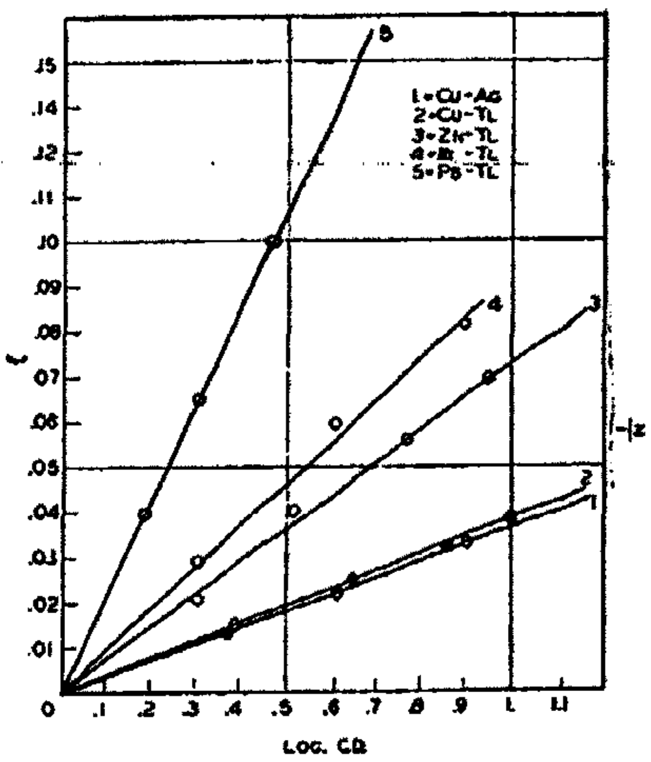

Fig. 5

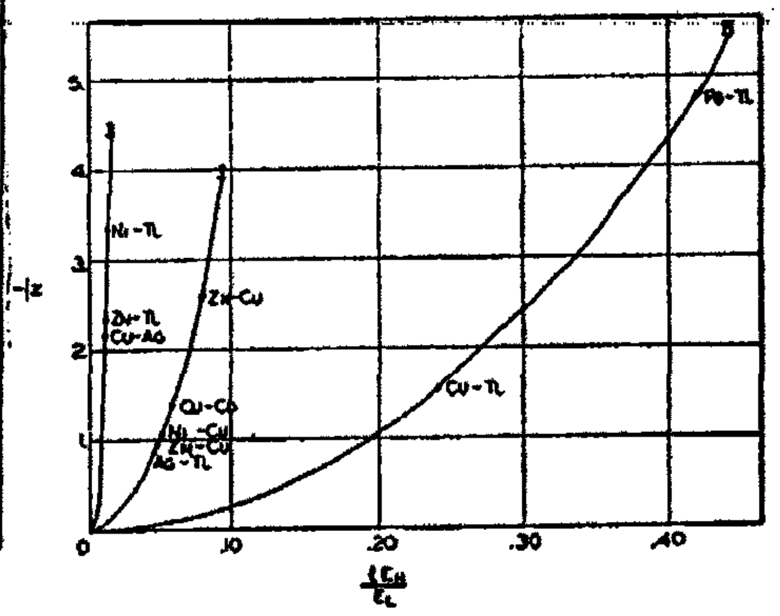

Fig.6

Fig. 5. Plot of l against the logarithm of the current density

Fig. 6. Plot of $\frac{lE_H}{E_L}$ against $\frac{1}{N}$ at constant current density

In the case where the valence of the two cations is the same

$$l\frac{E_H}{E_L} = 0.0524\sqrt{\frac{1}{N}}\log C.D. \qquad (1)$$

If we double the valence of the cation of lower cathode potential we will have Case III. The ratio of the charges will be doubled, and therefore the limit will be doubled if all the other variables are held constant. The ratio $\frac{E_H}{E_L}$ was doubled in the above operation, as E_L will be one-half its former value if its valence is doubled. With the stipulation that all variables excepting valence and limit be held constant, we must introduce a factor of 2 in order to take care of this change. We will then have,

$$l = 2 \times 0.0524 \sqrt{\frac{1}{N}} \times 2 \frac{E_L}{E_H} \log C.D. \tag{2}$$

or

$$l = 0.2046 \sqrt{\frac{1}{N}} \times \frac{E_L}{E_H} \log C.D. \tag{3}$$

This equation is in excellent agreement with the experimental data obtained.

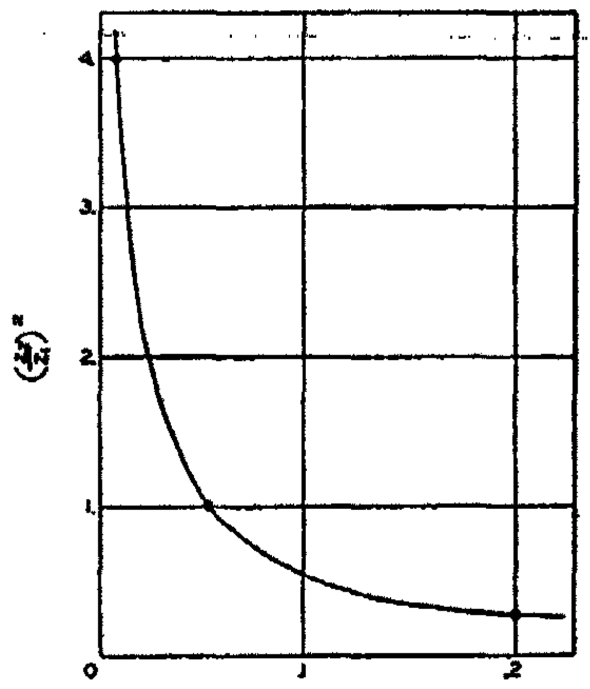

FIG. 7. Plot of $\left(\frac{Z_2}{Z_1}\right)^2$ against constant in equations I, II and III

For the second case, if we double the valence of the cation of higher cathode potential we will divide the ratio of the charges by 2. This will decrease the limit in the same proportion. Treating this case in the same manner as before, we have:

$$l = \frac{0.0524}{2} \sqrt{\frac{1}{N}} \times \frac{1}{2} \frac{E_L}{E_H} \log C.D. \tag{4}$$

or

$$l = 0.0132 \sqrt{\frac{1}{N}} \times \frac{E_L}{E_H} \log C.D. \tag{5}$$

This equation does not agree with the data, varying by a factor of approximately 2. It is most probable that the valence of the metal plating does have an effect not taken care of by the ratio of the equivalent weights. It would seem that the tendency is for two univalent ions to plate more readily than a bivalent ion. This tendency would be augmented in the last case by the fact that it was also the ion of higher cathode potential, with less tendency to plate out. Just what this discrepancy is due to is being investigated.

CONCLUSION

In order to obtain an empirical expression for the variation of the constant in equations I, II, and III, $\left(\frac{Z_2}{Z_1}\right)^2$ was plotted against the constant. Z_1 is the valence of the ion of lower cathode potential, and Z_2 is the valence of the ion of higher potential. Figure 7 shows the curve obtained. It is hyperbolic in form and fits the equation,

$$l = \frac{0.066\,Z_1^2 - 0.0087\,Z_2^2}{Z_2^2 + 0.059\,Z_1^2}\left(\sqrt{\frac{1}{N}} \times \frac{E_L}{E_H} \log C.D.\right) \tag{6}$$

where $C.\ D.$ is in milliamperes per square centimeter.

Substituting in equation 6 the following values for zinc-thallium and thallium-lead at 5 amperes per square foot,

	ZINC-THALLIUM	THALLIUM-LEAD
Z_1	1	2
Z_2	2	1
N	0.42	0.17
log $C.\ D.$	0.74	0.74
E_L	204	102.5
E_H	32.7	204

we obtain

$$l_{\text{Zn-Tl}} = \frac{0.66 \times 1 - 0.0087 \times 4}{4 + 0.059}\left(\sqrt{\frac{1}{0.42}} \times \frac{204}{327} \times 0.74\right) \tag{7}$$

from which the per cent of thallium at the limit is 5.4. Calculated in the same manner the per cent of lead at the limit is 18. The values obtained for thallium-lead by Fink and Conrad (1) and for zinc-thallium by Parks and LeBaron (3) are 19 and 5.3, respectively. The agreement is excellent and serves as a good check on the validity of the method employed to calculate these limits.

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THE SOLUBILITY AND ACTIVITY COEFFICIENT OF SILVER IODATE IN POTASSIUM NITRATE SOLUTIONS. THE STANDARD POTENTIAL OF THE SILVER-SILVER IODATE ELECTRODE

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In this study we have determined the solubility and activity coefficient of silver iodate in solutions of potassium nitrate up to an ionic strength of 1 molar, and have compared the experimental values with those calculated from the Debye-Hückel equation. We have also computed the standard potential of the silver-silver iodate electrode by combining the value obtained for the activity product of silver iodate with the standard potential of the silver electrode.

Silver iodate possesses distinct advantages, because the concentration both of the silver and of the iodate ions in the saturated solutions can be determined with an adequate degree of accuracy. In most studies of solubilities of slightly soluble salts the concentration of either the cation or the anion in the saturated solution is determined, and it is tacitly assumed that the equivalent concentration of the ion of opposite charge is equal to that of the ion which has been determined. When dealing with slightly soluble salts there are several reasons why an inequality of the concentrations of the cations and anions of the salt in the saturated solutions may be found. In the first place contamination of the slightly soluble salt by a salt having a common ion will cause such an inequality; in this case the difference between the concentration of the lattice cation and anion should increase with the amount of solid taken.

Furthermore, inequality may be caused by an exchange between lattice cations and cations in the surface of the glass container. Actually, it has been found in the present study that when the solubility of silver iodate is determined in uncoated glass containers, the concentration of the silver ions is smaller than that of the iodate. The error has been eliminated by coating the interior of the glass bottles with paraffin. Incidentally, it may be mentioned that Johnson (2) found an abnormally small value for the silver-ion concentration in a saturated solution of silver chloride in water, but in dilute nitric acid he obtained normal and reproducible values. The explanation of this abnormal behavior is that from neutral medium silver ions disappear by exchange with cations from the glass surface, whereas in acid medium hydrogen ions instead of silver ions give this exchange.

A third cause of inequality of the concentrations of lattice cation and anion in the saturated solutions in the presence of a foreign electrolyte is the possible exchange between foreign ions and lattice cations or lattice anions on the surface of the solid. A number of cases in which this type of exchange occurs have been studied in this laboratory (4). In the present study it was found that barium and thallium ions exchange with silver ions on the surface of silver iodate:

$$\underset{\text{surface}}{AgIO_3} + \underset{\text{solution}}{Tl^+} \rightleftharpoons \underset{\text{surface}}{TlIO_3} + \underset{\text{solution}}{Ag^+} \qquad (1)$$

MATERIALS

Silver iodate: This salt was prepared by rapid precipitation, using thrice-recrystallized potassium iodate and pure silver nitrate. The precipitation was carried out at room temperature from dilute solutions, the potassium iodate solution being added to a slight excess of the silver nitrate solution. The product was aged for four days in the mother solution and was then washed with twelve separate portions of conductivity water, each portion being removed by centrifuging. It was then dried in a vacuum oven for ten hours at 55°C.

Part of the original product was recrystallized from a large volume of 1 *N* nitric acid. The product consisted of relatively large crystals which were thoroughly washed and were dried over fused potassium hydroxide.

Potassium nitrate: Commercial C.P. samples of the salt were recrystallized five times from conductivity water. The mother liquor from the third recrystallization was free of chloride. The salt was dried for several hours in an oven at 150°C.

Barium, lead, and thallous nitrates: These salts were purified by several recrystallizations, and careful tests showed that they were free of chloride.

Water: Conductivity water with an average specific conductance of 1.4×10^{-6} ohms^{-1}, was used for preparing all solutions.

Solutions were prepared by weighing out the appropriate amounts of the dried salts. Carefully calibrated weights and volumetric glassware were used. Concentrations are expressed in moles per liter of solution at 25°C.

EXPERIMENTAL TECHNIQUE

The solubility determinations were carried out by rotating samples of the silver iodate with the various solutions in a water thermostat at 25.00° ±0.02°C. Brown glass bottles, coated inside with paraffin and closed with paraffined corks, were used.

The rate of solution of silver iodate was determined by placing 100 mg. of the unrecrystallized salt in 275 ml. of conductivity water in a conductance cell at 25°C. and measuring the decrease in resistance with time while the solution was stirred with purified nitrogen. It was found that the resistance dropped to within 2 per cent of its final value after only 30 min. and solubility equilibrium was reached after 60 min., even with this small amount of solid and relatively inefficient gas stirring. In the actual solubility experiments the samples were rotated for at least three hours, which was therefore an ample time.

Samples of the saturated solutions for analysis were obtained without removing the bottles from the thermostat by using a filter pipet with a plug of absorbent cotton affixed to its tip. The first portion of solution withdrawn was used to rinse the cotton filter and pipet and was then discarded.

Methods of analysis

The saturated solutions were analyzed for both silver and iodate, using 100-ml. samples.

The concentration of silver was determined by potentiometric titration with 0.001 *N* potassium iodide solution, delivered from a carefully calibrated 10-ml. microburet. This method of titration has been described elsewhere (5). The titrations were accurate to ±0.2 per cent.

The concentration of iodate was determined by iodometric titration with 0.01 *N* thiosulfate, using a calibrated microburet; the end point was readily detectable to ±0.03 ml. Thiosulfate solutions were prepared fresh each day, and were carefully standardized against dilute standard potassium iodate solutions under the same conditions as in the titrations.

Special experiments showed that the small amount of silver present in the saturated silver iodate solutions, which precipitated as silver iodide during the titrations, was entirely without influence on the accuracy (±0.3 per cent) of the iodate titrations.

INFLUENCE OF UNCOATED GLASS BOTTLES ON THE SOLUBILITY OF SILVER IODATE IN WATER

Two preliminary series of solubility determinations were carried out using plain uncoated glass bottles in one series and paraffined bottles in the other. The data obtained are given in table 1, in which the first column gives the amount of solid silver iodate used (original unrecrystallized product) and the third and fourth the silver- and iodate-ion concentrations in the saturated solutions. The observed solubility product L $(= C_{Ag^+} C_{IO_3^-})$ is given in the fifth column, and the square root of L is given in the last column.

These data show that the silver-ion concentration was about 15 per cent smaller than the iodate-ion concentration when plain glass bottles were used, whereas the concentrations were virtually equal in paraffined bottles.

It is interesting to note that the average solubility product using plain glass bottles was quite close to that using paraffined bottles, even though the individual ion concentrations were not equivalent.

TABLE 1

Influence of uncoated glass bottles on the solubility of silver iodate in water

Samples of the original unrecrystallized silver iodate rotated for at least three hours with 200 ml. of pure water at 25.00°C.

EXPT. NO.	$AgIO_3$ IN GRAMS	NO. OF DETERMINATIONS	AVERAGE CONCENTRATION IN MOLES PER LITER × 10^4		$L \times 10^8$	$\sqrt{L} \times 10^4$
			Silver	Iodate		
Plain uncoated bottles						
1......	0.05	4	1.633	1.839	3.00	1.73
2......	5.0	3	1.630	1.910	3.11	1.76
Paraffined bottles						
3......	0.1	5	1.750	1.796	3.143	1.773
4......	3.0	1	1.76	1.81	3.18	1.79
5......	0.05	1	1.76	1.80	3.17	1.78
Average of paraffined bottles............................					3.152	1.776

TABLE 2

Exchange adsorption of barium and thallous ions with silver iodate

Unrecrystallized silver iodate rotated with the solutions in paraffined bottles for three hours at 25.00°C.

EXPT. NO.	SALT	$AgIO_3$ IN GRAMS	CONCENTRATIONS IN MOLES PER LITER × 10^4		$L \times 10^8$
			Silver	Iodate	
1......	0.01 *M* $Ba(NO_3)_2$	0.05	2.11	2.14	4.52
		3.0	2.20	2.08	4.58
2......	0.01 *M* $TlNO_3$	0.05	2.00	1.98	3.96
		3.0	2.05	1.91	3.92

EXCHANGE ADSORPTION OF BARIUM AND THALLOUS IONS WITH SILVER IODATE

Experiments were carried out in which 0.05 g. and 3.0 g. of the original unrecrystallized silver iodate were rotated for three hours with 0.01 molar solutions of barium nitrate and thallous nitrate. At these concentrations the solubility products of barium and thallous iodates are not exceeded. The purpose of using the very small amount of solid was to obtain the solubility of the silver iodate in the salt solutions, since with a very small amount of solid the exchange is negligibly small. The experiments with the large amount of silver iodate show the extent of the exchange reactions. The data are given in table 2, and show that the concentrations of the silver and iodate ions were practically equal when the small amount of solid was used, but with the large amount of solid (much greater surface) the silver-ion concentrations were greater than the iodate-ion concentrations.

It is evident therefore that both barium and thallous ions exchange with silver ions on the surface of silver iodate, according to equation 1.

SOLUBILITY AND ACTIVITY COEFFICIENT OF SILVER IODATE IN POTASSIUM NITRATE SOLUTIONS

The solubility of silver iodate in potassium nitrate solutions in the concentration range from zero to 1 molar was next investigated. The recrystallized silver iodate and the paraffined bottles were used in these experiments. The data obtained are given in table 3. The square root of the solubility product is given in the fourth column, and the total ionic strength, S, in the fifth.

The relation between the activity product, K, the solubility product, L, and the ionic strength of the solutions, S, is given by

$$\log L^{1/2} = \log K^{1/2} + \frac{0.5045 S^{1/2}}{1 + 0.328 a S^{1/2}} \tag{1}$$

in which the last term is the Debye–Hückel expression for the negative logarithm of the activity coefficient, and a is the ion size parameter.

The value of K was obtained in the usual way by plotting $\log L^{1/2}$ against $S^{1/2}$, and extrapolating to zero ionic strength. The value of K found in this way was 1.744×10^{-4}, from which the value of the activity product K is $(1.744 \times 10^{-4})^2 = 3.042 \times 10^{-8}$.

The observed values of the activity coefficient, $f_{\text{obs.}}$, given in the sixth column of table 3 were computed by the relation

$$f_{\text{obs.}} = \frac{K^{1/2}}{L^{1/2}} \tag{2}$$

The values of $f_{\text{D.H.L.E.}}$ given in the seventh column were computed by the Debye–Hückel limiting expression, which at 25°C. is

$$-\log f = 0.5045 S^{1/2} \tag{3}$$

It will be observed that the activity coefficient is given accurately by the simple limiting Debye–Hückel expression up to an ionic strength of about 0.01 molar. At higher ionic strengths up to 1 molar the activity coefficient is given by the relation

$$-\log f = \frac{0.5045 S^{1/2}}{1 + 0.394 S^{1/2}} \tag{4}$$

which has been obtained from the Debye-Hückel equation by introducing the average value of a (1.2 A. U.) given in table 3. The values of a given in the last column of table 3 were obtained from $f_{\text{obs.}}$ at each ionic strength by means of the Debye-Hückel relation.

Kohlrausch (3) determined the solubility of silver iodate at a series of temperatures between 10°C. and 27°C., by the conductance method. A short interpolation of his data gives a value of 1.79×10^{-4} molar at 25°C., which is in good agreement with the value 1.771×10^{-4} molar found in the present study. Noyes and Kohr[8] found a value of 1.89×10^{-4} molar at 25°C. by a gravimetric method involving the precipitation and weighing of silver iodide. It is evident, in view of the good agreement between Kohlrausch's data and ours, that this value of Noyes and Kohr is too high, probably because of the analytical difficulties involved in their method.

TABLE 3

Solubility and activity coefficient of silver iodate in potassim nitrate solutions

Approximately 0.3 g. of recrystallized silver iodate rotated with 200 ml. of solution in paraffined bottles for at least three hours at 25.00°C.

EXPT. NO.	KNO_3 IN MOLES PER LITER	CONCENTRATIONS IN MOLES PER LITER $\times 10^4$		$\sqrt{I_s}$ $\times 10^4$	S	$f_{\text{obs.}}$	$f_{\text{D.H.L.E.}}$	a IN A.U.
		Silver	Iodate					
1....				1.744*		(1.000)	(1.000)	
2....	0	1.761†	1.780†	1.771	0.000177	0.985	0.985	
3....	0.001301	1.813	1.832	1.823	0.001483	0.957	0.957	
4....	0.003252	1.863	1.877	1.870	0.003439	0.933	0.935	
5....	0.006503	1.908	1.919	1.914	0.006694	0.911	0.910	
6....	0.01410	1.991	1.996	1.994	0.01430	0.875	0.871	0.9
7....	0.07050	2.302	2.300	2.301	0.07073	0.758	0.736	1.3
8....	0.1998	2.668	2.663	2.665	0.2001	0.654	0.598	1.5
9....	0.4995	3.345	3.284	3.314	0.4998	0.526		1.2
10....	0.9989	4.087	4.086	4.086	0.9993	0.427		1.1
Average......								1.2

* Extrapolated value.

† Average of three experiments.

From the value of K found in this study (3.04×10^{-8}) we find for the standard free energy change of the reaction

$$AgIO_3\ (S) \rightleftharpoons Ag^+\ (a = 1) + IO_3^-\ (a = 1)$$

$\Delta F^0_{298} = -2.303\ RT \log K = 10{,}250$ cal. From Kohlrausch's data we find

$$\left(\frac{\mathrm{d} \log K}{\mathrm{d}T}\right)_{298} = 0.03496\ \text{deg.}^{-1}$$

Therefore

$$\Delta H^0_{298} = 2.303\,RT^2\left(\frac{\mathrm{d}\log K}{\mathrm{d}T}\right) = 14{,}200\text{ cal.}$$

or the heat evolved in the precipitation of 1 mole of silver iodate from an infinite volume of solution in which the activities of the silver and iodate ions are both unity is + 14,200 cal. at 25°C.

Greensfelder and Latimer (1) derived from Kohlrausch's data the following values: $\Delta F^0_{298} = 10{,}233$ cal. per mole, and $\Delta H^0_{298} = 14{,}478$ cal. per mole, with which our values are in fair agreement.

THE STANDARD POTENTIAL OF THE SILVER–SILVER IODATE ELECTRODE

The relation between the standard potential of the silver–silver iodate electrode, IO_3^- (a = 1), $AgIO_3(S)/Ag$, the activity product of silver iodate, and the standard potential of the silver electrode is (7)

$$E^0_{AgIO_3} = E^0_{Ag^+,Ag} + \frac{RT}{F_v}\ln K \qquad (5)$$

Combining the value of K found in this study with the value $E^0_{Ag^+,Ag}$ = 0.7996 v., computed by Lingane and Larson (7), we find for the standard potential of the silver–silver iodate electrode, IO_3^- (a = 1), $AgIO_3(S)/Ag$

$$E^0_{AgIO_3} = 0.7996 + 0.05913 \log (3.04 \times 10^{-8}) = 0.3551\text{ v.} \qquad (6)$$

This result is 1.8 mv. less than the value 0.3569 v. obtained by Pearce and Wirth (9) by direct measurements of cells of the type

$$Hg \mid Hg_2Cl_2(S),\ KCl \mid KIO_3,\ AgIO_3(S) \mid Ag$$

which involve a liquid-junction potential. By keeping the concentration of the potassium chloride equal to that of the potassium iodate, Pearce and Wirth were able to correct for the liquid-junction potential by the Lewis and Sargent equation (6). They measured only three cells in the concentration range 0.01 to 0.10 M, in which the correction for the liquid-junction potential amounted to 7.5 to 8.7 mv. In obtaining their final value of $E^0_{AgIO_3}$ they discarded the results obtained with the most dilute electrolyte, so that the value 0.3569 v. is actually based on measurements of only two cells. It is interesting to note that the value obtained with the most dilute electrolyte which they discarded was 0.3553 v., which is in good agreement with the value that we have computed.

In view of the uncertainties involved in the measurements of Pearce and Wirth we believe that the value 0.3551 v. is the most reliable for $E^0_{AgIO_3}$.

We believe that the value of $K(3.04 \times 10^{-8})$ found in this study is correct to at least ±0.6 per cent. It follows therefore that the corresponding error in $E^0_{AgIO_3}$ due to this small uncertainty in K would be only

$$\Delta E^0_{AgIO_3} = 0.0591 \log \frac{K_2}{K_1} = 0.0591 \log 1.006 = \pm 0.15 \text{ mv.} \quad (7)$$

which is of the same order of magnitude as the uncertainty in $E^0_{Ag^+, Ag}$.

It is evident therefore that the value $E^0_{AgIO_3} = 0.3551$ v. is probably correct to at least ±0.2 mv.

SUMMARY

1. In this study the solubility and activity coefficient of silver iodate in potassium nitrate solutions have been investigated up to an ionic strength of 1 molar. The concentrations of both silver and iodate ions in the saturated solutions were determined. The activity product of silver iodate at 25°C. was found to be 3.04×10^{-8}.

2. It was shown that saturated solutions of silver iodate in pure water contain a greater concentration of iodate than of silver ions, when uncoated glass vessels are used. This is attributed to an exchange between cations in the glass surface and silver ions in the solutions. The error resulting from this exchange was eliminated by coating the glass vessels with paraffin.

3. It was found that barium and thallous ions exchange with silver ions on the surface of silver iodate.

4. The standard potential of the silver-silver iodate electrode IO_3^- ($a = 1$), $AgIO_3(S)/Ag$, was computed from the activity product of silver iodate and found to be 0.3551 ± 0.0002 v. at 25°C.

We express our appreciation to the Graduate School of the University of Minnesota for financial assistance in this work.

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ON THE MOVEMENT OF MATERIALS ACROSS LIVING MEMBRANES AGAINST CONCENTRATION GRADIENTS[1]

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The ability of living systems to move materials against concentration gradients is one of their most important characteristics. Life under changing circumstances would be impossible without this ability. This generalization is as valid for complex organisms as it is for the simplest forms. The living organism must maintain its internal environment relatively constant in spite of changes in its external environment in order to maintain its integrity. In order to keep its salt content constant an organism must be able to do osmotic work. One of the most important cases is in connection with sodium chloride. In order to maintain constancy of composition with respect to this important component of the body, higher organisms must be able to prevent its loss from the intestines and kidneys when the rate of its intake is low and bring about its excretion when its intake is high. The problem of how salt may be moved against its diffusion gradients in accomplishing these ends is the subject of this paper.

The problem has been approached by a study of the circumstances surrounding the movement of salts against their concentration gradients from the intestine to the blood. It has long been known that all of the phenomena of intestinal absorption could not be accounted for on the assumption that the intestinal epithelium behaves like a dialyzing membrane. Reid (9) showed that fluid is moved across various epithelial tissues when there is no difference in osmotic pressure on the two sides. Heidenhain (4) found that water is absorbed from hypertonic solutions in the intestine. Goldschmidt and Dayton (2) found that in the case of solutions containing both sulfate and chloride, the latter was absorbed when its concentration was less than the concentration of chloride in the blood. Burns and Visscher (1) made an exhaustive study of the influence of various anions upon the movement of chloride into and out of the gut in the living animal. They found that in the presence of a sodium salt of

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[1] Presented at the Fourteenth Colloid Symposium, held at Minneapolis, Minnesota, June 10-12, 1937.

sulfate, phosphate, citrate, or ferrocyanide, sodium chloride was very rapidly absorbed from the intestine against steep concentration gradients. Ingraham and Visscher (5, 6, 7, 8) have studied this problem further and have found, among other facts, that under favorable circumstances sodium chloride removal may proceed until the concentration ratio for chloride between blood and intestinal fluid may be 200 to 1. Details of methods will be found in these papers.

In figure 1 are the analytical results of a typical experiment showing sodium chloride removal. A solution isotonic with the blood plasma containing equi-osmotic fractions of sodium chloride and sodium sulfate was placed in a closed loop of lower small intestine. In one and one-half hours the concentration of chloride had fallen to 2.5 mg. per cent, or less than 1 per cent of the blood concentration. This occurred by movement into the blood. Obviously, osmotic work was performed by the system in moving chloride from a place of lower to one of higher concentration.

Also shown in figure 1 are the respective concentrations of ammonia in the intestinal fluid and in the blood. The ammonia is a product of the metabolism of the intestinal epithelium, and its relation to the activity of the intestine is seen in connection with the action of certain toxic substances which abolish the ability of the intestine to perform osmotic work; this will be referred to later.

The ability to do osmotic work is not specific for sodium chloride, for under suitable conditions it may be shown that sodium bromide moves at exactly the same rate against equally great concentration gradients (5). Moreover, this univalent ion impoverishment in the presence of polyvalent ions of the same sign is not limited to the anions, for when a polyvalent cation is present the univalent cation is likewise moved against large concentration gradients (8).

These phenomena are dependent upon certain specific properties of intestinal epithelium. This can be seen from results of the experiments in which specific poisons have been used (7). As little as 0.0001 *M* mercuric chloride stops the process of specific impoverishment, as does 0.0005 *M* Na_2HAsO_3. Somewhat higher concentrations of sodium fluoride, hydrogen sulfide, and sodium cyanide produce a similar poisoning. In figure 2 the results are presented of a typical experiment on this question. Two adjacent loops of small intestine (lower ileum) of a dog were filled each with 100 cc. of an isotonic solution containing initially equi-osmotic quantities of sodium sulfate and sodium chloride. To the fluid in one loop there was added 0.025 *M* sodium fluoride. The results of the two experiments are plotted together, the one marked "control" and the other "NaF." In the case of the control the chloride content of the intestinal fluid fell to 22 mg. per cent in the course of 90 min., whereas in the loop containing sodium fluoride the chloride concentration instead rose to approach the blood plasma level of 340 mg. per cent. The sodium fluoride destroyed the impermeability of the membrane to sulfate (not shown in the graph) and abolished the specific absorption. It also practically abolished the ammonia formation. These effects are produced by all of the poisons mentioned (7).

The conditions for the occurrence of specific absorption from the intestine are extremely exact. If the tissues are injured in any way, chemically, mechanically, or thermally, the epithelium is no longer able to perform osmotic work. The amount of work performed in a given time is not identical for different individual experiments, although from the same animal adjacent loops of intestine give almost identical results, and successive trials are in agreement. Occasionally the intestine of an animal shows spontaneously poor ability to do osmotic work. This might seem to be a disadvantage to the study of the phenomenon, and it is a disadvantage to the extent that a larger number of experiments have had to be performed than would have been necessary if the material were more uniform. However, one advantage has accrued from the instances of spontaneous failure of ability to do osmotic work, namely, that they have given opportunity for the study of means of bringing about more rapid performance of osmotic work. The most striking effect produced by any substance studied is that resulting from the addition of relatively small quantities of $Al(OH)_3$. As a routine procedure in a number of experiments two adjacent loops of small intestine were studied, being filled with the

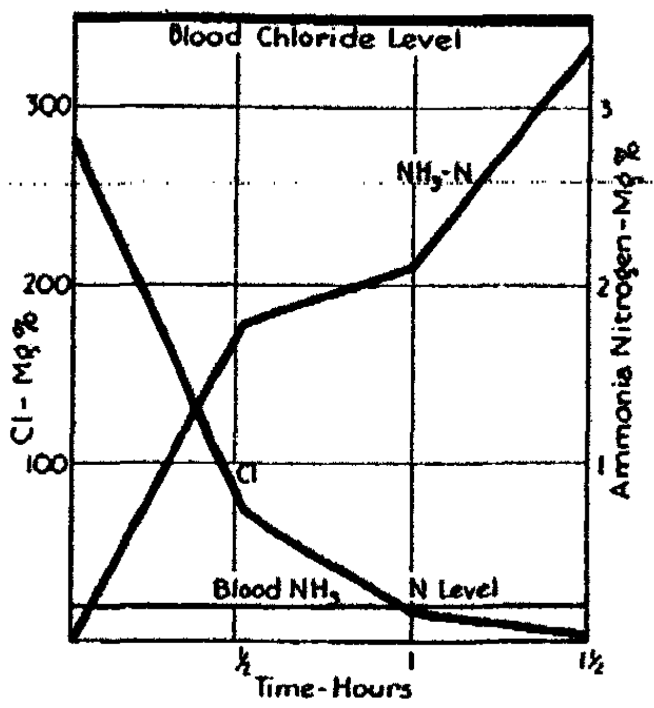

FIG. 1

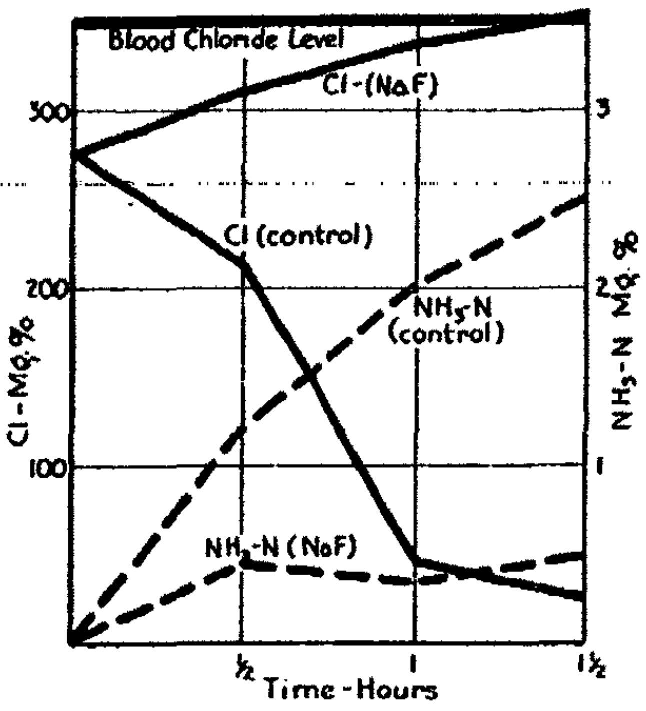

FIG. 2

FIG. 1. Results of a typical experiment showing sodium chloride removal. Also shown are respective concentrations of NH_3 in intestinal fluid and in the blood.

FIG. 2. Effect of sodium fluoride on intestinal membrane

usual isotonic mixture of sodium chloride and sodium sulfate. In the case of one of the loops there was an addition of 1.5 cc. of alumina cream per 100 cc. of fluid. It was regularly found that the rate of chloride removal was greater from the loop containing the $Al(OH)_3$ than from the control. This effect is shown in figure 3. In this instance there was very little Cl impoverishment in the control loop, whereas in that containing the alumina cream the chloride concentration fell to a low level. The same effect of aluminum was observed when small quantities of $Al_2(SiO_3)_3$ are employed. There is a suggestion that this effect depends upon the sign of the aluminum ion, since the negative colloidal dyes, trypan red and brilliant vital red, produce a reverse effect, whereas in a number of instances methylene blue has accelerated chloride impoverishment. The influence of methylene blue need not, of course, be due to the simple effect of charge, and the mechanism of the $Al(OH)_3$ effect cannot be considered to be settled.

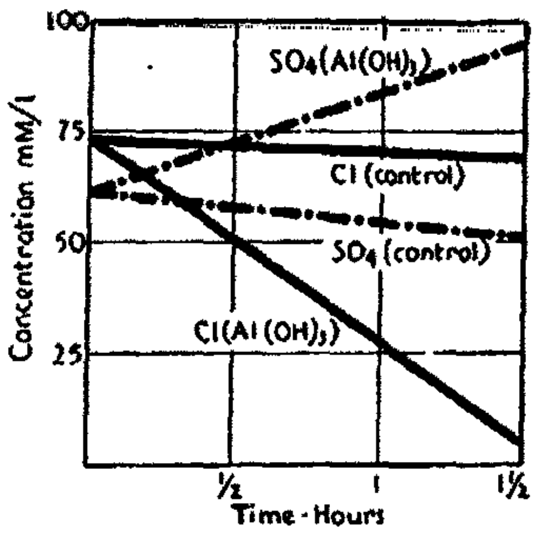

Fig. 3. Effect of $Al(OH)_3$ on chloride removal

As has been pointed out in a previous publication (6) it has been found to be impossible to account for univalent ion impoverishment on the basis of a membrane equilibrium of the Donnan type, or as resulting from processes going on in approaching such equilibrium. After exhaustively considering and subsequently rejecting every known type of process based on ion exchange or membrane equilibrium, a kinetic picture has been developed, which is based upon highly probable assumptions and which, as will be apparent from the data presented, will satisfactorily account in a quantitative way for the phenomena as observed.

The type of uni-univalent salt impoverishment which is observed in the small intestine can be accounted for by assuming that there is a flow of water into the blood carrying out the uni-univalent salt at the concentration at which it exists in the gut, and a simultaneous flow of water free from that salt into the intestine at another point. It is necessary to postulate a membrane which is in essence a mosaic, one portion of which is strictly semipermeable and through which water enters the gut, and another portion of which is permeable to uni-univalent salts through which the solution of such salts passes into the blood. This scheme is analogous to the physical model diagrammed in figure 4.

If the vessel contains originally V_0 liters of a solution of sodium chloride at a concentration C_0 millimoles per liter, and pure water flows into the vessel at some rate R_i and sodium chloride solution at a concentration C (the concentration at any time t) leaves the vessel at some rate R_0, the concentration, C, of sodium chloride in the vessel will decrease. If the rates of flow, R_0 and R_i, are constant or vary in a uniform manner with time, the concentration, C, will likewise decrease in a uniform way with time. In the following derivation only the case in which R_i and R_0 are constant is considered.

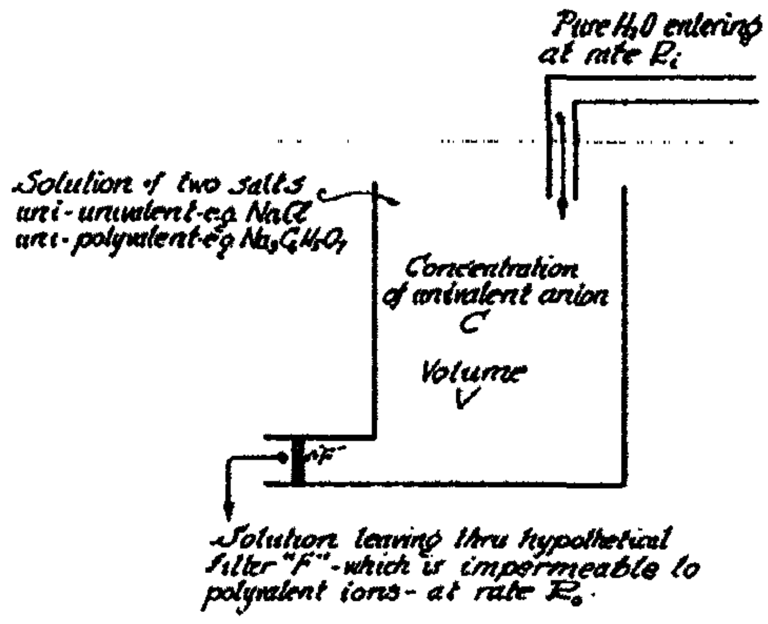

FIG. 4. Model for explaining the type of uni-univalent salt impoverishment which is observed in the small intestine.

In the case of the intestine the solution contains both sodium citrate and sodium chloride. The gut is freely permeable to sodium chloride but almost completely impermeable to sodium citrate. Then if a hypothetical filter, F, is assumed to be present at the outlet which is impermeable to sodium citrate, the above scheme will represent a physical model of the chloride-impoverishing mechanism of the small intestine on the basis of this theory.

If the rates R_0 and R_i are constant it is possible to derive the mathematical relationship between concentration and time in terms of the original volume and concentration of the fluid in the intestine and the rates of fluid movement. By comparing the concentration of sodium chloride experimentally determined at various intervals of time in the course of an actual experiment with those values of C calculated from the theoretical formulae at the same time, one can determine whether chloride impoverishment as it occurs in the small intestine can be quantitatively accounted for by the type of fluid movement postulated.

The formula relating time and concentration is derived as follows: Let

V_0 = the original volume of the solution in liters,
C_0 = the original concentration of sodium chloride in the solution in millimoles per liter,
V, C = the volume and concentration at any time t in the same units,
t = time in hours,
R_0 = rate of flow of sodium chloride solution, concentration C, from the intestine to the blood in liters per hour,
R_i = the rate of flow of pure water into the intestine from the blood in liters per hour,
$D = (R_0 - R_i)$ or the rate of volume decrease, since in all experiments the volume in the intestine decreases with time, and
I = the amount of salt present at any time.

In such a system it is evident that:

$$C = f(I, V) \tag{1}$$

I and V are functions of the third variable t. The total derivative of equation 1 in respect to t is then:

$$\frac{dC}{dt} = \frac{\partial C}{\partial I}\frac{dI}{dt} + \frac{\partial C}{\partial V}\frac{dV}{dt} \tag{2}$$

At any time

$$C = \frac{I}{V} \tag{3}$$

Therefore,

$$\frac{\partial C}{\partial I} = \frac{1}{V} \tag{4}$$

$$\frac{\partial C}{\partial V} = -\frac{I}{V^2} \tag{5}$$

The change in salt content in respect to time $\left(\frac{dI}{dt}\right)$ is equal to the rate of exit of salt solution multiplied by the concentration of salt in the moving fluid, or,

$$\frac{dI}{dt} = -CR_0 \tag{6}$$

The change of volume with time is equal to the difference in the rate of fluid leaving and fluid entering:

$$\frac{dV}{dt} = (-R_0 + R_i) = -D \tag{7}$$

Substituting equations 4, 5, 6, and 7 for the proper terms in equation 2:

$$dC = \left[\frac{1}{V}(-CR_0) + \left(-\frac{I}{V^2}\right)(-D)\right]dt \tag{8}$$

From equations 3 and 7:

$$dC = \left[\frac{-CR_0}{V} - \frac{C}{V}(R_i - R_0)\right]dt \tag{9}$$

Simplifying:

$$dC = \left(\frac{-CR_i}{V}\right)dt \tag{10}$$

$$\frac{dC}{C} = \frac{-R_i dt}{V} \tag{11}$$

Since $V = V_0 - Dt$ (12)

$$\frac{dC}{C} = \frac{-R_i dt}{V_0 - Dt} \tag{13}$$

On integration this yields:

$$\log C = \frac{R_i}{D}\log(V_0 - Dt) + \log A \tag{14}$$

Or

$$C = A(V_0 - Dt)^{\frac{R_i}{D}} \tag{15}$$

At zero time

$$A = \frac{C_0}{V_0^{\frac{R_i}{D}}} \tag{16}$$

Therefore

$$C = \frac{C_0}{V_0^{\frac{R_i}{D}}}(V_0 - Dt)^{\frac{R_i}{D}} \tag{17}$$

Simplifying and from equation 12

$$C = C_0\left(\frac{V}{V_0}\right)^{\frac{R_i}{D}} \tag{18}$$

Or, in logarithmic form,

$$\log_{10}\frac{C}{C_0} = \frac{R_i}{D}\log_{10}\frac{V}{V_0} \tag{19}$$

By plotting the log $\frac{C}{C_0}$ against log $\frac{V}{V_0}$ one should obtain a straight line, the slope of which represents $\frac{R_i}{D}$, if the formulation fits the real phenomenon. The results of three of the most complete experiments we have performed are plotted in this way in figure 5. The experimental data and some of the calculations are given for these experiments in table 1. For the period of the first hour in each case there is substantially a straight-line relation between log $\frac{C}{C_0}$ and log $\frac{V}{V_0}$, as is predicted from this reasoning. For the point at one and one-half hours, there was in two instances a very considerable deviation from the predicted straight line. This does not appear to be a serious discrepancy, however, because the assumption that the membrane through which the water enters the gut is absolutely impermeable to chloride might be in error to the extent that perhaps 1 per cent of the chloride in the blood could pass. Such a minor correction as this could completely account for the deviation when the chloride content of the intestine has fallen to such low figures as 2 per cent of the blood chloride level. It should also be mentioned in this connection that one is here approaching the limits of analytical accuracy for chloride in biological fluids.

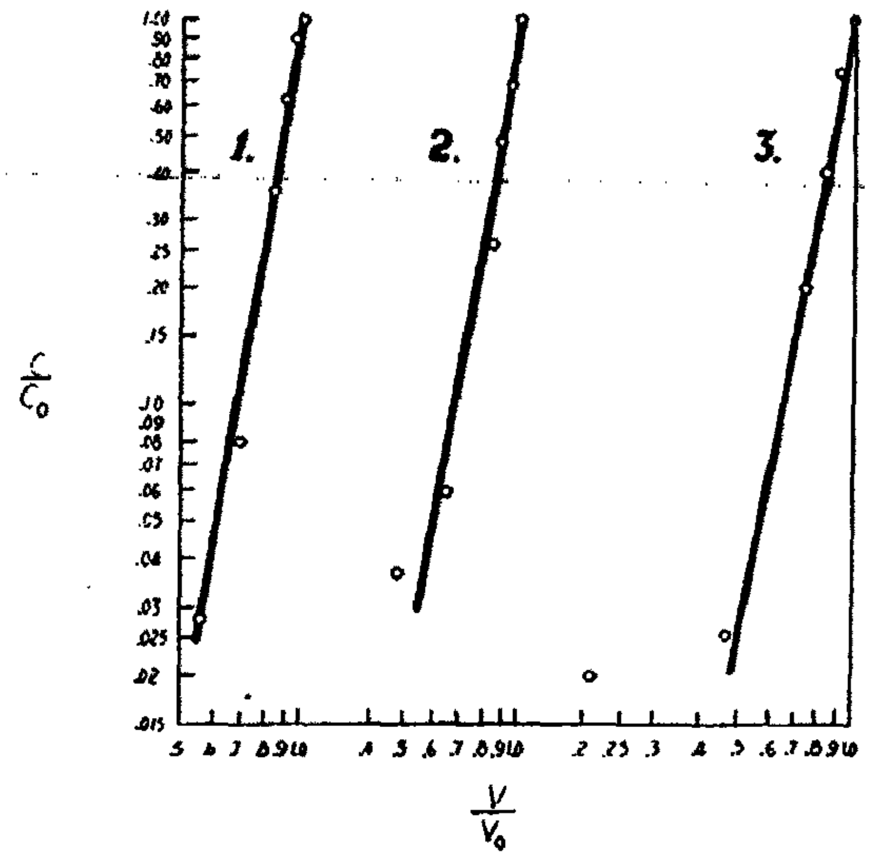

FIG. 5. Plot of log $\frac{C}{C_0}$ against log $\frac{V}{V_0}$

Summarizing the mathematical results, it seems that one is entitled to say that until extremely low chloride concentrations are reached the theory as developed will completely account for the phenomena observed.

From the values of $\frac{R_i}{D}$ the absolute value for R_i itself can be calculated because D is experimentally determined. In several experiments this value has ranged between 150 and 250 cc. per hour for a loop of intestine 25 cm. in length. It seems important to note that this is a distinctly reasonable result. R_i is in a mathematical sense an arbitrary constant as far as the data we have presented are concerned. It should be noted, however, that it is a factor amenable to measurement although not in a direct way, because fluid is both entering and leaving the intestine simultaneously. Up to the present time the best evidence that we have that water actually enters the intestine at the rate R_i is derived from the fact that values of this constant calculated from the movement of substances with widely different diffusion constants are in substantial agreement with one another.

TABLE 1

Observed and calculated data on the rate of active absorption

TIME	c_{Cl} (EXPERIMENTAL)	$\frac{C}{C_0}$	V	$\frac{V}{V_0}$
		Experiment 1		
hours	*millimoles per liter*		*cc.*	
0	77.9	1	50	1
0.167	69.2	0.89	47.5	0.95
0.383	48.2	0.62	44.4	0.89
0.583	28.1	0.36	41.4	0.83
1.00	6.24	0.08	35.3	0.70
1.50	2.2	0.028	28.0	0.56
		Experiment 2		
0	59.5	1.00	75.0	1.00
0.167	40.1	0.67	70.7	0.94
0.333	28.7	0.48	66.3	0.88
0.5	15.6	0.26	62.0	0.83
1.00	3.5	0.059	49.0	0.65
1.5	2.2	0.037	36.0	0.48
		Experiment 3		
0	59.7	1	75.0	1.00
0.17	43.5	0.73	68.3	0.91
0.33	23.8	0.40	62.0	0.82
0.50	12.05	0.20	55.3	0.74
1.00	1.56	0.026	35.7	0.47
1.50	1.2	0.020	16.0	0.21

The mechanism for driving water in this system has not been considered up to this point. Since in these experiments there is no difference in osmotic pressure between the two fluids, ordinary osmosis will not account for the flow. Abnormal osmosis can, however, occur. Practical difficulties have prevented us from making crucial studies on this question up to the present time, and it would be unprofitable to go into an extended discussion from a theoretical basis, since too many important points are unknown. It is nevertheless worth while to say that the theory of Söllner (10) and of Grollman and Söllner (3) offers possibilities for the solution of this aspect of the problem.

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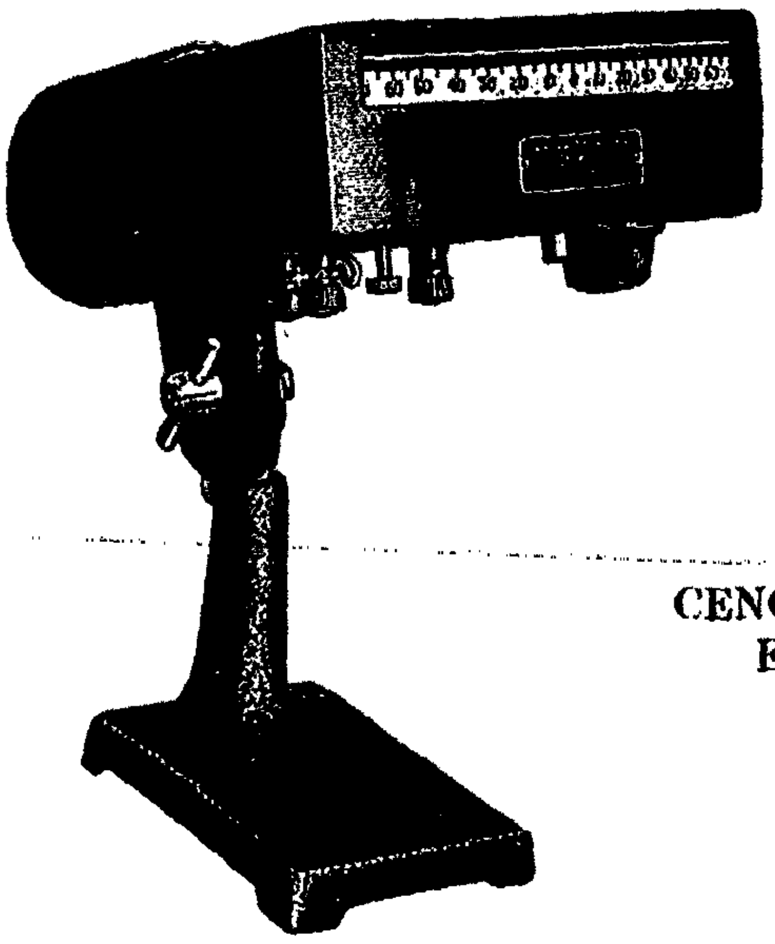

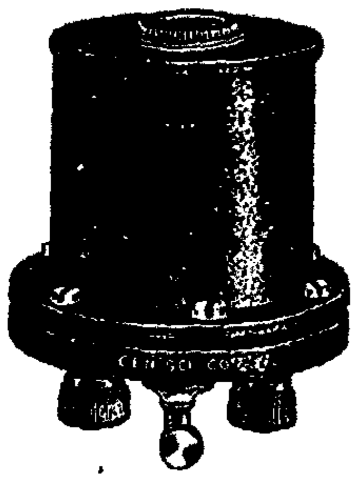

THE PERIODIC COAGULATION OF GOLD SOL IN THE PRESENCE OF COLLOIDAL SILICA

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The Liesegang phenomenon of periodic precipitation in gels has not as yet received a general explanation, and the four principal theories advanced have been applied with partial success only to specific systems (1, 2, 7, 8). In the earlier treatment attention was focussed upon electrolyte concentration in relation to conditions of solubility and supersaturation. It was later shown, however, that in many cases ring systems could be readily formed by coagulation of substances originally dispersed as colloids in gels (5), and it appears likely that even when electrolytes interact the compound formed may exist primarily as a colloid, protected to some extent by the material of the gel.

The theory proposed by Dhar and Chatterji explains the ring formation as due to adsorption of colloidal particles by the coagulum which forms the ring (2). As a consequence a portion of the gel succeeding the ring is depleted more or less completely of colloidal material and the diffusing electrolyte must proceed further before coagulation again ensues. The chief function of the gel is then to peptize or protect the colloidal dispersion, as well of course as to provide structural support to the system. In support of these ideas it is shown that freshly formed precipitates may adsorb their peptized sols, and that there is a parallel between the protective action of gels and their power to cause rhythmic formations (3). Whether or not this explanation applies in all cases of ring formation it is evident that there must exist some sort of concentration limit with regard to the diffusing ions which may be a metastable supersaturation limit or a coagulation limit, but which determines the agglomeration of the precipitate. There are also cases where the colloid theory would seem to have no application,—in the periodic deposition of sodium chloride by salting out in capillaries, and in the reactions of gases diffusing in narrow tubes.

It is important that further information be collected as to the behavior of simple colloidal systems in which ring structures are produced on coagulation. The present work deals with a study of colloidal gold prepared in the presence of silica sol, the system setting to a gel either in the course of time or through the influence of diffusing electrolytes. Stable red gold sols may be obtained in colloidal silica under carefully controlled conditions, the pH of the system being of prime importance. When setting was allowed to take place before introduction of electrolytes ring formation did not occur, the diffusing salts producing merely a change of color from red to blue. Apparently the protective action of the gel is sufficient to prevent extensive coagulation of the gold particles. It is possible, however, to adjust the pH of the gold-silica mixture to a point at which no gelation takes place on standing for a long period of time, and with these fluid mixtures the gold coagulated to form sharply defined rings when various electrolytes were allowed to diffuse in. Following the ring formation, setting to a gel took place under the influence of the advancing electrolyte and thus the structure was preserved. A study has been made of the conditions under which this interesting phenomenon takes place, and some conclusions have been drawn as to the bearing of these experiments on the theories of periodic structures.

EXPERIMENTAL

Materials

A commercial water-glass was diluted with three volumes of water and filtered through fuller's earth. A typical solution analyzed as follows: SiO_2, 12.75 per cent; Na_2O, 6.11 per cent.

The nuclear gold sol was prepared by using 240 ml. of double-distilled water, 3.7 ml. of 0.25 per cent gold chloride solution, 4 ml. of 0.18 *N* potassium carbonate, and 0.8 ml. of a saturated solution of phosphorus in ether; this gave a deep red and very stable sol.

Dialysis was carried out in collodion sacs, while for diffusion membranes du Pont Cellophane No. 300 was cut into small squares and allowed to soak in water for at least two days before use.

Preparation of gold-silica sols

Experiments with various concentrations of water-glass and acid showed that with equal volumes of 1.16 sp. gr. water glass and 3 *N* hydrochloric acid a clear sol was obtained which would set to a gel in three or four days.

Before introduction of the gold this sol was dialyzed until no test for chloride was obtained. Dialysis was found to decrease the rate of setting both by removal of electrolyte and through actual loss of silica. In one experiment 34 per cent of the silica was thus removed. To reduce this loss sols were allowed to age for some eight hours before dialysis, which was then carried out for about twenty hours.

Colloidal gold was prepared by Zsigmondy's method of reduction of gold chloride by formaldehyde at 100°C. in the presence of potassium carbonate. Reduction was carried out directly in the silica sol, and in most of the experiments 2 ml. of nuclear sol was added to produce uniform particle size. Following reduction the mixture was dialyzed for some forty-eight hours before the diffusion experiments were started.

It is important that the system be adjusted to a suitable pH before the gold is reduced. If the solution is too acid, reduction will be slow and incomplete, resulting in a blue or purple sol. On the other hand, the pH must not be too high if the silica is to set eventually. The influence of pH is shown in table 1, where 30-ml. samples of silica sol were adjusted to various pH values by addition of potassium carbonate and gold chloride, and the gold reduced by formaldehyde (without addition of nuclear sol). The results are somewhat variable but indicate that a pH in the neighborhood of 6.0 will produce a stable red gold sol which will set to a gel in a few days, whereas above this value stable silica sols may be maintained.

TABLE 1

Influence of pH upon set and stability of sols

pH	K_2CO_3 (0.5 *N*)	$AuCl_3$ (0.7 PER CENT)	SET	COLOR	STABILITY (AFTER 2 MONTHS)
	ml.	*ml.*			
4.70	0.3	2	Yes	Blue	
5.60	0.4	2	3 days	Red	Faded
5.90	0.45	2	5 days	Red	Blue-purple
5.90	0.6	2.5	4 days	Red	Good
5.95	0.60	2.5	4 days	Red	Murky
6.00	0.6	2	3 days	Red	Blue
6.00	0.7	2.5	5 days	Red	Purplish-red
6.05	0.55	2.5	4 days	Red	Good
6.20	0.75	2.5	9 days	Red	
6.30	0.8	2	No set	Red	
6.40	1.25	2	No set	Red	

pH values were obtained with the quinhydrone electrode, which is not entirely satisfactory in the presence of gold salts. It is possible to obtain the carbonate requirement by adding potassium carbonate to the silica sol before introduction of gold chloride and thus adjusting the pH, the buffer action of the carbonate being sufficient to prevent any large change. Some results from such procedure are shown in table 2 for a series of samples. All of these sols eventually set.

The preparation of a satisfactory sol which would not set on standing, but which could be set by electrolytes, was carried out as follows: A silica sol was made from 80 ml. of water-glass (1:3), 20 ml. of water, and 100 ml. of 3 *N* hydrochloric acid. After standing for nine hours it was dialyzed for twenty-four hours. To 150 ml. of this sol were then added 10 ml. of gold chloride solution (0.25 per cent) and 3 ml. of potassium carbonate solution

(0.5 *N*), bringing the pH to 6.2. Two ml. of nuclear sol was added, the mixture heated to 90°C., and 5 ml. of 0.2 per cent formaldehyde stirred in after removal of the flame. Reduction to clear red was complete in several minutes. Dialysis then took place for forty-eight hours. The resulting sol contained 1.79 per cent of SiO_2.

Diffusion experiments

A series of test tubes was prepared containing gold-silica sol of pH about 6. Setting was allowed to take place, and the gels were overlaid with solutions of sodium chloride, sodium sulfate, potassium dihydrogen phosphate, magnesium chloride, and aluminum chloride at concentrations from 1 *M* to 0.025 *M*. In every case a continuous change from red to blue without ring formation was observed. A sol of pH 6.5 was now placed in a collodion sac immersed in a phosphate buffer solution of pH 6.24. As diffusion progressed the normal change from red to blue was accompanied by the formation of a series of dark rings, and setting of the sol took place.

TABLE 2

Carbonate requirement in reduction of gold

TITRATION OF SILICA 75 ML.		REDUCTION OF 5 ML. OF $AuCl_3$ WITH 1.5 ML. OF NUCLEAR SOL IN 75 ML. WITH 5 ML. OF FORMALDEHYDE		
Volume of K_2CO_3	pH	Extent of reduction	Time of reduction	Color
ml.				
0.0	5.90			
0.4	6.50	Slight	Hours	Light blue
0.5	6.65	Slight	Hours	Purple
0.6	6.72	Complete	35 min.	Clear red
0.8	6.85	Complete	6 min.	Deep red
1.0	6.97	Complete	4 min.	Deep red

For more convenient study of this process pieces of Pyrex tubing ¾ in. in diameter and 6 to 8 in. long were capped with Cellophane membranes secured by rubber bands, and filled with about 30 ml. of the gold-silica sol. The tubes were then set into Erlenmeyer flasks containing the diffusing electrolyte, and the whole placed in an air thermostat which was kept between 25° and 30°C. to 0.2°C. by means of two lamps and a mercury thermoregulator. A small fan was used to prevent local heating. Some of the structures obtained are illustrated in figure 1 for various electrolytes. The reproducibility is surprisingly poor even under these controlled conditions, as is shown in figure 1c for the same concentration of potassium chloride. Some difference in the permeability of the membranes is indicated. In some of the experiments three tubes with the sol were allowed to dip into a large beaker containing the electrolyte solution, which was continuously stirred and covered with a layer of paraffin wax to prevent evaporation. Usually under these conditions the rings formed were observed to be regularly spaced, but even here puzzling discrepancies appeared. It appeared also that the light of the lamps was having an effect on the character of the rings but was not the prime cause, since similar periodic structures were also produced in the dark.

That there is some regularity in the spacing of the rings, at least in a considerable number of cases, is shown by the curves of figure 2, where the height of the ring as measured with a cathetometer is plotted against the ordinal number of the ring, starting with the lowest observable.

The effect of various electrolytes

With these sols, ring formation has been observed under the influence of sodium sulfate, sodium chloride, potassium chloride, silver nitrate, aluminum nitrate, aluminum chloride, and several buffer solutions at various concentrations. The behavior of the different electrolytes seems to be quite specific, and no direct effect of valence was noted, although some such effect is to be expected. Thus the same concentrations of potassium chloride and sodium chloride usually gave quite different results, and with the latter salt the results were much more uncertain than with the former, which could usually be relied upon to give regular systems. With barium chloride no definite rings were obtained, merely maxima and minima of density of coagulum. With 0.025 *N* aluminum chloride a system of very fine, closely spaced rings formed in the lower part of the tube and coarser rings in the upper part. Silver nitrate was found to produce effects like potassium chloride.

If the electrolyte is too concentrated the rings are indistinct. With decreasing concentration the ring system increases in sharpness to the point at which the silica will no longer set and the flocculated gold merely settles to the bottom of the tube. Comparison of ring systems was made using potassium chloride at a series of concentrations between 2 *N* and 0.015 *N*. Some of the results are shown in figure 3, and also in figure 1d. It is evident that decreasing the concentration of diffusing electrolyte decreases the number of rings, and increases the rate at which the distance between adjacent rings spreads out.

In some experiments the concentration of gold in the sol was varied by using amounts of gold chloride from 2.5 to 15 ml. per 150 ml. of sol. With increasing concentrations the rings increased in density, while at the highest concentration coagulation of the gold was incomplete, the spaces between the rings showing red gold colloid.

The setting of the silica was followed in a number of cases by means of a thin capillary tube of about 0.5 mm. outside diameter, which was carefully

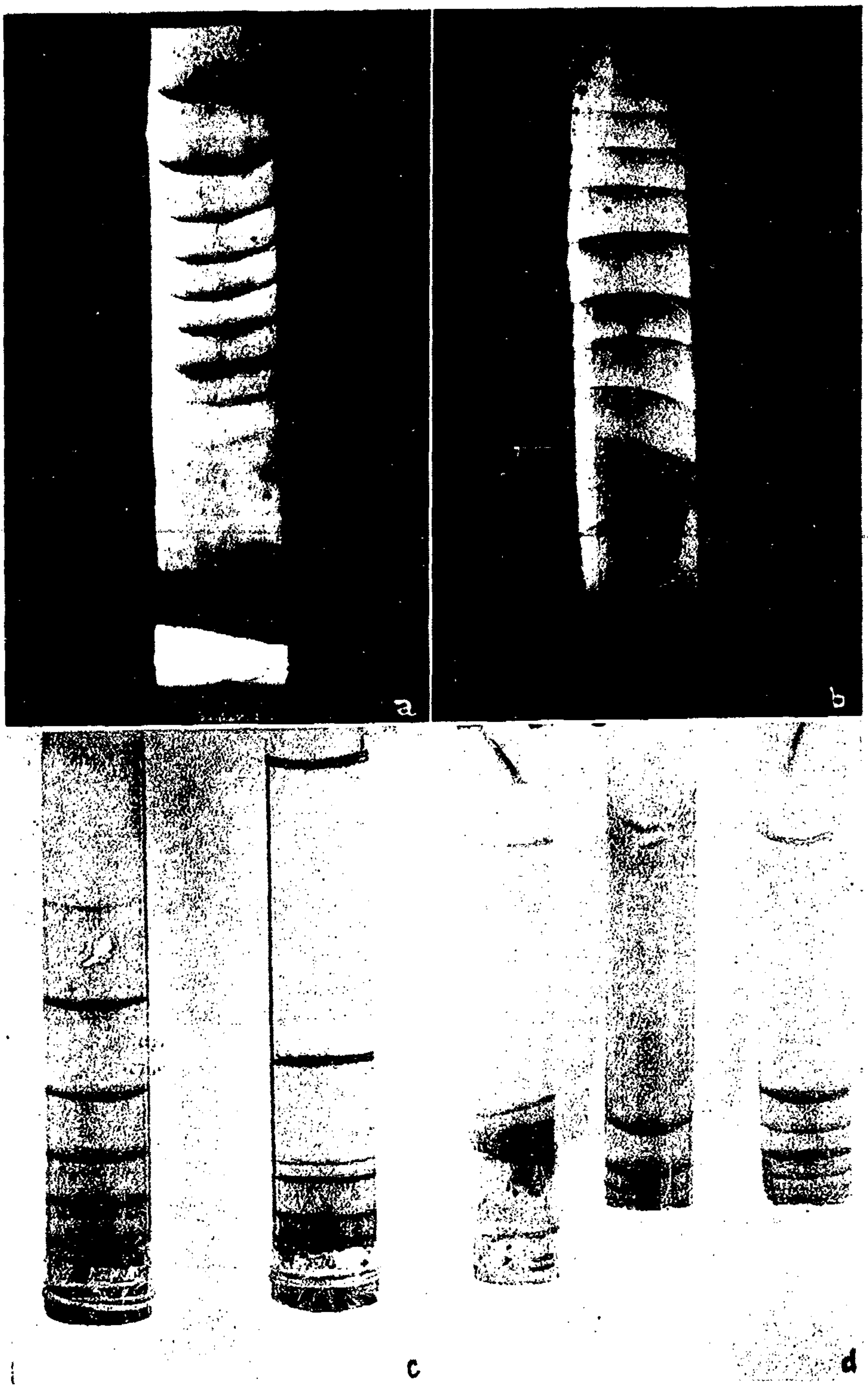

Fig. 1, a-d

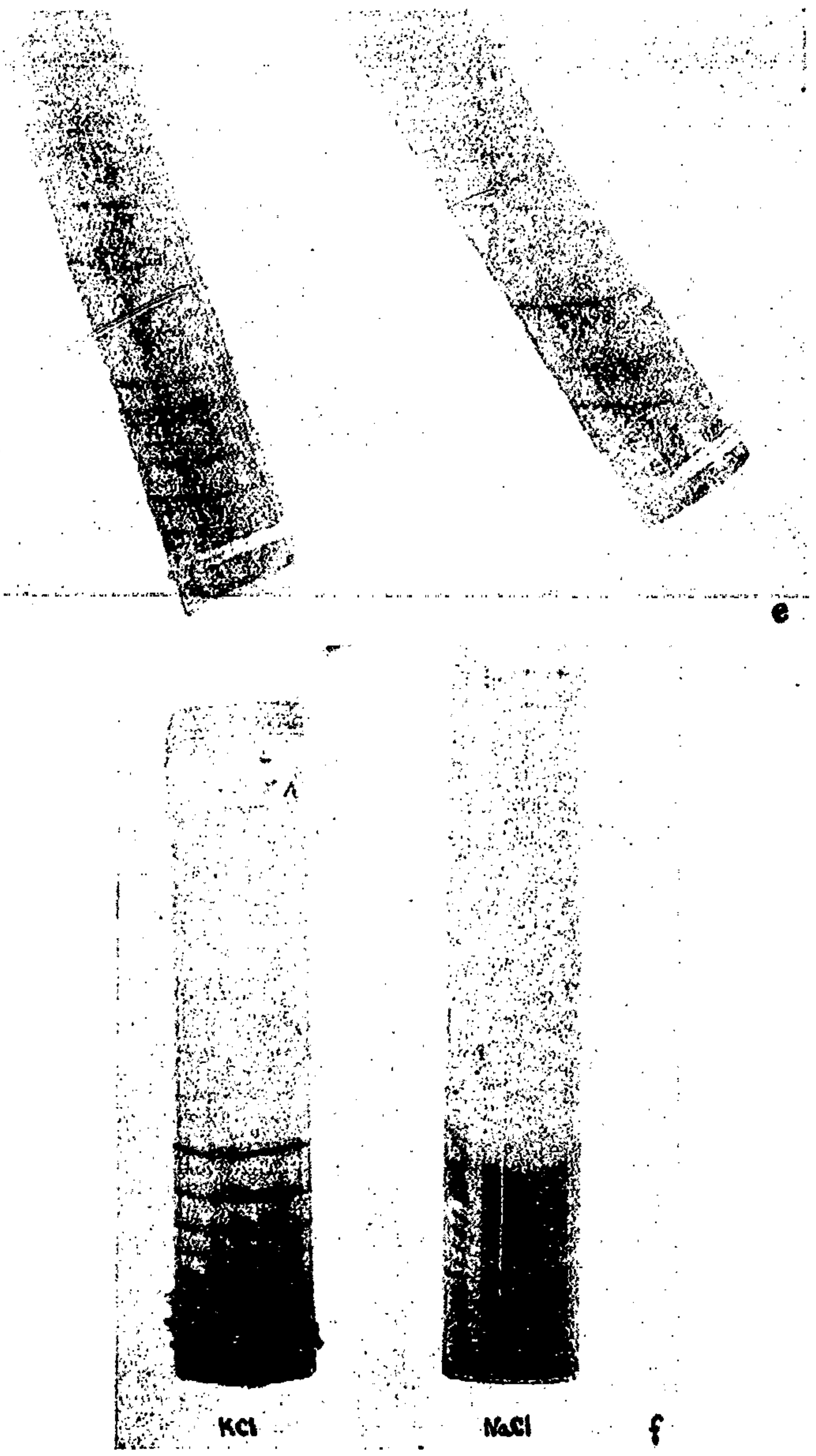

FIG. 1 e, f

FIG. 1. Ring formation in gold–silica sols in the presence of various electrolytes. (a) With phosphate buffer; pH 7.7. (b) With 0.2 *M* aluminum nitrate; no membrane. (c) Regular and irregular rings produced with potassium chloride. (d) Effect of varying electrolyte concentration (0.015, 0.020, and 0.025 *N* potassium chloride). The gel prepared with 0.015 *N* potassium chloride is so weak that it will not stick in the tube. (e) Diffusion at various angles. (f) Potassium chloride, 0.015 *N*; sodium chloride, 0.025 *N*.

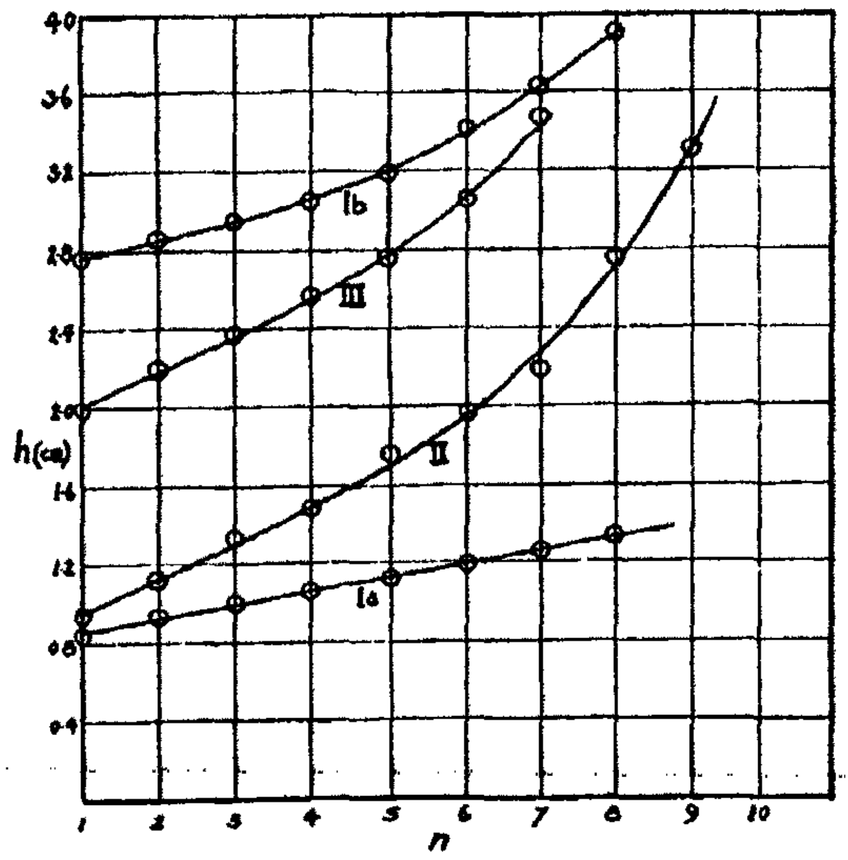

FIG. 2. Height of the ring plotted against the ordinal number of the ring. Curve I, 0.025 N aluminum chloride: (a) fine rings in lower part of tube; (b) coarser rings in upper part. Curve II, 0.025 N potassium chloride. Curve III, 0.025 N sodium chloride.

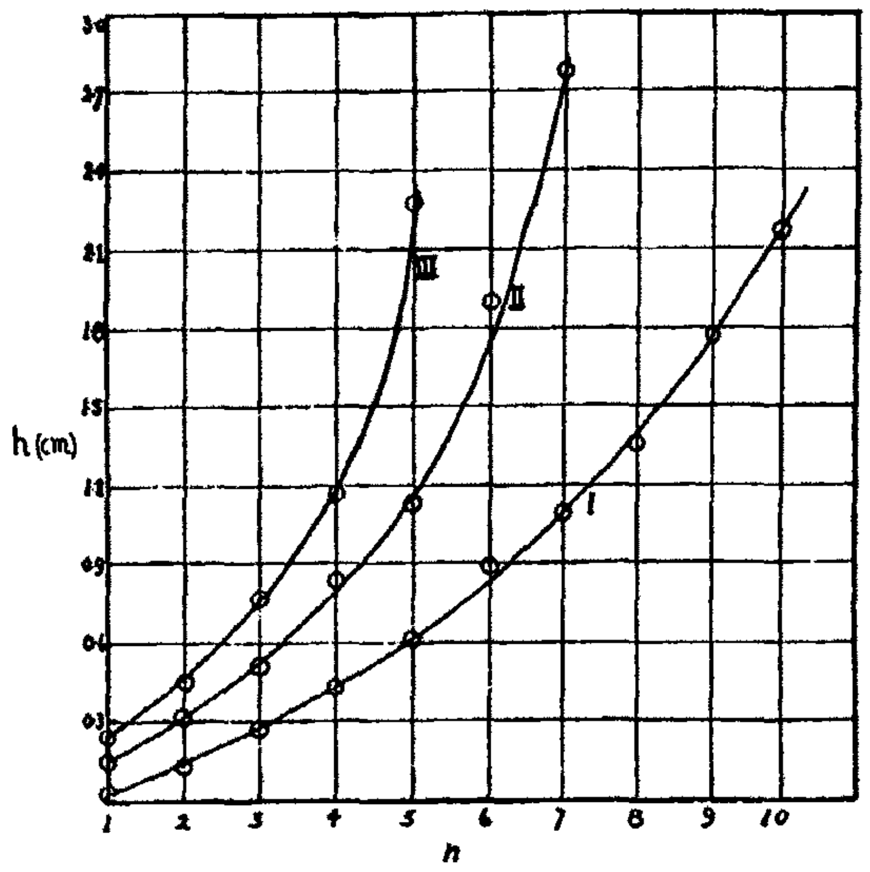

FIG. 3. Comparison of ring systems using potassium chloride in different concentrations. Curve I, 0.025 N; curve II, 0.020 N; curve III, 0.015 N.

thrust down the center of the tube as the rings were forming. The point at which the flexible tube began to bend as it was moved from side to side was taken as the approximate limit of the setting process. This was found to be about 2 mm. behind the ring which was forming, but it is probable that the silica coagulates sufficiently to give support at the ring itself. The gel first formed is somewhat fluid, as shown by experiments in which the tubes were tilted from the vertical (figure 1e).

The function of the gel

It is apparent from the above that gel formation is necessary in these experiments for structural support. In a case where the electrolyte was allowed to diffuse from the top of the tube the gold was completely coagulated and fell to the bottom. With a horizontal tube a layer of coagulum was formed on the lower side of the tube.

There exists the possibility that the periodic phenomenon is confined to the silica in its setting, and that the coagulated gold merely serves to indicate the boundary between sol and gel. Such a gelation process has not as far as we know been observed, and would distinguish the systems here studied from those involving gels.

A series of tubes containing silica sol without gold were set up with 0.025 *N* potassium chloride diffusing upwards. After some hours fine black sand was dropped in from the top at the rate of a few grains every half-hour for about two days. No discontinuities were observed in the distribution of the particles. Similar results were obtained using emery powder and sulfur. When, however, the setting sol was overlaid with a suspension of silver chloride, a series of rings were formed as the silver chloride particles settled down. The success of the last experiment may be due to the smaller size of the particles used, but does not unequivocally indicate periodic gelation, since coagulation of the silver chloride particles under the influence of the upwardly diffusing electrolyte probably took place.

Further tests of this idea were based on the following considerations. The diffusion rate of electrolytes is slightly less in gels than in sols. Coagulation of the silica may be accompanied by adsorption of electrolyte. It is therefore possible that measurable discontinuities in the diffusion stream may occur. The diffusion of an electrolyte, silver nitrate, was therefore followed potentiometrically. Three diffusion tubes were set up containing in the first 0.001 *N* sodium nitrate, in the second silica sol without gold, and in the third a gold-silica sol. The tubes were dipped into a large beaker of 0.002 *N* silver nitrate, which was constantly stirred and protected from evaporation. Silver electrodes were let into the sides of the three tubes about 4 cm. above the membrane, and a single silver electrode was placed in the large beaker. Measurements of potentials between the reference electrode and the electrodes in the tubes were made simultaneously over a period of one hundred fifty hours during which the potentials dropped from about 175 to 20 mv. as the silver-ion concentration tended to equalize between the electrodes. Any changes in the rate of diffusion in the tubes containing silica should be observable by comparison with the tube containing sodium nitrate solution. The curves obtained by plotting millivolts against time are not shown, since the values have no absolute significance. They were displaced from one another in the three cases, but were found to be almost parallel throughout. Certain irregularities in slope were found to be almost duplicated in the three cases, and must be attributed to changes in the membranes and in other external conditions. It is evident from this that no appreciable discontinuities of electrolyte diffusion are produced by the setting gel. During the course of the experiments a very regular ring system was formed in the tube containing the gold.

DISCUSSION

In common with other examples of the Liesegang phenomenon there appears to be in the systems studied here a general regularity with regard to the spacing of the rings. A number of expressions, mostly empirical, have been developed by various authors connecting the height, *h*, of the ring with its ordinal number, *n*. More fundamental treatment of periodic processes has been given by Morse and Pierce (6), and by Fricke (4). These authors, however, have confined their attention chiefly to the silver chromate rings in gelatin, and have treated the process from the point of view of opposing diffusion streams of electrolytes, with precipitation at supersaturation. In the present case we are dealing with the coagulation of a colloid by electrolytes, and it becomes necessary to consider a single diffusion stream and to replace the supersaturation limit of concentrations by some limit necessary to coagulation.

Using the same method of approach as that of Morse and Pierce, however, it is possible in our case to arrive at an equation for the distribution of the rings, which is based on the following assumption. There is necessary for coagulation of the gold particles a definite concentration of electrolyte, but, once started, coagulation can continue throughout the sol until some definite lower concentration of electrolyte is reached. This means, in effect, that the coagulum formed at the upper limit of concentration may remove particles by adsorption from a region between the higher and lower limits. It is also to be expected that the settling of the coagulated gold is rapid with respect to the advance of gelation, and that the latter corresponds to the advance of some definite concentration of electrolyte.

For the diffusion of the advancing electrolyte in the tube we have, according to Fick's equation,

$$a^2 \frac{\partial^2 u}{\partial x^2} = \frac{\partial u}{\partial t}$$

where a^2 is the diffusion coefficient, and u the concentration of electrolyte at the distance x from the starting point. It is assumed that the diffusion gradient is not affected by the formation of the coagulum, as the potentiometric measurements seem to show.

The solution of the equation is of the form

$$u = \frac{2U_0}{\sqrt{\pi}} \int_{\frac{x}{2a\sqrt{t}}}^{\infty} e^{-\beta^2}\, d\beta$$

where U_0 is the initial concentration of electrolyte and t is the time. Now if u is to be constant for the formation of each ring the lower limit of integration must be constant, and hence $x/\sqrt{t}$ must be constant.

Let c_1 represent the electrolyte concentration at which the silica will set to a gel, c_2 the concentration at which the coagulation of the gold will take place, and c_3 the lower limit of concentration necessary to removal of the gold to the ring. From the experiments it is probable that c_1 and c_2 are not far different. Let h_1, h_2, and h_3 be the corresponding values of x at which these concentrations are reached at the time t. The gold in the region h_2 to h_3 has coagulated and accumulated at h_1 to form the ring.

Now for coagulation to set in again the concentration at h_3 must rise to the value c_2. This will happen at a later time t'. Meanwhile the gelation has advanced to a point h_1'. The gold from h_3 to some higher point h_4 will coagulate and fall to h_1', forming the next ring.

From the previous considerations we may set

$$h_2 = k_2\sqrt{t} \qquad \text{and} \qquad h_3 = k_2\sqrt{t'}$$

where k_2 is a constant, and at the time t

$$h_3 = k_3\sqrt{t}$$

where k_3 is some other constant.

Hence

$$\sqrt{t'/t} = k_3/k_2$$

Also we have, at the rings themselves

$$h_1 = k_1\sqrt{t} \qquad \text{and} \qquad h_1' = k_1\sqrt{t'}$$

Then

$$h_1'/h_1 = \sqrt{t'/t} = k_3/k_2 = \text{a constant}$$

In general, for successive rings,

$$h_n/h_{n-1} = K$$

where n is the ordinal number of the ring. This equation has been proposed empirically by Schleussner (9). The final equation has been tested for these results by plotting the logarithm of h against n, since

$$h_n = Kh_{n-1} = K^{n-1}h_1$$
$$\log h_n = (n - 1) \log K + \log h_1$$

A straight line should be obtained. Some of the results obtained are shown in figure 4. While in a number of experiments little regularity was shown in the ring spacing, yet the more regular cases seemed to agree reasonably well with the equation given.

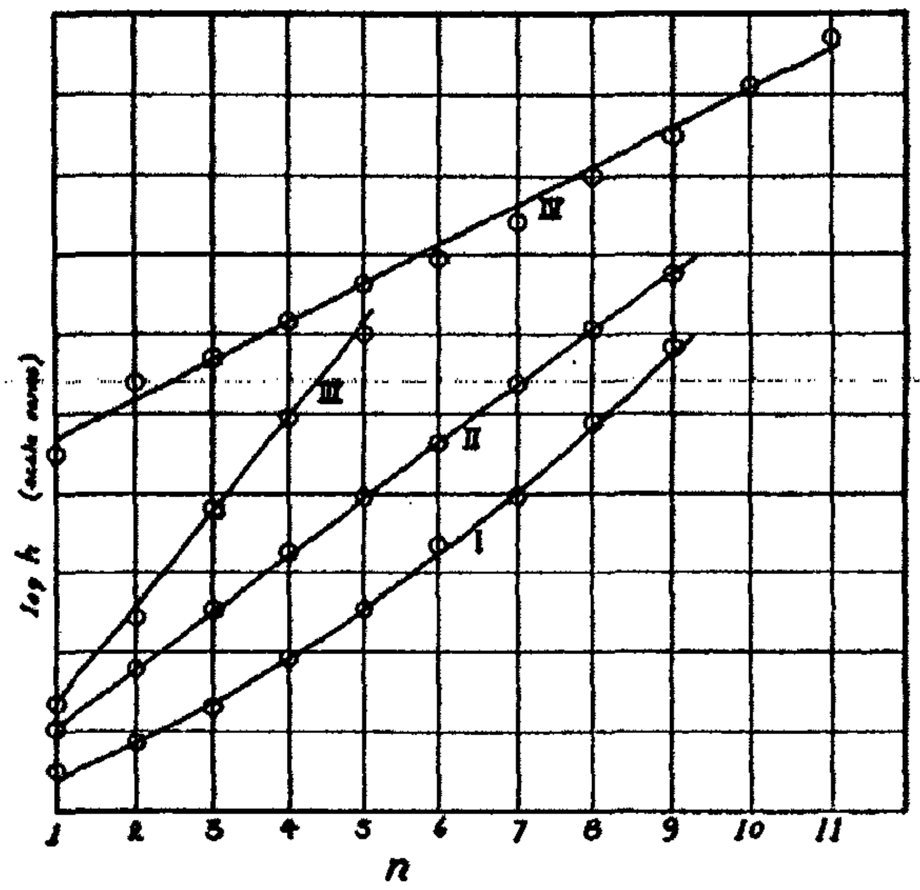

FIG. 4. Plot of log h against n. Curve I, 0.25 N potassium chloride; curve II, 0.025 N sodium chloride; curve III, 0.01 N potassium chloride; curve IV, 0.025 N potassium chloride.

In conclusion it should be noted that the mechanism outlined above is very probably not the only one which will lead to an equation for ring spacing of this type, and that similar results could be expected if the gel were setting in a discontinuous manner. The experiments described here may be interpreted to lend further support to the coagulation-adsorption theory as a reasonable explanation of a number of periodic processes.

SUMMARY

1. Experiments are described in which periodic coagulation is produced in colloidal gold in the presence of silica sol by diffusion of various electrolytes.

2. The effect of different electrolytes seems to be highly specific, but in general increase of concentration produces more closely spaced rings.

3. There appears to be no discontinuity in the diffusion of the electrolyte during ring formation and setting of the gel.

4. The results agree moderately well with the assumption that the coagulation of the colloid is accompanied by adsorption of colloidal particles in the adjacent region.

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THE SYSTEM SODIUM METASILICATE-WATER FROM 90°C. TO THE ICE POINT

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Sodium metasilicate seems to have been first reported by Fritzsche (2), who prepared the hydrates with six and nine molecules of water. Subsequent workers have reported more than a dozen different hydrates, the number of molecules of water ranging from two and a half to fourteen. The recent work of Baker, Woodward, and Pabst (1) indicates that probably only four hydrates exist. The characteristics of the hydrates with five, six, eight, and nine molecules of water as reported by them are given in table 1 for ready reference. Crystalline anhydrous sodium metasilicate has been prepared by Morey (5) from glasses and from hydrous systems at elevated temperatures. The characteristics of the anhydrous crystals as reported by Morey and Bowen (6) are also shown in table 1. The melting point for sodium metasilicate is that reported by Jaeger (4). The only published phase equilibrium studies involving hydrated sodium metasilicate are those of Harmon (3) for the system Na_2O-SiO_2-H_2O at 25°C.

MATERIALS

The most satisfactory source of sodium metasilicate for the present work was found in specially prepared crystals of $Na_2SiO_3 \cdot 9H_2O$. The lower hydrates are less desirable because they are apt to carry inclusions and also to occlude small amounts of excess alkali. A solution carrying about 30 per cent Na_2SiO_3 was made up from a specially purified grade of commercial silicate of soda and C.P. sodium hydroxide. This solution was then allowed to stand for two weeks at room temperature. The crystals which separated were washed and centrifuged. After recrystallization they were usually found to be quite pure.

PROCEDURE

The solutions were made up by melting the $Na_2SiO_3 \cdot 9H_2O$ crystals in silver flasks and either adding the required amount of water or boiling off any excess over that desired. The liquid was then adjusted to the thermostat temperature, and the flask was tightly closed and strapped onto a submerged rotor in the thermostat. Care was exercised to protect the metasilicate solutions from atmospheric carbon dioxide and never to bring them into contact with glass.

After a week or two of rotation in the thermostat, samples were taken of the aqueous phase and of the wet residue, and an analysis made of each. The particular flask was then replaced for another week or so, and then the contents again sampled and analyzed. This process was repeated until two or three successive analyses indicated that the system had come to equilibrium.

Once the approximate solubility was ascertained for a given temperature, two or more samples of undersaturated solution carrying in suspension an excess of crystals were usually started so as to approach equilibrium also from undersaturation. On the average, from six to ten weeks were required to establish the true solubility at any given temperature.

TABLE 1

Characteristics of sodium metasilicate and its hydrates

COMPOUND	CRYSTAL SYSTEM AND CLASS	DENSITY AT 20°C.	MEAN INDEX OF REFRACTION	MELTING POINT
				°C.
Na_2SiO_3	Orthorhombic		1.520	1088
$Na_2SiO_3 \cdot 5H_2O$	Triclinic pinacoidal	1.749	1.456	72.20
$Na_2SiO_3 \cdot 6H_2O$	Monoclinic sphenoidal	1.807	1.474	62.85
$Na_2SiO_3 \cdot 8H_2O$	Monoclinic prismatic	1.672	1.462	48.35
$Na_2SiO_3 \cdot 9H_2O$	Rhombic bipyramidal	1.646	1.455	47.85

No particular difficulty was experienced at the lower temperatures, but as the solutions worked with became more concentrated, they were more viscous, slower to reach equilibrium, and more difficult to sample. In order to secure samples of the more viscous solutions, it was necessary to employ a special centrifuge operating at 5600 revolutions per minute. The strong tendency for these solutions to remain supersaturated is well illustrated by the ease with which it was possible to obtain a metastable point on the solubility curves for the pentahydrate and the octahydrate.

The hydrated crystals showed only a very small tendency to occlude excess Na_2O, although it can be said that the tendency became greater with lower degree of hydration. The anhydrous crystals, however, often occluded an appreciable excess of Na_2O. In one case, a solution originally carrying equimolecular proportions of sodium oxide and silica was found, after partial crystallization, to have only 0.95 mole of Na_2O per mole of

SiO_2. The anhydrous crystals formed had a proportional excess of Na_2O. It was finally found necessary to prepare the required anhydrous metasilicate crystals, allow them to settle, drain off the mother liquor, add another saturated solution which was exactly congruent, allow the mixture to rotate in the thermostat for a week or so, and then again replace the mother liquor with a congruent one. This permitted the equilibrium solutions for each temperature study to be strictly congruent, although the crystals in equilibrium with them always contained a slight excess of Na_2O.

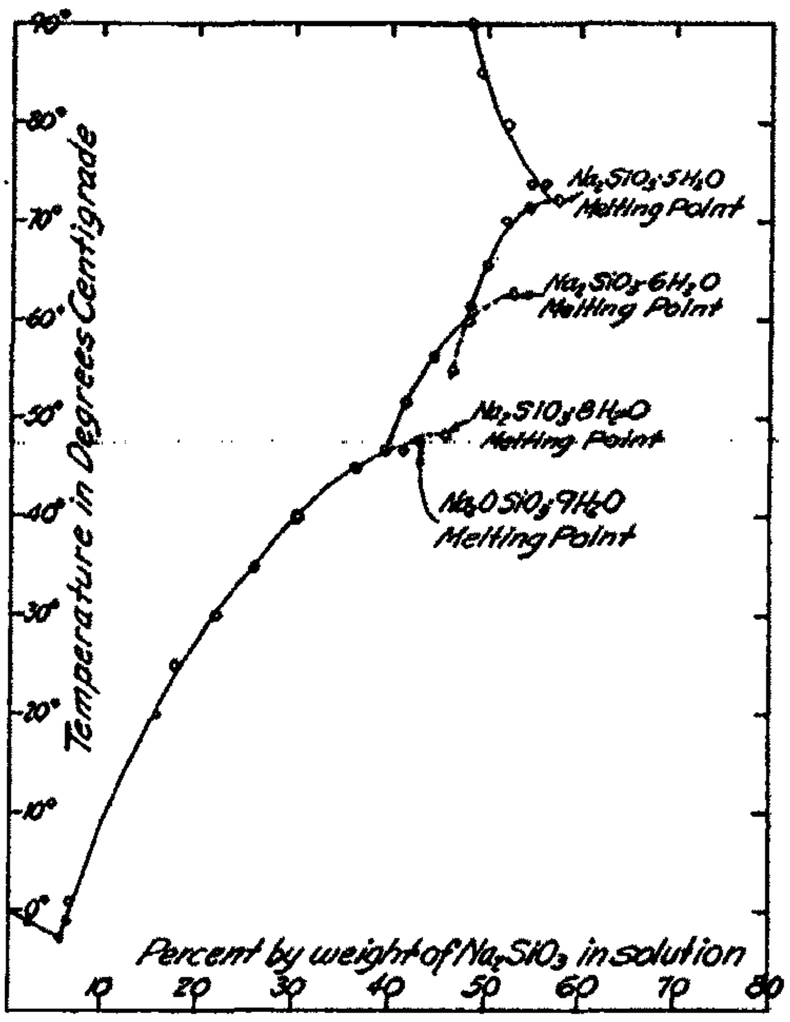

FIG. 1. The system sodium metasilicate-water from 90°C. to the ice point

The ice point was determined by rotating in a Dewar flask until analyses on successive days proved that equilibrium had been established. It is believed to be fairly accurate. The transition points were, in every case, determined by either extrapolation or interpolation, as indicated by the graphical representation (see figure 1). The melting points of the several hydrates are those earlier reported by Baker, Woodward, and Pabst (1).

SUMMARY

The phase equilibria for the system sodium metasilicate-water have been determined between 90°C. and the ice point. It is hoped that the phase equilibrium work on soluble silicate systems can be extended further and published in subsequent papers.

TABLE 2

Solubility data for the system sodium metasilicate-water

SOLID PHASE	TEMPERATURE	SOLUBILITY OF Na_2SiO_3
	°C.	*per cent by weight*
Ice	−1.00 ± 0.01	2.21 ± 0.1
Ice-$Na_2SiO_3 \cdot 9H_2O$	−2.7 ± 0.05	5.6 ± 0.1
$Na_2SiO_3 \cdot 9H_2O$	−1.00 ± 0.01	6.29 ± 0.1
	0.60 ± 0.01	6.63 ± 0.1
	20.00 ± 0.01	15.80 ± 0.1
	25.00 ± 0.01	18.20 ± 0.1
	29.90 ± 0.01	21.70 ± 0.1
	35.00 ± 0.01	25.66 ± 0.1
	39.90 ± 0.01	30.18 ± 0.1
	45.00 ± 0.01	36.18 ± 0.1
Melting point	47.85 ± 0.05	42.94
$Na_2SiO_3 \cdot 9H_2O$ $Na_2SiO_3 \cdot 8H_2O$ Metastable	47.6 ± 0.2	42.2 ± 0.5
$Na_2SiO_3 \cdot 8H_2O$	46.7 ± 0.01	41.3 ± 0.1
Melting point	48.35 ± 0.05	45.85
$Na_2SiO_3 \cdot 9H_2O$ $Na_2SiO_3 \cdot 6H_2O$	46.8 ± 0.1	39.80 ± 0.1
$Na_2SiO_3 \cdot 6H_2O$	47.00 ± 0.01	39.70 ± 0.1
	52.00 ± 0.01	42.00 ± 0.1
	56.00 ± 0.01	44.30 ± 0.1
	60.00 ± 0.01	48.31 ± 0.1
Melting point	62.85 ± 0.05	53.03
$Na_2SiO_3 \cdot 6H_2O$ $Na_2SiO_3 \cdot 5H_2O$	59.8 ± 0.1	48.0 ± 0.1
$Na_2SiO_3 \cdot 5H_2O$	55.00 ± 0.01	46.50 ± 0.1
	61.00 ± 0.01	48.25 ± 0.1
	65.00 ± 0.01	50.05 ± 0.1
	70.00 ± 0.01	52.40 ± 0.1
	71.30 ± 0.01	54.60 ± 0.1
Melting point	72.20 ± 0.05	57.53
$Na_2SiO_3 \cdot 5H_2O$ Na_2SiO_3	72.0 ± 0.1	56.6 ± 0.4
Na_2SiO_3	74.00 ± 0.01	55.75 ± 0.5
	74.00 ± 0.01	54.75 ± 0.5
	80.00 ± 0.01	61.63 ± 0.1
	85.00 ± 0.01	49.17 ± 0.1
	90.00 ± 0.01	47.97 ± 0.1

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STUDIES ON OVERVOLTAGE. IX

THE NATURE OF CATHODE AND ANODE DISCHARGE POTENTIALS AT SEVERAL METAL SURFACES[1,2]

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Polarization potentials have been measured, in general, by two methods commonly known as the direct and the commutator methods. Early investigators invariably found that the direct method gave higher values than the commutator method. For more than half a century the correct explanation has been sought for this discrepancy. The explanations offered fall largely into two groups. According to one group, the difference between the values given by the two methods is due to the existence of a resistance of some nature at the interface between electrode and electrolyte. This resistance has been named by different authors "surface resistance," "transfer resistance," "contact resistance," "film resistance," etc. According to the other group, the interrupting device used in connection with the commutator does not permit the total discharge potential to be measured because of the very rapid drop in potential during the interval between interruption of the current and measurement of the potential. Several years ago a thorough investigation of this subject was started in this laboratory. A brief summary of the work follows.

In the first paper (6) it was proven that the commutator gives values which are only averages. This provided a possible explanation for the observed discrepancies between the two methods since the commutator, therefore, could never give, directly, values as high as those obtained by the direct method.

In the second paper (7) a commutator of special design was used in an attempt to show that the potential at the beginning of the discharge interval is the same as that at the end of the charge interval. This was

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[1] This paper is a portion of the dissertation submitted by Stanley Kleinheksel to the Faculty of the Graduate School of the University of Michigan in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] The oscillograph used in these investigations was purchased with a grant from the Faculty Research Fund of the University of Michigan, which thus made this work possible.

not entirely successful, since it was not possible to measure the discharge potential at the instant the polarizing circuit was opened, and since the potential was dropping very rapidly at this time.

In the third paper (1) a new commutator was used that permitted charge potentials and corresponding discharge potentials to be measured within 0.0003 sec. from the time of interruption of the polarizing circuit. There was still, however, a discrepancy of a few millivolts between the measured potentials at the end of charge and the beginning of discharge. Certain other difficulties were also discovered that are inherent in the regular commutator potentiometer method and render it undesirable for the measurement of overvoltage and transfer resistance.

In the fourth paper (2) a commutator was used that permitted potentials to be measured practically simultaneously at several points during both the charge and discharge intervals. These results gave curves which could be extrapolated apparently with a high degree of accuracy to the instant of interruption of the polarizing circuit. The curves indicated that for platinized platinum in 2 *N* sulfuric acid at current densities between 3.8 and 150 ma. there is no surface resistance, but for smooth platinum the decrease in potential was so rapid as to make extrapolation highly uncertain.

The fifth paper (3) contains the description of a new device for the study of polarization potentials, known as a commutator oscillograph system. Actual photographs of the charge and discharge potentials throughout the complete cycle were obtained. This proved to be an excellent means for making a direct comparison of the commutator and direct methods. Oscillograms were taken by both the direct and commutator methods on the same film and practically at the same time and thus under identical conditions. These curves showed that the commutator gives a maximum value for charge potential that is identical with the value given by the direct method and confirmed the statement made in the second paper (7) that "the commutator and the direct methods would give the same values if measurements by the commutator method could be made at the instant the polarizing current is interrupted." The curves show, however, that for current densities of the order of 0.02 amp. it requires about 0.008 sec. for the cathode and 0.04 sec. for the anode to reach a maximum value. This means that, if the commutator is rotated at a speed too high to allow these time intervals for charge, correct values for charge will not be obtained. Investigators up to this time have generally used such high speeds in order to prevent the very rapid loss in potential at the beginning of discharge.

Those who support the idea that a resistance of some kind exists at the contact surface between electrode and electrolyte base their conclusions upon the presence of an instantaneous drop in electrode potential immediately after the polarizing circuit is opened. This point of view is probably best represented by the work of Newbery (8) in which he used a cathode-ray oscillograph. He states, "The existence of this gap (a vertical displacement between charge and discharge curves) proves conclusively that there is an instantaneous fall of potential at the electrode the moment the exciting current is interrupted.... This resistance—transfer resistance—may be measured by observing the vertical height of the gap in the curves." In the seventh paper (4) an electromagnetic interrrupter was substituted in place of the commutator. With this it was possible to determine the true nature of the decay curves by superimposing them directly upon another curve known to be due to an I.R. drop only, or on one known to be due to both an I.R. drop and the decay of a true electrode potential. It was evident, clearly, from the comparisons made of this nature, that there is no surface resistance at *platinized platinum* electrodes in 2 *N* sulfuric acid for current densities up to 0.017 amp.

In the eighth paper (5) the same method was used to study the nature of polarization phenomena at *smooth platinum* electrodes. It was found, however, that the early part of the potential decay curve dropped so rapidly that it could not be distinguished from a drop due to a pure resistance. It could not be demonstrated, therefore, that for such electrodes there is no surface resistance.

In the present investigation new equipment has been used with which it is possible to distinguish definitely between an I.R. drop and an electrode potential decay even for smooth platinum and several other materials investigated. With this equipment the decay of a true electrode potential may be distinguished from an I.R. drop in any case where the former requires more than 1×10^{-5} sec. per millivolt change in potential.

Overvoltage decay curves at the cathode were obtained for platinized platinum, smooth platinum, palladium, gold, silver, zinc, cadmium, antimony, and nickel. Decay curves at the anode were made for the first four. In each case curves were obtained at several current densities.

The method employed is fundamentally the same as that described in the last two papers (4, 5). In the present work, in order to be able to distinguish definitely in all cases between an I.R. drop and a true electrode potential decay, a new oscillograph vibrator (galvanometer) was used having a greatly increased frequency. In order to retain the desired sensitivity it was then necessary to construct a new amplifier having a much greater amplification; in fact, the sensitivity of the present system is actually 2.5 times that used previously.

The procedure is, essentially, to charge the cell under investigation for any desired period, then to interrupt the charging circuit at a definite instant by means of an electromagnet, and finally to record the decay of potential photographically with the oscillograph. No current is drawn from the electrode under investigation.

The cell assembly is represented in figure 1 and needs no explanation except to state that the electrodes have an area of 1 sq. cm. and the backs are covered with paraffin.

It was found desirable to be able to obtain several sensitivities from the one amplifier. This was accomplished through a variation in the potential on the suppressor grid, G2, of the R.C.A. 57 tube (figure 2). Each different voltage value applied to the grid G2 required, however, a corresponding definite potential for grid G4 of the 2A3 tube. Six different combinations of voltages were used for grids G2 and G4, giving as many amplifier sensitivities designated as systems I, II, III, etc.; the first system produced the largest and the sixth the smallest sensitivity.

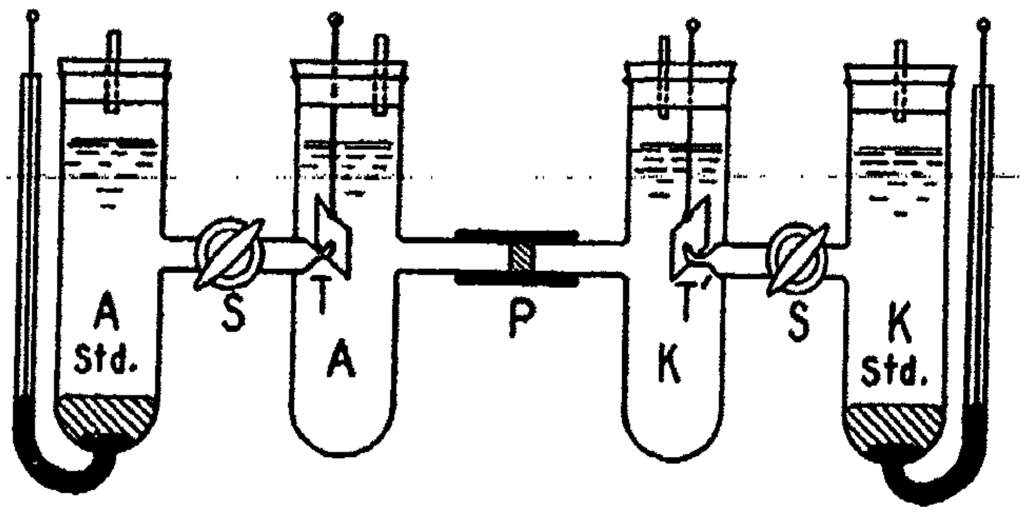

FIG. 1. Cell assembly

Each of the six systems required a separate calibration curve. A known potential Eg from a potentiometer applied to the control grid G1 of the amplifier, i.e., to the input leads (figure 2), produced a definite current Ip indicated by a milliammeter in the output circuit. A linear relation was found in the Eg–Ip curve between 60 and 130 ma. In order to locate the upper limit of the linear portion of the curve, it was only necessary, therefore, that the sum of all the potential differences in the input circuit should have a value such that the corresponding plate current was 130 ma. The oscillograph used required only 65 ma. for full scale deflection, which is well within the linear relationship. The upper limit of the linear portion for each amplification curve, in terms of milliampere output, and the approximate sensitivity in terms of millivolts per milliampere is given in table 1 for the six systems. The table contains, also, the corresponding Eg2 and Eg4 potentials.

A simplified diagram of the complete apparatus is given in figure 3. A potential divider, V, supplies the current for charging the electrodes. This circuit contains the cell under investigation and a standard 10-ohm resistance, and is closed through contacts B3 – – B4 of electromagnet B. The value of the charging current is obtained from the measured potential drop across the standard resistance. Switch E represents a group of switches so arranged that the potential difference between any pair of the four electrodes,—anode standard, anode, cathode, or cathode standard,—may be applied to either the potentiometer or the input of the amplifier. By means of the potential divider, V1, a potential may be placed in series with that of the cell under investigation. Since the potential to be measured is fixed, it is necessary to have this auxiliary potential from V1 in order to bring the current in the output circuit to the value corresponding to the upper limit of the linear portion of the characteristic curve of the

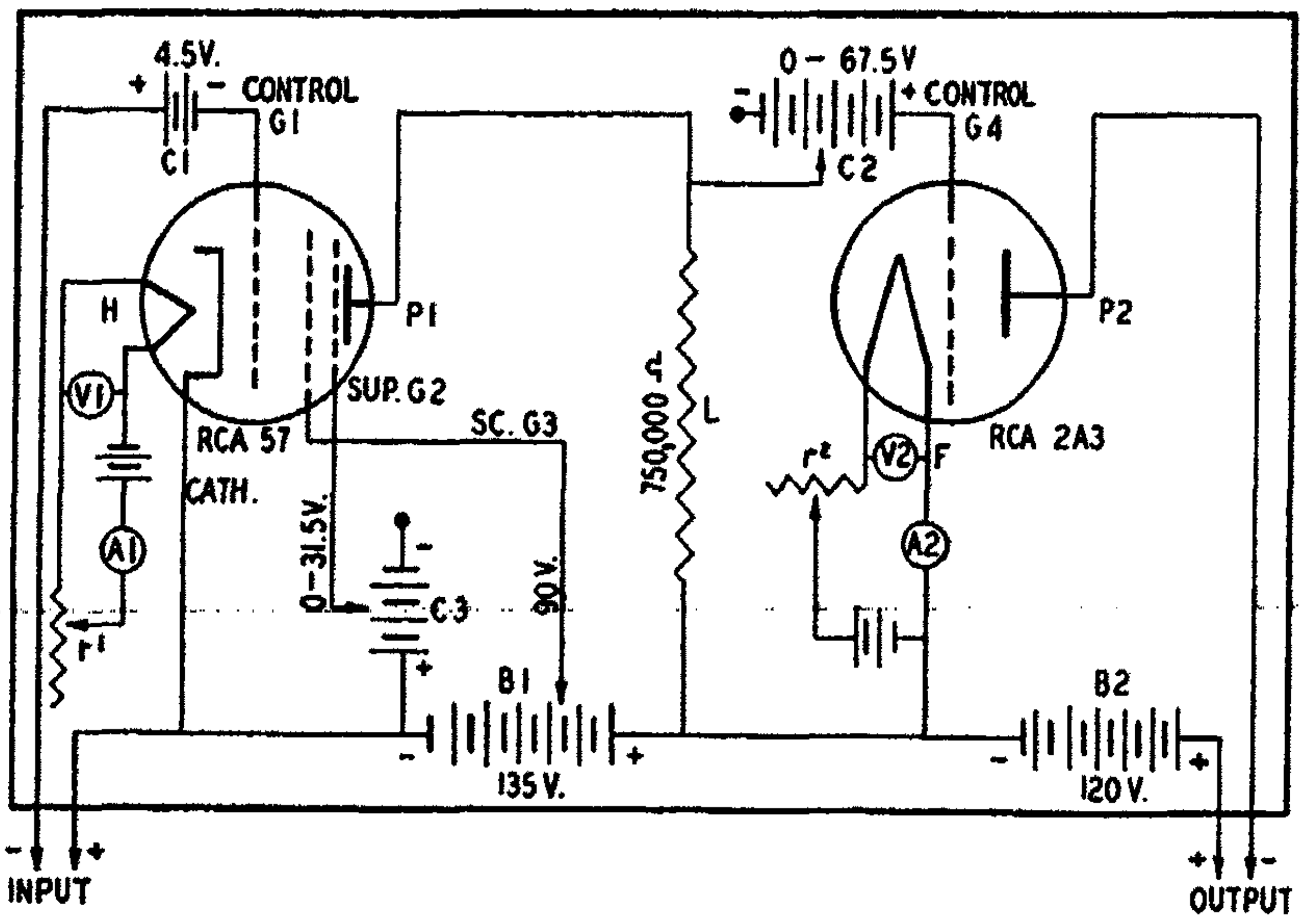

Fig. 2. d. c. amplifier

TABLE 1

Constants for the six amplification systems

SYSTEM NO.	Eg2	Eg4	OUTPUT CURRENT	APPROXIMATE SENSITIVITY
	volts	*volts*	*ma.*	*mv. per ma.*
I............	0.0	67.5	130	1.0
II............	–16.5	22.5	125	2.3
III............	–25.5	10.5	120	4.5
IV............	–28.5	6.0	120	7.3
V............	–30.0	3.0	105	9.4
VI............	–31.5	0.0	100	12.7

amplifier for the particular amplification system being used, i.e., 130 ma. for system I.

The output of the amplifier may be connected through switch A to either milliammeter Am or to the sensitive element of the oscillograph. Since the linear portion of the characteristic curve of the amplifier, for system I for instance, lies between 130 ma. and 60 ma., but the oscillograph requires only 65 ma. for full scale deflection, the output of the amplifier is first connected to the milliammeter and V1 adjusted to give 130 ma., and then an opposing potential from the divider V2 in the output circuit is inserted to reduce the current to the desired value, i.e., 65 ma. If the polarizing circuit of the cell is then opened, any potential drop in connection with this cell and included in the input potential of the amplifier results in a decrease in plate current along the linear portion of the characteristic curve starting from 130 ma., but appears on the ammeter as a corresponding decrease from 65 ma. After such preliminary adjustments the ammeter is replaced by the oscillograph, which produces a permanent record upon the rotating film.

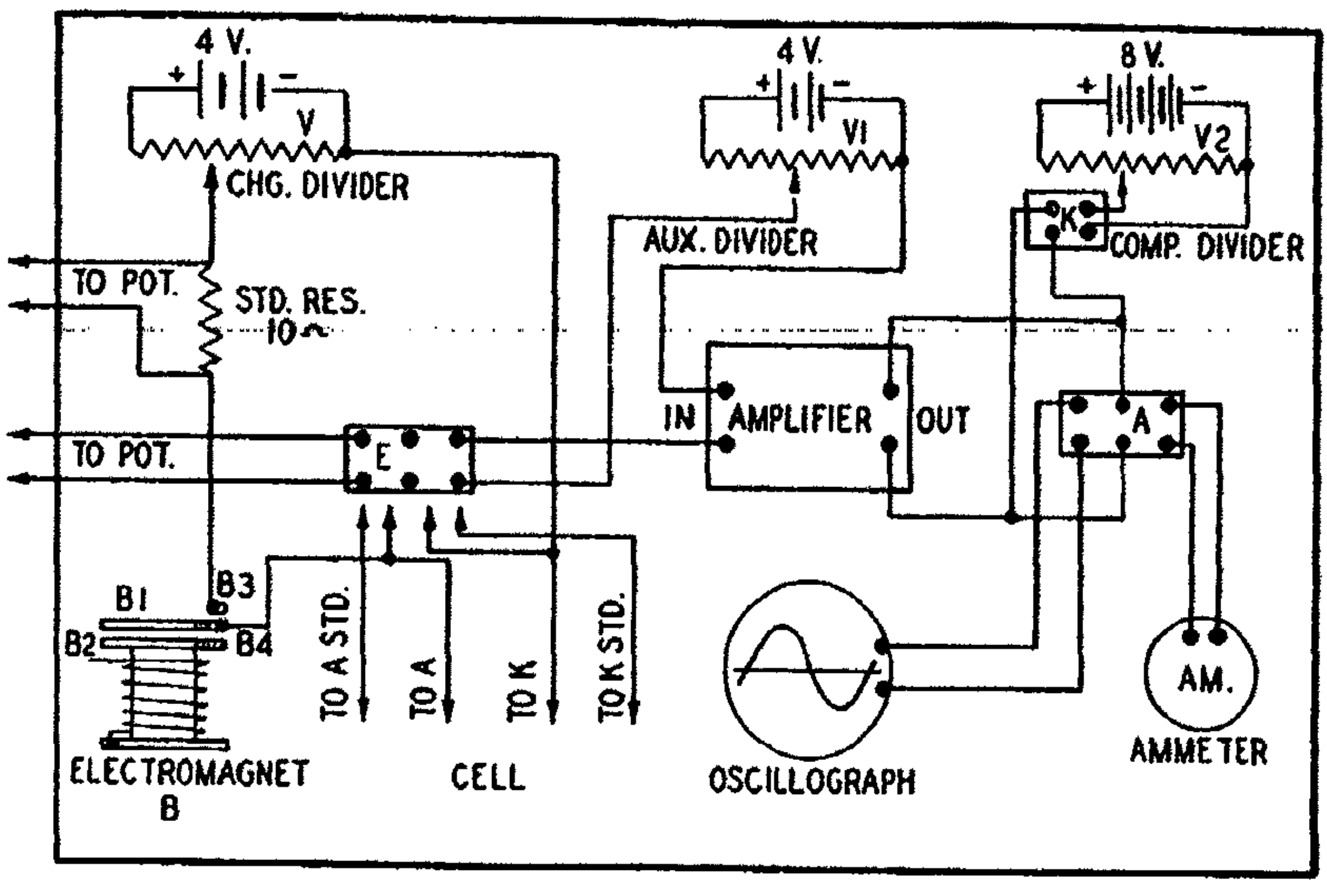

FIG. 3. Simplified diagram of apparatus

The resistances of the milliammeter and the oscillograph element are nearly equal, so that no change in total resistance of the circuit is made when one is replaced by the other. Since the element of the oscillograph is in series with a portion of the potential divider V2, however, the resistance of the latter must be large compared to the former in order that the current change in the output circuit of the amplifier may be truly represented by the deflection of the oscillograph element. At no time was the resistance included in the potential divider less than 200 times the resistance of the element. Experiments were carried out using various compensating potentials to shift the recorded curve to different positions from top to bottom of a calibrated film, and the potential indicated was entirely independent of the compensating potential, showing that the oscillograph records the true potential of the cell irrespective of the value of V2 used and therefore the position of the curve on the film.

In order to convert deflections of the light beam of the oscillograph which are recorded on the photographic film into volts, it is necessary to calibrate such recorded deflections in terms of applied potentials. To do this, first 60 mv. were applied from a potentiometer in the place of the cell. The potentials from V1 and V2 were then adjusted as described above to give 65 ma. through the oscillograph, which produced a line near the top of the film. With V1 and V2 left constant, the potential from the potentiometer was reduced 15 mv. and another line produced on the film which appeared slightly below the first. This operation was repeated until the whole film was calibrated. Separate calibrated films were made for each of the six amplification systems used. Samples of such films are shown in figure 4. New calibrations had to be made occasionally, owing to changes in the characteristics of the amplifier.

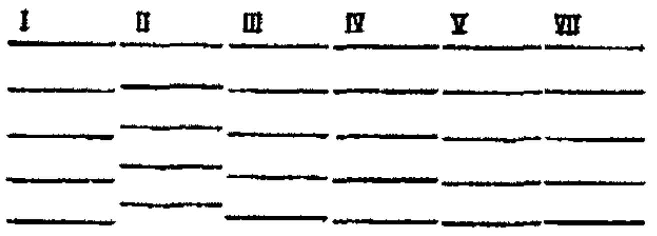

FIG. 4. Samples of calibrated films for the six amplification systems used

In all experiments the electrodes had an approximate exposed area of 1 sq. cm. and the back of the electrode was covered with paraffin. The electrolyte was 2 *N* sulfuric acid, which has a hydrogen-ion activity of nearly 1. Electrolysis was allowed to proceed for about one hour before measurements were taken. By this time the potentials had reached a constant value, the anode chamber had become saturated with oxygen and the cathode with hydrogen, and all other gases had been swept out.

Five different potentials were measured for each system used: anode vs. anode standard (A), anode vs. cathode standard (Ai), anode standard vs. cathode standard (I), cathode vs. cathode standard (K), and cathode vs. anode standard (Ki). The first gives the actual potential of the anode, the second gives this potential plus the I.R. drop through the solution, the third the I.R. drop through the solution alone, the fourth the actual cathode potential, and the fifth the cathode potential plus the I. R. drop through the solution.

The first electrodes worked with were platinized platinum. The various decay curves are shown in figures 5 and 6. The only difference between the systems represented in the two figures is in current density. Several other current densities were used, but these are typical of all.

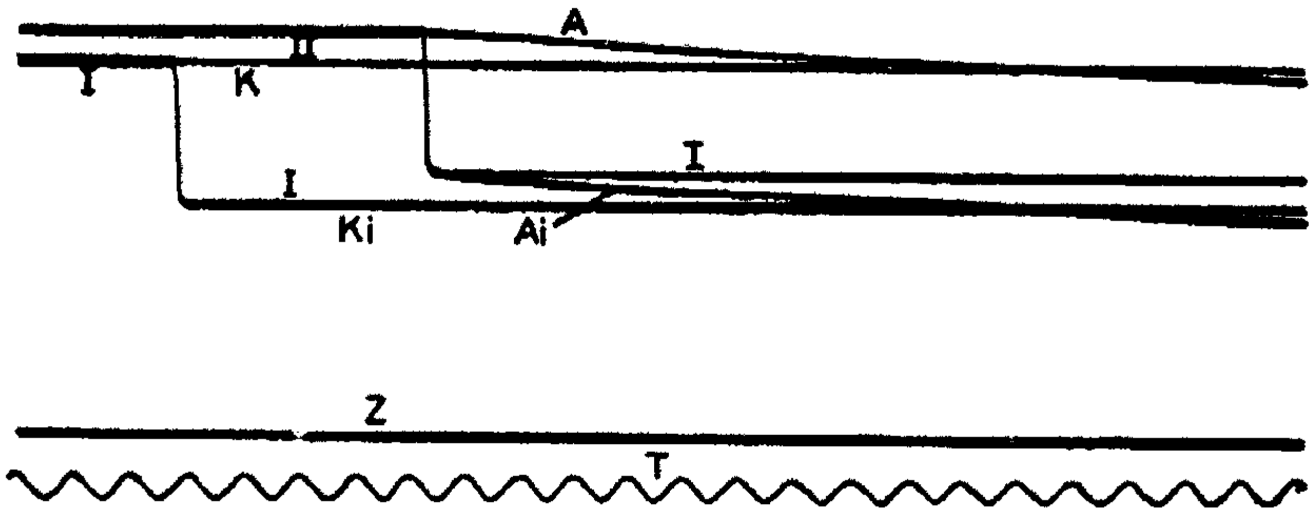

FIG. 5. Overvoltage decay curves for platinized platinum electrodes. Amplifier system I

Curve	Potential measured	Value in volts	C. D. in milliamperes
A	Anode vs. anode standard	1.616	0.485
Ai	Anode vs. cathode standard	1.637	0.485
K	Cathode vs. cathode standard	0.008	0.485
Ki	Cathode vs. anode standard	0.029	0.485
I	Anode standard vs. cathode standard	0.021	
Z	Zero line of vibrator		

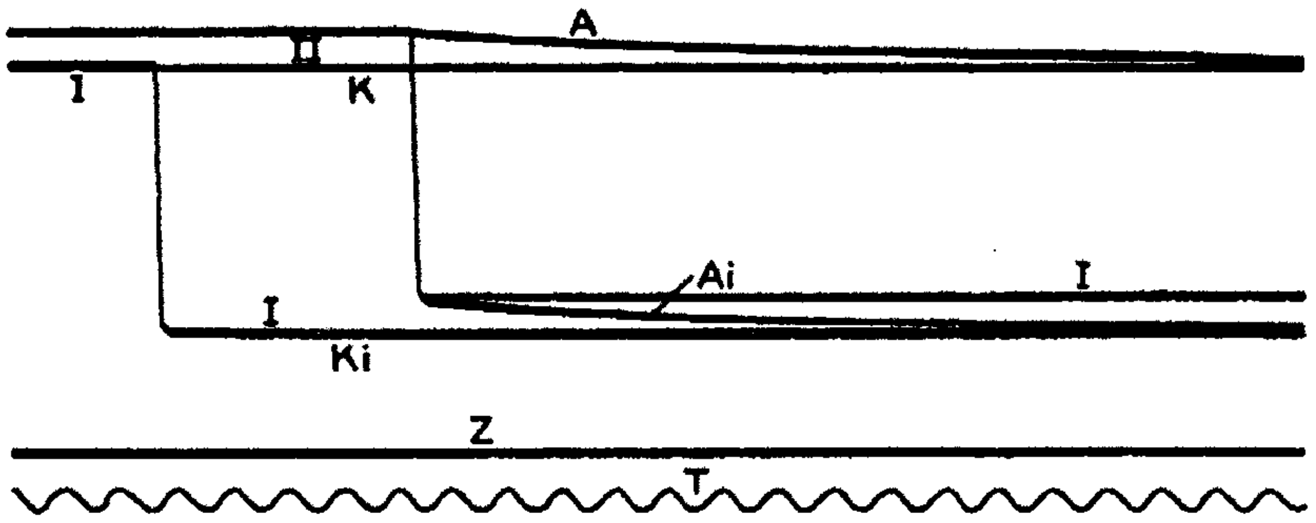

FIG. 6. Overvoltage decay curves for platinized platinum electrodes. Amplifier system VI

Curve	Potential measured	Value in volts	C. D. in milliamperes
A	Anode vs. anode standard	1.840	9.05
Ai	Anode vs. cathode standard	2.336	9.05
K	Cathode vs. cathode standard	0.043	9.05
Ki	Cathode vs. anode standard	0.540	9.05
I	Anode standard vs. cathode standard	0.497	9.05
Z	Zero line of vibrator		

On each film there are two groups of curves, I and II, each made up of three curves. For instance, group II of figure 5 contains the curves A, Ai, and I. These are all superimposed at the start by the proper adjustment of V2. The point of separation of the curves represents the instant at which the polarizing current for the cell under investigation is interrupted. By means of various contact points on the rotating film drum this can be located at any desired time during the rotation of the film. One exposure is made to record the potential represented by A, another for Ai, and another for I. Group I is a similar set for the cathode. The base line for the undeflected vibrator element is represented by Z. The curve T represents a 120-cycle circuit. The films represented in these figures were, therefore, exposed eight times. In general the film speed was adjusted so that 1 mm. on the original film represents about 0.0007 sec.

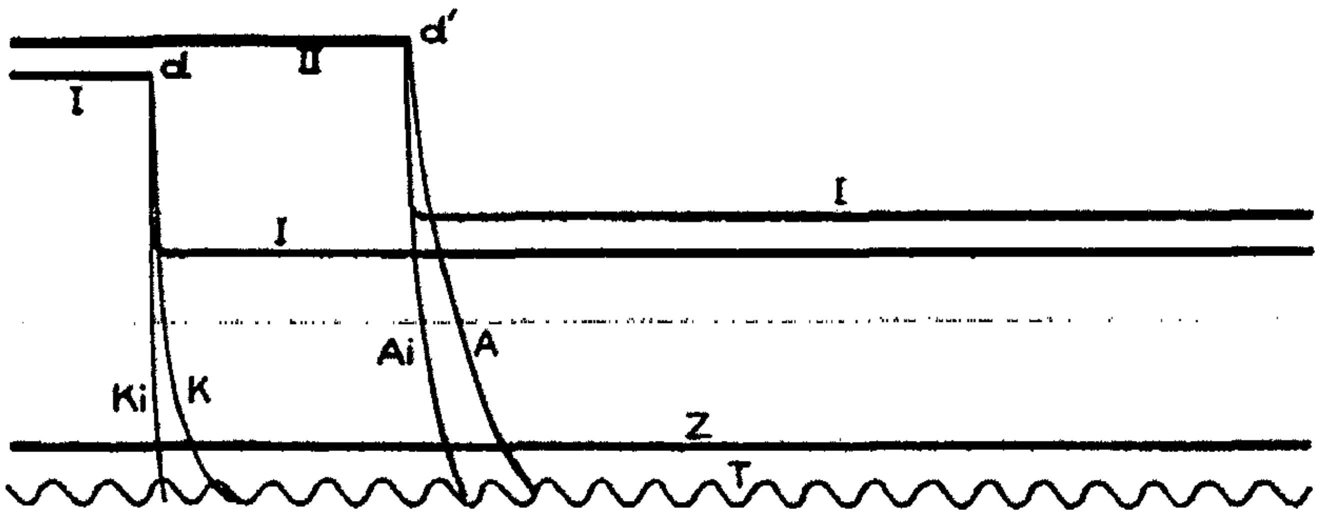

FIG. 7. Overvoltage decay curves for smooth platinum electrodes. Amplifier system I

Curve	*Potential measured*	*Value in volts*	*C. D. in milliamperes*
A	Anode vs. anode standard	1.970	0.30
Ai	Anode vs. cathode standard	1.996	0.30
K	Cathode vs. cathode standard	0.107	0.30
Ki	Cathode vs. anode standard	0.133	0.30
I	Anode standard vs. cathode standard	0.026	
Z	Zero line of vibrator		

In all cases the curve I represents a pure I.R. drop; it is the I.R. drop through the solution and may be measured by the potentiometer while the polarizing current is flowing. The value so measured agrees almost perfectly with the value calculated from a comparison of the drop in the I curve with the calibrated film. The curve A represents the decay of anode potential. It is to be noted that this decay is slow throughout its entire length, giving no indication of an I.R. drop. Curve Ai is the sum of the potentials represented by A and I, and shows the nature of a potential decay curve that does contain, also, a potential due to an I.R. drop. These curves indicate that the overvoltages, both at anode and cathode, are very small at these current densities, and that there is no I.R. drop through any kind of film at the electrodes.

Curves for smooth platinum are shown in figures 7 and 8. In agreement with previous findings in this laboratory, the initial overvoltage decay for smooth platinum is far more rapid than for platinized platinum. However, in contrast to the earlier work, in which the decay curves for the electrode potentials could not be distinguished from an I.R. drop, it is clearly evident from these figures that the present equipment is capable of making this separation. Both the anode and the cathode potentials, curves A and K respectively, diverge from the vertical line I, which is due to a pure I.R. drop, from the instant the polarizing current is interrupted. This appears to be conclusive evidence for the non-existence of a potential drop due to transfer resistance or any other resistance even at smooth platinum electrodes. These curves show, also, that the initial rate of overvoltage decay for smooth platinum electrodes is slower at the anode than at the cathode.

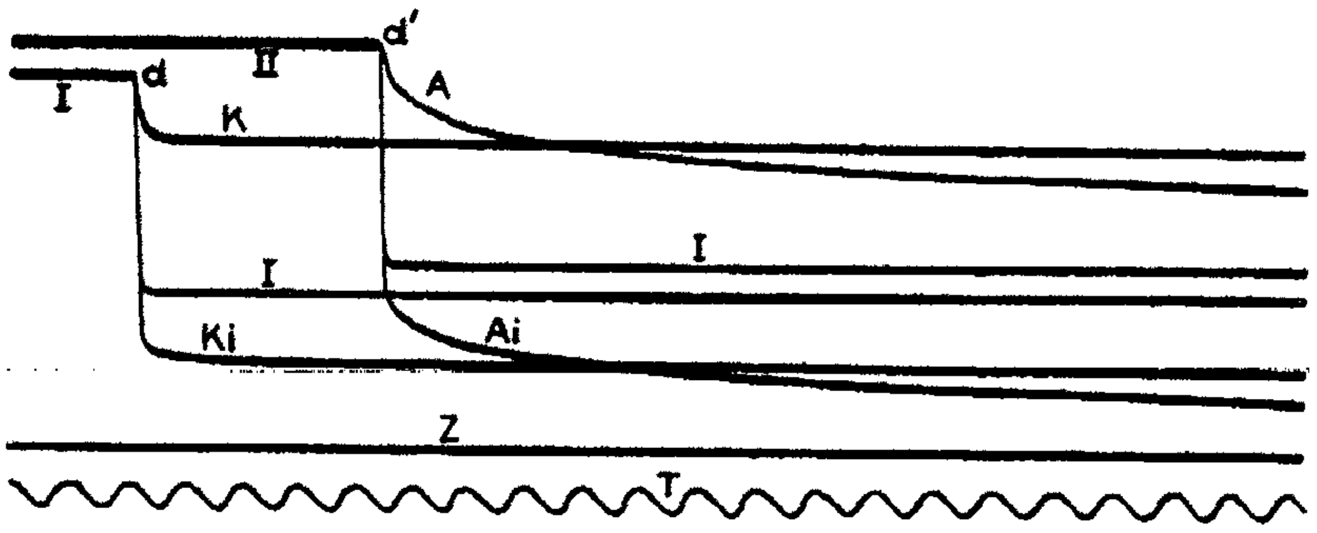

FIG. 8. Overvoltage decay curves for smooth platinum electrodes. Amplifier system VI

Curve	*Potential measured*	*Value in volts*	*C. D. in milliamperes*
A	Anode vs. anode standard	2.075	7.26
Ai	Anode vs. cathode standard	2.481	7.26
K	Cathode vs. cathode standard	0.162	7.26
Ki	Cathode vs. anode standard	0.569	7.26
I	Anode standard vs. cathode standard	0.406	7.26
Z	Zero line of vibrator		

When comparing the curves in different figures one must be sure to take into account the particular amplification system used. For the comparison factors see table 1.

The behavior of a palladium electrode during electrolysis differs from platinum in many respects. When a fresh palladium electrode, or one which has been used previously as an anode, is polarized cathodically, electrolysis must be continued during several hours at a current density of several milliamperes before a visible evolution of hydrogen occurs. With the appearance of hydrogen bubbles the cathode potential rises rapidly to a definite value. After an electrode has been used as a cathode it may be removed from the electrolyte for several hours, and if it is again polarized cathodically hydrogen evolution will begin almost immediately, followed by a rapid rise of potential to the normal overvoltage value.

Overvoltage decay curves for a palladium cathode at several current densities are shown in figure 9. These curves drop very rapidly to what appears to be a constant value, which would be explained if a compound of hydrogen were formed at the palladium cathode. It should be remembered that these experiments were designed to study the character of the extremely rapid initial drop of potential at the beginning of the discharge and that, therefore, the photographs were taken at high speeds. If a low speed were used a curve having a definite but small downward slope extending to the normal hydrogen value might be obtained. This matter is under investigation at the present time.

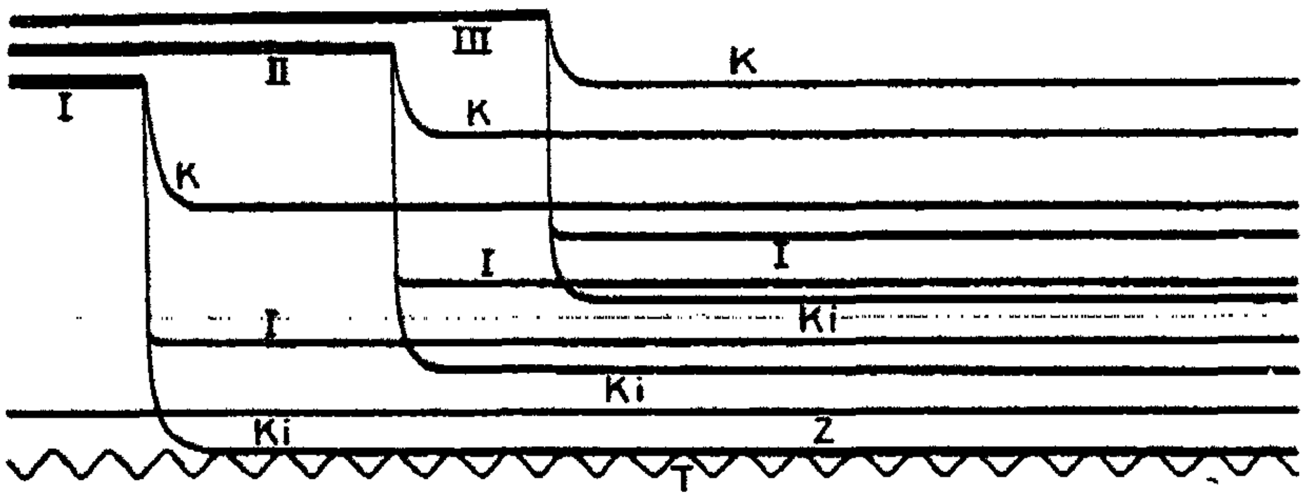

Fig. 9. Overvoltage decay curves for a palladium cathode at several current densities

Curve	*Potential measured*	*Group I, system I*	*Group II, system II*	*Group III, system III*
K	Cathode vs. cathode standard	0.046 v.	0.062 v.	0.081 v.
Ki	Cathode vs. anode standard	0.086 v.	0.143 v.	0.232 v.
I	Cathode standard vs. anode standard	0.040 v.	0.082 v.	0.152 v.
	Current density	1.0 ma.	2.08 ma.	3.85 ma.
Z	Zero line of sensitive vibrator			
T	120-cycle timing curve			

A comparison of the K curves with the vertical portion of the I curves proves that no surface resistance exists at the cathode-electrolyte interface.

The behavior of a palladium anode during electrolysis is similar to that of a cathode. A new electrode, or one which has been used previously as a cathode, requires several hours before visible oxygen bubbles appear. Prolonged electrolysis results in a tarnishing of the surface.

Curves representing the anodic overvoltage decay for palladium are given in figure 10. The anode curves, A, slope gradually downward throughout the time of the exposure in contrast with corresponding curves for the cathode, where a rapid initial drop is followed by a very slow change. The overvoltage at the anode is much larger than at the cathode.

Curves for gold as cathode are represented in figure 11 and as anode in figure 12. Again the anode overvoltage is much greater than the cathode. Upon prolonged electrolysis the gold anode is tarnished to a dull chocolate color.

The cathode decay curves for silver are shown in figure 13. Reproducible curves could not be obtained for silver as anode.

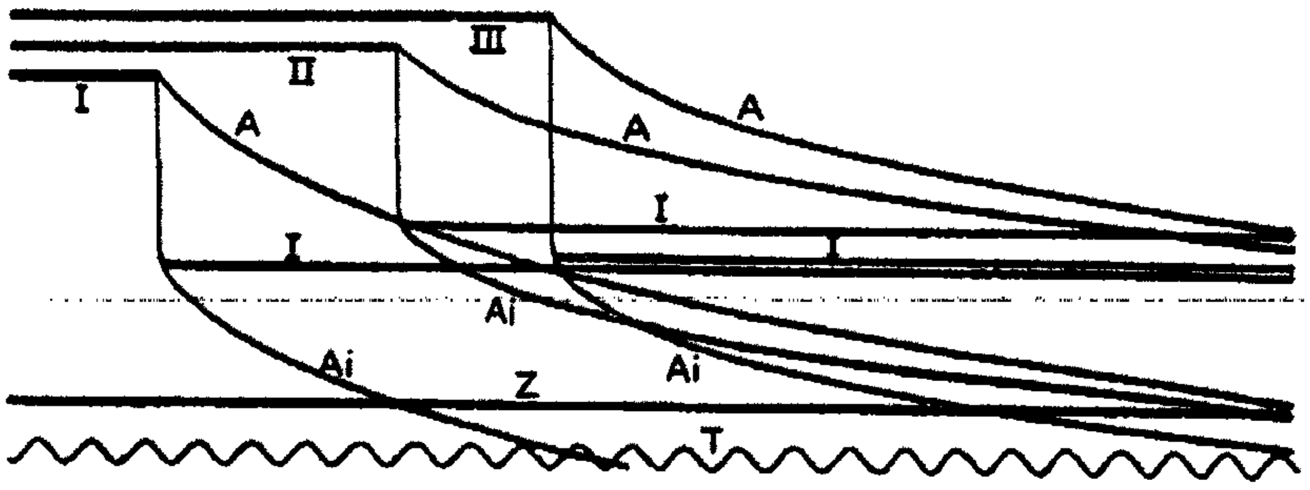

Fig. 10. Overvoltage decay curves for a palladium anode

Curve	*Potential measured*	*Group I, system II*	*Group II, system III*	*Group III, system III*
A	Anode vs. anode standard	1.842 v.	1.864 v.	1.873 v.
Ai	Anode vs. cathode standard	1.909 v.	1.991 v.	2.044 v.
I	Anode standard vs. cathode standard	0.068 v.	0.126 v.	0.171 v.
	Current density	1.70 ma.	3.18 ma.	4.37 ma.

Z	Zero line of sensitive vibrator
T	120-cycle timing curve

Zinc under ordinary conditions displaces hydrogen from 2 *N* sulfuric acid solution. Preliminary cathodic polarization of pure zinc, followed by buffing with clean cotton, results in a smooth surface which is passive. In most cases an electrode treated in this manner may be used as a cathode for hours without showing any tendency toward solution. Overvoltage curves for zinc as cathode are given in figure 14. Zinc shows an extremely rapid initial drop and then remains nearly constant.

The curves for cadmium are given in figure 15. These curves show that cadmium has an unusually high overvoltage, a large part of which disappears very rapidly.

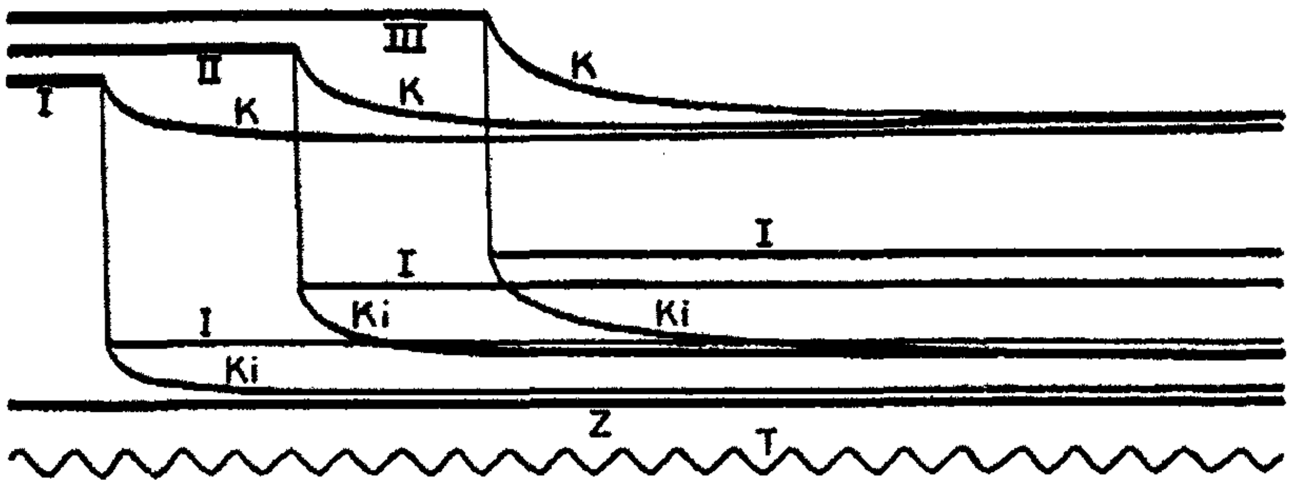

Fig. 11. Overvoltage decay curves for gold cathode

Curve	*Potential measured*	*Group I, system VI*	*Group II, system V*	*Group III, system IV*
K	Cathode vs. cathode standard	0.491 v.	0.485 v.	0.484 v.
Ki	Cathode vs. anode standard	1.003 v.	0.831 v.	0.747 v.
I	Cathode standard vs. anode standard	0.512 v.	0.346 v.	0.263 v.
	Current density	12.26 ma.	8.87 ma.	6.75 ma.

Z Zero line of sensitive vibrator
T 120-cycle timing curve

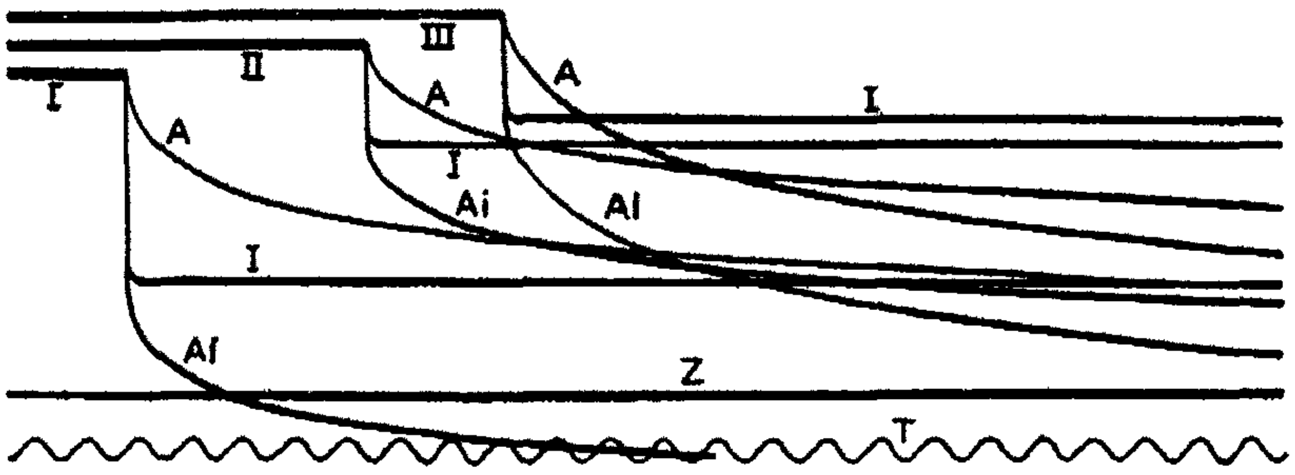

Fig. 12. Overvoltage decay curves for gold anode

Curve	*Potential measured*	*Group I, system III*	*Group II, system III*	*Group III, system II*
A	Anode vs. anode standard	2.046 v.	2.027 v.	2.010 v.
Ai	Anode vs. cathode standard	2.196 v.	2.096 v.	2.044 v.
I	Anode standard vs. cathode standard	0.150 v.	0.069 v.	0.034 v.
	Current density	2.9 ma.	1.38 ma.	0.73 ma.

Z Zero line of sensitive vibrator
T 120-cycle timing curve

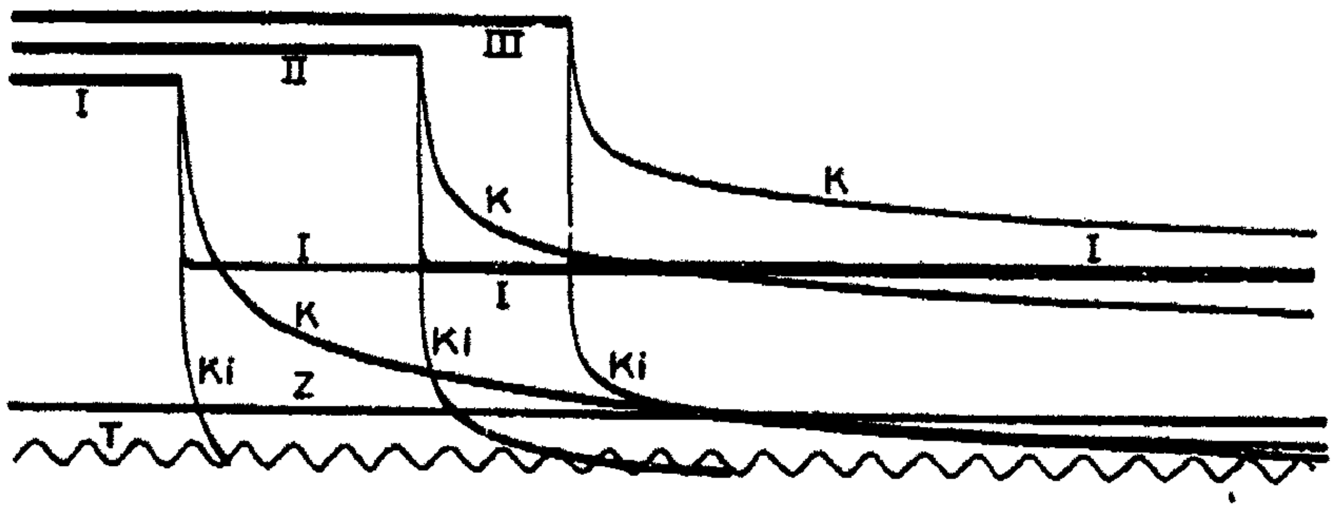

Fig. 13. Overvoltage decay curves for silver cathode

Curve	*Potential measured*	*Group I, system III*	*Group II, system IV*	*Group III, system V*
K	Cathode vs. cathode standard	0.480 v.	0.506 v.	0.520 v.
Ki	Cathode vs. anode standard	0.609 v.	0.749 v.	0.873 v.
I	Cathode standard vs. anode standard	0.128 v.	0.243 v.	0.348 v.
	Current density	2.40 ma.	4.4 ma.	6.5 ma.
Z	Zero line of sensitive vibrator			
T	120-cycle timing curve			

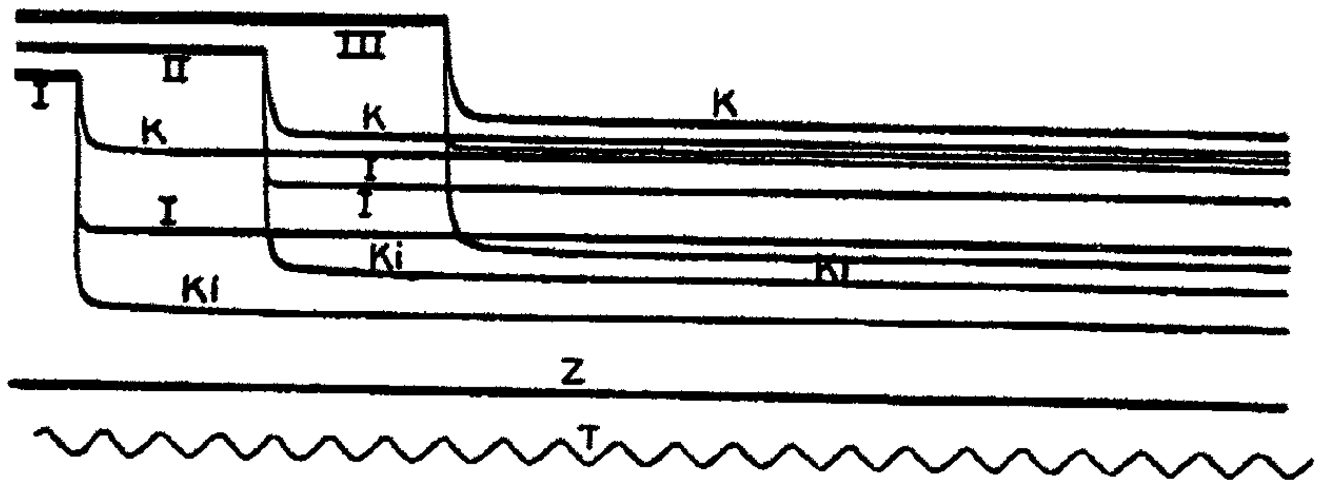

Fig. 14. Overvoltage decay curves for zinc cathode

Curve	*Potential measured*	*Group I, system VI*	*Group II, system V*	*Group III, system IV*
K	Cathode vs. cathode standard	0.985 v.	0.942 v.	0.930 v.
Ki	Cathode vs. anode standard	1.302 v.	1.150 v.	1.086 v.
I	Cathode standard vs. anode standard	0.317 v.	0.205 v.	0.147 v.
	Current density	7.15 ma.	4.62 ma.	3.33 ma.
Z	Zero line of sensitive vibrator			
T	120-cycle timing curve			

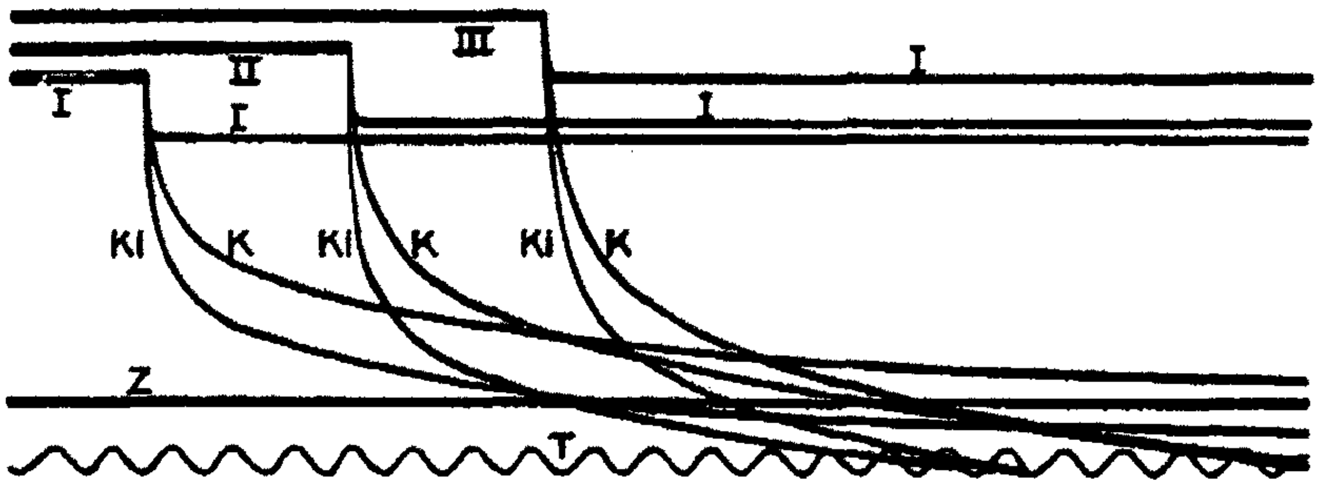

FIG. 15. Overvoltage decay curves for cadmium cathode

Curve	*Potential measured*	*Group I, system VI*	*Group II, system V*	*Group III, system IV*
K	Cathode vs. cathode standard	1.117 v.	1.116 v.	1.078 v.
Ki	Cathode vs. anode standard	1.234 v.	1.210 v.	1.149 v.
I	Cathode standard vs. anode standard	0.117 v.	0.094 v.	0.071 v.
	Current density	3.0 ma.	2.42 ma.	1.79 ma.

Z	Zero line of sensitive vibrator
T	120-cycle timing curve

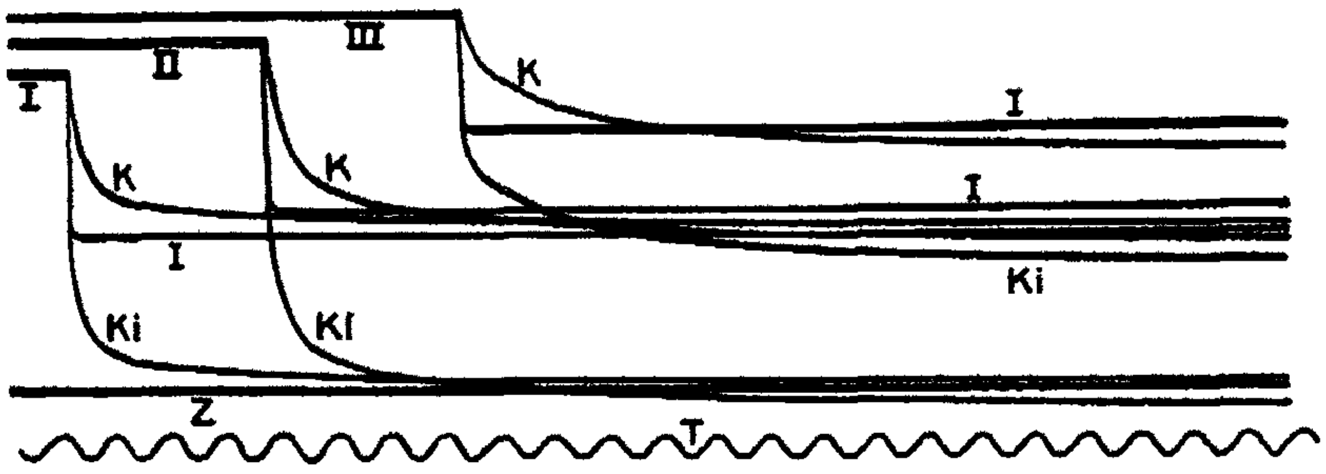

FIG. 16. Overvoltage decay curves for antimony cathode

Curve	*Potential measured*	*Group I, system III*	*Group II, system II*	*Group III, system I*
K	Cathode vs. cathode standard	0.615 v.	0.579 v.	0.525 v.
Ki	Cathode vs. anode standard	0.731 v.	0.641 v.	0.544 v.
I	Cathode standard vs. anode standard	0.116 v.	0.062 v.	0.019 v.
	Current density	2.94 ma.	1.55 ma.	0.46 ma.

Z	Zero line of sensitive vibrator
T	120-cycle timing curve

Cathode curves for antimony and nickel are shown in figures 16 and 17, respectively.

In every case studied the decay curves diverge from the corresponding I.R. drop curves immediately. These facts show conclusively that no part of the overvoltage decay is as rapid as an I.R. drop and, therefore, the possibility of the inclusion of a potential drop through some kind of resistance at the electrode solution interface in the measured electrode potential is excluded.

From a careful analysis of the cathode decay curves presented here and many others not included in this paper, it appears probable that at least two different causes are responsible for the total measured overvoltage. The first of these appears as an extremely rapid potential drop which, for most materials studied, is completed in less than 0.01 sec. This extremely rapid initial drop is followed by a slow decay, probably to the value of the normal hydrogen electrode. Only the initial rapid drop and the first portion of the slow decay were investigated in this research; thus it is not possible to arrive at conclusions regarding the later stages of the slow decay.

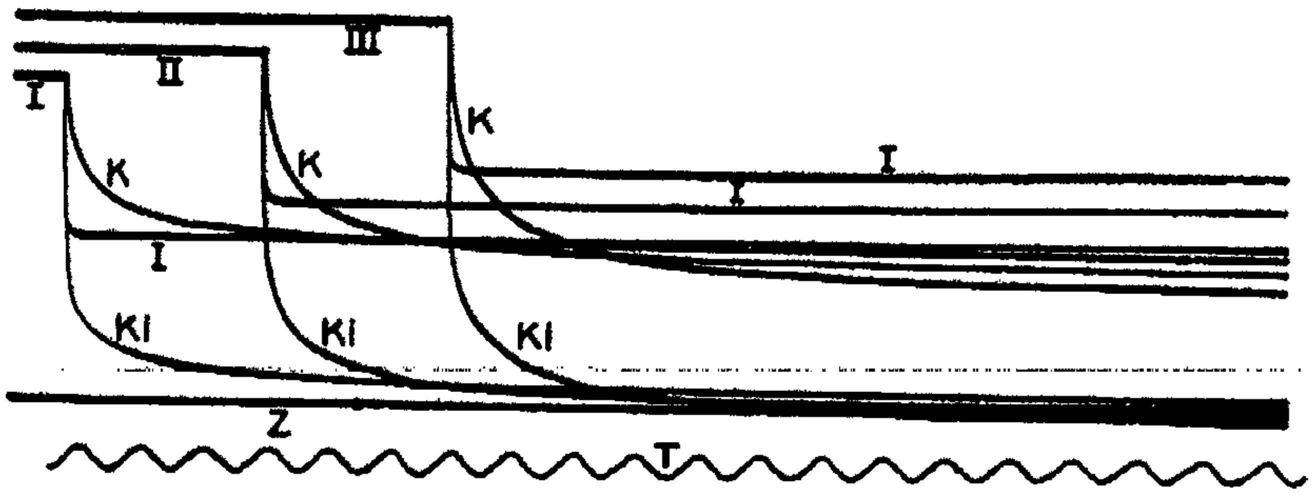

FIG. 17. Overvoltage decay curves for nickel cathode

Curve	*Potential measured*	*Group I, system VI*	*Group II, system V*	*Group III, system IV*
K	Cathode vs. cathode standard	0.520 v.	0.509 v.	0.494 v.
Ki	Cathode vs. anode standard	0.817 v.	0.723 v.	0.656 v.
I	Cathode standard vs. anode standard	0.297 v.	0.214 v.	0.162 v.
	Current density	5.72 ma.	4.09 ma.	3.1 ma.
Z	Zero line of sensitive vibrator			
T	120-cycle timing curve			

The value of the total hydrogen overvoltage increases with current density for all the materials used. The value of the initial rapid drop also increases with current density; but the residual overvoltage, i.e., the difference between the total overvoltage and that represented by the initial rapid drop, is nearly constant for a given metal and is independent of current density. This is the first time that such an observation has been noted, because it is the first time that it has been possible to measure the very rapid initial overvoltage drop. Values for the initial overvoltage, the residual overvoltage, and total overvoltage are collected in table 2. This table contains data, also, from several curves not included in this paper. The variation of initial overvoltage with current density is evident from the values in column 3, and the constancy of residual overvoltage is evident from column 5. Both types of overvoltage depend to a pronounced degree upon the material used as electrode.

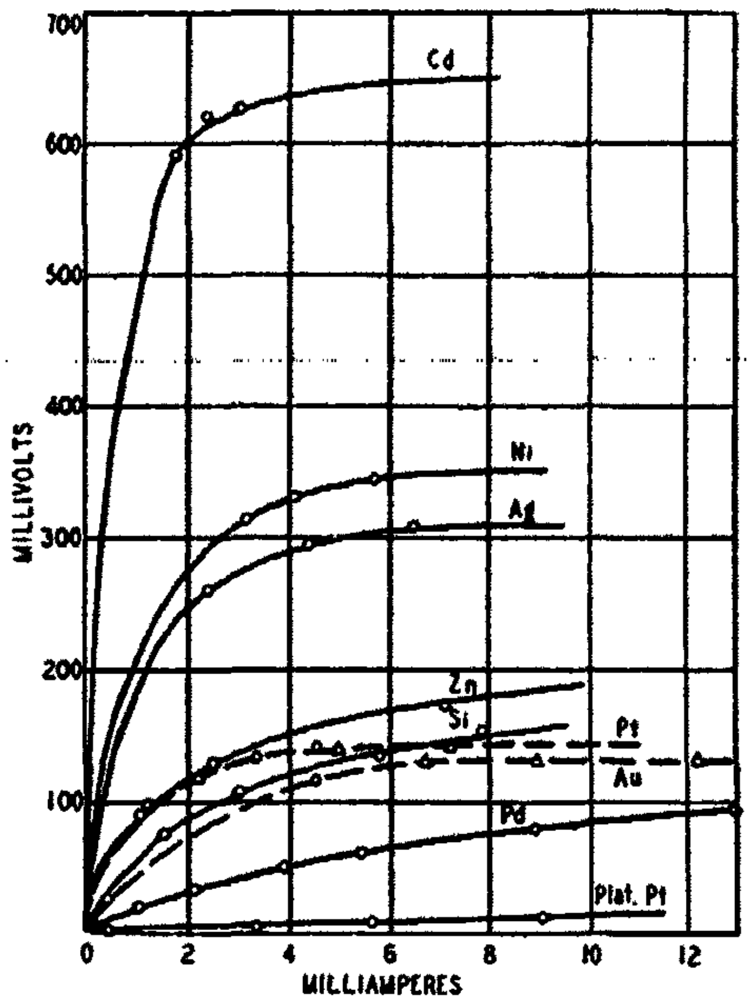

FIG. 18. Initial rapid overvoltage drop vs. current density

Curves showing the relation between current density and the overvoltage corresponding to the early rapid drop, data for which are contained in columns 1 and 3 of table 2, are given in figure 18. It is assumed that this type of hydrogen overvoltage is zero at zero current density and thus all the curves pass through the origin. These curves show considerable regularity, but no special significance is attached to them by the authors.

It is interesting to consider the data in this paper in the light of modern theories of overvoltage. The most interesting recent experimental work has been done by Bowden and coworkers. Bowden based his theory of overvoltage upon results obtained within the range of current densities from 10^{-8} to 10^{-3} amp. per square centimeter. Using a mercury electrode and

TABLE 2

Summary of hydrogen overvoltage values

CATHODE	(1) CURRENT DENSITY	(2) TOTAL OVER-VOLTAGE	(3) INITIAL OVERVOLTAGE DROP	(4) PER CENT OF TOTAL	(5) RESIDUAL OVER-VOLTAGE
	ma.	*mv.*	*mv.*		*mv.*
Platinized platinum	0.485	8	0	20	8
	3.32	29	4		25
	5.58	38	7		31
	9.05	43	13		30
Smooth platinum	2.20	140	120	86	20
	5.02	162	138		24
	7.26	162	142		20
Palladium	1.00	46	20	65	26
	2.08	62	33		29
	3.85	81	52		29
	5.43	93	61		32
	8.94	111	79		32
	13.54	127	95		32
Gold	6.75	484	128	26	356
	8.87	485	126		359
	12.26	491	131		360
Silver*	2.40	480	260	57	220
	4.40	506	295		210
	6.50	520	310		210
Zinc	1.05	897	92	14	805
	1.24	901	97		804
	2.84	939	127		812
	3.33	939	129		810
	4.62	942	140		802
	7.15	985	175		810
Cadmium*	1.79	1078	590	55	488
	2.42	1116	620		496
	3.00	1117	625		492
Antimony	0.460	525	27	17	498
	1.55	579	75		504
	2.95	615	105		510
	4.55	617	117		500
	5.80	632	135		497
	7.88	652	154		498
Nickel	3.10	494	315	65	179
	4.09	509	332		177
	5.72	520	346		174

* Curves still have a distinct slope. Values correspond to a time one-sixth of a second after the interruption of the charging circuit.

a current density of 0.04 ma. he reported that there was no rapid initial drop in the cathode decay curve, but only a gradual drop from the moment the charging current was interrupted. In the light of the data presented in table 2 of the present paper this would be expected, since, at the current density used, probably only the type of overvoltage included in column 5 is effective.

In the same paper Bowden found that at current densities between 10^{-8} and 10^{-4} amp., $n = a + b \log i$, where n is the overvoltage, i the current density, and a and b are constants. Within this current density range, b was found to equal 0.120. At higher current densities, roughly 10^{-4} to 10^{-3} amp., the relation became $n = a + 2b \log i$. The data in table 2 offer a qualitative explanation for these observations. Within the range of low current densities, where the relation is $n = a + b \log i$, only the residual type of overvoltage corresponding to values in column 5 is effective; in the higher range of current densities both types of overvoltage represented by columns 3 and 5 are increasing simultaneously, giving a constant for b about twice the former. This explanation is supported by the fact that the portion of the cathode decay curve between the rapid initial drop and the subsequent slow decay shows a gradual change in slope, as would be expected if two potential drops, one rapid and one slow, were superimposed. The type of overvoltage represented by the values in column 3 appears at current densities above about 10^{-4} amp., and therefore was not studied or recognized by Bowden. At these high current densities the logarithmic relation does not hold, the overvoltage changing less rapidly with current density.

Bowden and Rideal assumed a difference between the apparent and "accessible area" of a metal surface to explain the difference in the quantities of electricity required to cause an equal increase in overvoltage at different metal electrodes having the same apparent area. For instance, they found that the "accessible area" of a platinized platinum electrode was as much as 2000 times the apparent or regularly measured area. Yet, in developing their relations between overvoltage and current density they used the apparent area, as have all previous workers in attempts to develop such relationships. If there is the great variation between the actual, effective, or accessible area and the geometric area, which is the only one that can be accurately measured, it appears to the authors that relationships such as above expressed between overvoltage and the geometric area should have no significance.

Probably the most plausible theory of overvoltage, based upon experiment, is the dipole theory proposed by Bowden. It was developed, however, with the aid of data obtained at current densities below those employed in this research. It is not surprising, therefore, that the data submitted here do not fit well into his theory. They do show conclusively that his theory as postulated cannot be complete.

Probably the most promising theory of overvoltage from a theoretical point of view is based upon the recent considerations of Butler, Gurny, Fowler, and their associates, in which attempts are made to interpret electrode phenomena including overvoltage by the application of quantum mechanics.

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A PHYSICOCHEMICAL STUDY OF BLOOD SERA. II

Analyses of Five Hundred Cases

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The change in the total protein of the blood serum under different conditions has been studied by Peters, Eisenman, and Bulger (18) in normal individuals and under miscellaneous conditions. Rowe (20) studied the effect of venous stasis on the proteins of human serum. The same author (21) studied the effect of muscular work, diet, and hemolysis on the serum proteins. Holman, Mahoney, and Whipple (11) have studied the change in plasma proteins caused by starvation, diet, and intravenous injection of plasma proteins. Bruckman, D'Esopo, and Peters (1) have reported the same changes in malnutrition. Wiener and Wiener (27) have made a general study of the plasma proteins in many conditions. Marriott (15) has observed and reviewed the literature of blood changes in anhydremia. Peters and Van Slyke (19) have discussed and further reviewed the general literature on the subject.

The author (29) has described a physicochemical method for the study of blood serum and has suggested the direct application of that method in differentiating various pathological conditions. This differentiation can be made with exclusive physicochemical data; definite groups can be formed. The present paper includes the analyses and grouping of five hundred consecutive cases from over fifteen hundred mental and nervous cases that have been studied at the Gladwyne Research Laboratories.

The normal amount of total protein in human serum or plasma has been studied by many investigators. Salvesen (22), Linder, Lundsgaard, and Van Slyke (14), Bruckman, D'Esopo, and Peters (1) are among those who have reported data comparable to ours, for they have used the method of Howe (12) for the fractionation of the albumin and globulin and determined the nitrogen by the Kjeldahl method. The average of all these determinations gives 7 per cent total protein, 4.39 per cent albumin, and 2.61 per cent globulin, including fibrinogen. The figures which we have used as our normal average are those of Handovsky (8), which are similar to those obtained by ourselves in normal average people, namely 7.00 per cent total protein, 4.15 per cent albumin, 1.60 per cent pseudoglobulin, and 1.25 per cent euglobulin, making albumin 60.0 per cent of the total protein, pseudoglobulin 22 per cent, and euglobulin 18 per cent.

The grouping of our cases was based on the deviation of a normal average distribution of the proteins and total amount of protein. Group II contains those cases with a euglobulin per cent of 21 or more; group III, those with a pseudoglobulin per cent of 25 or over; group IV, those cases with an albumin percentage of 65 or over; group I, those cases that did not fall in any of the other groups and which imply an average normal distribution of the proteins with a plus or minus of 3 per cent for the euglobulin and pseudoglobulin and of 5 per cent for the albumin. We have further subdivided each group according to the amount of total protein in each case. In subgroups A we considered the cases with a total protein between 6.70 per cent and 7.49 per cent as a normal average amount; in subgroups B, cases with a total protein higher than 7.49 per cent; and in subgroups C, cases with a total protein lower than 6.70 per cent. This selection has been arbitrary, but seems logical, considering the normal average variations that we have observed.

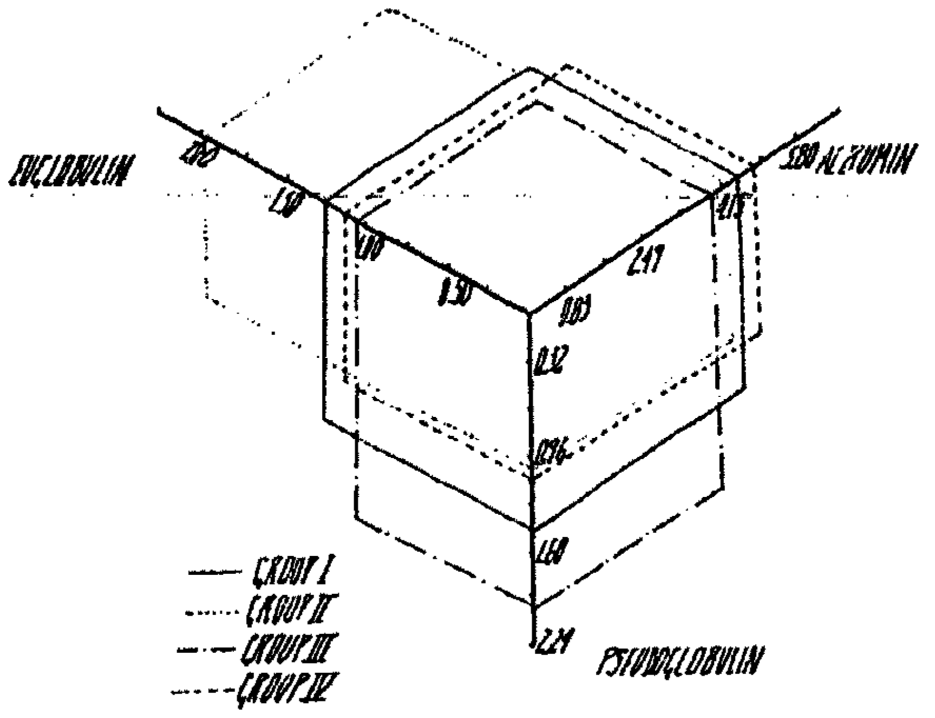

FIG. 1. Chemical chart of the averages of groups I, II, III, and IV

In figure 1 we have plotted in a three-dimensional diagram the chemical distribution of the total average of the different protein fractions in the four main groups. This plotting gives an approximate equilateral cube which shows the average normal distribution.

The quantitative and qualitative mixture of these protein fractions gives different colloidal properties to the serum. These in turn change the general physiology of the organism, especially in its relation to the water interchange between blood and tissues, for there is no doubt that the interstitial fluid is produced from the blood serum. Krogh, Landis, and Turner (13), studying the movement of fluid through the human capillary wall in relation to colloidal osmotic pressure, support the view that there is a gradient of pressure which permits filtration at the arterial end and reabsorption at the venous end of the capillary, thus producing a continuous circulation of fluid between capillaries and tissues. Direct measurements of capillary pressure and serum colloid osmotic pressures definitely provide the circulation of fluid, which has been anticipated by theoretical considerations. Thus the colloidal osmotic pressure of a serum, which is usually directly proportional to the quantitative and qualitative distribution of the protein fractions of a serum, becomes of direct importance in the study of movement of water between blood and tissues. This subject has been treated in detail by Peters (17).

There also exist changes in the protein fractions and their amounts in immune reactions. There seem to be sufficient data concerning the two fundamental types of immune reactions (28). One type has to do with substances which are essentially active poisons and whose toxicity is neutralized by direct chemical action. To this group belong the antitoxins from bacterial toxins, such as diphtheria, tetanus, botulinus, etc., snake venoms, vegetable toxins, etc. The substances in this group are similar in that, while having a chemical structure more simple than that of a true protein, they resemble more a colloidal aggregate. The protein change that occurs in this form of immunity reaction is a definite increase in the pseudoglobulin fraction, for it is in this fraction of the protein complex that we find the greatest amount of the antitoxic substance. This fact is recognized, for it is used in the concentration of the antitoxins for commercial use.

The other group of immunity reactions consists of those which are concerned with the defense of the body to definite foreign proteins, polysaccharides, or lipoid complexes, whether toxic or non-toxic in themselves. To this group belong the whole protoplasmic bodies of bacteria, their different lipoid or carbohydrate fractions, animal or vegetable proteins, etc. In this type of immunity reaction we find a definite increase in the euglobulin fraction of the whole plasma protein of the immunized animal, and the majority of the antibodies produced are found in this fraction. This fact is used in the preparation of purified therapeutic bacterial antibodies.

The difference in chemical response in these two types of immunity reactions by these two groups of substances suggests the direct effect of the chemical structure of the antigen on the reaction of the body to the administration of these substances. In the separation of our groups we have taken this fact into consideration; in group II we have included the cases with a euglobulin increase (second group of immunity reactions) and in group III those with a pseudoglobulin increase (first group of immunity reactions).

The chemical difference between the pseudoglobulins and the euglobulins suggested by Chick (4) and confirmed by Sørensen and some of his coworkers (24) is that euglobulin in serum is a complex material, formed from pseudoglobulin by association with some serum lipoid, to the presence of which it owes its phosphorus content.

Hardy and Mellanby (9) made studies many years ago on the solubility of serum globulin in salt solution, and more recently Sørensen (24) did likewise. The last author believes that in the serum itself, as well as in the special globulin fractions prepared from it, the globulins do not occur as mixtures of two or more globulins but as readily dissociable combinations of the same. As a simple and general term for the composition of such a combination the formula EpPq was utilized, where E indicated a euglobulin complex and P a pseudoglobulin complex, and where previously the probable difference between the individual euglobulin and pseudoglobulin complexes was disregarded.

The study of serum as a readily dissociable component system of protein and the differences observed in our cases give us a fundamental physicochemical point of view which is of general practical and theoretical value. Sørensen (24) says that in serum an interaction must be presumed to occur between all the protein systems present, an interaction which may lead to the formation of new systems possibly containing components from albumin systems as well as from globulin systems and perhaps capable, to a limited extent, of giving rise to the formation of systems even larger than those known as albumins and globulins. Not only proteins, which as ampholytes have a particularly marked tendency to mutual interaction, but also to a greater or less extent, dependent on concentration conditions and other circumstances, many of the other substances present in biological liquids must be supposed to be more or less closely knit to the, in all probability, highly hydrated protein systems. The views here advanced apply not only to serum but also to plasma and blood, for the blood corpuscles and other form elements in the blood,—readily dissociable complexes consisting of proteins,—and also, to a greater or less extent, other substances present in the blood have to be taken into account. For these large complexes which condition many of the physical properties of the blood plasma, for example, its great viscosity and its comparatively low colloid osmotic pressure, must be imagined in continuous reversible dissociation, dependent on the ever-changing composition of the blood.

The marked changes in amount of pseudoglobulin and euglobulin in serum give the serum different physicochemical properties. The lipoid complex in euglobulin gives this substance marked hydrophilic properties, as Chick (3) has found in the study of the hydration numbers of the different serum fractions, establishing for the euglobulin 5.8 cc. per gram, for pseudoglobulin 3.8 cc. per gram, and for albumin 2.1 cc. per gram. These differences in hydration of the various protein fractions affect their holding power for water. We are aware of the work of Grollman (7), Sunderman (6), and Greenberg (6), who do not believe that there is any appreciable amount of "bound water" in serum. But we agree with Gortner (5) and Bull (2), who point out that the concept of "bound water" has a substantial theoretical basis, and it is with this viewpoint that we have used the term here.

TABLE 1

Averages of physicochemical observations of the blood serum in 500 mental and nervous cases

GROUP	NO. OF CASES	PER CENT OF TOTAL CASES	VISCOSITY	SPECIFIC GRAVITY	TOTAL PROTEIN	ALBUMIN	PSEUDO-GLOBULIN	EUGLOBULIN	ALBUMIN	PSEUDO-GLOBULIN	EUGLOBULIN	BOUND WATER	FREE WATER	TOTAL WATER	OSMOTIC PRESSURE	ALBUMIN/GLOBULIN
									per cent	*per cent*	*per cent*					
I	94	17.8	1.70	1.0272	7.05	4.38	1.42	1.25	62.1	20.1	17.8	21.8	73.7	95.5	29.6	1.64
I A	58	11.0	1.70	1.0273	7.07	4.38	1.41	1.28	61.9	20.0	18.1	22.0	72.4	94.4	29.7	1.62
I B	14	2.6	1.81	1.0284	7.89	4.88	1.50	1.51	61.8	19.0	19.2	24.7	70.0	94.7	23.0	1.62
I C	22	4.1	1.67	1.0266	6.55	4.02	1.29	1.24	61.3	19.7	19.0	20.5	75.4	95.9	27.3	1.59
II	231	43.7	1.74	1.0276	7.24	4.22	1.08	1.94	58.2	14.9	26.9	24.2	71.1	95.3	28.8	1.39
II A	104	19.7	1.72	1.0274	7.12	4.22	1.07	1.83	59.2	15.0	25.8	23.5	71.9	95.4	28.6	1.45
II B	85	17.0	1.81	1.0283	7.94	4.37	1.18	2.39	55.0	14.8	30.8	27.5	67.2	94.7	30.5	1.22
II C	42	8.0	1.66	1.0266	6.36	3.72	0.93	1.71	58.1	14.6	[illegible].3	21.3	74.8	96.1	25.3	1.41
III	48	9.1	1.72	1.0276	6.81	3.78	1.99	1.0	55.5	28.9	15.6	21.5	74.2	95.7	27.5	1.24
III A	26	4.9	1.72	1.0278	7.04	3.92	2.12	1.00	55.7	30.1	14.2	22.1	72.4	94.5	23.2	1.25
III B	2	0.3	1.80	1.0285	7.80	3.67	2.04	2.08	47.0	26.1	26.9	27.5	67.3	94.8	27.6	0.89
III C	20	3.8	1.72	1.0266	6.37	3.61	1.83	0.93	56.6	28.7	14.7	19.9	76.2	96.1	26.1	1.31
IV	155	29.4	1.68	1.0273	7.00	4.82	1.08	1.10	69.0	15.4	15.6	20.6	74.9	95.5	30.9	2.21
IV A	83	15.7	1.67	1.0273	7.07	4.87	1.09	1.11	68.9	15.4	15.7	20.7	74.7	95.4	31.3	2.21
IV B	28	5.3	1.73	1.0283	7.79	5.24	1.06	1.49	67.2	13.6	19.2	23.7	71.1	94.8	33.7	2.05
IV C	44	8.3	1.67	1.0270	6.40	4.48	1.04	0.88	70.0	16.2	13.8	18.4	77.7	96.1	28.7	2.33
Total	528	100.0	1.71	1.0278	7.09	4.38	1.20	1.51	61.7	16.9	21.4	22.5	74.0	96.5	29.4	1.61

Group I: Distribution of protein fractions average.
Group II: Percentage of euglobulin 21 or more.
Group III: Percentage of pseudoglobulin 25 or more.
Group IV: Percentage of albumin 65 or more.
Subgroup A: Total protein between 6.70 and 7.50.
Subgroup B: Total protein higher than 7.49.
Subgroup C: Total protein lower than 6.70.

METHODS

The methods used in this work are the same as those described in our previous work (29). The mean average for each observation in each group is shown in table 1.

PHYSICOCHEMICAL CHARACTERISTICS OF THE DIFFERENT GROUPS

The physicochemical characteristics of the four main groups can be observed from the average figures for each group.

Group I, the average normal group, can be used as a comparison for the other three groups. In group I we get the general average of the average normal distribution of the protein fractions, as seen in figure 2, where the three-dimensional diagram of each of the subgroups shows a cube with its sides fairly equal. Subgroup A appears, as expected, midway between subgroups B and C. The general physicochemical characteristics of this subgroup are those which are typical of a normal serum with, the variations expected due to dilution of the total blood. For example, we find in subgroup B a more concentrated serum than in subgroup C. The concentration of the blood usually occurs through some physiological process, such as anhydremia, malnutrition, etc. The variation of "free water" in each of these subgroups is of interest. The difference between subgroups B and C is 5 cc. of "free water" in 100 cc. of serum. We take subgroup A as our standard of comparison, for it shows the general averages found among normal persons.

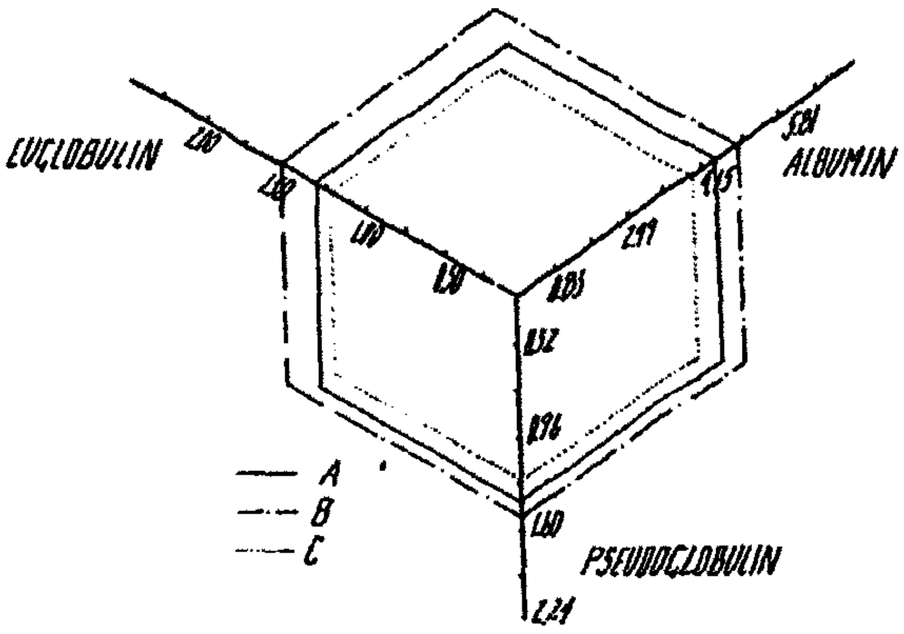

Fig. 2. Chemical chart of subgroups I A, I B, and I C

In group II we find higher viscosity, higher specific gravity, higher total protein, increase in euglobulin per cent, a large amount of "bound water," low "free water," and a low albumin-globulin ratio. This type of colloidal mixture is a more definite hydrophilic one. With this type of protein system is usually associated a certain definite physiology.

To this whole group we have given the name "hyper-reactive." This hyper-reaction, which is based on the increase of the euglobulin fraction, suggests an immunity response to a stimulation of some sort. This response is similar to that found in immunity reactions produced by a protein complex. The larger the amount of euglobulin in the serum, the more phospholipins there are bound to the protein fraction. This union alters the general physicochemical properties of the serum. With this kind of protein complex (euglobulin), we find changes in the water interchange between the blood and tissues, thus disturbing one of the most important of body functions. We find the same condition in subgroups B and C, to a more marked degree in subgroup B, and to a less extent in subgroup C. The main difference between these two subgroups is in the amount of total protein, which suggests in the last group (C) a definite dilution, as is indicated in changes in specific gravity and viscosity. For the chemical-fractional plotting of the three subdivisions of group II, see figure 3.

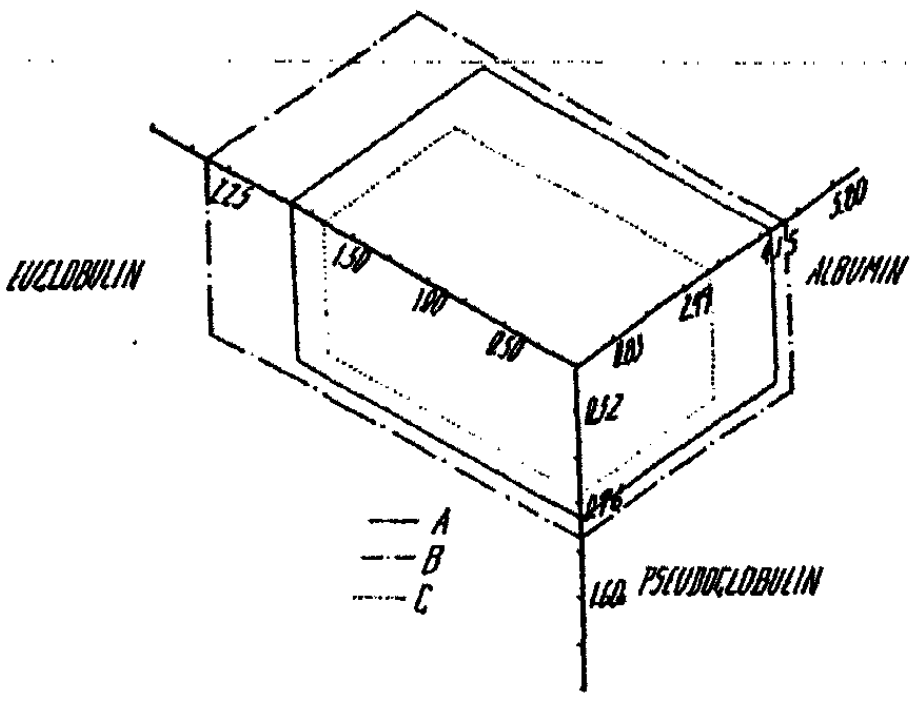

FIG. 3. Chemical chart of subgroups II A, II B, and II C

Group III is characterized by an increase of above 25 per cent in the pseudoglobulin fraction in relation to the total protein. To this group belong the general reactions that from immunological experience are expected to come from stimulation by toxic substances of a simple chemical composition. These substances may come from any by-product of digestion (absorption through the intestine), from some substance that is not properly assimilated by the liver (as we often find the pseudoglobulin fraction markedly increased in diseases of the liver), or from any other substance which is absorbed and has the characteristics mentioned above.

In subgroup B we have only two cases out of the five hundred. In these two cases there is an increase in the pseudoglobulin fraction as well as an increase in the euglobulin fraction. This double increase makes the colloidal properties of this subgroup an exceptional one. The specific gravity and the "bound water" are high, while the "free water" is low. From the immunological point of view this shows a double reaction, which suggests a definite liver involvement with a probable generalized reaction to an infection. The low albumin-globulin ratio is typical of this subgroup.

Subgroup C has definite characteristics: low total protein, low "bound water," low specific gravity, and high "free water." This suggests a marked dilution of the blood. For the chemical plotting of the subdivisions of group III, see figure 4.

Group IV, the high albumin percentage group, is of general interest because of the low pseudoglobulin and euglobulin in the mixture. With a preponderance of the albumin fraction, we expect this group to be proportionately less hydrophilic than the others, so we find high "free water" and a high osmotic pressure. Chemically it is the direct opposite to group II, and, owing to the low concentration of the pseudoglobulin and euglobulin fractions, we have termed it, from an immunological point of view, the "non-reactive" group. It seems that the individuals in this group do not react immunologically. Probably the reticulo-endothelial system in this group of cases is blocked or markedly deficient.

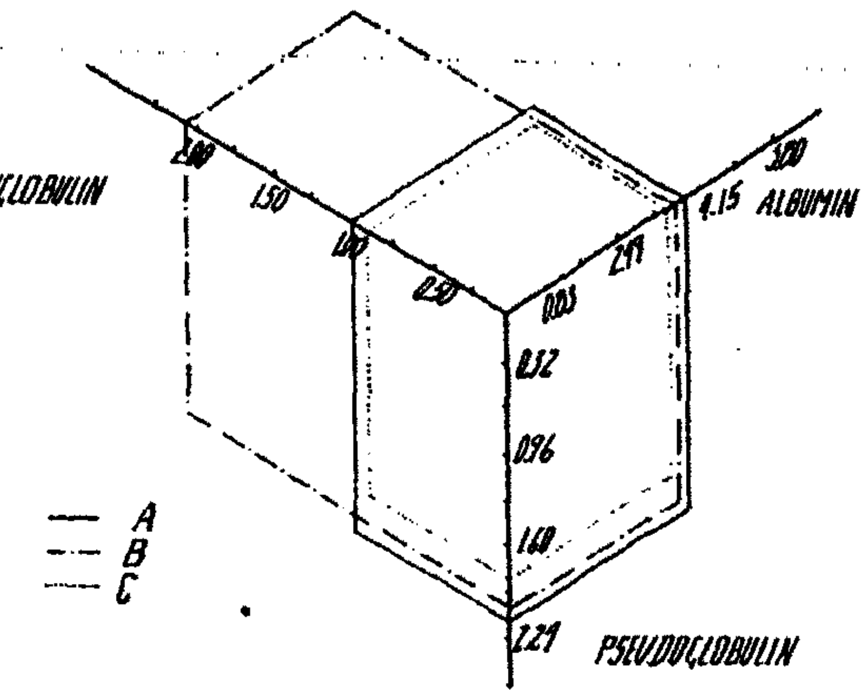

FIG. 4. Chemical chart of subgroups III A, III B, and III C

The chemical distribution of the subgroups is seen in figure 5.

Subgroup B has the general characteristics of the group except that it has a high total protein. Subgroup C is directly opposite to subgroup B. It is between these two opposite groups that we find the most marked differences. The main characteristics of this subgroup (IV C) are a low total protein, low "bound water," high "free water," high albumin-globulin ratio, and a relatively high osmotic pressure.

In order to understand further the physicochemical differences between the various groups, we study the relation between specific gravity and the total protein per cent. The results are shown in figure 6. The total average of each group falls lowest for group I and highest for group III. Groups I and II follow a straight line. Groups III and IV are askew,

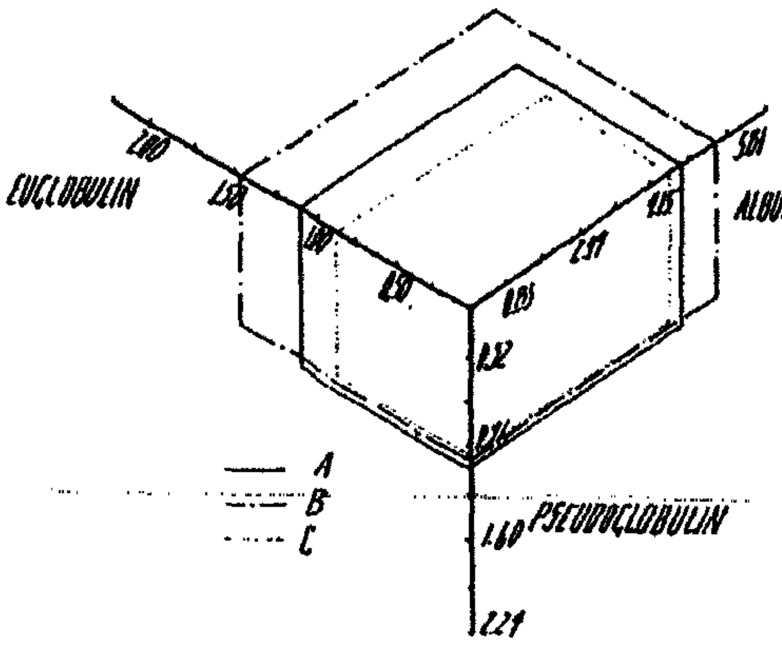

Fig. 5. Chemical chart of subgroups IV A, IV B, and IV C

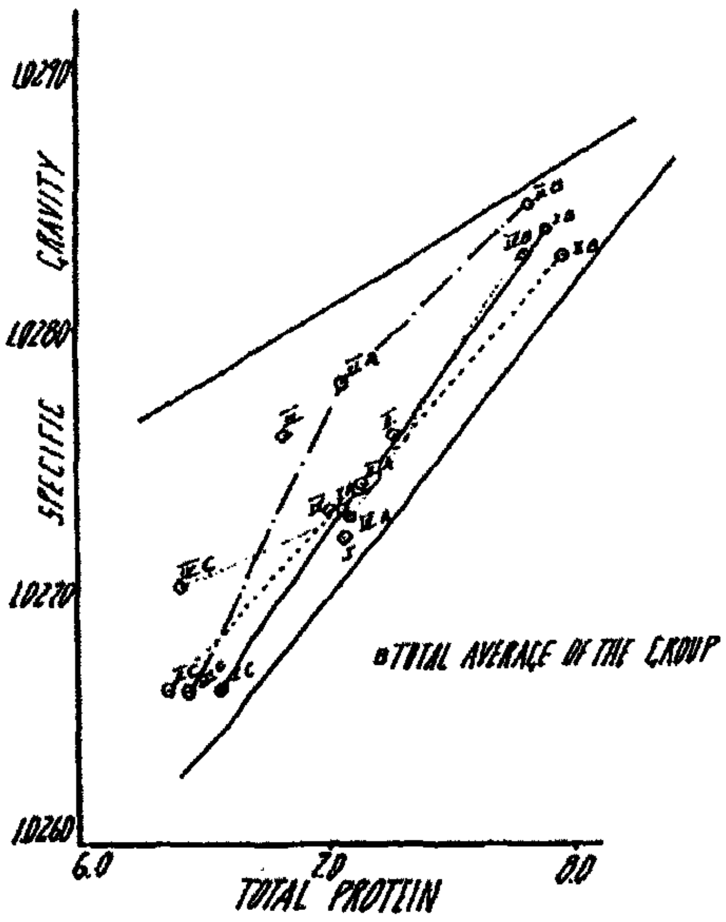

Fig. 6. Relation between specific gravity and total protein in all the groups

subgroup III A being out of line as well as subgroup IV C. The corresponding subgroups of all the different groups fall within reasonable expectation.

The study of these cases in groups shows a different relation between specific gravity and total protein, for in our previous work (29) we found the index of correlation between these two measurements to be 0.282 ± 0.062. From this chart we can assume that in the present distribution we would expect a much higher correlation when the cases are grouped by chemical characteristics. The heavy solid lines are drawn to show the apparent band of distribution, expecting greater discrepancies between specific gravity and total protein in the cases of lower total protein with increased albumin percentage than in the other groups.

In studying further the relation of specific gravity to some of our other measurements or calculations, we used "bound water" as the other relation, because by the method we use in calculating it we get a quantitative-qualitative evaluation of the protein fractions in the particular mixture.

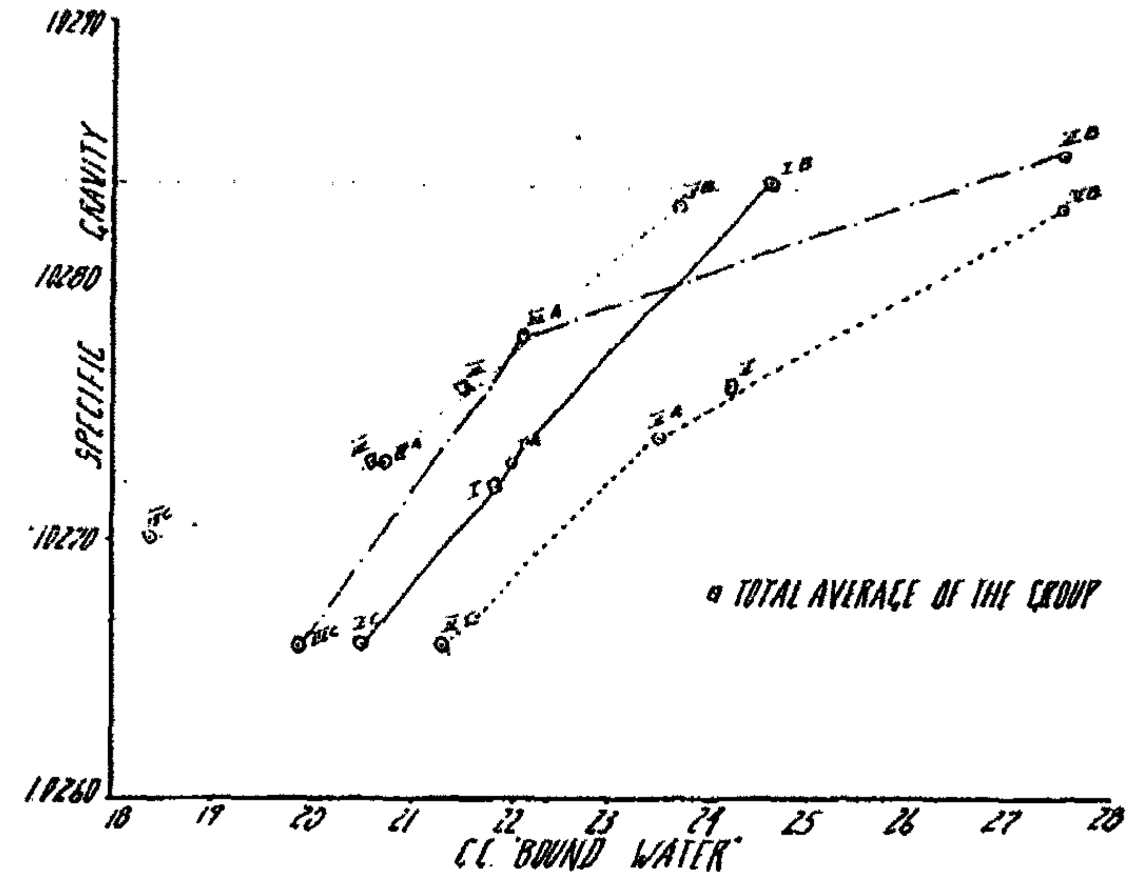

FIG. 7. Relation between "bound water" and specific gravity in all the groups

Using this value we could study the effect of this difference and specific gravity. Our results are plotted in figure 7.

As expected from the theory, group I is in the middle, group II below (plus euglobulin), and group IV above (plus albumin). Group III shows a different trend, but group III B returns to line. (In group III B we have only two cases, which we believe are definitely abnormal.) The total average of each group falls close within the line of general trend.

Chick's studies (3) on the volume occupied by 1 g. in solution of the different protein fractions used Hatschek's (10) formula, modified to apply to emulsoids of the protein type. The formula as given by Chick is as follows:

$$A = \left(\frac{n}{n-1}\right)^3, \quad A' = \frac{100}{d \times c'}, \quad \frac{A'}{A} = \frac{v}{c}$$

where n = viscosity of the protein solution, d = specific gravity of the protein solution, and c = concentration of the protein in per cent. The relation A'/A is the expression of the volume occupied by unit weight of the dissolved substance.

We are aware that this formula of Hatschek's does not directly apply to our systems, because the formula appears to hold true only when the disperse phase occupies more than one-half of the total system. In greater dilution it is probable that relatively more "bound water" than that indicated by the formula is closely associated with the protein molecule. Nevertheless we thought it of interest to use it here and test its general theory.

TABLE 2

The value of A'/A to express the volume occupied by unit weight of the dissolved substance in each one of the groups

GROUP	c*	d	n	A	A'	A'/A
I	7.05	1.0272	1.70	14.3	13.8	0.96
A	7.07	1.0273	1.70	14.3	13.7	0.96
B	7.89	1.0284	1.81	12.2	12.3	1.01
C	6.55	1.0266	1.67	15.6	14.8	0.95
II	7.24	1.0276	1.74	12.8	13.4	1.04
A	7.12	1.0274	1.72	13.6	13.6	1.00
B	7.94	1.0283	1.81	11.1	12.2	1.10
C	6.36	1.0266	1.66	15.8	15.3	0.96
III	6.81	1.0276	1.72	13.6	14.3	1.05
A	7.04	1.0278	1.72	13.6	13.8	1.01
B	7.80	1.0285	1.80	11.2	12.4	1.10
C	6.37	1.0266	1.72	13.6	15.3	1.12
IV	7.00	1.0273	1.68	15.0	13.9	0.92
A	7.07	1.0273	1.67	15.6	13.7	0.88
B	7.79	1.0283	1.73	13.3	12.4	0.93
C	6.40	1.0270	1.67	15.6	15.2	0.97

*c = concentration of protein in per cent.
d = density of system.
n = coefficient of viscosity.

$$A = \frac{\text{volume of 100 g. of system}}{\text{volume of disperse phase } (=v)}.$$

$$A' = \frac{\text{volume of 100 g. of system}}{\text{weight of dissolved substance } (=c)}.$$

A'/A = volume occupied by 1 g. of dissolved substance ($=v/c$).

In table 2 we find the values of A and A', and the ratio A'/A, and in figure 8 we show the plotting of these values in relation to cubic centimeters of "bound water" per 100 cc. of serum.

In the study of the figure we note the normal trend of the subgroups in groups I and II and the marked skewness of the curves of the subgroups in groups III and IV. The abnormal point seems to be in both cases in subgroup C. It may well be that the relation A'/A does not hold true in the lower concentration of albumin and pseudoglobulin, for Chick found that in the lower concentrations of the different protein fractions this ratio increased in abnormal proportion as the concentration decreased. Why should albumin and pseudoglobulin in this particular property behave so differently from euglobulin? Probably the "bound water"-"free water" relationship is markedly disturbed, as is also suggested by the specific gravity-total protein relationship. From Chick's work (3) the volume occupied by 1 g. of protein solution in high concentration is for serum albumin 2.8 cc., for pseudoglobulin 4.5 cc., and for euglobulin 6.5 cc. Therefore, the curve for the different groups as shown in figure 8 follows the general theory, although the concentration is much below the one used by Chick.

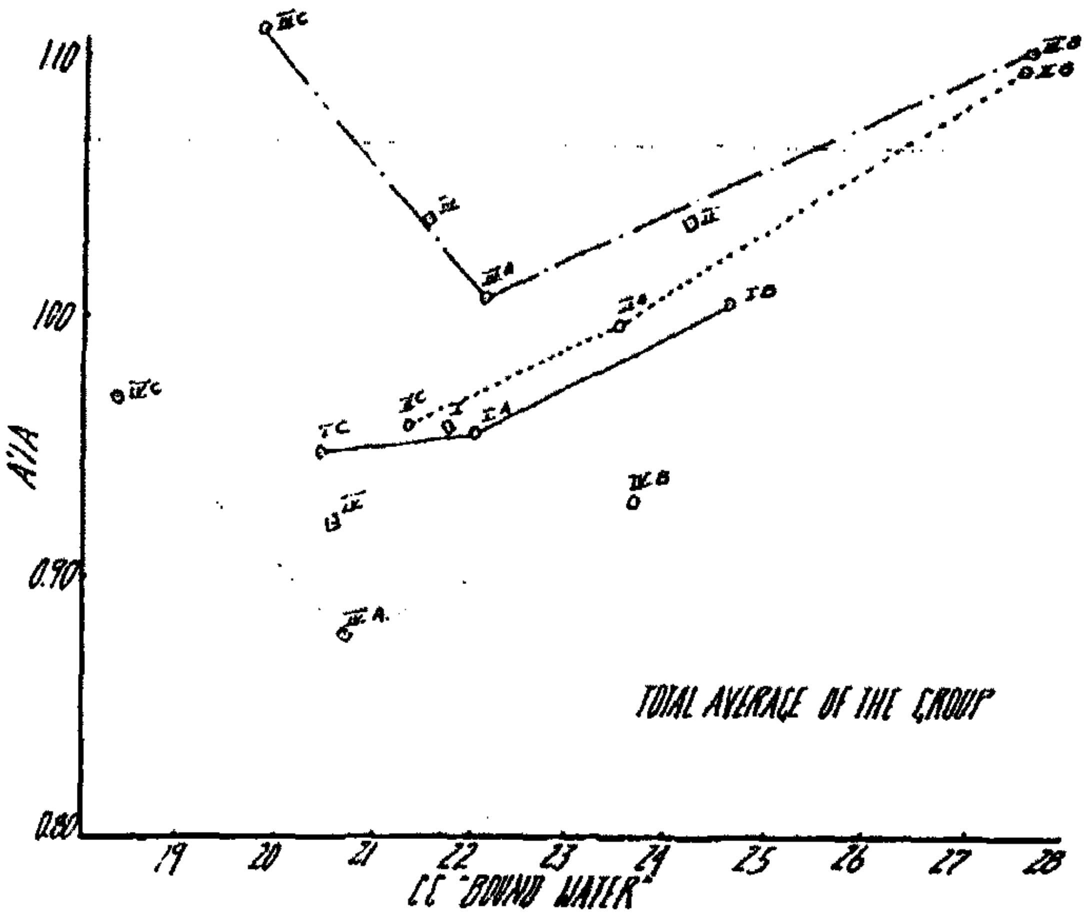

FIG. 8. Relation between A'/A and "bound water" in all the groups

Viscosity measurements are of great significance in the study of colloids and any change in these measurements suggests change in the internal colloidal system.

The relation between specific gravity and viscosity has been used as a general estimate of the relation of total protein and the albumin-globulin ratio. In our previous paper (29) we found that the index of correlation between these two measurements was 0.075 ± 0.06, that is, there was no correlation. This result was obtained from the ungrouped cases studied then. In figure 9 we have plotted the observations from our different groups. Here the total average of the whole group plots according to the expected theory as far as viscosity is concerned, in which the albuminous group (group IV) has the lowest viscosity for a given concentration, then group I (average mixture), then group III (pseudoglobulin), and the highest is group II (euglobulin). The trend followed by the different subgroups is of interest. As in other observations, the subgroups in groups I and II follow a more or less straight curve, while the low concentrations of total protein in the subgroups of groups III and IV show a marked skewness. From the observed facts we can generalize that groups I and II follow in all of our analyses an expected course, which agrees with the theoretical expectations, while in groups III and IV (specifically in subgroup C in both cases) there is always a marked discrepancy as to the expected course of events. In the case of the viscosity–specific gravity relationship we observe that groups III C and IV C give a higher viscosity than expected. In the higher concentrations of protein (subgroups B), all of the groups show a close similarity in their behavior, with the exception of subgroup IV B, which, as we have already stated, has a lower viscosity than the similar subgroups, as might be expected. There is a similar variation in specific gravity in the comparative groups (subgroup IV C excepted), but the viscosity changes follow the laws of protein behavior rather more closely (subgroup III C excepted).

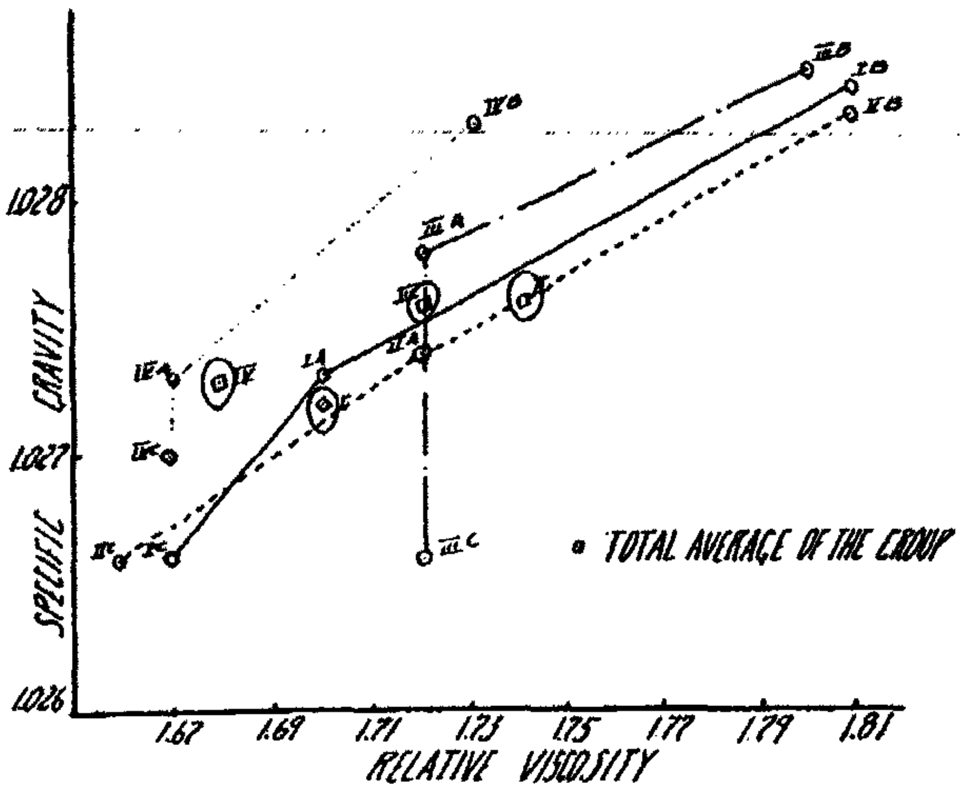

Fig. 9. Relation between specific gravity and relative viscosity

To study further the effect of the chemical constitution of the different groups on viscosity, we selected cubic centimeters of "bound water" as an indication of relative evaluation of the different protein fractions, as we have done before in figure 8, and we plotted the relation between these two measurements, as shown in figure 10. Here we find the same observation as discussed before, all of the groups behaving according to theory with the exception of subgroups III C and IV C. It is of interest to note that the albuminous group (group IV) comes below group I. Comparing this observation with that found in figure 7, we note that in the relationship of specific gravity to cubic centimeters of "bound water" group IV comes above all the groups, suggesting the high specific gravity in relation to the "bound water"; and in relation to the viscosity, group IV has higher "bound water" than expected. Groups IV A and IV C are similar in viscosity but different in "bound water," the same as in groups III A and III C. We cannot account for this similarity in viscosity except that in the lower dilutions the "bound water" probably increases above our calculation, as shown by Chick in her experiments.

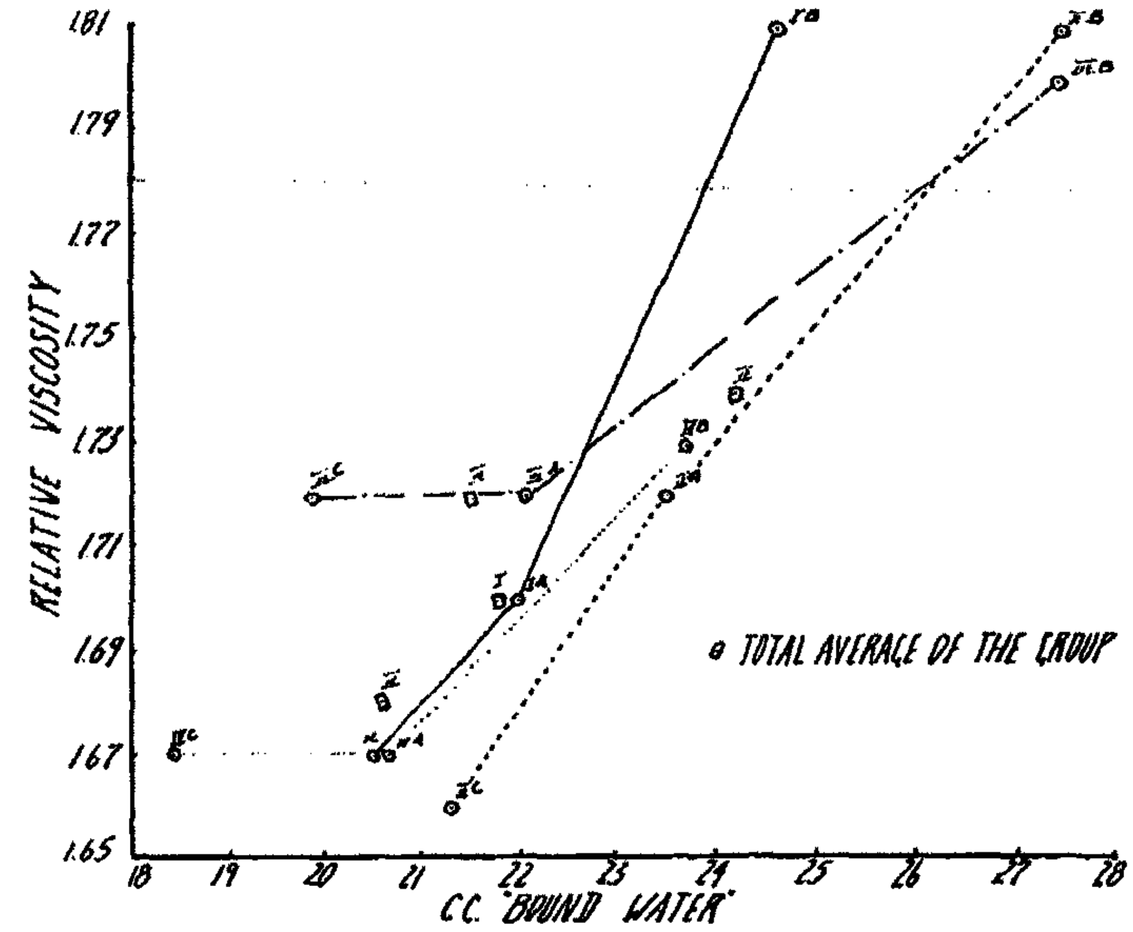

FIG. 10. Relation between relative viscosity and "bound water" in all the groups

In order to study the relation of specific gravity and the volume occupied by unit weight of the dissolved substances in each of the different groups we plotted our results, which are shown in figure 11. We observe the same phenomena that we observed before, that is, that groups I and II follow the expected relationship between the specific gravity and the ratio A'/A, but that groups III C and IV C show a marked skewness, for the specific gravity does not agree with the volume occupied by the unit of the dissolved proteins. No doubt in these lower concentrations a new factor enters, which may probably be the proportion in which water enters into the protein molecule or "bound water," for this same skewness is found in figure 8, where the relation between "bound water" and A'/A is shown.

A definite gradient between group II B and group IV C is found, as shown diagrammatically in figure 12, where we have a definite and opposite relation between the hydration of the protein mixture in the serum and its dilution, depending on the chemical composition of the serum. The euglobulin, of the serum proteins, is the one which takes up more water of hydration ("bound water"), while albumin takes up the lowest amount. It would follow that the "free water," or the dilution of the serum, would run opposite to the hydration of the proteins. For one of the most important functions of serum protein resides in the osmotic

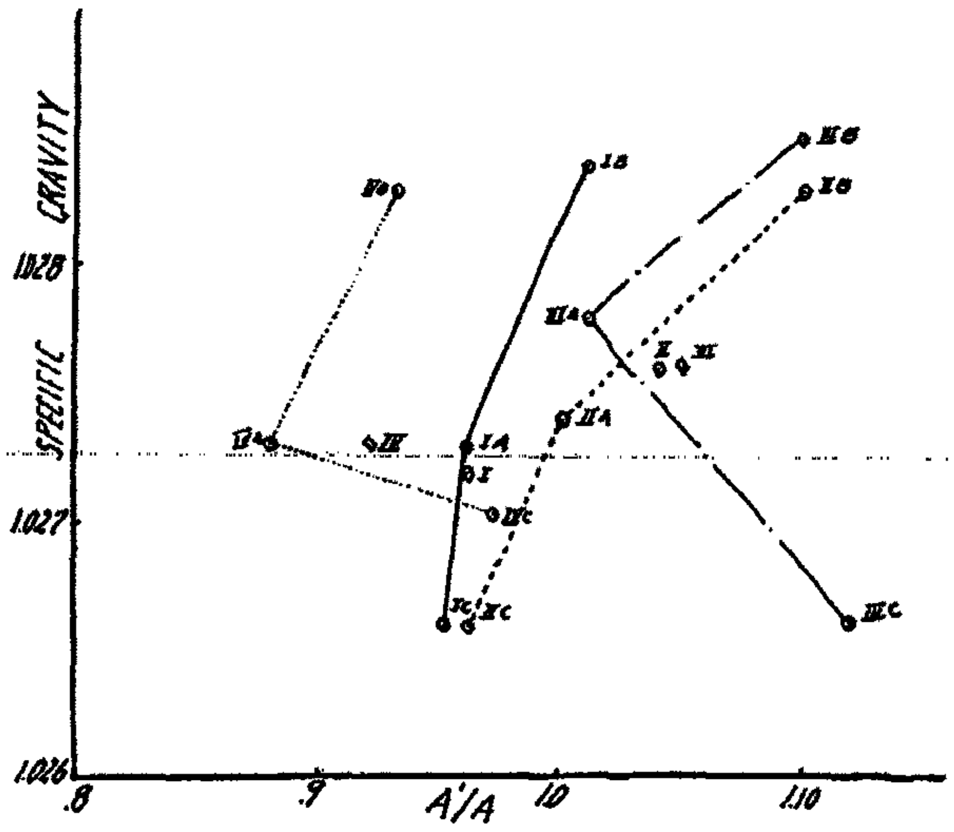

FIG. 11. Relation between A'/A and specific gravity in all the groups

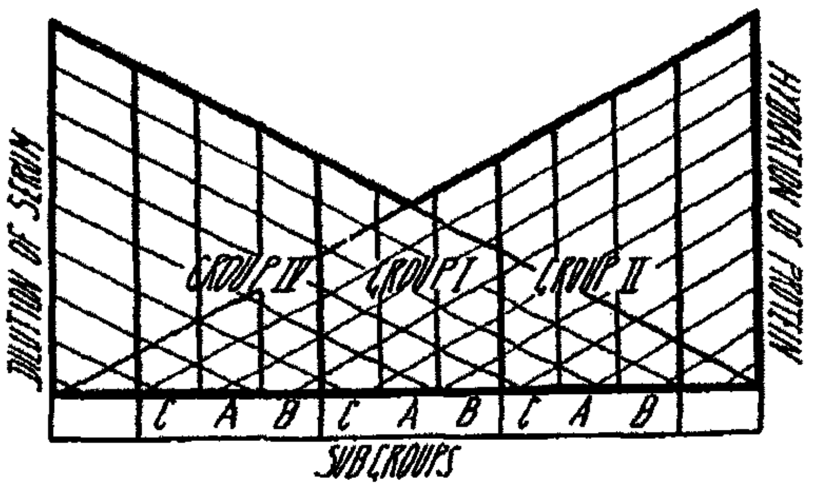

FIG. 12. Graphic representation of the relation between hydration of proteins and dilution of serum

attraction for water, and this property of the serum is the most effective agent in maintaining the fluid balance between the blood and intercellular tissues. Smith, Belt, and Whipple (23) have found that intensive and prolonged plasmapheresis results in symptoms resembling those of shock. Stanbury, Warweg, and Amberson (25) have emphasized the importance of the colloidal osmotic pressure of the plasma in maintaining a normal blood volume. Melnick and Cowgill (16) have further shown the important rôle of the serum protein complex as a factor in regulating blood volume. All of the above authors have taken into consideration the *amount of total protein and have not given any consideration to the chemical* composition of the serum. This factor is probably as important as the amount of total protein, on account of the marked differences in the hydration of the various fractions, as well as in the different volume occupied by each one of the fractions in solution.

The variation in chemical patterns observed in this group of cases is relatively moderate, owing to the selection of our material (nervous and mental cases), but similar studies done with sera from a general hospital would bring out more distinctly the chemical differences found here. As an example, we can refer to marked variations in the total protein between a case of nephrosis (4.0 per cent) and a case of myeloma with a total protein of 14.5 per cent.

SUMMARY

The data resulting from the physicochemical study of the serum of five hundred cases can be put into groups with definite differences which correspond to specific reaction or non-reaction of the organism to well-accepted immunological responses. The differences in the chemical results further suggest differences in the constitution of the individuals.

The chemical groups that we have found behave according to the general laws of protein chemistry, depending upon the chemical constitution.

I wish to thank Dr. S. DeW. Ludlum for his valuable suggestions and help in the development of this work, as well as Dr. V. Alvarez-Hussey and Dr. Robert A. Lichtenthaeler for their technical assistance.

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SURFACE-BOUND VERSUS CAPILLARY-CONDENSED WATER IN WOOD[1]

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It is generally conceded that the water held by cellulose and by wood with a reduction in the equilibrium relative vapor pressure is held either by direct surface molecular forces or by capillary condensation. The extent to which each of these is effective is, however, still controversial. Sheppard and Newsome (6) and Stamm (8) have taken the stand that the inflection point in the sigmoid moisture content–relative vapor pressure curves roughly represents the transition point between surface-bound and capillary-held water, the curve being a combination of an adsorption curve, which tends to become parallel to the relative vapor pressure axis, and a capillary condensation curve, which becomes effective in capillaries just slightly exceeding molecular dimensions and tends to become parallel to the moisture content axis. On this basis the surface-bound water would vary from 3 to 7 per cent for different celluloses and wood, and the capillary-condensed water would amount to 12 to 25 per cent.

Other evidence that the surface-bound water is of this order of magnitude is obtained from the thermodynamic calculations of Stamm and Loughborough (10). The temperature coefficient of the differential heat of swelling–moisture content relationship becomes significant above this moisture content. Presumably the temperature coefficient of capillary condensation is appreciably greater than that of surface adsorption. The entropy change–moisture content relationship further has an inflection point around 6 per cent moisture content, indicating a change in the energy relationship. Extrapolation of the relationship between moisture sorption and temperature at saturated vapor pressures to the critical temperature should give a strictly surface adsorption value. Although this extrapolation cannot be made with any degree of accuracy, available data (10) indicate that the surface-bound water on this basis cannot exceed a few

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[1] Presented before the Division of Colloid Chemistry at the Ninety-fourth Meeting of the American Chemical Society, Rochester, New York, September, 1937.

[2] Maintained at Madison, Wisconsin, in coöperation with the University of Wisconsin.

per cent. Predicted values of the surface-bound water of 20 per cent (2) are quite incompatible with these data, as the sorption only slightly exceeds 20 per cent at the experimental temperature of 100°C.

A number of investigators have differentiated between surface-bound water, capillary-held water, and free water on the basis of the first not acting as a solvent for solutes (5). From studies of the effect of salts (7) and sugars (9) upon the shrinking of wood, Stamm concluded that practically all the sorbed water would act as a solvent. These solutes reduced the shrinkage of wood to the oven-dry condition by an amount which would be obtained if the treating solution attained a concentration within the swelling structure practically equal to the bulk concentration and the solute were subsequently deposited within this structure on drying. The accuracy of these measurements is such as to indicate that selective adsorption of water cannot exceed a few per cent.

Barkas (1, 2) has made measurements of the selective adsorption from sugar solutions by wood, from which the air was removed by a special vacuum device to avoid all capillary effects, using an interferometer method to determine the concentration changes. From these data he calculated a minimum value for the bound water for each concentration by considering that sugar is not adsorbed.[3] He concluded that approximately 20 per cent of water does not act as a solvent. This value is about three times the estimated value of the surface-bound water from the relative vapor pressure–moisture content curves and the thermal data and is incompatible with measurements of the retardation of shrinkage caused by solutes deposited in the cell wall. It thus seemed desirable to repeat Barkas' measurements with sugar and also to make them with other solutes.

ADSORPTION MEASUREMENTS

The measurements of the selective adsorption of water from aqueous solutions by wood were made with a Hilger-Raleigh gas cell interferometer adapted for use as a liquid cell interferometer in a manner somewhat similar to that used by Ford and McBain (3) and Hall and Jones (4). A water bath was built into the tube zone of the instrument with plate glass windows at the two ends set in adjustable rubber diaphragms. This made possible the perfect alignment of the fringes when the bath was full of water. The cells were made by sealing a piece of 10-mm. Pyrex tubing concentrically into a piece of 40-mm. tubing with an inner seal connection serving for filling (4). Ground Pyrex glass plates were sealed to the parallel ground ends of tubes with silver chloride cement. The cells used ranged

[3] What seems to be a typographical error occurs in the derivation of Barkas' equation. The final form of the equation and the calculations made therefrom, however, are correct.

from 7 to 12 cm. in length. This simple construction makes it readily possible to set the cell in such a position that the two beams which give fixed reference fringes and the comparison beam all pass through the solution of lowest refractive index in the large outer tube part of the cell and the adjustable fringe beam passes through the solution of higher index of refraction in the inner tube part of the cell. In all cases investigated the fringe displacement was found to be directly proportional to the concentration.

Sugar pine, in the form of small thin sections about 1 mm. in the fiber direction, was used for the measurements. To insure the removal of all extractives the sections were extracted in a continuous extractor with each of the following solvents for seven days: benzene, methyl alcohol, and water. They were then oven-dried prior to use. Chemically pure sucrose (in the form of rock candy), glycerol, and sodium chloride were used as the solutes. Precautions were taken in the case of the sucrose to perform all operations under sterile conditions. For each measurement 0.3 to 2.5 g. of oven-dry wood was used and enough solution to give ratios of the weight of solution to that of the wood of 20 to 200. A vacuum device, very similar to that of Barkas (2), was used for removing the air from the thin wood sections and for running the solution of known concentration on the wood without loss of solvent. The solutions were allowed to stand in contact with the wood for a minimum time of twenty-four hours at 25°C., after which the equilibrium concentration of the solution was determined with the interferometer, using the original solution as the reference solution.

In the three different solutions used in this investigation, selective adsorption of water took place. Preliminary measurements with other solutions indicate that water is selectively adsorbed from all aqueous solutions that cause a negligible swelling of the wood beyond the water-swollen dimensions, whereas the solute is selectively adsorbed from aqueous solutions that cause an appreciable swelling of the wood beyond water-swollen dimensions. The calculations of the minimum amount of selectively adsorbed water were made by assuming that the adsorption of solute was negligible (2). On this basis the weight of the adsorbed water per gram of dry wood that does not act as a solvent is given by the following equation

$$w_a = \frac{M}{X}\frac{\Delta C}{C_2} \qquad (1)$$

in which M is the weight of solution in grams in contact with X grams of dry wood, ΔC is the concentration change, and C_2 the equilibrium concentration in grams of solute per gram of solution.

In figure 1 the percentage by weight of water held by the wood that does not act as a solvent is plotted against the concentration of the solution in equilibrium with the wood in weight per cent. The data for the sugar solutions are very scattered but are in fairly good agreement with the data of Barkas except at low concentrations.

The different solutions, on a weight concentration basis, give different values for w_a. This would be expected, as the capacity of the wood to take water from the different solutions should depend upon the activity of the water in these solutions rather than their concentration. This activity is measured by the relative vapor pressure of water over the solutions. In curve B of figure 2 the percentage of water in the wood not acting as a solvent is plotted against the relative vapor pressure of the solution in equilibrium with the wood. In this case all the data can be reasonably well represented by a single curve which seems to be approaching a limiting value of w_a between 3 and 4 per cent; that is, 3 to 4 per cent of water is held by the wood without acting as a solvent when in equilibrium with solutions that depress the equilibrium relative vapor pressure by at least 25 per cent.

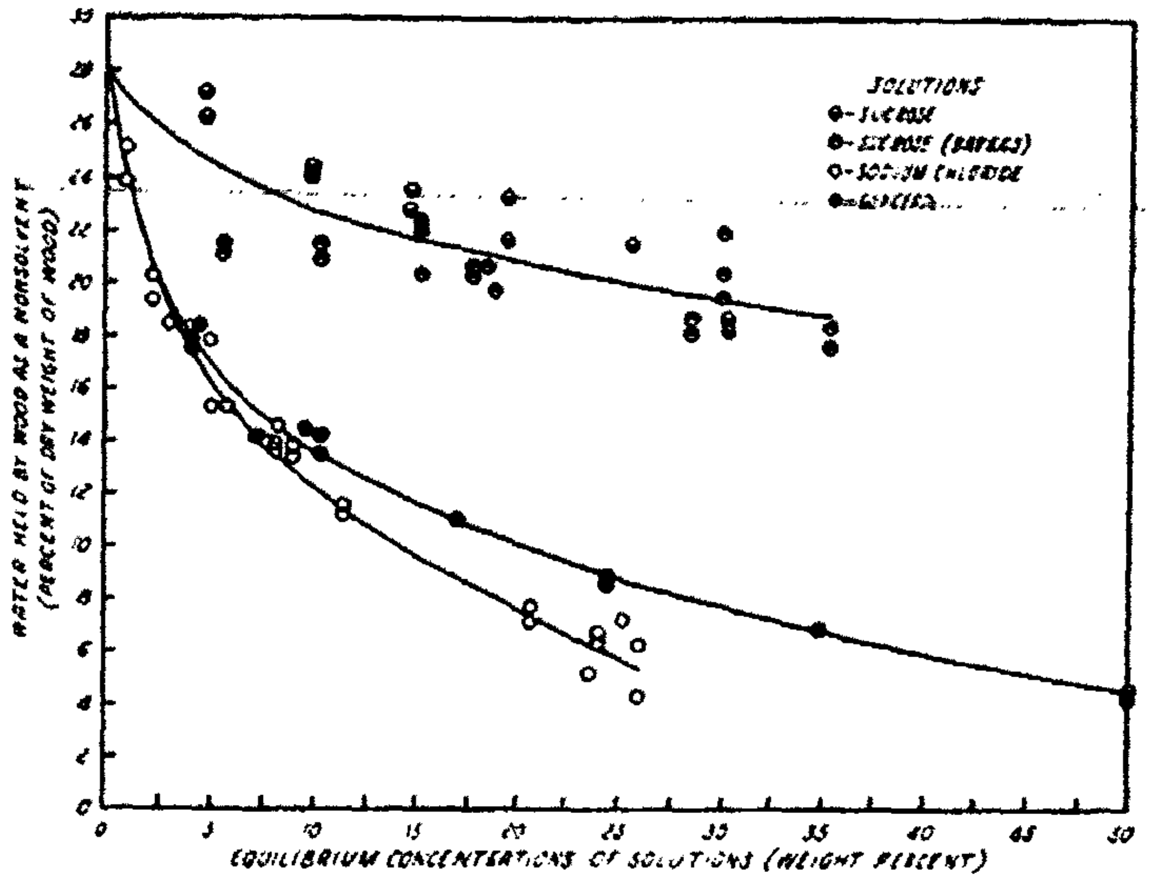

FIG. 1. Selective adsorption of water from aqueous solutions of different concentrations

DISCUSSION

If the adsorption of water from solution were strictly a monomolecular surface adsorption of a single constituent on a fixed surface, the adsorption would follow a curve such as curve C of figure 2. The experimental variation from this curve might be explained in several different ways:

(*1*) The swelling of the wood may increase the internal surface available for water as adsorption continues. Such an increase in surface, however, should give a curve similar to curve C except that it does not become parallel to the relative vapor pressure axis.

(2) The solute may be simultaneously adsorbed with the solvent. This would tend to raise curve B and make it more like curve A than curve C.

(3) The force of primary adsorption may extend beyond molecular dimensions, causing polymolecular adsorption at high relative vapor pressures. All recent experimental evidence on innumerable systems, however, indicates that polymolecular adsorption does not take place.

(4) Capillary condensation may not have been completely eliminated, even though the greatest precautions were taken to do so.

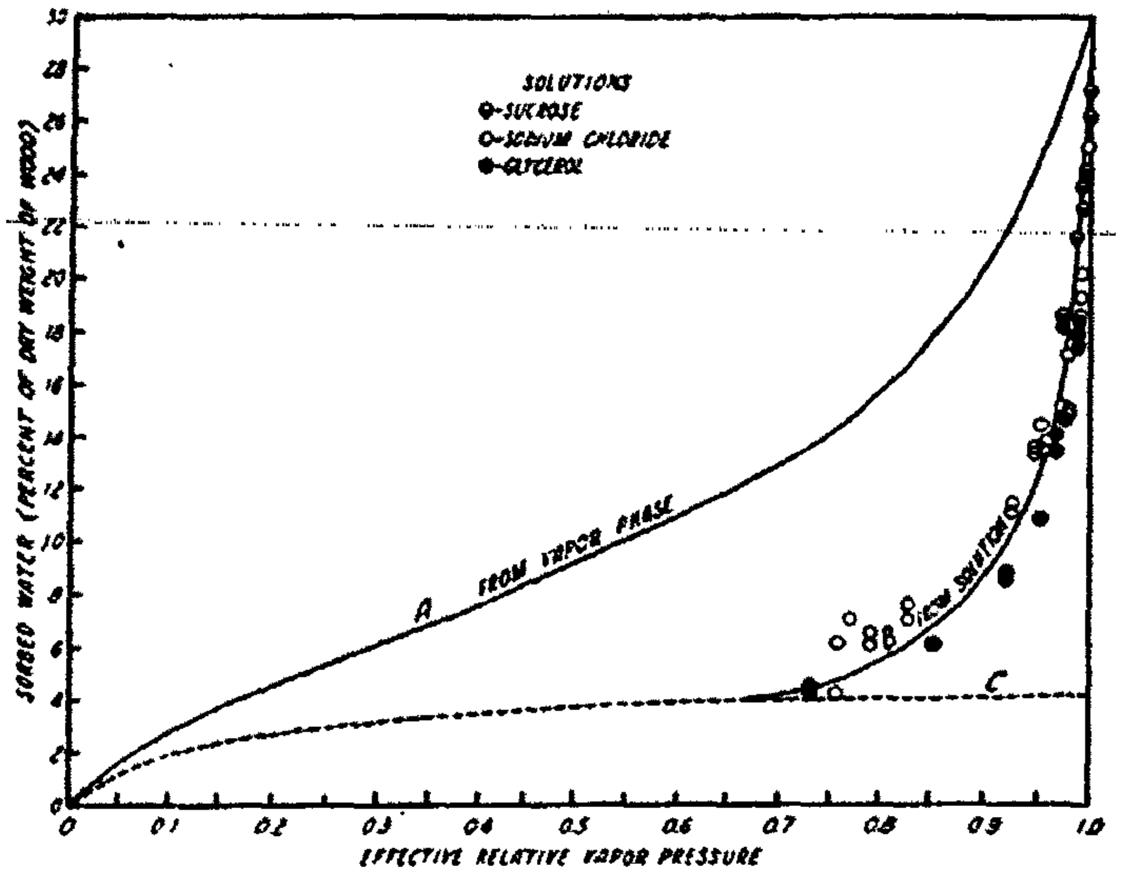

Fig. 2. Water sorbed from the vapor phase and from aqueous solution under different relative vapor pressure conditions.

(5) Complete equilibrium in the distribution of solvent and solute may not have been attained. It has been demonstrated that water is adsorbed from aqueous solutions by wood, followed by diffusion of the solute into the water within the fine structure (7). The amount of water that can be taken from the solution in this manner will be some function of the relative vapor pressure of the solution. Greater deviations from the true equilibrium condition may thus exist in the least concentrated solutions.

The last two explanations both account for the general nature of curve B. Further experimentation will be necessary, however, to prove that either or both are effective. The data nevertheless show that measurements like those of Barkas (2) in concentrations that do not appreciably depress the relative vapor pressure do not measure the true surface-bound water, and that only in solutions that depress the relative vapor pressure more than 25 per cent can approximations of the surface-bound water be made. Innumerable other investigations in which the "bound water" has been obtained by determining the non-solvent water or water that does not freeze at an arbitrary temperature are subject to the same error of neglecting the activity of the water. This would be especially true in the case of water-insoluble capillary-active materials in which capillary effects would be most appreciable.

The adsorption of water from solution by the wood, if extended to solutions in equilibrium with zero per cent relative vapor pressure, should follow approximately the dashed part of curve B, figure 2. At relative vapor pressures below 20 to 30 per cent the solution should begin to remove surface-bound water from the wood. Curve B falls below curve A in the low relative vapor pressure range, presumably because the surface-bound water shares its bonds between the wood and the adjacent solute molecules. If half of the bonds were shared in this manner, the surface-bound water would be twice the non-solvent water. In such a case the data would be in excellent agreement with the predictions.

SUMMARY

Adsorption measurements from aqueous solutions of sucrose, glycerol, and sodium chloride by wood all give selective adsorption of water. In none of these solutions is wood swollen beyond the water-swollen dimensions. Preliminary measurements of adsorption from solutions causing swelling beyond the water-swollen dimensions indicate that positive adsorption of solute is taking place. The selective adsorption of water from aqueous solutions is a function of the activity of the water in the solution. A constant value of 3 per cent is approached in equilibrium with reductions in the relative vapor pressure exceeding 25 per cent, which presumably is the adsorption value free from residual capillary condensation and non-equilibrium effects. This value is about half of the predicted surface-bound water. The difference between the values is explained on the basis of the surface-bound water acting as a partial solvent, sharing its bonds between the wood and adjacent solute molecules.

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THE RATE OF REACTION OF AMALGAMS WITH ACIDS. II

SODIUM AMALGAMS[1]

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In a previous paper (3) it was shown that the rate of reaction of lithium amalgams with acids in the general sense followed two different kinetic laws. For the strong acids and the weak acids, with the exception of *o*-chlorophenol, it was found that the rate of appearance of the alkali metal ion in the solution was given by the relationship

$$\frac{dx}{dt} = kSC_A \qquad (1)$$

where S is the surface and x is the number of ions of alkali metal formed at time t by way of the reaction

$$M + H_3O^+ \rightarrow M^+ + H_2O + 1/2\,H_2$$

or

$$M + HOOCR \rightarrow M^+ + RCOO^- + 1/2\,H_2$$

The rate appeared to be independent of the concentration of the alkali metal in the amalgam, and k varied with the acid used.

For the reaction with water or with buffer solutions of primary and secondary phosphate the rate equation is

$$-\frac{dC_M}{dt} = k'SC_A \cdot \sqrt{C_M} \qquad (2)$$

where C_M is the concentration of the alkali metal in the amalgam and the reaction presumably is

$$M + HOH \rightarrow M^+ + OH^- + 1/2\,H_2$$

and

$$M + H_2PO_4^- \rightarrow HPO_4^{--} + M^+ + 1/2\,H_2$$

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[1] This paper is abstracted in part from the dissertation of Wilbur G. Dunning presented to the Faculty of the Graduate School of the University of Pennsylvania in partial fulfillment of the requirements for the degree of Doctor of Philosophy, December, 1935.

Equation 2 is in agreement with the results of Brönsted and Kane (2). These authors worked with dilute (0.024 molar) sodium amalgam and practically constant acid concentration. Moriguchi and Mitsukuri (11), working with amalgams ranging from 0.6 to 1.2 molar, found the velocity of reaction in hydrochloric acid solutions to be independent of the amalgam concentration and approximately proportional to the acid concentration. Klein (8) worked with high and practically constant concentrations of sodium in the amalgam and found that the results could be expressed by an equation equivalent to the first two terms in equation 1 of the paper of Fletcher and Kilpatrick (3). However, the first term could not be evaluated exactly, as the results in alkaline solution were not reproducible. This lack of reproducibility for the water reaction has been observed by others. Baker and Parker (1, 12) observed that the rate of reaction of sodium with water varied with the purity of the water. They ascribed this to the presence of traces of hydrogen peroxide.

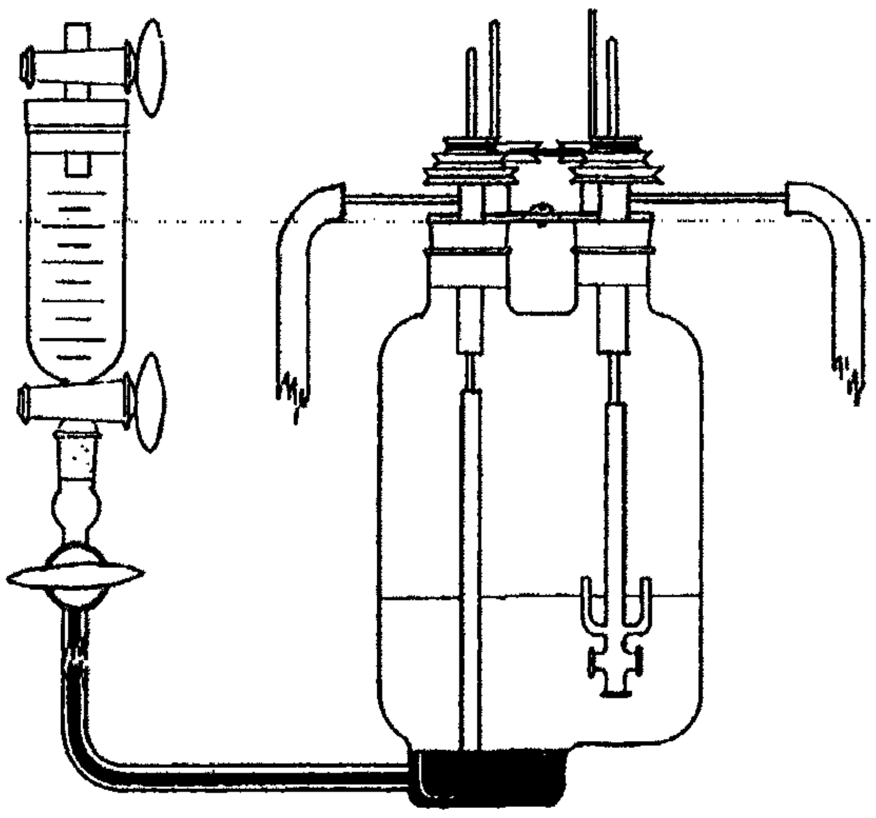
FIG. 1. Reaction vessel for amalgams

The purpose of the present work is to provide a further experimental test of equations 1 and 2, and to attempt to elucidate the results obtained by other workers. To do this a series of experiments has been carried out under different experimental conditions with various acids.

EXPERIMENTAL METHOD

The preparation of amalgams and the general procedure have been given by Fletcher and Kilpatrick (3). Three different reaction vessels were used and will be referred to as vessels D, F, and H. Figure 1 shows apparatus H equipped with stirrers for both solutions. In most experiments the stirrer for the amalgam was removed. The area of the interface was 12.3 cm.^{2} and 300 cc. of aqueous solution was used in most experiments. Apparatus D was similar in size and shape to apparatus H, the essential

TABLE 1

Experiments with hydrochloric acid at 25°C.

INITIAL CONCENTRATION OF ACID	INITIAL CONCENTRATION OF AMALGAM	REVOLUTIONS PER MINUTE OF STIRRERS		k	REMARKS
		Aqueous layer	Amalgam layer		
Apparatus D—area, 3.8 cm.^{2}					
moles per liter	*moles per liter*			*cm. min.*$^{-1}$	
0.0150	0.31	2450	0	2.91	
0.0250	0.35	2450	0	1.79	
0.0250	0.35	2450	0	2.41	
0.0150	0.31	1650	0	1.48	
0.0300	0.31	1650	0	1.56	
0.0090	0.31	1650	0	1.74	
0.0100	0.24	1650	0	1.21	
0.1610	0.35	1650	0	1.31	
0.3220	0.35	1650	0	1.13	
0.0250	0.35	1650	0	1.78	
0.0250	0.35	1650	0	1.60	
0.0250	0.35	1650	0	1.39	
0.0300	0.56	1650	0	1.36	
0.0200	0.56	1650	0	1.35	
0.0260	0.56	1650	0	1.39	
0.0500	0.56	1650	0	1.39	
0.0300	0.66	1650	0	1.32	
0.0204	0.35	1660	0	1.65	
0.0204	0.35	1660	0	1.60	
0.0300	0.56	1650	0	1.41	T = 20°C.
0.0500	0.56	1650	0	1.54	T = 20°C.
0.0300	0.56	1650	0	1.61	T = 30°C.
0.0500	0.56	1650	0	1.76	T = 30°C.
0.0250	0.35	1150	0	1.17	
0.0250	0.35	1150	0	1.18	
0.0100	0.24	980	0	1.28	
0.0150	0.31	975	0	1.15	
0.0150	0.31	520	0	0.59	
0.073	0.57	500	0	0.67	
0.029	0.57	500	0	0.66	
0.010	0.57	500	0	0.60	
0.0250	0.35	500	0	0.69	
0.0250	0.35	500	0	0.65	
0.0540	0.27	500	0	0.65	
0.0540	0.27	500	0	0.87	In 0.95 M NaCl
0.0540	0.27	500	0	0.89	In 0.95 M NaCl
0.0540	0.27	500	0	1.03	In 0.95 M $NaClO_4$

TABLE 1—*Concluded*

INITIAL CONCENTRATION OF ACID	INITIAL CONCENTRATION OF AMALGAM	REVOLUTIONS PER MINUTE OF STIRRERS		k	REMARKS
		Aqueous layer	Amalgam layer		
		Apparatus D—area, 3.26 $cm.^2$			
moles per liter	*moles per liter*			$cm.\ min.^{-1}$	
0.0412	0.56	2000	100	1.92	
0.0927	0.56	1950	0	1.62	
0.0927	0.56	1940	97	1.98	
0.0309	0.56	1900	95	2.00	
0.0618	0.56	1900	95	1.84	
0.0206	0.56	1900	95	2.14	
0.0399	0.90	800	75	1.88	
0.0250	0.90	850	60	2.10	In 1 *M* NaCl
		Apparatus H—area, 12.3 $cm.^2$			
0.0299	0.33	1600	80	1.12	Volume = 200 cc.
0.0199	0.33	1600	80	1.42	In 0.1 *M* NaCl
0.00997	0.33	1600	80	1.33	
0.0299	0.33	1600	160	1.18	
0.0199	0.33	1500	75	1.28	
0.0299	0.33	1500	75	1.37	
0.0399	0.33	1500	75	1.44	
0.0100	0.24	1000	0	1.02	
0.0100	0.24	980	0	0.81	

difference being the cross section of the amalgam well, which was 3.26 in the early experiments and 3.8 in the later experiments. Apparatus F has already been described by Fletcher and Kilpatrick (3). The cross section of the well was 9.63 $cm.^2$ The general method of carrying out an experiment has already been given.

Table 1 summarizes the results with hydrochloric acid solutions. The velocity constants are calculated by the integrated form of equation 1.

Table 2 gives the results with perchloric acid. Inspection of the results with aqueous solutions of hydrochloric and perchloric acids indicates that the velocity constant is independent of the concentration of sodium in the amalgam, and from the agreement of the results with the two acids the rate of reaction is approximately proportional to the hydrogen-ion concentration with the possibility of an electrolyte effect. It is also evident that the rate of reaction is proportional to the surface of the amalgam. The effect of stirring of the amalgam is small and may be due to a change in the surface exposed to the aqueous solution. These results are essentially in agreement with the results with lithium amalgam.

Table 3 gives a comparison of the results with potassium and lithium amalgams.

From these results we can conclude that the velocity constants for all three amalgams are the same under the same experimental conditions. This suggests that the rate-controlling process is independent of the alkali metal in the amalgam, and we might conclude that this process is the transport of the acid to the amalgam surface. If this is the case, the effect of stirring, according to Roller (13), should be in agreement with the relation

TABLE 2

Experiments with perchloric acid at 25°C.

INITIAL CONCENTRATION OF ACID	INITIAL CONCENTRATION OF AMALGAM	REVOLUTIONS PER MINUTE OF STIRRERS		k	REMARKS
		Aqueous layer	Amalgam layer		
		Apparatus D—area, 3.8 cm.^{2}			
moles per liter	*moles per liter*			*cm. min.*$^{-1}$	
0.0400	0.56	1650	0	1.45	
0.0300	0.56	1650	0	1.31	
0.0200	0.56	1650	0	1.30	
0.0300	0.67	1650	0	1.29	
0.0050	0.60	500	0	0.83	
0.051	0.60	500	0	0.85	
0.010	0.60	500	0	0.82	
0.030	0.60	500	0	0.80	
0.030	0.60	500	0	0.88	
0.030	0.60	500	0	1.11	In 0.17 *M* $NaClO_4$
0.030	0.60	500	0	0.91	In 0.34 *M* $NaClO_4$
		Apparatus D—area, 3.26 cm.^{2}			
0.0410	0.90	700	60	1.28	
0.0308	0.90	700	60	1.28	
0.0205	0.90	665	45	1.24	
0.0103	0.90	665	55	1.28	
		Apparatus H—area, 12.3 cm.^{2}			
0.0103	0.90	1600	80	1.16	
0.0205	0.90	1600	80	1.11	
0.0410	0.90	1600	80	1.20	
0.0103	0.33	1600	80	1.20	
0.0205	0.33	1600	80	1.16	
0.0308	0.33	1600	80	1.14	
0.0308	0.90	1560	78	1.07	
0.0410	0.33	1560	78	1.13	

$$\frac{k_{\text{obs.}}}{s^{0.8}} = \text{a constant}$$

where s is the rate of stirring. An examination of the results for apparatus D in table 1 gives an exponent which is approximately 0.7, but in the case of perchloric acid the exponent is considerably lower. Application of the equation

$$k_{\text{obs.}} = As^{0.8}(1 - e^{-k/As^{0.8}})$$

where $k_{\text{obs.}}$ is the observed velocity constant, k the chemical velocity constant, and A an empirical constant. If A is taken as 0.005 and the chemical velocity constant as 3.00, there is fair agreement between $k_{\text{obs.}}$ and the calculated velocity constants for the results in apparatus D. But if $k_{\text{obs.}}$ is the same for the three alkali metal amalgams in three different vessels, it would seem that the chemical k for lithium, sodium, and potassium would be the same. This seems hardly likely, so that one may conclude that an exponent of 0.67 is probably more nearly correct in the derivation of Roller. If that is the case, since $\frac{k_{\text{obs.}}}{s^{0.67}}$ is fairly constant, the conclusion that the controlling process is the transport of the acid to the surface of the amalgam seems justified. If one considers a mechanism similar to that proposed by Sclar and Kilpatrick (14) for the dissolution of magne-

TABLE 3

Comparison of velocity constants for alkali metal amalgams

AMALGAM	R.P.M.	k	REMARKS
		Apparatus D—area, 3.8 cm.²	
		cm. min.$^{-1}$	
Na	1650	1.43	Average of 14 experiments
K	1650	1.58	
Li	1650	1.43	
Li	500	0.78	
Na	500	0.66	Average of 7 experiments
		Apparatus F—area, 9.63 cm.²	
Na	975	1.06	
K	975	1.01	
Li	975	1.07	Average of 7 experiments
		Apparatus H*—area, 12.3 cm.²	
Na	1980	1.43	
K	1980	1.42	Average of 10 experiments
Li	1980	1.43	

* The experiments in apparatus H were carried out by Mr. K. Hoff, to whom due acknowledgement is made.

sium in alcoholic solutions of acids, the same general conclusion can be drawn.

EXPERIMENTS WITH WEAK ACIDS

In the experiments with weak acids buffer solutions were used at constant ionic strength for each series, so that the hydrogen-ion concentration was constant and negligible, as will be shown in a later section. The experiments with acetic acid buffers are shown in table 4.

TABLE 4

Experiments with acetic acid at 25°C.

INITIAL CONCENTRATION OF ACID	INITIAL CONCENTRATION OF ACETATE	INITIAL CONCENTRATION OF CHLORIDE	INITIAL CONCENTRATION OF AMALGAM	REVOLUTIONS PER MINUTE OF STIRRERS		k	REMARKS
				Aqueous layer	Amalgam layer		
Apparatus D—area, 3.8 cm.^{2}							
moles per liter	*moles per liter*	*moles per liter*	*moles per liter*			*cm. min.*$^{-1}$	
0.0210	0.0210	0.170	0.56	1650	0	0.64	
0.0350	0.0350	0.150	0.56	1650	0	0.71	
0.0490	0.0490	0.130	0.56	1650	0	0.80	
0.0630	0.0630	0.110	0.56	1650	0	0.87	
0.0250	0.0250	0.175	0.56	1650	0	0.67	
0.0490	0.0490	0.151	0.56	1650	0	0.78	
0.0350	0.0350	0.150	0.56	1650	0	0.64	T = 20°C.
0.0250	0.0250	0.175	0.56	1650	0	0.64	T = 20°C.
0.0350	0.0350	0.150	0.56	1650	0	0.79	T = 30°C.
0.0250	0.0250	0.175	0.56	1650	0	0.71	T = 30°C.
0.0490	0.0490	0.130	0.34	1650	0	0.86	
0.0250	0.0250	0.175	0.31	1650	0	0.74	
0.0150	0.0150	0.185	0.31	1650	0	0.65	
0.20	0.20	0	0.60	500	0	0.41	
0.15	0.15	0.05	0.60	500	0	0.42	
0.05	0.05	0.15	0.60	500	0	0.54	
0.05	0.05	0.15	0.60	500	0	0.55	
0.05	0.05	0	0.60	500	0	0.51	
Apparatus H—area, 12.3 cm.^{2}							
0.054	0.0250	0.0250	0.33	1560	80	0.92	
0.027	0.0125	0.0375	0.33	1600	80	0.67	
0.036	0.0166	0.0334	0.33	1650	80	0.78	

Again the rate is independent of the amalgam concentration, and velocity constants are calculated in the same way as for the strong acids. The possibility that equation 2 might apply to these results will be considered after the presentation of the results for the water reaction.

Tables 5 and 6 present the results with other weak acids, and table 7 summarizes the results.

As in the case of lithium amalgams, the velocity constants are not very different. This can be interpreted to mean that we are dealing with a rate-controlling process involving a transport of the molecules of the carboxylic acid to the surface of the amalgam. If this were the case, however, the order of the velocity constants should be perchloric acid, hydrochloric acid, formic acid, acetic acid (7) and if hydrochloric acid is taken

TABLE 5

Experiments with weak acids at 25°C.

Apparatus D except as indicated

INITIAL CONCENTRATION OF ACID	INITIAL CONCENTRATION OF ANION	INITIAL CONCENTRATION OF CHLORIDE	INITIAL CONCENTRATION OF AMALGAM	REVOLUTIONS PER MINUTE OF STIRRERS		k
				Aqueous layer	Amalgam layer	
			Mandelic acid			
moles per liter	*moles per liter*	*moles per liter*	*moles per liter*			*cm. min.*$^{-1}$
0.017	0.017	0.175	0.56	1650	0	0.54
0.024	0.024	0.165	0.56	1650	0	0.58
0.035	0.035	0.165	0.56	1650	0	0.59
			Glycolic acid			
0.034	0.034	0.165	0.56	1650	0	0.61
0.024	0.024	0.175	0.56	1650	0	0.62
0.015	0.015	0.185	0.31	1650	0	0.61
0.040	0.040	0.160	0.31	1650	0	0.81
0.040	0.040	0.160	0.31	1650	0	0.71
0.100	0	0	0.60	500	0	0.44
0.100	0.100	0.100	0.60	500	0	0.40
			Apparatus H—area, 12.3 cm.^{2}			
0.0370	0.0380	0.0125	0.33	1680	84	0.62
0.0122	0.0125	0.0375	0.33	1600	80	0.72
0.0244	0.0250	0.0250	0.33	1600	80	0.51
0.0489	0.0500	0	0.33	1600	80	0.67
			Formic acid			
0.0260	0.0260	0.175	0.56	1650	0	0.78
0.0365	0.0365	0.165	0.56	1650	0	0.77
0.030	0.030	0.170	0.35	1650	0	0.70
0.015	0.015	0.185	0.35	1650	0	0.71
0.100	0.100	0.100	0.60	500	0	0.36
0.050	0.050	0.150	0.60	500	0	0.33

as unity the ratios of the k's to k for hydrochloric acid should be perchloric acid 1.1, formic acid 0.26, acetic acid 0.23. The actual ratios of the velocity constants at 1600 R.P.M. are perchloric acid 0.94, formic acid 0.52, acetic acid 0.52, and at 500 R.P.M. the ratios are perchloric acid 1.3, formic acid 0.54, acetic acid 0.75. From the data of Kilpatrick and Rushton (6)

TABLE 6

Experiments with weak acids at 25°C.

INITIAL CONCENTRATION OF ACID	INITIAL CONCENTRATION OF ANION	INITIAL CONCENTRATION OF CHLORIDE	INITIAL CONCENTRATION OF AMALGAM	REVOLUTIONS PER MINUTE OF STIRRERS		k
				Aqueous layer	Amalgam layer	
			Phenylacetic acid			
moles per liter	*moles per liter*	*moles per liter*	*moles per liter*			*cm. min.*$^{-1}$
0.035	0.035	0.165	0.56	1650	0	0.58
0.025	0.025	0.175	0.56	1650	0	0.56
0.015	0.015	0.185	0.31	1650	0	0.52
0.030	0.030	0.170	0.31	1650	0	0.53
0.050	0.050	0.150	0.56	500	0	0.38
0.050	0.050	0.050	0.56	500	0	0.40
			Propionic acid			
0.035	0.035	0.165	0.56	1650	0	0.82
0.010	0.010	0.190	0.56	1650	0	0.76
0.035	0.035	0.165	0.56	1650	0	0.66
0.022	0.022	0.178	0.56	1650	0	0.58
0.025	0.025	0.175	0.31	1650	0	0.63
0.015	0.015	0.185	0.31	1650	0	0.61

TABLE 7

Summary of experiments with weak acids

ACID	R.P.M.	AVERAGE k	AVERAGE DEVIATION
			per cent
Mandelic	1650	0.57	4
Formic	1650	0.74	5
	500	0.35	5
Glycolic	1650	0.65	10
	500	0.42	5
Phenylacetic	1650	0.55	4
	500	0.39	3
Acetic	1650	0.75	10
	500	0.49	11
Propionic	1650	0.68	12

with magnesium, the corresponding ratios are: perchloric acid 0.74, formic acid 0.33, acetic acid 0.21, while from the data of King and Cathcart (7) we have perchloric acid 0.97, formic acid 0.34, acetic acid 0.28. Whatever the relation between the velocity constant and the diffusion coefficient, these ratios should be the same for the dissolution of magnesium and of sodium amalgam. If we apply an equation of the type $k = \alpha D^x$, the value of x is approximately 0.45 for sodium amalgam. These computations indicate a lack of correlation between dissolution constants and diffusion coefficients. Further experiments with weaker acids indicated that the rate law was not that of equation 1, but that the kinetic law given by equation 2 was followed. In all previous experiments when the reaction was carried to completion the hydrogen evolved was found to correspond to the number of equivalents of sodium reacted. This was not true in the case of monochloroacetic acid or with cacodylic acid. The latter acid is very easily reduced. With solutions of tertiary and secondary sodium phosphate the volume of hydrogen was always less than that calculated from the sodium reacted. In the case of the primary phosphate and mixtures of primary and secondary phosphates, the gas evolved corresponded to the sodium reacted. Table 8 gives these results, the acid concentration being constant. The velocity constant in column 4 is the sum of the water constant and the acid constant multiplied by the acid concentration.

TABLE 8

Experiments with phosphates

AQUEOUS SOLUTION	INITIAL CONCENTRATION OF AMALGAM	R.P.M.	$10^3 (C_A k + k_w)$
0.030 *M* NaH_2PO_4	0.31	1650	2.0
0.030 *M* Na_2HPO_4			
0.20 *M* NaCl			
0.050 *M* NaH_2PO_4	0.31	1650	2.6
0.050 *M* Na_2HPO_4			
0.175 *M* NaH_2PO_4	0.56	1650	12.5
2.0 *M* NaH_2PO_4	0.56	500	62.0

In all cases the velocity constants have been calculated from the integrated form of equation 2 and confirm the results of Fletcher and Kilpatrick (3) with *o*-chlorophenol and those of Brönsted and Kane (2) with very weak acids.

THE WATER REACTION

With the exception of a few experiments which were followed by the gas evolution method, the experimental method for the water reaction was that used by Kilpatrick and Rushton (6) and by Fletcher and Kilpatrick (3). In view of the fact that the purity of the water seemed to make a marked difference, all experiments were carried out with conductivity water and in most cases the water used was from a special batch having a specific conductance of 5 × 10^{-7} mhos at 25°C. Air was not excluded from the solution except in the case of the experiments followed by gas evolution. The indicators used were bromophenol blue, methyl red, bromothymol blue, phenolphthalein, and thymol blue. The velocity constants were calculated from the integrated form of equation 2. C_{H_2O}, being a constant, is included in k. The results are presented in table 9.

TABLE 9

The water reaction

INITIAL AMALGAM CONCENTRATION	H_3O^+ CONCENTRATION	R.P.M. (AQUEOUS LAYER)	$k_w \times 10^3$	REMARKS
moles per liter	*moles per liter*			
0.31	1×10^{-9}	2450	1.60	
0.31	1×10^{-9}	1650	0.86	
0.31	1×10^{-9}	1650	2.20	
0.56	1×10^{-5}	1650	0.65	
0.35	1×10^{-6}	1650	1.00	
0.31	1×10^{-9}	1000	1.50	
0.05	1×10^{-6}	1000	0.70	
0.05	1×10^{-5}	800	0.68	
0.05	4×10^{-10}	500	0.26	
0.26	1×10^{-9}	500	0.16	
0.04	1×10^{-9}	500	0.45	
0.05	1×10^{-7}	500	0.40	
0.06	1×10^{-6}	500	0.55	
0.06	1×10^{-5}	500	0.30	
0.06	1×10^{-5}	500	0.32	Apparatus H—area, 12.3 cm.^{2}
0.01	1×10^{-5}	500	1.10	
0.01	1×10^{-5}	500	1.00	
0.01	1×10^{-5}	500	0.71	
0.04	1×10^{-4}	500	0.36	
0.01	1×10^{-4}	500	0.89	
0.60	Range 10^{-7} to 10^{-12}	500	0.18	By gas evolution
0.60		500	0.18	
0.25		500	0.12	
0.56		500	1.00	
0.26	1×10^{-9}	500	0.18	In 1 *M* KCl
0.26	1×10^{-9}	500	0.29	In 1 *M* LiCl
0.26	1×10^{-9}	500	0.17	In 1 *M* NaCl
0.26	1×10^{-5}	500	0.59	In 0.003 *M* $CaCl_2$
0.26	1×10^{-6}	500	0.34	In 1.14 *M* $CaCl_2$
0.33	1×10^{-9}	500	0.40	In 0.33 *M* $SrCl_2$

All experiments are at 25°C., but it should be stated that there is very little effect of temperature.

A plot of the logarithm of the velocity constant against the logarithm of the stirring speed gives a line of slope of approximately 0.7. The velocity constant seems to be independent of the hydrogen-ion concentration within the reproducibility of the experiments. Since the average value of the velocity constant is smaller for the experiments carried out by the gas evolution method, the possibility of a reaction with oxygen was tested in a special series of experiments. In addition the effect of hydrogen peroxide was studied.

The results in table 10 are in qualitative agreement with those for lithium amalgams and indicate that there is a reaction with oxygen as well as with hydrogen peroxide (9). The reduction of oxygen would result in the formation of hydrogen peroxide (4) in acid solution.

TABLE 10

Effect of oxygen and hydrogen peroxide

Initial concentration of amalgam, 0.78; R.P.M. = 1650; temperature = 25.0°C.

INITIAL CONCENTRATION OF H_2O_2	HYDROGEN-ION CONCENTRATION	10^3k	$\frac{10^3(k - k_w)}{C_{H_2O_2}}$
moles per liter	*moles per liter*		
0	10^{-7} to 10^{-12}	0.53	By gas evolution
0	1×10^{-9}	0.67	Open to air
0	1×10^{-9}	1.06	Oxygen bubbled through the solution
0.036	1×10^{-9}	2.15	42
0.11	1×10^{-9}	3.15	23
0.11	1×10^{-5}	3.66	27
0.18	1×10^{-9}	6.05	30

Our experimental test of equation 2 was carried out at constant acid concentration. To test the possibility that equation 2 might be applied to the acetic acid buffer we have

$$-\frac{dC_M}{dt} = (k_w + k_A C_A) S \sqrt{C_M}$$

so that upon plotting $\frac{1}{C_M}\left(\frac{dC_M}{dt}\right)$ versus C_A a straight line of slope $- k_A S$ and intercept $- k_w S$ should result if the law is obeyed. Computations with the data for acetic acid indicate this law is not obeyed.

In calculating velocity constants for the strong and weak acids, with the exception of primary phosphate, equation 1 was used and the water reaction was neglected in the calculation. It was realized that this neglect would lead to some discrepancies in the determination of the velocity constants. Computation by means of the equation

$$\frac{dx}{dt} = \frac{\bar{v}S}{1000}[k_w + k_{HB}C_{HB}]\sqrt{C_M} + S[k_{H_3O^+} \cdot C_{H_3O^+}] + S[k_A C_A]$$

(where $\bar{v}$ is the volume of amalgam in cubic centimeters, HB represents an acid such as the primary phosphate, and A represents an acid such as phenylacetic) yields information concerning the portion of the alkali metal appearing in the solution by the various reactions. dx/dt is the number of gram-ions of sodium appearing per minute in the aqueous solution. These calculations indicate that the water reaction comes in to as much as 25 per cent in the lowest concentrations of acids following the law represented by equation 1. In the case of acids following the square-root law, the correction for the water reaction is carried out without difficulty, as shown elsewhere (2). For all the experiments with buffer solutions, computations show that the reaction with hydrogen ion is quite negligible. Equation 2 does not seem to fit any mechanism of the reaction which the present authors can offer (5, 10). One or two observations may be worth recording. In many cases an island of bubbles formed on the amalgam surface, and the larger the island the more rapid was the rate of reaction, as a rule. In cases of excess of strong acid over the number of moles of sodium in the amalgam, the reaction rate is practically constant, and just before the sodium has all reacted there is a sudden increase in rate. Here we have a reaction which is of the first order, but under the experimental conditions appears to be of zero order and completed in finite time.

From the results of this paper and the preceding one (3) it is evident that the rate of reaction of alkali metal amalgams with strong and fairly weak acids follows a first-order law, in agreement with the findings of earlier workers in the field. The velocity constants are independent of the concentration of the alkali metal in the amalgam. In solutions of weaker acids and low hydrogen-ion concentration the rate is proportional to the square root of the concentration of alkali metal in the amalgam, and the results may be interpreted as a chemically controlled rate of reaction between electrons and protons from the weak acids (2). In both cases the results can be interpreted from the point of view of the general theory of acids. In addition, one must also consider the process

$$\Theta + \text{oxidant} \rightarrow \text{reductant}$$

analogous to

$$\Theta + H^+ \rightarrow H$$

SUMMARY

1. The earlier and the more recent work on the dissolution of amalgams has been confirmed.

2. For strong acids and certain weak acids the rate of solution is independent of the concentration of the alkali metal in the amalgam if the experimental conditions are such that the water reaction is negligible. The rate is proportional to the concentration of strong acid above 1×10^{-4} moles per liter, is proportional to the surface, and is dependent upon the stirring. For the weaker acids the increase in rate above the water reaction is proportional to the acid concentration.

3. For the water reaction and the reaction with primary phosphate the rate of solution is proportional to the square root of the alkali metal concentration, independent of the hydrogen-ion concentration, and proportional to the acid concentration and to the surface.

4. In the presence of oxygen, hydrogen peroxide is formed and reacts with the sodium amalgam. This reaction explains in part the lack of reproducibility in the rate of reaction of amalgam with water.

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THE ADSORPTION OF THE VAPORS OF DIMETHYL, DIETHYL, AND DI-*n*-PROPYL ETHERS BY ACTIVATED CHARCOAL[1]

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The theory of adsorption which is most in favor at the present time is the Langmuir hypothesis, or modifications of it, in which adsorption is recognized as due to physical or chemical forces acting through distances comparable with molecular dimensions. There are cases in which this theory is difficult to apply, owing perhaps to a lack of knowledge of all the factors involved, but no other hypothesis affords an explanation so general in scope and yet so definite in its applicability to individual adsorption phenomena. Attempts to correlate adsorption data with physical properties, such as surface tension, van der Waals constants, boiling points, molecular volumes, and dipole moments, have proved successful in isolated instances. Undoubtedly many of these are factors which influence adsorption, but adsorption processes are generally so complex that it is difficult to establish the dependence of such phenomena upon a single physical property.

In spite of the large amount of published data upon adsorption of vapors by charcoal there has been little possibility of comparison of results, owing to the differences in activities of the charcoals used, as well as in operating technique, and other variable factors. Some years ago a series of investigations was begun in this laboratory during which measurements of adsorption of a number of vapors have been made upon a specially prepared charcoal under standardized operating conditions, in an attempt to learn the influence of molecular structure of the vapor upon adsorption, and to test the various mathematical treatments of adsorption magnitudes. Papers published before the death of the senior author included investigations upon water, alcohols, ammonia, and amines (7), methane and its chlorine derivatives (6), monochloro derivatives of saturated aliphatic hydrocarbons (8), dichloro derivatives of saturated aliphatic hydrocarbons

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[1] This paper is an abstract of a portion of a thesis submitted by P. E. Peters to the Graduate College of The State University of Iowa in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Deceased November 14, 1936.

[3] Present address: North Shore Coke and Chemical Company, Waukegan, Illinois.

(4), and various ketones and esters (5). This paper briefly outlines the results obtained in a study of the adsorption of the vapors of dimethyl, diethyl, and di-*n*-propyl ethers.

From our present knowledge of adsorption processes it appears probable that these attractive forces act largely through certain atoms or groups in the vapor molecule. In the chlorinated hydrocarbons adsorption is influenced by the number and position of the chlorine atoms; with ketones and esters the C=O group appears to be the center of attraction. Analogously, we should expect adsorption forces to act through the —O— atom in the adsorption of ethers.

If adsorption does occur through the oxygen atom it is evident that the cross-section area of the adsorbed molecule in a plane perpendicular to the direction of the adsorption force increases by definite increments as we proceed through the ether series. The number of molecules of any ether adsorbed at or near saturation will be influenced by this cross-section area, or covering power, per molecule. Hence we should expect in this series, as in previous series, that at higher pressures the smallest molecules would be most highly adsorbed. At lower pressures, where this steric effect is practically inoperative, and where the adsorption forces appear somewhat similar to van der Waals forces, we should expect the most complex molecules to be most highly adsorbed.

The apparatus and technique employed are the same as previously described (6).

The dimethyl ether was obtained as a 40 per cent solution in sulfuric acid from the Eastman Kodak Company. This solution was introduced directly into an evacuated system, and the ether was released by the careful addition of water. The ether was dried before admission to the adsorption apparatus. The diethyl and di-*n*-propyl ethers were purified by washing and by distillation in a special fractionating column (2, 9) until products having substantially constant boiling points were obtained.

In tables 1, 2, and 3 x/m is the number of cubic centimeters (N.T.P.) of vapor adsorbed per gram of charcoal at the equilibrium pressure p (in millimeters).

At 183.14°C. diethyl ether appeared to decompose slowly in the presence of the charcoal. After admission of a sample of the vapor to the charcoal the pressure decreased to a minimum, and then gradually increased. At 235°C. this decomposition became so rapid as to render the results valueless. For the 183.14°C. isotherm the values of p recorded are the minimum values. At 181.66°C. di-*n*-propyl ether begins to show very slight evidence of decomposition. The di-*n*-propyl ether isotherms could not be continued to equilibrium pressures higher than the vapor pressure of the compound at 50°C. (the temperature of the air bath), owing to condensation in the adsorption apparatus.

TABLE 1

Adsorption of dimethyl ether vapor by charcoal

At 0.00°C.

p	2.58	5.41	9.48	20.49	51.50	124.29	256.17	636.55
x/m	29.71	43.98	58.88	78.72	97.11	110.23	117.70	126.26

At 50.00°C.

p	2.18	5.35	15.50	33.49	61.12	84.85	125.21	211.55	426.26
x/m	8.68	17.56	31.75	45.03	56.55	63.60	70.97	80.95	92.30

At 99.37°C.

p	3.82	10.62	18.40	34.69	74.47	125.88	205.06	258.95	397.52
x/m	4.44	9.20	13.92	20.54	30.05	37.84	46.15	50.20	57.76

At 139.41°C.

p	16.17	32.25	89.11	170.53	213.85	350.69
x/m	5.53	9.12	17.77	25.50	28.70	35.95

At 182.64°C.

p	30.07	115.90	243.09	305.01	429.48
x/m	3.99	10.70	17.39	20.25	24.39

TABLE 2

Adsorption of diethyl ether vapor by charcoal

At 0.00°C.

p	0.35	1.59	2.04	3.57	15.77	51.55	97.25	138.62	181.60	186.91	187.01
x/m	25.74	48.64	58.14	69.03	79.62	84.34	87.89	91.29	94.06	97.10	100.73

At 34.60°C.

p	0.45	1.94	12.66	54.89	94.01	210.39	452.01	652.31
x/m	32.36	55.14	68.08	74.89	76.64	79.79	84.06	87.84

At 40.00°C.

p	0.52	0.65	1.94	5.18	34.69	130.99	252.35	399.95	551.48
x/m	19.50	34.31	51.64	59.94	70.52	75.31	77.88	79.91	82.24

At 99.65°C.

p	0.94	2.73	10.32	33.10	98.98	196.18	286.24	374.90	649.27
x/m	14.52	26.52	38.46	49.27	57.95	61.71	63.68	65.51	67.88

At 138.85°C.

p	4.09	18.90	37.12	85.79	175.05	318.03	637.76
x/m	15.94	28.68	35.12	43.02	49.00	53.22	56.27

At 183.14°C.

p	13.19	29.52	50.81	90.05	143.09	188.09	236.18	329.60	507.62
x/m	8.20	16.50	22.42	28.54	33.59	36.37	38.77	41.72	45.44

Equilibrium pressures for the ethers were attained in a relatively short time. At the higher pressures the time for the attainment of equilibrium was from five to six hours. The rate of adsorption decreased with an increase in the size of the adsorbed molecule.

We have attempted by graphic methods to fit our data to various mathematical equations, but we have found no formula which fits the data throughout the temperature and pressure ranges studied. Langmuir's equation expressing adsorption on amorphous adsorbents (1), such as charcoal, becomes so complex that it cannot be satisfactorily subjected to experimental verification without more knowledge of the nature of such surfaces. As an alternative we have plotted our data according to Langmuir's simplest relation, $x/m = abp/(1 + bp)$, for adsorption on plane surfaces. A plot of $p/(x/m)$ against p should be a straight line if this relation is applicable.

TABLE 3

Adsorption of di-n-propyl ether vapor by charcoal

At 0.00°C.									
p	0.25	0.30	3.22	8.83	16.25	16.29			
x/m	29.07	49.23	60.87	65.00	70.25	74.96			
At 50.00°C.									
p	0.10	0.30	0.40	1.78	11.00	36.36	92.33	149.38	187.53
x/m	6.60	19.21	38.62	52.17	56.89	60.35	62.77	65.39	69.97
At 99.66°C.									
p	0.10	0.50	4.36	22.98	34.63	51.71	147.71		
x/m	11.06	25.98	41.85	47.53	48.59	49.07	51.19		
At 139.55°C.									
p	0.25	1.68	12.04	37.94	81.88	110.95	142.69		
x/m	13.27	26.06	37.64	42.23	44.62	45.56	46.27		
At 181.66°C.									
p	1.24	5.20	17.23	37.99	50.52	73.45	133.04		
x/m	14.57	23.02	29.02	33.91	35.52	37.30	39.78		

The isotherms plotted according to this method are shown in figure 1. For all isotherms except those of dimethyl ether at the higher temperatures this relation expresses the experimental points fairly well. The failure to comply with the formula at temperatures near and above the critical temperature is in disagreement with the results of McBain and Britton (3), who found the Langmuir equation to hold for the adsorption of nitrous oxide, ethylene, and nitrogen at temperatures well above the critical temperature and at pressures up to 60 atm. It should be noted that the data for ethers fit the equation satisfactorily over a wider pressure range than did those for ketones and esters (5).

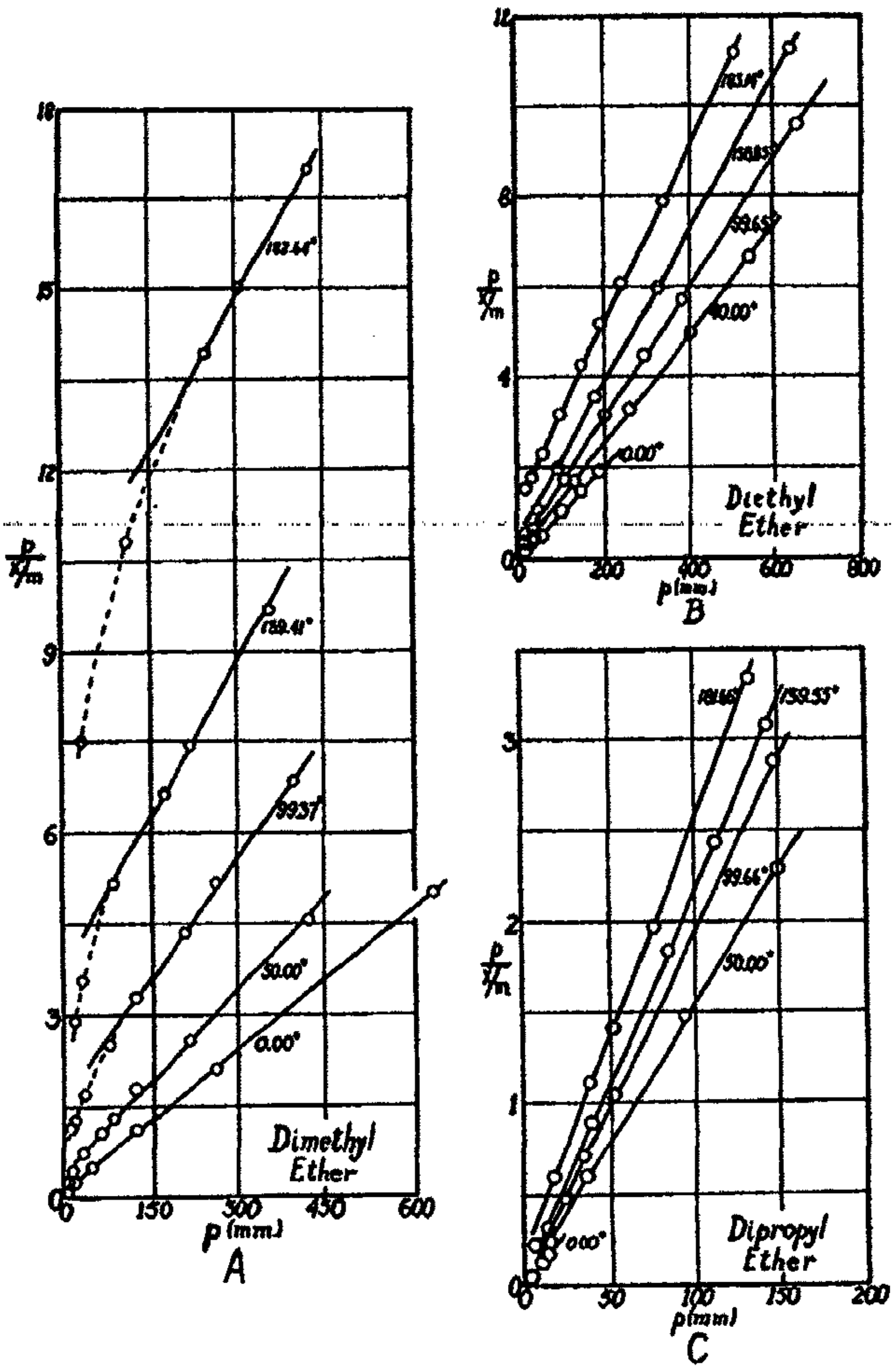

FIG. 1. The Langmuir adsorption isotherms for vapors of dimethyl, diethyl, and di-*n*-propyl ethers at various temperatures.

We have chosen the isotherms at the natural boiling pointsof the ethers for purposes of comparison of the adsorption magnitudes. At these temperatures the thermal energies of the molecules are equal, and the amounts of vapors adsorbed should be significant. Such a comparison is based upon the premise that the adsorption forces existing upon the surface of the adsorbent do not change throughout the temperature range investigated, and that the amount of adsorption of any vapor depends upon the extent to which its thermal agitation prevents orientation of its molecules by the natural adsorption forces of the adsorbent.

The boiling point for dimethyl ether (−24.9°C.) lies somewhat below the experimental temperature range. The isotherm for dimethyl ether at that temperature has been determined by extrapolation of the adsorption isobars (plot of log x/m against temperature).

The order of adsorption of the three ethers at their boiling points is shown in figure 2, in which log x/m is plotted against log p. At low pressures, below about 0.5 mm., the order of increasing adsorption is dimethyl, diethyl, and di-n-propyl ethers; at higher pressures the order is reversed. These relations are similar to those previously found to exist in the series of ketone, ester, and chloride adsorptions. It is hardly necessary to point out the correlation at lower pressures between the order of increasing adsorption and the order of increasing van der Waals constants. At higher pressures this relation is reversed.

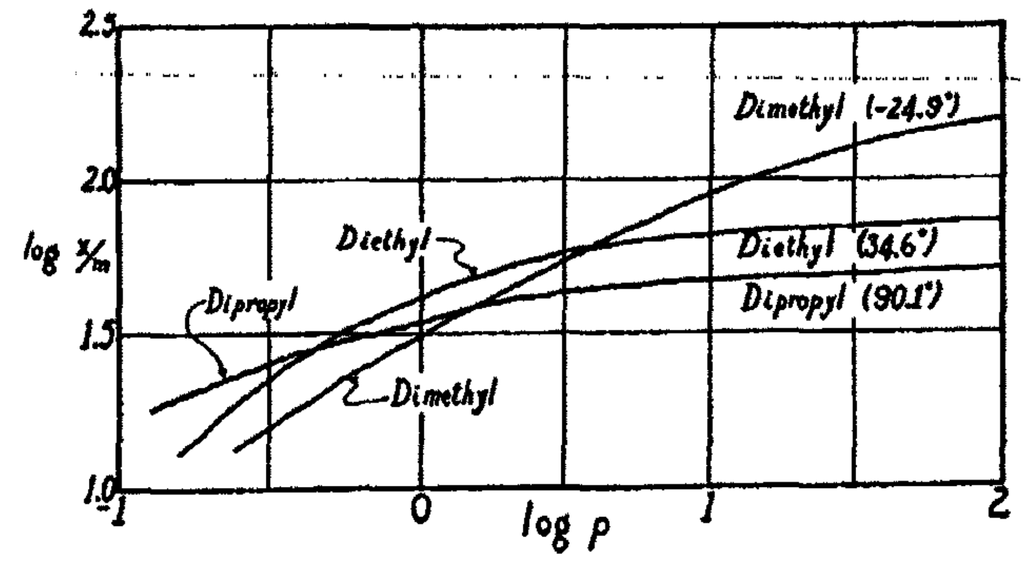

FIG. 2. Double-log isotherms of dimethyl, diethyl, and di-n-propyl ethers at their natural boiling points.

It should be noted that at higher pressures the order of adsorption may be correlated with van der Waals constant b more logically than with van der Waals constant a, as has been done in a previous publication (5). The constant a is a measure of the intermolecular attractive force between molecules of the vapor. The constant b is a measure of the volume of the vapor molecule. Hence if the adsorption magnitude is correlated with van der Waals a it should logically be a direct correlation. At low pressures this is true, since a for the ethers increases in the order dimethyl, diethyl, and di-n-propyl, which is the same as the order of adsorption. At higher pressures this has been cited previously (5) as an inverse correlation. When van der Waals b is considered, however, the correlation becomes logical at higher pressures, since it is in this range that steric effects become operative. The constant *b* for the ethers increases in the order dimethyl, diethyl, and di-*n*-propyl. In other words, for the pressure range in which steric effects are present, the molecules having the largest volume (large values of *b*) are the least adsorbed. At pressures below this range we would expect no correlation between *b* and adsorption magnitudes. While this correlation appears applicable in all of the series studied, and may be useful for comparative purposes, it is not to be inferred that adsorption processes are dependent upon these factors alone.

From the slopes of the isosteres for the ethers the heats of adsorption have been calculated as follows: dimethyl ether, −8,280 cal.; diethyl ether, −12,050 cal.; and di-*n*-propyl ether, −12,830 cal. No experimental data are available for comparison with the above values. They are probably of the right order of magnitude, although in general it has been found that experimentally determined heats of adsorption are slightly higher than those calculated from the slopes of the isosteres.

SUMMARY

The adsorption of vapors of dimethyl, diethyl, and di-*n*-propyl ethers has been investigated at temperatures between 0° and 183°C. Except for the dimethyl ether isotherms at higher temperatures the Langmuir equation for adsorption on plane surfaces satisfactorily expresses the adsorption magnitudes through the pressure range studied. At low pressures the higher boiling ether is adsorbed more strongly; as the pressure is increased the order of adsorption is reversed. Heats of adsorption of the three ethers have been calculated from the slopes of the isosteres.

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STUDIES ON AGING OF FRESH PRECIPITATES. XVIII

THE MIXED-CRYSTAL FORMATION BETWEEN BARIUM SULFATE AND POTASSIUM PERMANGANATE

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According to Grimm *et al.* (4, 5, 6, 10, 11) mixed-crystal formation between two chemical individuals may occur when the following conditions are satisfied: (*1*) the chemical building types of the two compounds must be the same; (*2*) the lattice types must be the same; (*3*) the lattice constants must be of the same order of magnitude. Similarity of chemical building types refers to pairs of compounds with the same number of cations and anions in which the corresponding ions are made up of the same number of atoms. The above conditions include not only the classical ones of mixed-crystal formation but also the formation of Grimm's "neuartige Mischkristalle." Examples of systems forming this new kind of mixed crystals are barium sulfate–potassium permanganate; barium sulfate–potassium fluoborate; calcium carbonate–sodium nitrate; lead sulfide–sodium bromide, etc. Grimm and his coworkers (4, 6) studied especially the new kind of mixed-crystal formation between barium sulfate and potassium permanganate. They coprecipitated potassium permanganate with barium sulfate and studied the properties of the red precipitate. Briefly, they found that the crystals were homogeneously colored; that the permanganate in the crystals was inert towards various reagents; that the rate of solution in concentrated sulfuric acid increased with the potassium permanganate content of the crystals; that the amount of potassium permanganate in the crystals was approximately proportional to the concentration of potassium permanganate in the precipitating solutions; that it was possible to obtain precipitates containing as much as 80 mole per cent of potassium permanganate; that the x-ray pictures made by the Debye method showed a regular displacement of lines (6, 11), such as would be produced if the potassium permanganate were dissolved in the barium sulfate lattice; finally, that equivalent amounts of potassium and permanganate are coprecipitated. The latter fact is strongly indicative of mixed-crystal formation; the results of the x-ray investigation of

Wagner (6, 11), however, give conclusive evidence of the formation of solid solutions of potassium permanganate in barium sulfate.[1]

Various authors (1, 2, 3) have tried to invalidate Grimm's conclusions. Balarew (1), for example, criticizes Grimm's work and attributes the coprecipitation of potassium permanganate to an internal adsorption during the growth of barium sulfate. Balarew's claim that the coloring of barium sulfate by potassium permanganate is not completely homogeneous does not disprove mixed-crystal formation. Even in cases in which mixed crystals of the classical type are formed, a heterogeneous distribution often occurs (compare, e.g., Kolthoff and Noponen (8, 9) for the systems barium sulfate–lead sulfate and barium sulfate–barium chromate). It depends upon the manner of preparation of the mixed crystals whether they are homogeneous or not. Neither Wagner *et al.* nor his opponents have considered the conditions under which homogeneous mixed crystals are obtained, and therefore one cannot arrive at any exact statement of the rules determining the distribution of permanganate between solution and solid. Benrath and Schackmann (2), criticizing Grimm's conclusions, showed that fairly perfect barium sulfate, on being shaken for five weeks with potassium permanganate solutions, incorporated hardly any potassium permanganate. Such a result was to be expected, as hardly any recrystallization occurs upon shaking the fairly perfect barium sulfate. Interesting studies on the coprecipitation of permanganate with barium sulfate have been made by Karaoglanov (7), the results of which are in harmony with the concept of the formation of solid solutions.

It is peculiar that the authors criticizing Grimm's conclusions ignore the conclusive evidence of mixed-crystal formation obtained by him and Wagner from the x-ray diagrams.

In the present study the authors have made a preliminary study of the incorporation of potassium permanganate in recrystallizing barium sulfate with the ultimate purpose of learning the rules governing the distribution of potassium permanganate between the solid and liquid phases. In previous work by the authors (8, 9) it was shown that *homogeneous* mixed crystals of barium sulfate and lead sulfate and of the former with barium chromate could be obtained upon adding lead nitrate or sodium chromate, respectively, to a fresh suspension of barium sulfate and shaking for considerable periods of time until distribution equilibrium was attained. The fresh, imperfect barium sulfate is subject to repeated recrystallizations upon aging in the mother liquor, thus incorporating the mixed-crystal-

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[1] After this paper was submitted for publication, P. R. Averell and G. H. Walden, Jr., (J. Am. Chem. Soc. 59, 906 (1937)) reported conclusive evidence, based upon x-ray investigations, that hydronium permanganate (H_3OMnO_4) forms a solid solution in barium sulfate.

forming component in the recrystallizate, and eventually yielding homogeneous crystals. In the present study an attempt was made to reach distribution equilibrium from two sides: (*1*) by shaking freshly precipitated barium sulfate with solution containing potassium permanganate until the concentration of the latter in the solid became constant, (*2*) by shaking barium sulfate containing coprecipitated potassium permanganate with the supernatant liquid until the permanganate concentration in the solid became constant.

EXPERIMENTAL

A 0.5 molar solution of potassium permanganate was prepared and filtered through an asbestos filter after one day of standing. The general procedure was to precipitate barium sulfate quickly at room temperature from 0.3 *M* solutions of barium nitrate and sodium sulfate, using a slight excess of barium. Immediately after precipitation, various volumes of 0.5 *M* potassium permanganate were added and the suspensions shaken at room temperature (8, 9). After various periods of time the mixtures were centrifuged and the mother liquor was poured off. The precipitate was washed four or five times with 50-ml. portions of C.P. acetone which did not contain impurities reacting with permanganate. It was found that water could not be used for washing the precipitate, as permanganate was extracted continuously. With acetone, on the other hand, the fourth or fifth washing was always colorless. The washed precipitate was dried at 130°C. for twenty-four hours. Weighed amounts of the dried precipitate (from 0.3 to 0.8 g. depending upon the permanganate concentration) were treated with 10 ml. of concentrated sulfuric acid in a glass-stoppered iodine flask. After the crystals had completely dissolved, 40 ml. of water and 0.25 g. of potassium periodate were added, and the contents of the flask were heated for ten to fifteen minutes. The solution was then cooled and made up to a volume of 100 ml. The permanganate content of the solution was determined colorimetrically by comparing with suitable standards in a colorimeter, taking the average of ten readings.

The rate of entrance of permanganate into freshly precipitated barium sulfate

To 26 ml. of 0.3 *M* barium nitrate were added 25 ml. of 0.30 *M* sodium sulfate and 25 ml. of 0.5 *M* potassium permanganate. The mixtures were shaken for various periods of time and further treated as described above. The amounts of permanganate found in the precipitate after various periods of time are given in table 1. The occurrence of a maximum in the amount of permanganate in the precipitate after one day of shaking is comparable to that of lead in the precipitate upon shaking fresh barium sulfate with lead nitrate (8).

The rate of exit of coprecipitated potassium permanganate from barium sulfate

To a mixture of 26 ml. of 0.3 *M* barium nitrate and 25 ml. of 0.5 *M* potassium permanganate was added 25 ml. of 0.3 *M* sodium sulfate. The suspensions were shaken for various periods of time and further treated as described above. The amounts of permanganate found in the precipitate are reported in table 2. Apparently, the fresh precipitate obtained in the presence of permanganate contains much more permanganate than corresponds to equilibrium conditions. Grimm *et al.* (4, 5, 6) filtered their precipitates within half an hour after the preparation. Therefore their results do not correspond to a state of equilibrium, and no exact relation can be inferred from them regarding the distribution of the permanganate between the solid and liquid phases. Comparing the data in tables 1 and 2 shows that the same state of distribution of permanganate is approached from both sides after sufficient periods of time of shaking, indicating that distribution equilibrium can be attained from both sides.

TABLE 1

Rate of entrance of permanganate into barium sulfate

Time of shaking	1 hour	22 hours	6 days	15 days	1 month
Milligrams of $KMnO_4$ per 1 g. of $BaSO_4$	9.6	11.3	8.1	8.3	8.3

TABLE 2

Rate of exit of coprecipitated permanganate

Time of shaking	10 minutes	1 hour	25 hours	7 days
Milligrams of $KMnO_4$ per 1 g. of $BaSO_4$	19.3	17.3	11.5	9.2

The amount of potassium permanganate in the mixed crystals as a function of the concentration of the former in solution

The experiments described in table 1 were duplicated, except that different volumes of 0.5 *M* potassium permanganate were added after the precipitation. The suspensions were shaken for one month, centrifuged, washed with acetone, etc. The results of table 3 tend to show that there is no linear proportionality between the amounts of permanganate in the solid and liquid phases. However, they are not quite conclusive, since it will be shown below that the amount of permanganate taken up by the solid decreases upon addition of sodium nitrate to the solution. In the above experiments the supernatant liquid contained sodium nitrate, the concentration of which decreased with increasing volumes of permanganate added. Moreover, it may be expected that the relative effect of sodium nitrate upon the amount of permanganate incorporated in the solid will decrease with increasing concentration of potassium permanganate in the liquid. This effect of sodium nitrate may explain why the amount of incorporated permanganate increases more than linearly with the potassium permanganate concentration in the solution (table 3). The experiments will be repeated under conditions in which the effect of sodium nitrate is eliminated.

Effect of other salts upon the amount of potassium permanganate incorporated in barium sulfate

The experiments of table 1 were repeated, except that in addition weighed amounts of some electrolytes were added immediately after the precipitation to give mother liquors of various compositions. The suspensions were shaken for one month in order to attain distribution equilibrium of the permanganate. It is seen (table 4) that the amount of permanganate incorporated in the barium sulfate decreases upon addition of sodium nitrate and sodium chloride, the effect of the former being greater than that of the latter. On the other hand, the distribution into the solid phase is favored by the addition of potassium nitrate.

TABLE 3

Relation between concentration of permanganate in solid and in solution

Milliliters of 0.5 M $KMnO_4$ added	50	10	5
Milligrams of $KMnO_4$ per 1 g. of $BaSO_4$	31.9	2.55	1.2

TABLE 4

Effect of salts upon distribution of permanganate

Composition of mother liquor*	0.2 M $NaNO_3$	1.6 M $NaNO_3$	1.3 M KNO_3 + 0.2 M $NaNO_3$	1.3 M NaCl + 0.2 M $NaNO_3$
Milligrams of $KMnO_4$ per 1 g. of $BaSO_4$	8.3	3.9	12.5	6.5

* The concentration of potassium permanganate in the mother liquor was 0.17 M.

DISCUSSION

It has been shown that the rate of establishment of the distribution equilibrium of potassium permanganate between barium sulfate and solution is small. The same equilibrium distribution is reached upon shaking when potassium permanganate is added to the fresh suspension of barium sulfate as when it is coprecipitated, indicating the formation of a solid solution. In the case of mixed-crystal formation in the classical sense ($BaSO_4$ + $PbSO_4$; $BaSO_4$ + $BaCrO_4$) we have shown (8, 9) that large concentrations of electrolytes in solution, the ions of which do not participate in the exchange with ions in the lattice, do not affect the distribution of the isomorphous ion between the solid and the solution, if the added electrolyte does not change the ratio of the activities of the two isomorphous ions in the solution. Thus, it was found that the distribution of lead ion between barium sulfate and solution was not affected by 1 molar sodium nitrate and the distribution of chromate was not affected by 2 molar ammonium acetate. The system barium sulfate–potassium permanganate differs from the above classical systems in as much as indifferent electrolytes, such as sodium nitrate and sodium chloride, decrease the amount of permanganate taken up by the solid under equilibrium conditions. In interpreting these results it should be considered that Walden and Cohen (12) found that barium nitrate can be incorporated into barium sulfate in the form of a solid solution. Although barium nitrate, and possibly also other salts, which are not expected to form solid solutions in barium sulfate according to the classical rules or those of Grimm, do not affect the distribution of an isomorphous ion, they apparently do affect the distribution in the case of the formation of the new kind of mixed crystals of the type described by Grimm. The decreasing effect of sodium nitrate upon the distribution of the potassium permanganate in the barium sulfate may be responsible for the fact that no linear relation has been found between the concentration of potassium permanganate in solution and in the solid under equilibrium conditions. If such a linear relation exists within a certain range of mole per cent of potassium permanganate in the solid, it might be represented by the following expression:

$$(c_{\mathrm{K}^+} \cdot c_{\mathrm{MnO}_4^-})_{\mathrm{solution}} = K(c_{\mathrm{KMnO}_4})_{\mathrm{solid}}$$

in which concentrations are written instead of activities. According to this expression addition of potassium salt to the solution should favor the distribution of permanganate in the solid phase. Actually, addition of potassium nitrate to the solution was shown to have the expected effect (table 4). Apparently the increasing effect of the potassium ions is greater than the decreasing effect of nitrate ions upon the distribution of the potassium permanganate in the solid phase.

From this preliminary study it may be inferred that the factors determining the distribution are much more involved in the case of the formation of the "new kind of mixed crystals" than in the case of the distribution of an isomorphous ion between solid and solution. The investigations are being continued.

SUMMARY

1. Upon shaking freshly precipitated barium sulfate with a potassium permanganate solution, distribution equilibrium is reached after fifteen

days to one month. The same equilibrium is reached when the permanganate is coprecipitated with the barium sulfate and the suspension shaken for a period of about fifteen days. The amount of coprecipitated permanganate decreases considerably during the time of shaking.

2. Sodium nitrate, and to a lesser degree sodium chloride, in the solution decreases the equilibrium concentration of potassium permanganate in the solid phase.

3. The presence of sodium nitrate in the mother liquor may account for the fact that the concentration of potassium permanganate in the barium sulfate under equilibrium conditions was found to increase more than linearly with the potassium permanganate concentration in the solution.

4. Potassium nitrate added to the liquid increases the distribution of potassium permanganate in the solid phase. This is accounted for by assuming that within certain limits the distribution of potassium permanganate is given by the expression

$$(c_{K^+} \cdot c_{MnO_4^-})_{\text{solution}} = K(c_{KMnO_4})_{\text{solid}}$$

5. The factors affecting the distribution are more involved in the case of the formation of the "new kind of mixed crystals" than in the case of the distribution of an isomorphous ion between solid and solution.

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THE SYSTEM ZINC OXIDE-TITANIUM DIOXIDE. ZINC ORTHOTITANATE AND SOLID SOLUTIONS WITH TITANIUM DIOXIDE

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INTRODUCTION

A previous paper from this laboratory (1) reported data on the crystal structure, temperature of formation, etc., of the yellowish pigment lead titanate. The data showed that lead titanate exists only in the metatitanate modification, $PbTiO_3$. Zinc titanate also is of interest as a white pigment. The size of the unit cell of zinc orthotitanate, Zn_2TiO_4, has been reported in the literature at various values. Holgerrson and Herrlin (3) reported $a_0 = 8.44$ A.U. for the product of the reaction $2ZnO + TiO_2$ using sodium chloride as a fluxing agent. Passerini (6) obtained a value of $a_0 = 8.41$ A.U. when $2ZnO + TiO_2$ was calcined at 900°C. for short periods of time. Taylor (8) reported $a_0 = 8.46$ A.U. for mixtures of $ZnO + TiO_2$ and $2ZnO + TiO_2$ after twenty-four hours' calcination at 1050°C. and indicated that zinc orthotitanate, Zn_2TiO_4, was the only compound formed. The several investigators reported that the calcined product had a spinel structure typical of other compounds of the A_2BX_4 composition.

The existence of zinc metatitanate, $ZnTiO_3$, has been claimed by Levy (4), Piperaut and Helbronner (7), Mellor (5), and Goodlass Wall and Lead Industries (2), but no experimental data were offered in substantiation. Zinc metatitanate, if formed, would be expected to have a crystal lattice resembling one of the other titanates of the $MTiO_3$ type, e.g., ilmenite, perovskite, etc.

In view of the discrepancies noted above, mixtures of titanium dioxide and zinc oxide from the composition $2ZnO \cdot TiO_2$(ZnO, 67 per cent; TiO_2, 33 per cent) to $5ZnO \cdot 7TiO_2$ (ZnO, 41 per cent; TiO_2, 59 per cent) have been investigated over a rather wide range of temperature and time of calcination. The size of the unit cell for the several mixtures and calcinations was obtained as a means of observing the initial reaction temperature and other changes occurring during calcination.

METHOD OF PREPARATION AND EXAMINATION

Titanium dioxide precipitated from ilmenite solution and washed free of impurities was used as the source of pure oxide (over 99.8 per cent titanium dioxide, calcined basis). The principal impurity (silicon dioxide) in the titanium dioxide did not interfere in the reaction with zinc oxide, which was of highest purity, being over 99.9 per cent zinc oxide. The various mixtures were thoroughly mixed by blending in water, then filtering and drying. The calcinations were carried out in electrically heated muffles with the temperature controlled to within ±5°C.

The x-ray diffraction patterns were obtained by mounting the samples on copper wire in a camera having a diameter of 57.30 mm. Copper radiations from a Ksanda gas type tube were used to obtain the pattern. The diffraction patterns were prepared in duplicate for each sample, so as to have a more correct value for the unit cell. The differences in the unit cell size never exceeded ±0.005 A.U. in two different runs, and normally agreed within ±0.002 A.U.

The determination of the titanium dioxide in the calcined samples was in accordance with standard methods: namely, dissolving the sample in concentrated sulfuric acid, reducing with zinc amalgam in a Jones reductor, and titrating the reduced solution with ferric ammonium sulfate using potassium thiocyanate as indicator. The titanium dioxide value is correct to within ±0.1 per cent.

DISCUSSION

The initial reaction temperature between zinc oxide and titanium dioxide was found to be 430°C. Below this temperature, i.e., 400°C., only ZnO and TiO_2 patterns resulted after heating for 144 hours. The reaction was 30 per cent completed at 450°C. after seventy-two hours. After 144 hours at 430°C., the product was found to be a mixture of zinc oxide, titanium dioxide, and about 10 per cent of a compound having a spinel pattern with a unit cell size = 8.35 A.U. Heating a mixture of $2ZnO + TiO_2$ at higher temperatures yielded a product having different values for the unit cell and uncombined zinc oxide, as will be shown. The unit cell size increased and the uncombined zinc oxide decreased as the calcination temperature was raised.

The reactions occurring at 600°C., 800°C., and at 1000°C. are postulated to be as follows:

At 600°C.: $8ZnO + 4TiO_2 \rightarrow 2(Zn_2TiO_4 \cdot TiO_2) + 4ZnO$

At 800°C.: $2(Zn_2TiO_4 \cdot TiO_2) + 4ZnO \rightarrow (3Zn_2TiO_4 \cdot TiO_2) + 2ZnO$

At 1000°C.: $(3Zn_2TiO_4 \cdot TiO_2) + 2ZnO \rightarrow 4Zn_2TiO_4$

The range of stability of the solid solution, as will be shown, explains the discrepancies in the data reported by previous investigators. No evidence was obtained which showed that zinc orthotitanate was the first product of the reaction, with excess titanium dioxide then reacting with it to yield a solid solution. The initial reaction product is, therefore, considered to be a solid solution of titanium dioxide in zinc orthotitanate of approximately the empiric composition $ZnTiO_3$, i.e., $Zn_2TiO_4 \cdot TiO_2$ rather than $ZnTiO_3$. Reaction of the excess zinc oxide with the solid solution is not rapid until the temperature is raised above 600°C. The reaction ($2ZnO + TiO_2$) is complete at 1000°C. (after twenty hours).

The solid solution series were heated at 700°C., 800°C., 900°C., 950°C., and 1000°C. The size of the unit cell and the composition at the temperature of stability for each mixture are given in table 1 and shown in figure 1. The value reported by Taylor for zinc orthotitanate, Zn_2TiO_4, i.e., 8.46 A.U., was checked. He reported that the mixture $ZnO + TiO_2$ after twenty-four hours at 1050°C. gave Zn_2TiO_4 and TiO_2 patterns; this also was found to be in agreement with our results. The limit of stability of the solid solution with respect to temperature increases as the composition approaches $2ZnO \cdot TiO_2$.

TABLE 1

Size of unit cell of various compositions in the system TiO_2-Zn_2TiO_4

NO.	COMPOSITION PER CENT TiO_2	MOLECULAR RATIO $ZnO:TiO_2$	SIZE OF UNIT CELL	TIME AND TEMPERATURE OF CALCINATION	
			A.U.	*hours*	*°C.*
A	32.96	2:1	8.460	20	1000
B	36.42	1.73:1	8.440	3	850
C	41.04	1.42:1	8.412	4	800
D	45.79	1.13:1	8.405†	4	900
E	47.64	1.09:1	8.380	4	800
F	50.15	1.04:1	8.372	16	750
G	52.8	0.97:1	8.371	4	750
H*	52.33	0.9:1	8.380	48	750
I	55.92	0.78:1	8.355†	16	750
J	59.00	0.7:1	8.344†	16	750

* Mixture of zinc orthotitanate and titanium dioxide before calcination.

† About 5 per cent uncombined titanium dioxide observed from diffraction patterns.

Diffraction patterns of ZnO, TiO_2, Zn_2TiO_4, and $Zn_2TiO_4 \cdot TiO_2$ are shown diagrammatically in figure 3. The data are calculated to d in Ångström units and the intensity is estimated for the lines.

The compositions marked F, G, H, I, and J dissociate above 800°C. into titanium dioxide and a solid solution poorer in titanium dioxide. The approximate field of stability of the solid solution has been indicated in figure 2, as based on results so far obtained. The upper limits of stability were obtained by heating a given mixture for four hours at several temperatures and then obtaining the size of the unit cell for each heating

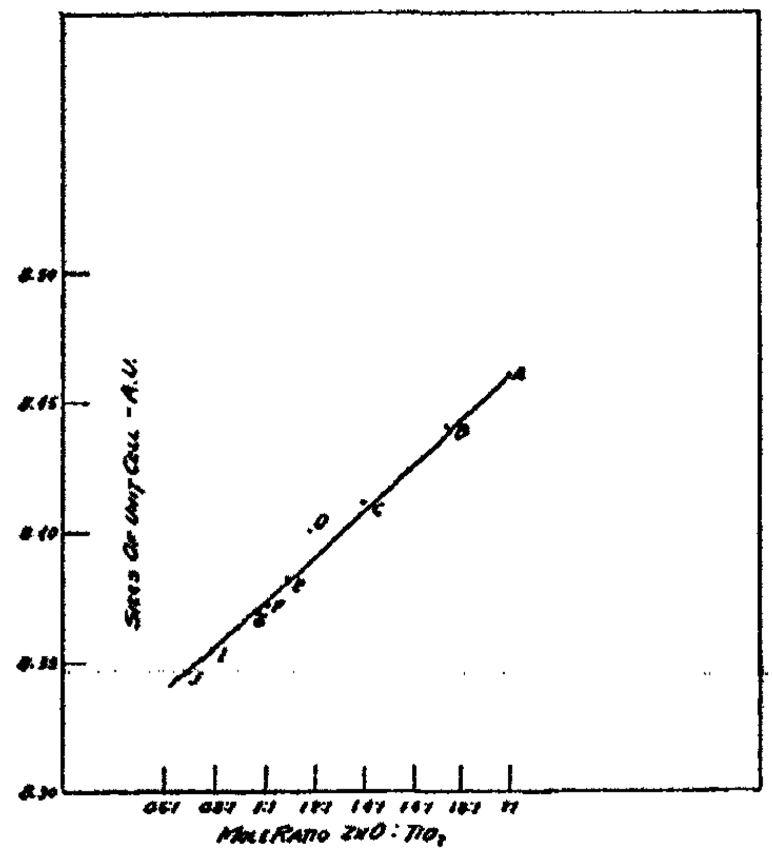

FIG. 1. Change of unit cell size in relation to composition

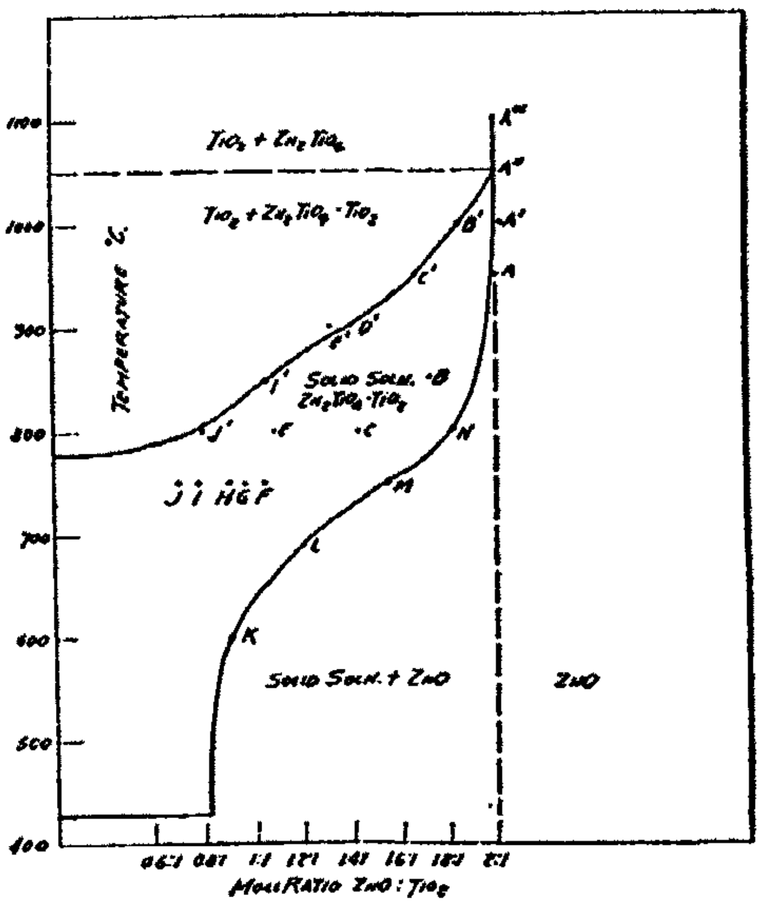

FIG. 2. Proximate limits of stability of solid solution $Zn_2TiO_4 \cdot TiO_2$

period. The dissociation of the solid solution could be determined from the change in the unit cell size. The composition of the product was obtained from the curve in figure 1. For example, the composition of $1.73ZnO \cdot TiO_2$ (No. B) was heated at 1000°C. The unit cell size obtained was 8.45 A.U., which would compare with composition $1.86ZnO \cdot TiO_2$ according to the curve in figure 1. The proportion of zinc oxide in the composition has been increased by the splitting off of titanium dioxide from the solid solution which was stable at the lower temperature. Again, composition $1.04ZnO \cdot TiO_2$ (No. F) after heating at 950°C. had a unit cell of 8.43 A.U., which would be composition $1.65ZnO \cdot TiO_2$. All compositions except Nos. A and B, when heated at 950°C. gave 8.43 to 8.44 A.U. for the unit cell size. No comprehensive study of the stability of these solid solutions has been attempted, so that these temperatures are only indicative of probable limits. The minimum temperature for dissociation of the solid solution is about 775°C. in the field rich in titanium dioxide.

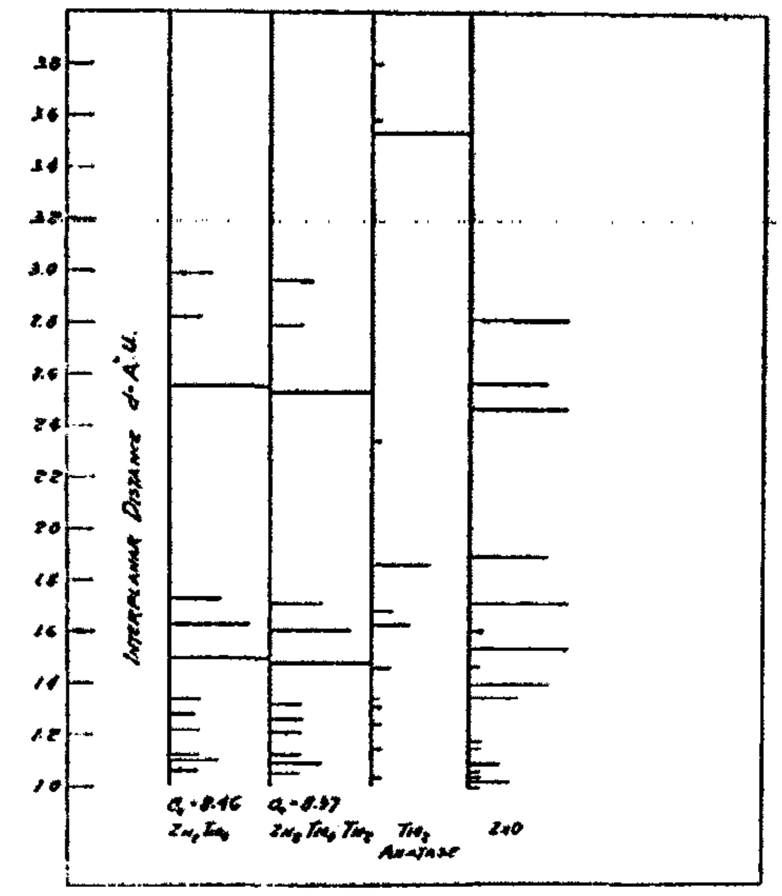

FIG. 3. Estimated intensity of principal diffraction lines

Since the solid solution was found to be unstable, it was desirable to determine if the reaction was reversible. Consequently, the mixture (No. H) $Zn_2TiO_4 + TiO_2$ was heated for sixteen and forty-eight hours at 750°C. The Zn_2TiO_4 had been heated previously at 800°C. for sixteen hours and had a unit cell size of 8.45 A.U. The unit cell values became 8.42 A.U. and 8.38 A.U., respectively, showing that the titanium dioxide had been taken up slowly by the zinc orthotitanate. No TiO_2 lines were observed after forty-eight hours. The time required to bring about the change in the unit cell shows that the reaction is slow, but the final product is similar to the initial product of the reaction of $ZnO + TiO_2$ at 750°C.

The change in size of the unit cell of the reaction product of the mixture $2ZnO + TiO_2$, when heated for 24-hour periods at various temperatures, is given in table 2. The mixture was carefully blended so that the two reactants were in close contact. The data obtained check the results found in the calcination studies on mixtures having different $ZnO:TiO_2$ ratios. The reaction of $2ZnO + TiO_2$ is not completed until the temperature is above 900°C. for twenty-four hours. The reaction goes very slowly to completion, but is nearly complete above 800°C. with short periods of calcination (three to six hours) as observed from other data obtained but not reported.

TABLE 2

Size of unit cell of reaction product of $2ZnO + TiO_2$ *at various temperatures*

NO.	TIME	TEMPERATURE	SIZE OF UNIT CELL	REMARKS
	hours	*°C.*	*A.U.*	
K	24	600	8.360	Approximately 30 per cent uncombined ZnO
L	24	680	8.382	Approximately 30 per cent uncombined ZnO
M	16	750	8.433	Approximately 15 per cent uncombined ZnO
N	16	800	8.450	Approximately 10 per cent uncombined ZnO
A	20	1000	8.459	
O	24	1100	8.460	

TABLE 3

Specific gravity of $Zn_2TiO_4 \cdot TiO_2$ *and* Zn_2TiO_4

	SOLID SOLUTION	ZINC ORTHOTITANATE
Composition	$(Zn_2TiO_4 \cdot TiO_2)$	Zn_2TiO_4
Observed gravity	4.76	5.12
Calculated gravity	4.79	5.28

In table 3 the observed and calculated specific gravity data for Zn_2TiO_4 and the solid solution $Zn_2TiO_4 \cdot TiO_2$ are given. The calculated value of $Zn_2TiO_4 \cdot TiO_2$ is based on the assumption that it is a mixture of 75 per cent Zn_2TiO_4 (sp. gr. 5.12) and 25 per cent TiO_2 (sp. gr. 3.85). The calculated gravity of Zn_2TiO_4 is obtained, by the regular calculation, from the size of the unit cell (8.46), assuming eight molecules to the unit cell. The observed and calculated values for $Zn_2TiO_4 \cdot TiO_2$ are in close agreement.

SUMMARY

1. The size of the unit cell of zinc orthotitanate has been checked and found to be 8.46 A.U.

2. The solid solution of titanium dioxide in zinc orthotitanate extends to the composition $Zn_2TiO_4 \cdot 1.5TiO_2$, with spinel structure persisting.

3. The solid solution is not stable at higher temperatures, dissociating into titanium dioxide and a solid solution poorer in titanium dioxide. The lowest dissociation temperature observed was 775°C.

4. An approximate field of stability has been indicated based on data so far obtained.

5. The initial temperature of reaction of titanium dioxide with zinc oxide is about 430°C.

6. The first product of the reaction is a solid solution with a unit cell size the same as the lower limit of the solid solution.

7. The specific gravity of zinc orthotitanate was calculated as 5.28 and observed as 5.12.

8. Titanium dioxide will react with zinc orthotitanate in the stable range of the solid solution to yield a product richer in titanium dioxide.

9. Zinc orthotitanate was the only compound found in the composition range studied.

The writers wish to acknowledge the advice and keen interest of J. L. Turner, Director of Research, National Lead Company—Titanium Division, in connection with this investigation, and to thank H. Espenschied, who determined the specific gravities.

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THE VISCOSITY OF OIL-WATER EMULSIONS[1]

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INTRODUCTION

Although the viscosity of concentrated emulsions is of considerable interest, it has received inadequate industrial and theoretical study. This may be traced to the complexity of the subject, many variables undoubtedly being of importance. Of these, the outstanding appear to be (*1*) volume concentration of the disperse phase, (*2*) rate of shear, or shearing force, (*3*) viscosity of the continuous phase, (*4*) viscosity of the disperse phase, (*5*) the stabilizer or emulsifying agent used, and (*6*) the particle size of the emulsion. Most investigators have considered the effects of the first and second variables, paying but little attention to the others involved. As will be seen, the nature of the disperse phase and the emulsifying agent cannot be neglected. For dilute suspensions, in which the small spherical particles can be considered to be rigid and substantially independent of each other, the viscosity is dependent only upon the volume concentration of the disperse phase. Einstein (3, 4) theoretically obtained the relation[2]

$$\mu = \mu_0(1 + 0.025V) \tag{1}$$

For dilute emulsions and suspensions this holds with a fair degree of accuracy (9). Besides mutual interference, deformation of the dispersed particles may occur, and Taylor (13) has shown theoretically that to correct for this Einstein's equation may be written

$$\mu = \mu_0\left\{1 + 0.025V\left(\frac{\mu_i + 2/5\mu_0}{\mu_i + \mu_0}\right)\right\} \tag{2}$$

However, small drops behave substantially as solid bodies if their radius does not exceed a certain critical radius (1),

$$r = \sqrt{T/(\rho_i - \rho)g}$$

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[1] This article is based on the work of the late Kenneth R. Moll (Thesis, Massachusetts Institute of Technology, 1933).

[2] For nomenclature see table 1.

For most ordinary stable emulsions the drop size lies below this critical radius, making any experimental test of Taylor's expression difficult.

Hatschek (5) derived an expression for concentrated emulsions

$$\mu = \mu_0 \left[\frac{1}{1 - \sqrt[3]{V}} \right] \tag{3}$$

which he was able to show held for an emulsion of paraffin oil in 0.75 per cent soap solution. With concentrated emulsions the rate of shear used in the viscosity determination becomes of importance, a point emphasized by Hatschek. As it is increased the apparent viscosity decreases, becoming almost constant at high shear. Most investigators have, therefore, attempted to correlate the viscosities at infinite shear. Sibree (10) attempted to verify the Hatschek equation, using paraffin-water emulsions to which 1 per cent of sodium oleate had been added as an emulsifier. The paraffin phase was weighted with bromoform, so that both phases possessed the same density.[3] By insertion of a correction factor h, so that equation 3 becomes

TABLE 1

Table of nomenclature

μ = viscosity of emulsion
μ_0 = viscosity of solvent or continuous phase
μ_i = viscosity of internal or disperse phase
μ' = limiting viscosity of emulsion
μ_r' = limiting relative viscosity of emulsion
μ_y' = limiting relative viscosity of emulsion at which yield point appears
V = volume concentration, per cent
T = surface tension of disperse phase
ρ_i = density of disperse phase
ρ = density of continuous phase
h = volume concentration correction factor (Sibree)
k = calibration constant in R.P.M. centipoises per degree MacMichael
M = deflection in degrees MacMichael
R = R.P.M.
M_y = yield point
a, b, c = constants

$$\mu = \mu_0 \left[\frac{1}{1 - \sqrt[3]{hV}} \right] \tag{4}$$

substantial agreement with experiment was obtained. Sibree was of the opinion that this correction factor, about 1.3, was an expression of the

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[3] It will be noted that this prevents creaming and tends to make the drops deformable when the emulsion is under shear.

increased volume of the drops due to a hydrated film of the emulsifier around their surface. Although he stated that the value of the volume factor might be specific for a given emulsion, no attempt was made to use different emulsifying agents and disperse phases beyond comparing the viscosities of emulsions made with limpid and viscous paraffins. These were found to have substantially the same viscosity at equal volume concentrations (11). Air entrainment leads to greatly increased viscosity (7), which apparently accounts for the observation of Sibree that coarse emulsions had much lower viscosities than fine ones. When all air was carefully removed, both coarse and fine emulsions had substantially the same viscosity.

More recently Richardson has deduced on theoretical grounds the equation

$$\mu/\mu_0 = e^{cV} \tag{5}$$

obtaining good agreement with benzene in water emulsions stabilized with sodium oleate (8). Richardson again investigated but one dispersed phase and one emulsifying agent. Sibree's data, when plotted in the form log μ/μ_0 against V, give straight lines which do not pass through the origin, although data of some other workers (8) conform to the Richardson formula. In view of the fact that most of the investigators to date have studied but one emulsion or one variable, it was felt that investigation of several emulsions at varying rates of shear using different stabilizing agents would be of value.

EXPERIMENTAL

The preparation of emulsions

Seven types of emulsions were prepared, using aqueous solutions of sodium oleate, saponin, and triethanolamine oleate (1, 2, and 3 per cent by weight, respectively) as continuous phases, and Nujol, benzene, and olive oil as the disperse phases. The materials used were of C.P. grade oı its equivalent. To prevent creaming or separation of the disperse phase on standing, all the oils were weighted with α-bromonaphthalene to a specific gravity of 1.00, so that on standing for several days the most dilute emulsions showed no tendency to cream.

Emulsification was performed by adding appropriate quantities of the weighted oil to the solution of the emulsifier, and thoroughly stirring the mixture in a high-speed electric stirrer. Intermittent stirring was found to be most effective, and a definite schedule of 1 min. of stirring followed by 1 min. of rest was selected. For some of the emulsions, particularly those stabilized by triethanolamine oleate, little or no stirring was necessary, emulsification being almost spontaneous.

The emulsions prepared in this way were sometimes coarse and always contained an appreciable amount of air. For removal of this a vacuum homogenizer, such as recommended by Briggs (2), was found satisfactory. All emulsions were given four or more passes through the homogenizer and showed no change in viscosity on standing for several weeks.

Viscosity determinations

The MacMichael viscosimeter was used in this investigation. It consists of an inner disc, suspended by a torsion wire inside an outer cup, which can be rotated at any constant speed desired. In all the experiments the viscosimeter was allowed to run at the indicated speed until the deflection of the wire became constant, four or more points in all being taken on the R.P.M.-deflection curves. The temperature is maintained constant (25° ± 1°C.) by means of the water bath surrounding the cup.

TABLE 2

Viscosity of liquid phases at 25°C.

PHASE	VISCOSITY
	centipoises
Benzene	0.82
Nujol	33.2
Olive oil	121.0
1 per cent sodium oleate solution	0.983
3 per cent sodium oleate solution	1.138
2 per cent saponin solution	1.001
3 per cent triethanolamine oleate solution	4.730

Three torsion wires were required to cover the range of viscosities encountered in this investigation. The viscosity was calculated from the R.P.M. and deflection by the relation

$$\mu = k \cdot \frac{M}{R} \tag{6}$$

the calibration constants, k, of the wires being obtained by measurements at 25°C. against a 60 per cent sugar solution. The value of the viscosity of this solution was taken as 44 centipoises (6).

The viscosities of the phases, listed in table 2, were determined in an Ostwald viscosimeter, except that of the weighted olive oil, which was measured in the MacMichael viscosimeter.

RESULTS

When the viscosities of the various emulsions are calculated it is found, in agreement with the results of other investigators, that this quantity is not a constant for any given emulsion, but varies with the rate of shear. All the emulsions behave as non-Newtonian liquids, e.g., figure 1 shows the variation for an emulsion containing 50 volume per cent of weighted Nujol in 3 per cent aqueous triethanolamine oleate solution. Thus the asymptote of the viscosity rate of shear curve (the limiting viscosity) or viscosity at infinite shear will be chosen as the quantity for consideration in the following discussion.

The experimental data for all the emulsions were plotted as R.P.M.-deflection curves, representative straight lines being drawn through the points. Typical curves are shown in figure 2. It is obvious that the slopes of the straight-line portions are inversely proportional to the limiting viscosities. These slopes were determined, and the limiting viscosities are listed in column 4 of table 3. At very high rates of shear the points begin to deviate from this straight line, becoming concave to the deflection axis.[4]

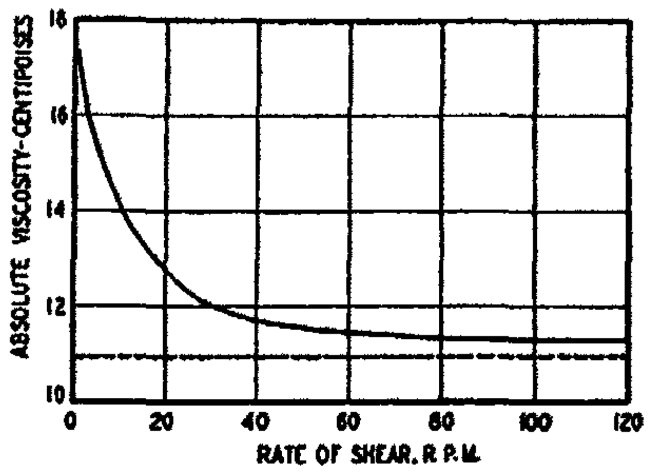

FIG. 1

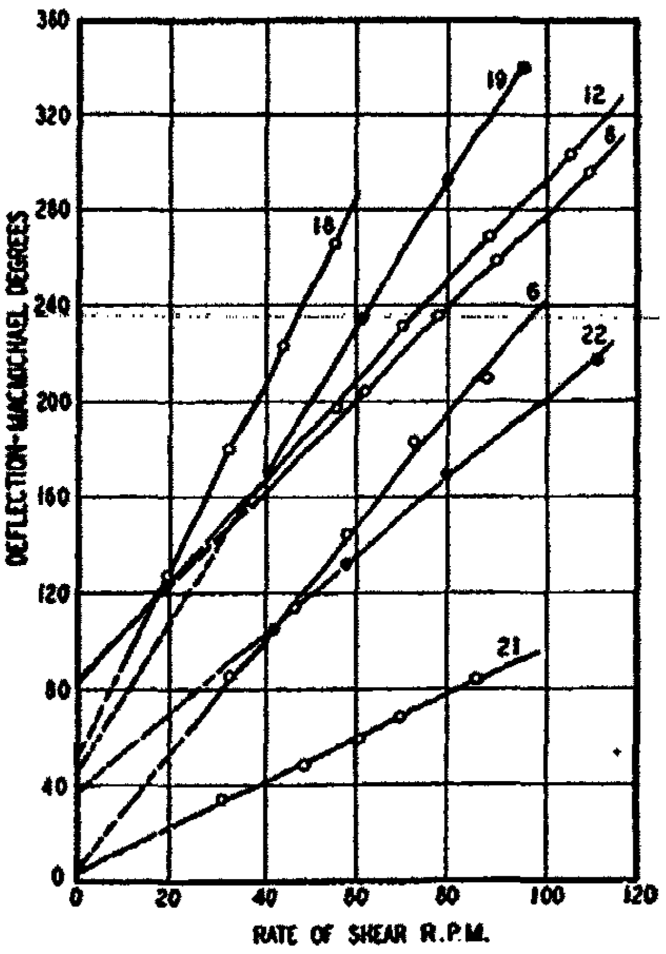

FIG. 2

FIG. 1. Effect of rate of shear on viscosity for emulsion 10

FIG. 2. Torque-rate of shear diagram. Wire X; temperature = 26° ± 1°C. See table 3 for key to figures

If the R.P.M.-deflection curves are extrapolated to low rates of shear it is found, in most cases, that they do not pass through the origin but

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[4] Taylor (12) has shown that this condition occurs when the flow ceases to be laminar and becomes vertical or turbulent.

intersect the torque axis at a definite positive value. This point of intersection has been termed the yield point, and represents the theoretical distorting force necessary to initiate flow. While there is doubt as to whether this extrapolated value is a definite physical entity, nevertheless it is obvious that, knowing the value of the yield point and the limiting viscosity, the flow characteristics of the emulsion can be calculated over the range where the R.P.M.-deflection relation is linear. In such cases,

TABLE 3

Summary of calculated data

EMULSION	VOLUME PER CENT (OIL)	YIELD POINT	LIMITING VISCOSITY	RELATIVE LIMITING VISCOSITY
			centipoises	
Nujol-sodium oleate				
4	50	1.94	8.94	9.09
2	60	5.0	14.75	15.0
8	70	84.0	29.9	30.4
3	75	178.5	37.5	38.15
Nujol-saponin				
5	50	0.54	10.97	10.97
6	60	5.0	36.3	36.3
9	70	440	78.5	78.5
7	75	838	143.8	143.8
Nujol-triethanolamine oleate				
10	50	2.9	10.97	2.31
11	60	8.0	18.85	3.98
12	70	83.0	32.45	6.87
27	80	1320	92.3	19.5
Benzene-triethanolamine oleate				
14	50		8.02	1.70
15	60		12.07	2.55
16	70		32.10	6.78
26	75	27.5	66.5	14.05
Benzene-sodium oleate				
20	50	0.97	9.05	7.95
21	60	4.0	14.13	12.42
22	70	36.0	25.2	22.1
Olive oil-triethanolamine oleate				
17	50	24	22.95	4.85
18	60	50	60.30	12.72
Olive oil-sodium oleate				
24	50	0.32	8.90	7.82
24	55	8.0		20.9

over wide ranges the two quantities,—the extrapolated yield point and the limiting viscosity,—define the viscous behavior of the emulsion. In column 3 of table 3 are listed the yield points determined by extrapolating the R.P.M.-deflection curves and expressed in terms of the equivalent deflection that would have been produced had one common wire been used for all the emulsions.

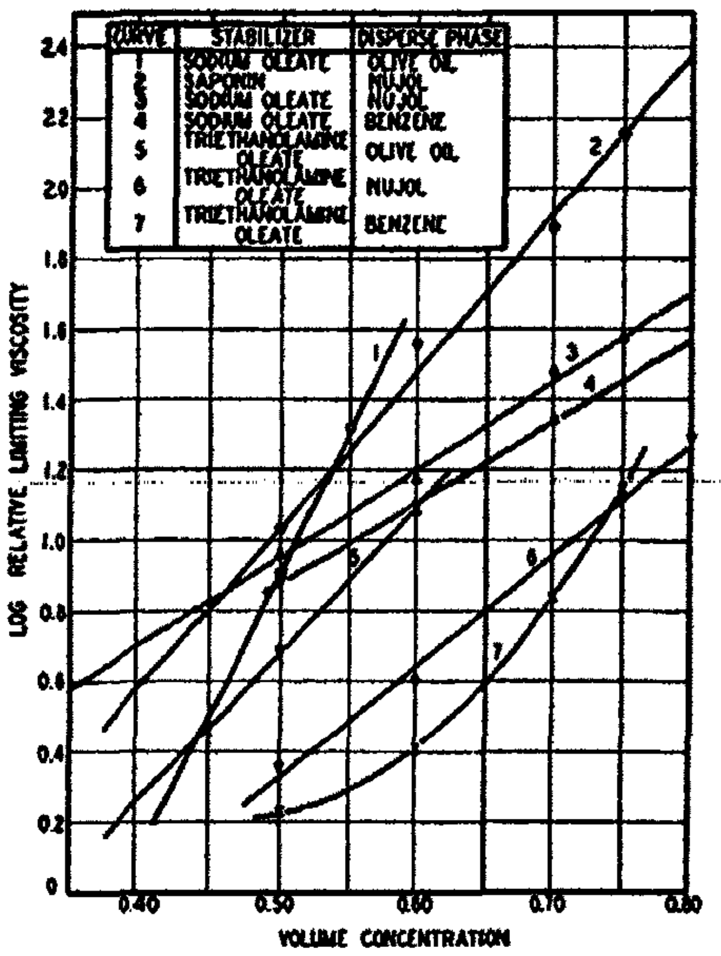

FIG. 3

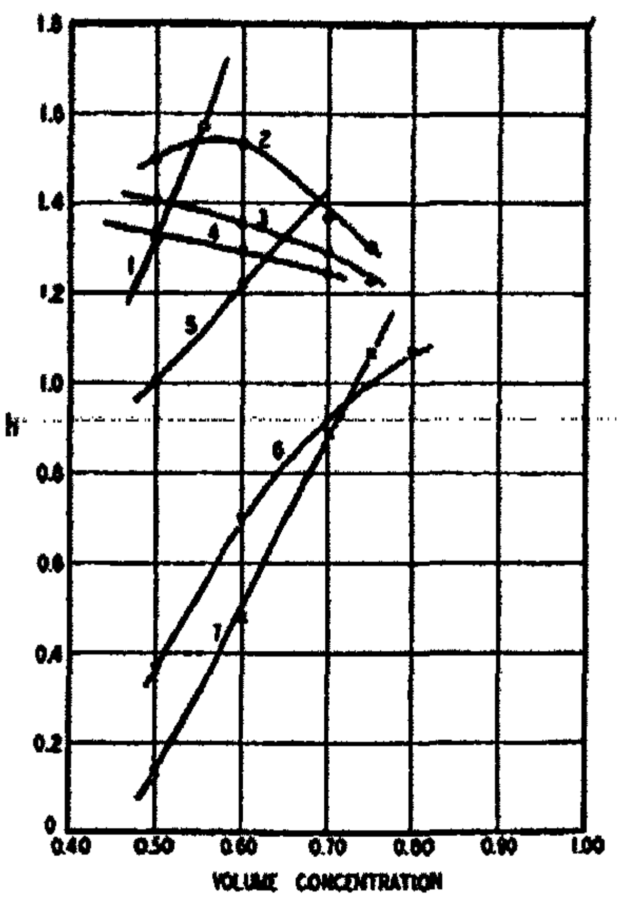

FIG. 4

FIG. 3. Relative viscosity versus volume concentration

FIG. 4. Sibree correction factor *h* versus volume concentration of disperse phase. See figure 3 for key to figures

DISCUSSION OF RESULTS

The effect of volumetric concentration

Inspection of the values of the limiting viscosity given in column 4 of table 3 shows that this quantity varies with the concentration over a wide range of values. It is therefore more convenient to plot not the limiting viscosity itself but its logarithm. Furthermore, to place the various emulsions on a comparative basis it is preferable to plot the logarithm of the limiting relative viscosity, defined as the ratio of the limiting viscosity to the viscosity of the continuous phase.

Examination of figure 3 shows that the logarithm of the limiting relative viscosity is linear in the volumetric concentration for the majority of the emulsions studied and hence may be represented by the equation

$$\text{Log}\ \mu_r' = a + bV \tag{7}$$

This relationship is somewhat analogous to that of Richardson (equation 5). Since the present data when extrapolated to $V = 0$ do not show relative limiting viscosity of unity, equation 5 does not hold.

Curve 7 of figure 3, showing the viscosity for the benzene–triethanolamine oleate emulsion, cannot be represented by a straight line and is an exception to the generalization given above. This may be related to the fact that this emulsion shows no yield point up to 70 per cent concentration.

The Hatschek equation, as modified by Sibree, may be expressed as

$$h = \left(\frac{\mu_r' - 1}{\mu_r'^{3}}\right)^3 \Big/ V \qquad (8)$$

Figure 4 shows the value of h calculated according to this equation plotted against the volumetric concentration for the data of table 3. If the data followed equation 2, h would lie uniformly on the line $h = 1$. If it followed equation 3 a series of straight lines parallel to the concentration axis, but having a different value for each emulsion, would be obtained. It is evident that no such behavior was found; in some cases h decreased with increasing concentration and for the Nujol–saponin emulsion even exhibited a maximum. If h were a measure of the percentage increase in volume of the disperse phase due to the layer of hydrated stabilizer around each particle, as suggested by Sibree, it would necessarily always be greater than unity. However, curves 6 and 7 of figure 4 show values of h far below unity at the lower volumetric concentrations, excluding such an interpretation. Hence, it can be seen that the Hatschek equation or its modification is not of general applicability.

It is interesting to note that h is most nearly constant for emulsions of hydrocarbons stabilized by sodium oleate (curves 3 and 4), which are the type Sibree prepared. While the slopes of the lines in figure 4 are smallest for these types, even in them considerable variation in h occurs. In fact, Sibree's own data show a variation in h from 1.45 at a volume concentration of 0.5 to 1.28 at 0.75 volume concentration for the viscous paraffin emulsion. Furthermore, for his data h always decreased with increasing volumetric concentration, although in many cases the decrease was not so marked as in the example quoted above. Considering figure 4, this change in h is significant and corroborates the present data, although Sibree concluded from his experiments that h was constant.

The results as shown in figures 3 and 4 indicate that the volumetric concentration of the emulsion is not the only important variable influencing the limiting relative viscosity.

Variation of the yield point

Inspection of column 3 of table 3 shows that the yield point as defined above varies even more widely with concentration than does the limiting viscosity. It is well known that relatively dilute emulsions behave like true liquids, showing no yield point and hence no variation in viscosity with rate of shear. Above a fairly definite concentration, however, the viscosity becomes a function of the rate of shear and a yield point develops.[5] All the emulsions studied were in a concentration range well above this limit, with the exception of the benzene-triethanolamine oleate emulsion (curve 7, figure 3). This emulsion showed no yield point up to a volume concentration of 0.70. In table 4 are listed the estimated concentrations at which a yield point appeared, obtained by linear extrapolation of the yield point-concentration curve. The third column of table 4 also shows the limiting relative viscosity of the emulsion at this concentration.

TABLE 4

Volume concentration and viscosity at initial yield point

EMULSION	VOLUME CONCENTRATION AT WHICH YIELD POINT APPEARS	CORRESPONDING LIMITING RELATIVE VISCOSITY, μ'_y
		centipoises
Nujol-sodium oleate	0.437	5.5
Nujol-saponin	0.489	11.0
Nujol-triethanolamine oleate	0.440	1.65
Benzene-triethanolamine oleate	0.718	8.7
Benzene-sodium oleate	0.465	6.0
Olive oil-triethanolamine oleate	0.407	1.8
Olive oil-sodium oleate	0.445	6.0

If the logarithm of the yield point is plotted against the logarithm of the difference between the limiting relative viscosities at the corresponding concentration and at the concentration at which the yield point appears, the curves shown in figure 5 are obtained. While it is to be admitted that these calculations are based on somewhat questionable extrapolations, the plot indicates an interesting though approximate correlation, the points seriously off the curve lying at low volume concentrations where accurate estimation of the yield point is difficult. It will be observed that the logarithm of the yield point is linear with the logarithm of the viscosity difference and that the curves have the same slope. This would indicate that the yield point is a function of the type of stabilizer and limiting vis-

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[5] In certain emulsions the behavior may be more complex, the fluid showing anomalous viscosity before development of a yield point.

cosity of the resulting emulsion. Hence it would appear that if, at one volumetric concentration, the yield point and limiting viscosity were known together with μ'_{v_1} the viscous behavior over a wide range of concentrations could be quantitatively predicted by the relations shown in figures 3 and 5.

No generalizations can be made as to the influence of the viscosity of the disperse phase on the resulting viscosity of the emulsion. Curves 5, 6, and 7 of figure 3 show that the viscosities of emulsions at the same volumetric concentration and for the same stabilizer are in the order of the viscosities of the disperse phases. However, this relation is reversed for the benzene and Nujol emulsions at 75 volume per cent. Again, comparing curves 1 and 4 for olive oil and benzene stabilized by sodium oleate, the viscosities of the more concentrated emulsions are in the order of the viscosities of the disperse phases, but at 50 volume per cent the viscosities of the two emulsions are identical.

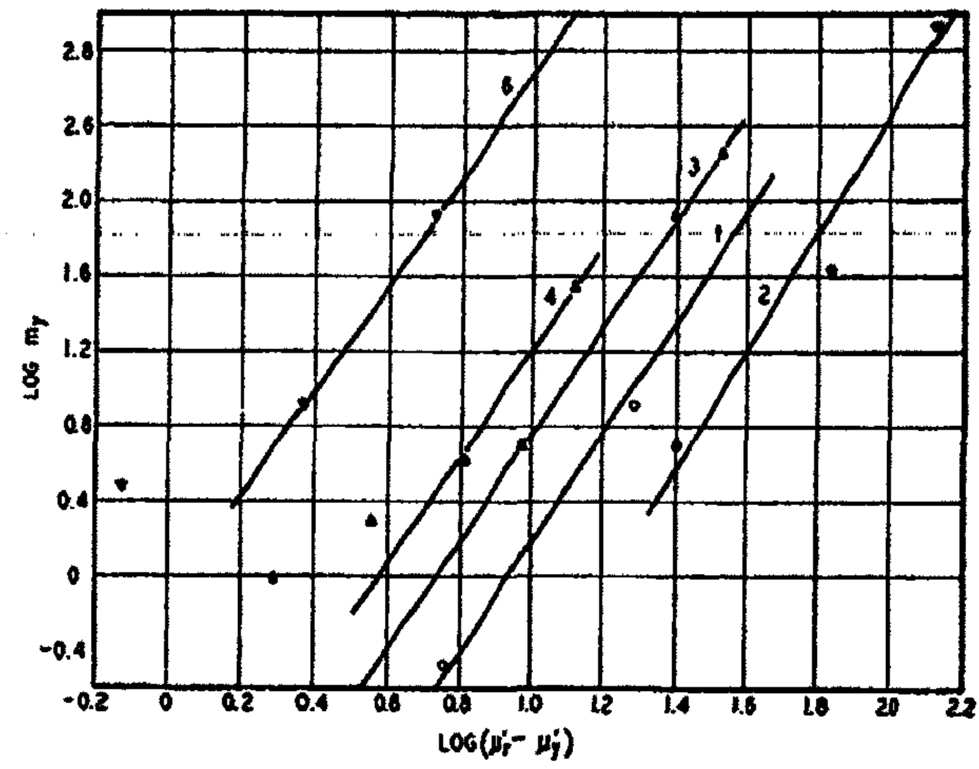

FIG. 5. Logarithm of the yield point plotted against the logarithm of the difference between the limiting relative viscosities at the corresponding concentration and at the concentration at which the yield point appears. See figure 3 for key to figures.

The effect of stabilizers

The effect of the type of stabilizer on the viscosity of a given phase pair may be observed by comparison of the appropriate curves of figure 3 (curves 2, 3, and 6 for Nujol-water, curves 4 and 7 for benzene-water, and curves 1 and 5 for olive oil-water). It will be seen that for a given phase pair the limiting relative viscosity at a definite concentration varies widely with the type of stabilizer employed. For curves 2, 3, and 6 the variation in viscosity at the same concentration is in the order of increasing ease of emulsification, the most efficient stabilizer producing the emulsion of lowest viscosity. Thus triethanolamine oleate emulsified Nujol practically spontaneously, but the saponin emulsion was quite difficult to prepare. The same order is shown in curves 4 and 7 for the benzene emulsions and in curves 1 and 5 for the olive oil emulsions.

Without doubt, the effect of the stabilizer is exceedingly important. Thus, the relative viscosity at 70 volume per cent of Nujol-water emulsions stabilized with saponin and triethanolamine oleate varied thirteenfold. It is true that difference in particle size may, in part, account for this variation but, in view of the work of Sibree already referred to, this appears unlikely. The influence of the stabilizer may, however, well account for some of the confusing results obtained in the past by different investigators.

CONCLUSIONS

1. The viscosity of a concentrated emulsion is a function of the rate of shear, approaching an asymptote as the rate of shear is increased. Over wide ranges the relation between shearing stress and rate of shear is linear. For a given emulsion, i.e., a given phase pair and stabilizer concentration (based on the dispersing medium), the limiting viscosity at infinite rate of shear increases with the volume concentration of the disperse phase. The quantitative relation between the concentration and the limiting viscosity is best represented by a modified form of the Richardson equation. The Hatschek equation, as modified by Sibree, does not apply.

2. Other than volumetric concentration, the type of stabilizer employed seems to be the variable of most significance in determining the magnitude of the viscosity of any phase pair. Stabilizers producing the best emulsification give emulsions of the lowest limiting relative viscosity.

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THE SYSTEM GALLIUM-INDIUM

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During the past two years the writers have studied a series of some forty alloys of gallium and indium covering the entire range of composition from pure gallium to pure indium. Search of the literature reveals no previous study of such alloys, this lack of study being due, no doubt, to the previous scarcity of the two metals.

In 1936 a progress report[2] was presented covering the determination of the eutectic in the system gallium–indium. The present paper includes that work (which was not published) and completes the study of this alloy system.

EXPERIMENTAL

Because of the relatively high cost of the metals involved it was essential to work with small amounts and to develop a technique suitable to such work. In the customary methods for studying alloy systems amounts up to 15 or 20 g. are used and time–temperature curves are plotted. The eutectic alloy may be squeezed out and analyzed.

In place of the usual time–temperature curve, the writers used *temperature-temperature* curves in which the temperature of the alloy was plotted against the temperature of its bath. This method is, of course, possible only where the alloys concerned have low melting points. Time was kept as nearly constant as possible in all determinations, the rate of temperature change being approximately one degree per minute.

An iron–constantan thermocouple prepared of fine wire and coated with high-grade white shellac was used for determining the temperature of the alloy. During the work on the gallium side of the curve the alloy was used as the variable cold junction, the hot junction being placed in a constant-temperature bath of boiling water. The hot junction assembly was specially prepared and consisted of a Kjeldahl flask, to one side of the

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[2] "The Eutectic in the Gallium–Indium System," presented before the Division of Industrial and Engineering Chemistry at the Ninety-second Meeting of the American Chemical Society, Pittsburgh, September, 1936.

neck of which an arm carrying a reflux condenser was sealed in. The thermocouple was inserted through a lower opening, so that the junction was immersed in water in an inner glass tube, the tube having an opening in the side to admit the thermocouple and to maintain a constant water level (see figure 1). A thermometer for checking the temperature was suspended in the tube. However, during the work on the indium side of the curve, with temperatures above 100°C., it was found more convenient to reverse the thermocouple junctions. The constant cold junction was a specially constructed ice bath, consisting of a Dewar flask containing a test tube of cottonseed oil; this in turn contained the thermocouple junction which was admitted to the tube by an adequate length of glass tubing (see figure 2). The alloy itself became the variable hot junction. It was placed in a thin-walled closed glass tube of 5 mm. bore with a pointed, rather than a snub-nosed, end to relieve the expansive effect of the freezing alloy. The tube was attached to the bulb of the standardized thermometer by rubber bands, and was heated in a cottonseed oil bath to the required temperatures. In each case a sensitive d'Arsonval wall galvanometer, suitably damped, a potentiometer, and a standard cell with the usual accessories completed the assembly.

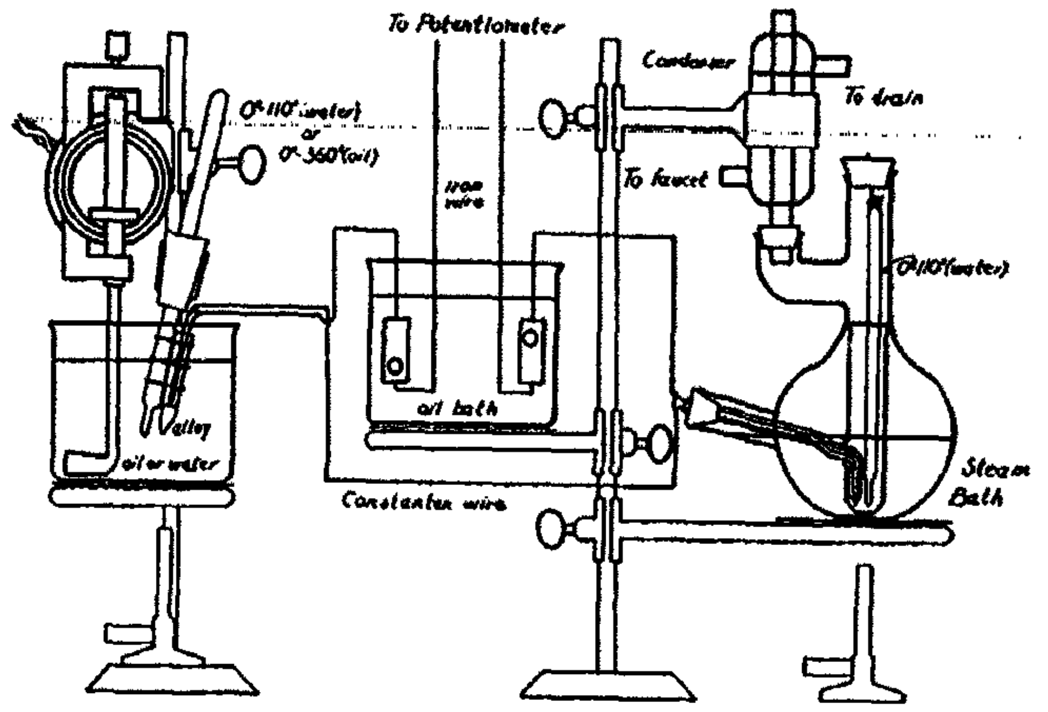

FIG. 1. Apparatus showing constant hot junction

The thermocouple was calibrated by placing the cold junction first in ice water, while the hot junction was in the boiling bath assembly. The cold junction was next attached to the bulb of the standardized thermometer, and both were immersed in an 800-cc. water bath, the temperature of which was slowly raised to 100°C., while the E.M.F. was plotted against the recorded temperature of the bath. The values obtained agreed with the commonly assigned values for this thermocouple. The thermocouple was next checked by putting it in the thin-walled glass tube containing a little mercury, the tube being attached to the bulb of the thermometer. Again the whole was immersed in the water bath, which was stirred by a motor-driven stirrer. The bath was slowly heated and cooled several times while simultaneous readings of the thermometer and the E.M.F. were taken. The E.M.F. readings were translated to equivalent temperatures and plotted against temperatures of the bath recorded by the thermometer. This data indicated that there was no time lag in the temperature changes of the alloy, for temperatures of bath and alloy agreed at all points and gave practically a straight-line graph.

The method used, in which temperature of alloy is plotted against that of a neutral body, gives a differential curve known as the Roberts-Austen differential curve. The chief advantage of the differential curve over the time-temperature curve lies in the fact that over a considerable range of temperatures the differential curve gives a *straight* line. If the same temperature interval is used in plotting temperature both of alloy and of bath, the line has a slope of 45°, the only deviations from a straight line coming at points which indicate a phase change in the alloy.

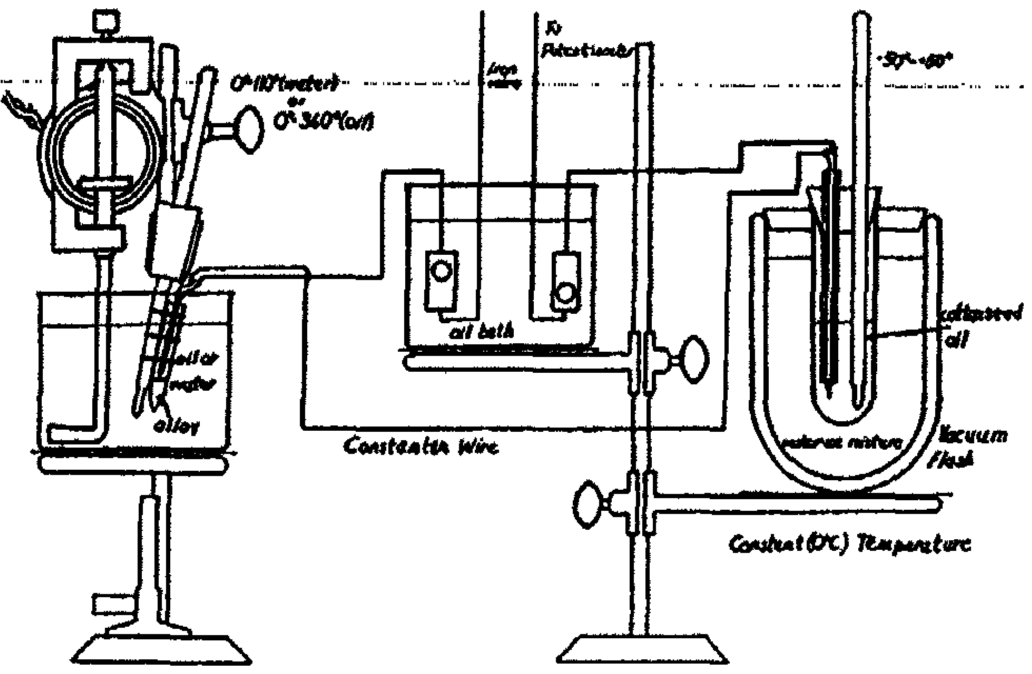

Fig. 2. Apparatus showing constant cold junction

The gallium used was obtained from Eimer and Amend, the indium from the Indium Corporation of America. Since the cost of gallium prohibited the preparation of a large number of *separate* alloys, the method used was to add successive small increments of either gallium or indium to the original small amount of the other pure metal. Starting with 0.94 g. of gallium and adding successive increments of 0.01 g. of indium gave a series of gallium-rich alloys on the gallium side of the curve. Although gallium is difficult to handle and cut, since it melts at a low temperature and is quite brittle, an analogous procedure was used to give a corresponding series of indium-rich alloys on the indium side of the curve.

In use, the thermometer with tube attached was immersed in the 800-cc. water or oil bath which was stirred with a motor-driven stirrer. Since gallium-rich alloys showed a strong tendency to supercool, it was necessary when working with such alloys to bring the temperature of the bath down to 0°C. to insure solidification of the alloy. The bath was then warmed up regularly with a small flame, and the corresponding E.M.F. for every degree increase in temperature was recorded. Water was placed above the alloy in the tube to prevent the metal from clinging to the glass and climbing.

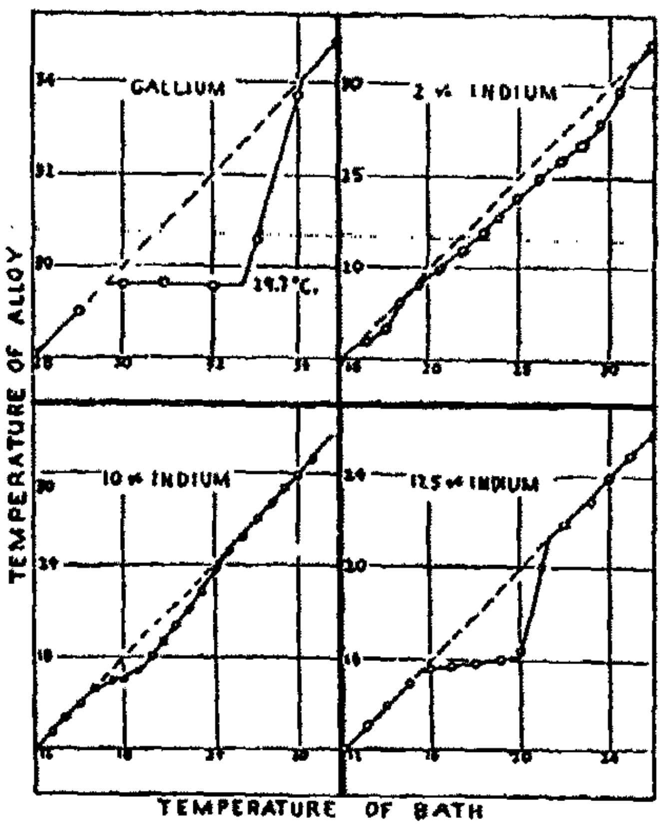

FIG. 3

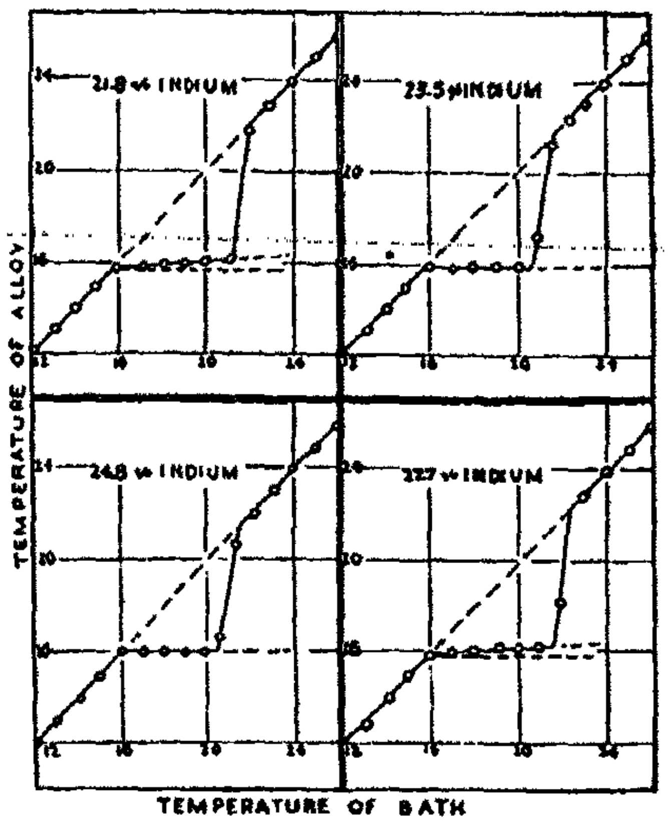

FIG. 4

FIG. 3. Melting curves of gallium and of alloys of indium with gallium

FIG. 4. Melting curves of alloys of gallium and indium approximating the eutectic composition

By this method the melting point of pure gallium was determined and was found to be 29.7°C. The melting curve is shown in figure 3 (upper left). Successive increments of 0.01 g. of indium were then added. In each case the alloy was warmed up to about 50°C. to insure solution of the indium, though the indium appeared to dissolve in molten gallium at temperatures as low as 30°C. without difficulty. The alloys were kept molten for some time while the tube was vibrated to insure complete mixing. A minimum of three determinations was made on each alloy. The procedure with the indium-rich alloys on the indium side of the curve was similar, with similar precautions taken to insure complete solution.

Since any error in weighing the increments of either metal would be cumulative, producing errors in the calculated percentage of each succeeding alloy, great care was exercised in weighing the samples of indium and gallium. Later, several check alloys were prepared on either side of the eutectic range to determine, if possible, whether mistakes had been made in previous weighings. Since the curves for these alloys agreed with those of the former alloys, it was concluded that no errors had been made in the successive weighings.

Throughout an entire series of operations it was not necessary to remove the thermocouple from the alloy; thus it was assured that none of the alloy was lost during the work.

Because of the marked tendency of gallium-rich alloys to supercool, it was impossible to use cooling curves on the gallium side of the eutectic range. Instead, melting curves were used for these alloys. For the indium-rich alloys, however, it was possible to use both melting and cooling curves and thus determine the liquidus points with a high degree of accuracy. Readings of the thermometer were taken at 1° intervals, together with the corresponding thermocouple readings. With a little practise, it was found that one observer could take both readings. There appeared to be little or no oxidation of the alloys in the course of the work. This is undoubtedly due to the fact that only low temperatures are necessary.

DETERMINATION OF THE EUTECTIC COMPOSITION

Since it was impossible to squeeze out sufficient eutectic alloy from the small amounts used to conduct an analysis, and since, even were this possible, there are no satisfactory methods developed for the quantitative separation and estimation of these metals, and finally, since the use of such a scheme would alter the composition of the residual alloy and prevent the use of the method involved, i.e., that of adding successive increments to a previous alloy, it was necessary to determine the eutectic composition as nearly as possible by the temperature studies.

Alloys closely approximating the eutectic composition give curves indistinguishable from the curve of a true eutectic alloy. Hence it is not possible to determine the exact eutectic composition by means of temperature curves. However, it is possible by such means to "bracket" the eutectic composition, by noting those alloys lying on either side of the eutectic composition in which the curve first deviates slightly from that of the alloys within the eutectic range. Of the alloys studied the only ones which gave perfectly horizontal lines during phase change were those containing 23.6 and 24.8 per cent indium (see figure 4). Those nearest on either side containing respectively 22 and 27.7 per cent indium were definitely outside the eutectic zone (see figure 4). This narrows the eutectic range down to that lying between about 23 and 26 per cent indium.

A check on those values is obtained when the entire system has been worked out and the liquidus curves plotted on both sides of the eutectic range. Using smooth curves through the liquidus points in the temperature–composition diagram, it is found that these curves meet the proper temperature ordinate of 16°C. at a composition ordinate representing 24 per cent indium (see figure 7). Points on the gallium side of this curve may, however, be slightly in error, owing to the fact that they had to be taken from melting-curve data rather than cooling-curve data. However, they yield a smooth curve and are probably accurate to within a degree.

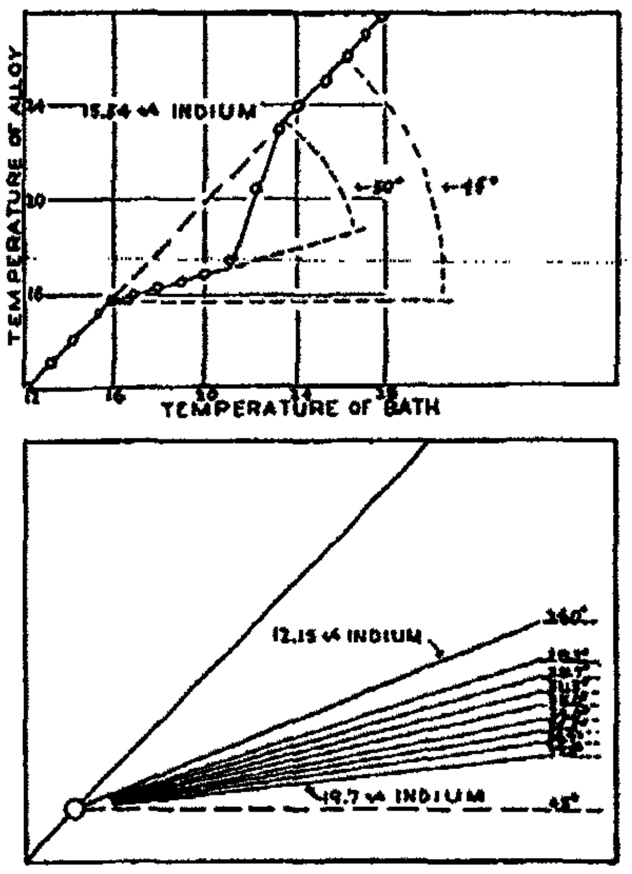

FIG. 5

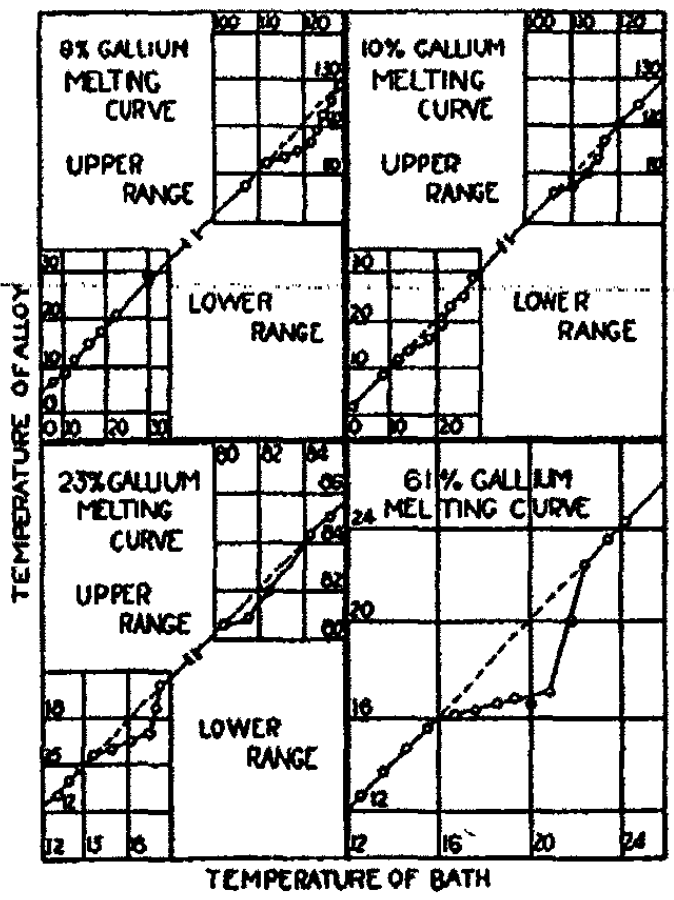

FIG. 6

FIG. 5. The upper part of the diagram illustrates the method used to determine the minimum eutectic range composition; the lower part gives the slopes of the melting curves of pro-eutectic alloys.

FIG. 6. Melting curves of indium-rich alloys

(The points used are those at which there is a definite deviation toward the perpendicular in the melting curve.)

There appeared to be another method for checking the eutectic composition which became evident when the differential curves were plotted for a number of the gallium-rich alloys. It was found that such alloys containing 12 per cent or more (up to 20 per cent) indium gave curves which during phase change were perfectly straight lines based on four or more points (see figure 5, upper portion). The slope of this line appeared to bear a simple relationship to the percentage of indium present, approaching the horizontal as the indium increment was increased. Knowing the percentage of indium present and the slope of the line, it was a simple matter to calculate the percentage of indium necessary to give a line with

TABLE 1

Calculation of eutectic range

PER CENT INDIUM IN ALLOY	ANGULAR SLOPE OF MELTING CURVE	MEAN SLOPE	CALCULATED VALUE OF EUTECTIC RANGE PER CENT INDIUM
	degrees	*degrees*	
12.15	23	24	22.70
	24		23.40
	25		22.00
14.55	29	28.2	22.70
	28		23.40
	28		23.40
15.34	31	29.7	22.30
	30		23.00
	29		24.00
16.07	33	31.3	22.00
			24.10
			23.30
16.80	34	33	22.20
	33		23.00
	32		23.70
17.54	35	34	22.50
	32		25.00
	35		22.50
18.26	34	35.3	24.20
	36		22.80
	36		22.80
19.00	36	36.7	23.80
	37		22.80
	37		22.80
19.66	37.5	37.8	23.60
	38.0		22.50
	38.0		22.50
Mean value			23.00

a zero slope. Actually the angles were calculated from the diagonal line of the pure liquid phase.

The percentage calculated in this manner would not be that of the true eutectic alloy but rather would mark the beginning of a eutectic range within which the curves are indistinguishable from that of the true eutectic range. Figure 5 (upper diagram) shows a typical alloy within the range used and the slope of the line and (lower diagram) angular slopes for all alloys containing between 12 and 20 per cent indium. Table 1 shows the results of the several calculations and the variation in individual results. The mean value of 23 per cent agrees well with the observed value of 22.7 per cent in marking the beginning of the eutectic range.

Using such a check method, the most accurate values should be obtained when the composition of the alloy lies about half way between that of a pure constituent and that of the eutectic alloy. As the percentage falls too low the curve fails to give a discernable straight-line portion (see figure 3, lower left). As the percentage approaches that of the eutectic composition too closely, the slope of the line approaches the horizontal too closely to permit of accurate measurement. Obviously, too, this method is limited to the differential curve method, which alone gives a straight-line curve for the pure phase, and to cases where the flattening of the curve during phase change is sufficient to yield a straight line the slope of which can be measured. It was found that the indium-rich alloys did not give such curves; hence this method could not be used to determine the other end of the eutectic range.

GALLIUM-RICH ALLOYS

On the gallium side of the curve there was no evidence of the formation of solid solutions, for the alloy containing but 2 per cent indium showed a definite bulge at the eutectic temperature of 16°C. (see figure 3). The alloy containing 1 per cent indium showed a similar though less pronounced bulge. Any solid solution formed must, therefore, contain less than 1 per cent indium. Like gallium itself, the gallium-rich alloys have a marked tendency toward supercooling. In spite of the fact that the eutectic alloy freezes normally at 16°C., it was possible to maintain some of these alloys in a liquid state at temperatures several degrees below 0°C. As was previously noted, this necessitated the use of melting curves in place of the more common cooling curves and made it more difficult to determine accurately points on the liquidus curve. Figures 3 and 4 show melting curves for several typical gallium-rich alloys.

INDIUM-RICH ALLOYS

The indium-rich alloys were studied in a manner similar to that used with the gallium-rich alloys, but fewer alloys were necessary to establish the liquidus and solidus curves. Since there was no supercooling, both melting and cooling curves were used. It was thus possible to determine points on the liquidus curve with a higher degree of accuracy than in the case of gallium-rich alloys. It was found that gallium forms solid solutions in indium, such alloys containing up to 9.5 per cent gallium by weight. Beyond this, the eutectic alloy consisting of α-indium (solid solution of gallium in indium) and gallium appears. Figure 6 shows the cooling and melting curves for alloys containing 9 and 10 per cent of indium, together with other examples in the indium-rich range.

THE SYSTEM GALLIUM-INDIUM

Figure 7 shows the complete constitution diagram for the system gallium-indium based on the data obtained in the study of some forty distinct alloys covering the range from pure gallium to pure indium. The eutectic temperature is 16°C., and the eutectic composition consists of 24 ± 0.5 per cent indium and 76 ± 0.5 per cent gallium. The solid solution range of indium in gallium is zero (or less than 1 per cent), while the solid solution range of gallium in indium extends up to 9.5 per cent gallium by weight.

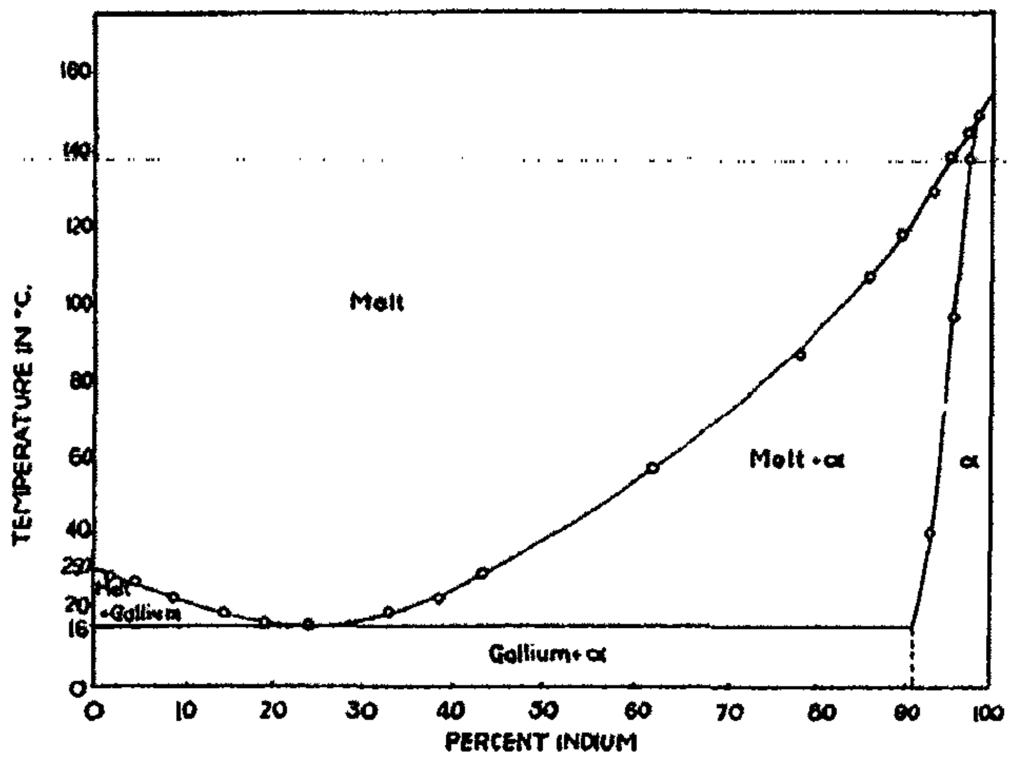

FIG. 7. Constitution diagram of gallium-indium system

CORRELATION OF RESULTS WITH THE HUME-ROTHERY THEORY OF SOLID SOLUTION PROBABILITY

According to the theory developed by Hume-Rothery, the range of solid solution of one metal in another is determined largely (other factors such as valence and crystal structure being somewhat similar) by the relative atomic (or ionic) radii of the constituent metal atoms. Where the difference in atomic radii is slight, the probability of solid solutions is high. Where the difference is greater than 13.5 per cent, the probability of solid solutions is low. Within the range 0 to 13.5 per cent, the amount of solid solution formed might be expected to vary inversely with the increase in percentage difference in the atomic radii of the constituent metals.

If we take the Goldschmidt values of 3.14 A.U. and 2.75 A.U. for the radii of the indium and gallium atoms, respectively, we find a mean difference in radius of 13.3 per cent. This would indicate the probability of limited or border-line solid solutions in the system. It is evident that the results predicted by the Hume-Rothery rule are in qualitative agreement with the observed results. On the other hand, the use of other obtainable values for atomic radii all indicate the probability of no solid solutions, for in all such cases the mean difference in atomic radii is greater than the limiting value of 13.5 per cent.

FLUIDITIES AND CHANGES IN VOLUME OF THE BINARY SYSTEMS ISOPROPYL ALCOHOL-BENZENE AND ISOPROPYL ALCOHOL-WATER[1]

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The extension of the laws governing dilute solutions to a variety of components in concentrated solutions has attracted considerable attention in recent investigations. A critical scrutiny of the derived equations, which are thermodynamically sound and which in a measure have correlated changes in colligative properties with changes in concentration, reveals that these were deduced for ideal mixtures containing one component greatly in excess of the other.

The applications of the generalizations of van't Hoff, Raoult, and Henry to property-composition relations have been the subjects of many research problems. These are problems of great importance, from both theoretical and practical standpoints, and much of physical chemistry is concerned with them.

The problem of solubility may be considered from two angles. In the first place, one may consider how the escaping tendency of any component of a solution varies with the composition of the solution, and in the second place, one may consider how this escaping tendency depends upon the specific character of the components.

As a part of a comparative study of binary and ternary systems made up of water, a hydrocarbon, and a lower alcohol, the following observations have been made on solutions of isopropyl alcohol in benzene and isopropyl alcohol in water.

MATERIALS

The methods of purification and the physical constants of these materials have been discussed and recorded in a previous article (10).

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[1] Presented at the Mid-West Sectional Meeting of the American Chemical Society, held at Omaha, Nebraska, April 29-May 1, 1937.

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EXPERIMENTAL

Viscosity

The viscosities of alcohol-water and alcohol-benzene systems were determined with a modification of the Ostwald viscometer designed to prevent evaporation, and the usual procedures were observed (4). The viscometer was suspended in a thermostatically controlled water bath, kept at 25.00°C.

TABLE 1

Fluidity-composition and change in volume for the system isopropyl alcohol-benzene

PER CENT ALCOHOL		SPECIFIC VOLUME			FLUIDITY			$K\Delta V$ ($K = 1700$)	CHANGE IN VOLUME EXPANSION IN PER CENT
By weight	By volume	V (Observed)	V (Calculated by equation 1)	V (Calculated by equation 4)	φ (Observed)	ϕ (Corrected by equation 9')	ϕ (Theoretical, equation 10)		
00.00	00.00	1.1445	1.1445	1.1445	165.5	165.5	165.5	0.0	0.00
8.99	9.95	1.1593	1.1567	1.1580	167.0	164.8	153.8	2.2	0.21
18.36	20.10	1.1736	1.1695	1.1719	165.1	161.0	141.9	4.1	0.36
27.33	29.61	1.1846	1.1817	1.1848	154.4	150.0	130.7	5.4	0.39
37.42	40.08	1.2000	1.1954	1.1990	142.0	135.9	118.4	6.1	0.38
47.06	49.86	1.2124	1.2085	1.2124	128.2	121.6	106.9	6.6	0.31
57.53	60.25	1.2260	1.2224	1.2266	111.9	104.8	94.7	7.1	0.27
67.90	70.30	1.2393	1.2359	1.2402	94.0	86.7	82.9	7.3	0.19
78.69	80.51	1.2531	1.2516	1.2543	76.9	72.3	71.9	4.6	0.13
89.22	90.25	1.2665	1.2650	1.2673	62.8	58.9	59.5	3.9	0.05
100.00	100.00	1.2806	1.2806	1.2806	48.0	48.0	48.0	0.0	0.00

Equation 9′ is $\phi = \varphi - K\Delta V$.

TABLE 2

Fluidity-composition and change in volume of the system isopropyl alcohol-water

PER CENT ALCOHOL		SPECIFIC VOLUME			FLUIDITY			$K\Delta V$ ($K = 1700$)	CHANGE IN VOLUME CONTRACTION IN PER CENT
By weight	By volume	V (Observed)	V (Calculated by equation 1)	V (Calculated by equation 4)	φ (Observed)	ϕ (Corrected by equation 9)	ϕ (Theoretical, equation 10)		
00.00	0.00	1.0029	1.0029	1.0029	111.74	111.74	111.74	0.0	0.00
7.85	9.80	1.0164	1.0245	1.0300	78.0	87.4	105.5	9.4	0.80
14.95	18.32	1.0262	1.0442	1.0536	57.9	73.9	100.1	16.0	1.73
25.20	30.06	1.0440	1.0727	1.0861	43.1	65.9	92.6	22.8	2.68
33.93	39.60	1.0640	1.0969	1.1126	36.1	62.8	86.5	26.7	3.01
44.08	50.14	1.0909	1.1250	1.1418	33.2	61.8	79.8	28.6	3.03
53.97	59.94	1.1194	1.1524	1.1683	32.3	59.3	73.5	27.0	2.87
64.81	70.15	1.1528	1.1825	1.1973	33.2	58.4	67.0	25.2	2.48
75.83	80.01	1.1884	1.2130	1.2245	36.9	56.5	60.7	19.6	2.03
87.51	89.94	1.2297	1.2454	1.2515	42.9	53.3	54.3	10.4	1.27
100.00	100.00	1.2801	1.2801	1.2801	48.0	48.0	48.0	0.0	0.00

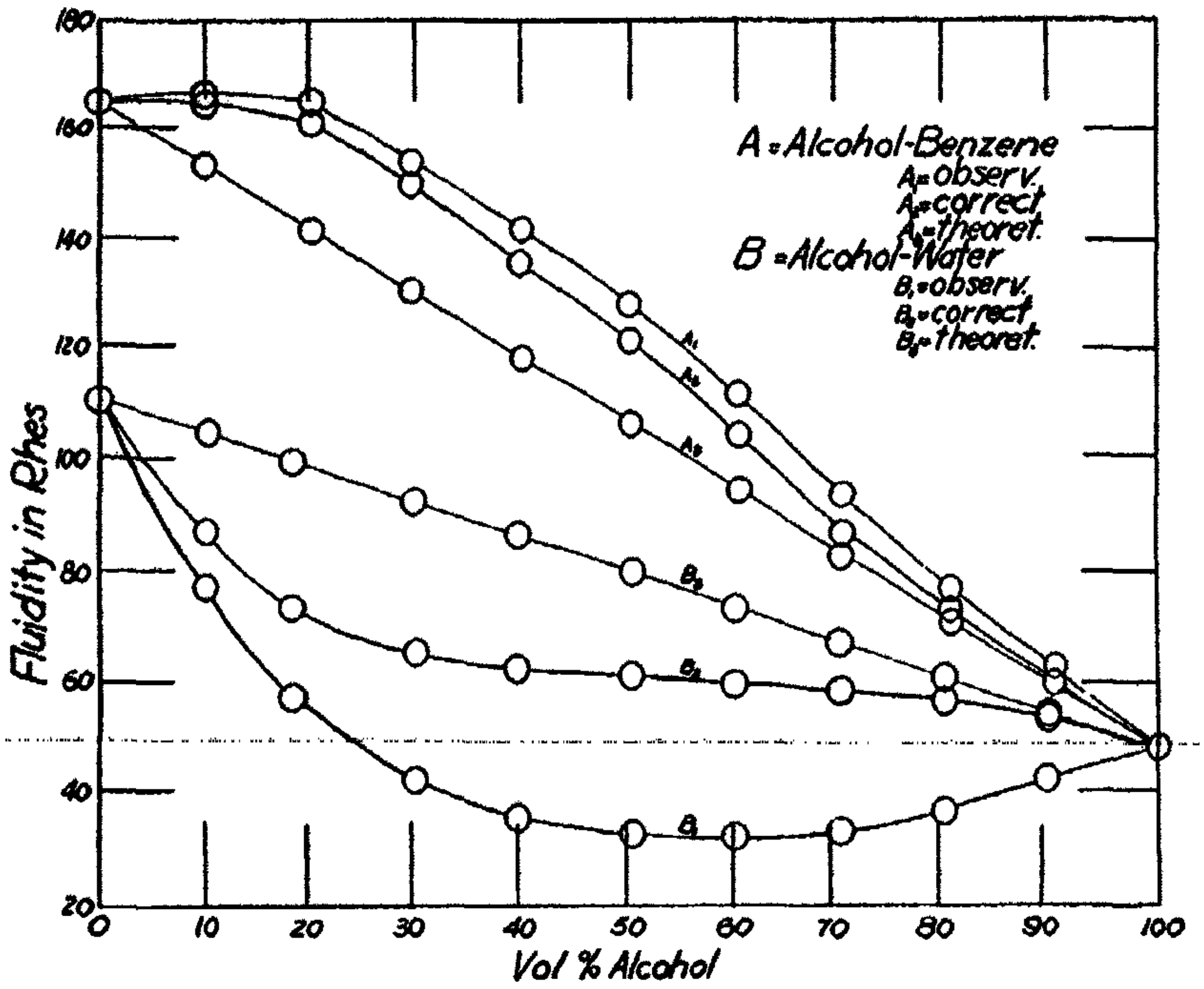

FIG. 1. Fluidity curves for isopropyl alcohol-benzene and isopropyl alcohol-water systems

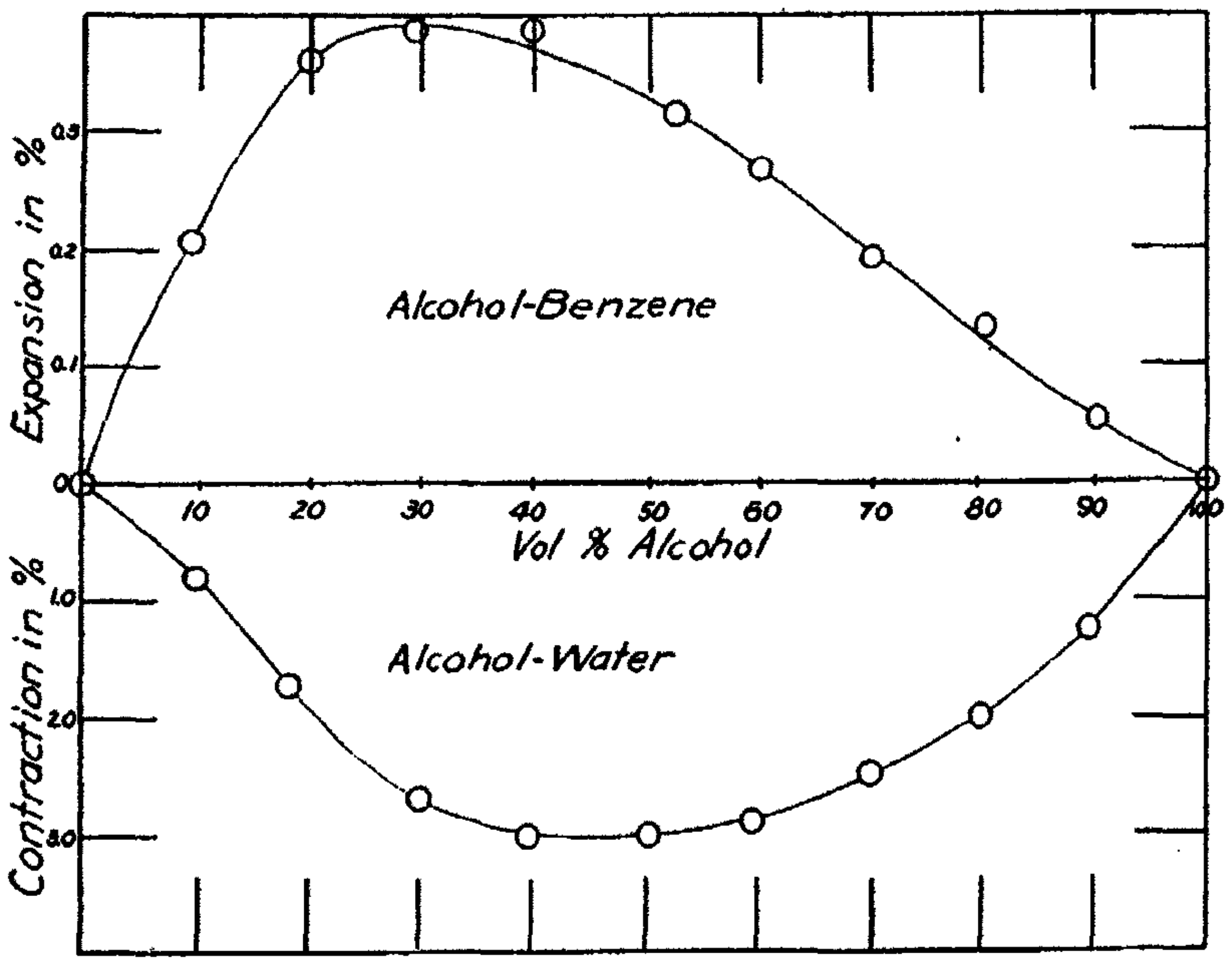

FIG. 2. Change in volume curves for isopropyl alcohol-benzene and isopropyl alcohol-water systems

The viscosities were calculated relative to water as unity at the same temperature. The fluidity of water at 25.00°C. was taken as 111.74 rhes, the value calculated from viscosity data given by the International Critical Tables (7). The product of this value and the reciprocal of the viscosity value gave the fluidity for each respective determination. The method of calculating the theoretical and corrected fluidities and the nomenclature followed in recording the data are those given by Bingham and Brown (3).

Equation 1 $V = mV_1 + nV_2$
Equation 4 $V = aV_1 + bV_2$
Equation 9 $\phi = \varphi + K\Delta V$
Equation 10 $\phi = a\varphi_1 + b\varphi_2$

a and b = volume fractions
m and n = weight fractions
V_1 and V_2 = specific volumes
ϕ = volume-corrected fluidity
φ = fluidity

$K = 1700$ = fluidity when the free volume is unity

The fluidity-composition data are recorded in tables 1 and 2 and are plotted on figure 1. In the first two columns of the tables the weight and volume concentrations of the first component are given. In the third column are given the observed specific volumes, in the fourth column are the specific volumes calculated by equation 1, and in the fifth column there are given for comparative purposes the specific volumes which would be expected by equation 4, if the specific volumes were a linear function of the volume concentration. The difference between columns four and five multiplied by 1700 gives the value in column 9, i.e., $K\Delta V$. The observed fluidity is given in column 7, while the volume-corrected fluidities immediately derived from them by equation 9 are also regarded as observed and are given in column 7. If an expansion in volume accompanies the mixing of a pair of liquids, the value in column 9 must be subtracted from the observed fluidity in column 6; this is the case with the isopropyl alcohol-benzene system.

Change in volume

The weights and densities of the components and the densities of the liquid mixtures of the two binary systems provided one with the necessary data with which to calculate the change in volume accompanying the mixing process. The method of calculation was that given by Washburn (12).

The data for the changes in volume are given in column 10 in tables 1 and 2 and are plotted on figure 2.

DISCUSSION

From a consideration of internal pressures (5) and dielectric constants (8) one might arrange these liquids in order of their decreasing polarities: water $\gg$ isopropyl alcohol $>$ benzene, $\gg$ indicating the rather high polarity of water itself. On the basis of polarity measurements, the alcohol and water, which have high dielectric constants, are termed polar, and the hydrocarbon with a low dielectric constant is termed non-polar. There is no sharp distinction between the two classes, since one class gradually merges into the other. The fundamental distinction between the normal (non-polar) and associated (polar) lies in the greater symmetry of the fields of force surrounding the molecules of the former, the field surrounding the latter being unsymmetrical or polar.

Isopropyl alcohol-benzene

From Hildebrand's concept of solubility (6), an ideal solution is defined as one in which Raoult's law is obeyed at all temperatures and pressures.

The alcohol-benzene system deviates in a positive manner from Raoult's law. The polar molecules of alcohol have an abnormally great attraction for each other, producing greater surface tension, cohesion, etc., and tend to "squeeze" out non-polar molecules from their midst. As a result of the tendency of a liquid of high internal pressure to "squeeze" out a liquid of low internal pressure, it is expected that the partial pressure would deviate in a positive manner from Raoult's law.

This concept of association does not admit any definite polymers like double molecules. The polar affinities act within the liquid to form groups of molecules which become impregnable to a non-polar molecule like benzene.

Bancroft (1, 2) stated that he believed the disturbing factor in the solution was the tendency to form liquid layers. Bancroft calculated from positive deviations from Raoult's law for the system ethyl alcohol-benzene that, in order to explain this phenomenon, polymers of both benzene and alcohol would have to be assumed; in fact, a polymer of six molecules of alcohol and eight molecules of benzene would have to be assumed. If the polarities of the two components are sufficiently different, immiscible layers will be formed, and it is found that the greater the difference in polarity, the greater is the deviation from Raoult's law. The tendency to separate into two liquid layers is a measure of the deviation from Raoult's law.

In the study of volume change with the corresponding change in temperature, Madgin, Peel, and Briscoe (9) advance the idea that the following equilibria may exist:

$$\left.\begin{array}{l} \mathrm{A}_x \leftrightarrows x\mathrm{A} \\ \mathrm{B}_y \leftrightarrows y\mathrm{B} \end{array}\right\} z\mathrm{A}_n\mathrm{B}_m$$

where A_x and $x\mathrm{A}$ represent associated molecules and simple molecules in pure liquid A, and B_y and $y\mathrm{B}$ represent the same in pure liquid B. $z\mathrm{A}_n\mathrm{B}_m$ represents a compound molecule formed from A and B. If the dissociation to simple molecules is accompanied by a drop in temperature and if the observed volume depends upon the relative number of simple, complex, and compound molecules, then the expansion in volume and a drop in temperature favor a concept of partial dissociation. There is no evidence that benzene, a non-polar liquid, is associated, whereas alcohol gives evidence of polymerization. These concepts are directly in line with the observed measurements, for in the binary mixture it is observed that there is a positive deviation from Raoult's law (11), a maximum in fluidity, an expansion in volume, a drop in temperature, and a normal freezing depression at small concentrations of alcohol (10).

Isopropyl alcohol–water

The polarities of water and isopropyl alcohol are sufficiently alike for the liquids to be miscible in all proportions. The high polarities of the alcohol and water give some measure as to the degree of association. A negative heat of dilution, a contraction in volume, a normal freezing-point depression, and a minimum in fluidity are indicative of a smaller number of molecules.

On the assumption that a greater affinity gives rise to larger complexes, the system of molecules becomes

$$\left.\begin{matrix} xA \leftrightarrows A_x \\ yB \leftrightarrows B_y \end{matrix}\right\} A_xB_y$$

causing the smaller particles to become associated with the possibility of a union to A_xB_y. The shift in equilibrium results in an evolution of heat and a contraction in volume. If an associated molecule of alcohol and an associated molecule of water united to form a loose aggregate of A_xB_y, the free space would be diminished, thereby resulting in a decreased fluidity. Such a union, providing the correct relation in fractional removal of molecules took place, would result in a normal freezing-point depression.

SUMMARY

1. The fluidities of the isopropyl alcohol–benzene and isopropyl alcohol–water systems have been measured.
2. The changes in volume of isopropyl alcohol–benzene and isopropyl alcohol–water throughout the entire range have been calculated.
3. Attempts have been made to correlate the physicochemical properties of these systems.

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STUDY OF ELECTROLYSIS OF METALLIC PERCHLORATES IN CELLOSOLVE[1]

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The study of the electrolysis of solutions of metallic perchlorates in organic solvents conducted by Mann and Chaney (1) showed that in general these salts are very highly soluble, that their solutions in the monoethyl ether of ethylene glycol are of relatively high conductivity, and that from them many metallic elements can be electrodeposited.

It is well-known that from anhydrous solutions in organic solvents it is possible to electrodeposit some of the metals which are too reactive to be deposited from aqueous solutions. The alkalies and alkaline earths have been deposited from their halides and thiocyanates in alcohol, in acetone, or in pyridine solution. Patten and Mott (13, 14, 15, 16) and Müller and his associates (7 to 12) have investigated the electrolysis of many inorganic salts in common organic solvents by determining cathodic polarization curves, i.e., curves showing the influence of current density upon cathode potential. From the forms of these curves and the values of the potentials they were able to observe the electrodeposition of metals even though they were so reactive that it was difficult to confirm the deposition by chemical analysis after the cathode had been removed from the cell and freed from its solution.

During the course of the investigation by Mann and Chaney some evidence was obtained which indicated that aluminum might be electrodeposited from the solution of its perchlorate in the monoethyl ether of ethylene glycol. The scarcity of solutions, other than fused salts, from which aluminum can be deposited made this of interest. It was thought well to investigate deposition from this solvent further by using the polarization curve method of Patten and Mott and of Müller. This paper presents these results. In addition, the dielectric constant of the monoethyl ether of ethylene glycol and the conductivities of solutions of salts in it, even highly concentrated solutions, are reported.

MATERIALS

The monoethyl ether of ethylene glycol was obtained from the Carbide and Carbon Chemicals Corporation under the trade name of Cellosolve.

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[1] Submitted by John L. Beal to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

It was dried with soluble anhydrite (5), filtered, and vacuum-distilled from fresh turnings of metallic calcium. Fractionation with a 90-cm. packed column and discarding of the initial product gave a constant-boiling fraction whose boiling point at 738 mm. was 133.8°C. By use of the manufacturer's vapor pressure-temperature chart this was corrected to 134.7°C. at standard pressure. Solvent purified in this manner had a conductivity as low as 9.3×10^{-8} reciprocal ohms. Its physical properties are given in the literature (17).

Silver perchlorate was prepared from silver oxide and 70 per cent perchloric acid. The silver oxide was obtained by treating silver nitrate with sodium hydroxide. After two recrystallizations the silver perchlorate was evaporated to dryness on a water bath and then further dried in a flask heated to 125–130°C., through which dry purified air was drawn. The salt so obtained showed 52.02 per cent of silver as compared with the theoretical value of 52.03 per cent. Since it is very hygroscopic it was heated to above 100°C. after each time that it had been exposed to the atmosphere.

Barium perchlorate was prepared by the method of Willard and Smith (18, 19). It was dried at 250°C. in a current of dry air. By analysis it contained 40.83 per cent of barium as compared with the theoretical value of 40.85 per cent.

Lead perchlorate was prepared from white lead and 70 per cent perchloric acid. After two recrystallizations as the trihydrate any excess acid was steamed out by the method of Willard and Kassner (20). It was dried at 160°C. in a current of dry air, and was found to contain 51.01 per cent of lead as compared with the theoretical value of 51.02 per cent.

Zinc perchlorate was obtained from the G. Frederick Smith Chemical Co. of Columbus, Ohio, as the hexahydrate. The anhydrous salt is not known.

Aluminum perchlorate in the anhydrous form is not known. All attempts to dry the hydrated salt by heat and vacuum led to decomposition, and drying agents, such as phosphorus pentoxide, do not remove the moisture. An electrolytic method of preparation of anhydrous solutions in the monoethyl ether of ethylene glycol is reported by Mann and Chaney (1). This consists in electrolyzing a solution of lead perchlorate in the solvent using an aluminum anode and a lead cathode, the electric current causing the replacement of the dissolved lead by aluminum from the anode. Preparation of such solutions was attempted by this method, but decomposition was indicated by the presence of traces of chlorides in the resulting solutions.

An alternative method for the preparation of solutions of aluminum perchlorate was devised which depends upon the replacement of silver from an anhydrous silver perchlorate solution by contact with aluminum activated with mercury. This is a very slow process and several months are required for its completion. The solution remains colorless, chlorides are absent, and the solvent, after removal by evaporation in a vacuum, is of unchanged boiling point. A solution made from 20 g. of silver perchlorate and 50 cc. of solvent in contact with an excess of granular amalgamated aluminum for thirteen months was found to contain no silver and the number of equivalents of aluminum was the same, within the limits of experimental error, as that of the perchlorate. This solution was used in the polarization measurements.

DIELECTRIC CONSTANT OF THE MONOETHYL ETHER OF ETHYLENE GLYCOL

The dielectric constant of the monoethyl ether of ethylene glycol was determined by means of a capacity bridge supplied with alternating current of approximately 3500 frequency and tuned to the point of balance with two stage amplified ear phones. One arm of the bridge, figure 1, contained two fixed condensers, C_1 and C_2, each of 200 $\mu\mu f$ capacity. The other arm contained a variable air condenser, C_3, of approximately 400 $\mu\mu f$ capacity with a sensitive vernier. The two variable air condensers, C_4 and C_5, in parallel were of 375 $\mu\mu f$ and 35 $\mu\mu f$ capacity. These latter two alone required calibration, and only the ratio of their capacities at one setting to that at any other was needed. This calibration was accomplished by comparison with a small fixed condenser.

The alternating current was supplied by the oscillator using a 171A tube in a circuit similar to the one described by Jones and Josephs (6). Its transformer consisted of three inductances,—L_1 of 700 turns of No. 28 enameled wire, L_2 of 800 turns tapped at 350, 500, and 650, and L_3 of 100 turns, all wound on the same soft iron core but insulated from each other by several thicknesses of paper. A condenser of 0.1 μf was placed across L_1. The power supplied to the bridge was controlled by varying the turns in L_2 by means of taps. The oscillator was shielded by a grounded copper box.

Across C_2 a variable resistance, R, was used to balance any current which leaked through the cell containing the solution. This resistance consisted of two binding posts between which pencil lines were drawn joining the posts until the proper balancing conductance was obtained.

The cell consisted of two smooth platinum electrodes 25 mm. in diameter and 1 mm. apart enclosed in a Pyrex container. By first balancing the bridge to the point of minimum sound and then placing the cell with its dielectric in parallel with condensers C_4 and C_5 and rebalancing by changing only the setting of these latter condensers, the capacity of the cell could be determined; it was equal to the change in capacity of the condensers C_4 and C_5.

The cell was standardized by using air and benzene as two media of known value and establishing the straight-line relation between dielectric constant and capacity. This relation was checked by measuring the constants of chloroform, ethyl bromide, and water. Measurements upon the monoethyl ether of ethylene glycol showed its dielectric constant to be 29.6 ± 0.1. The results are shown in table 1.

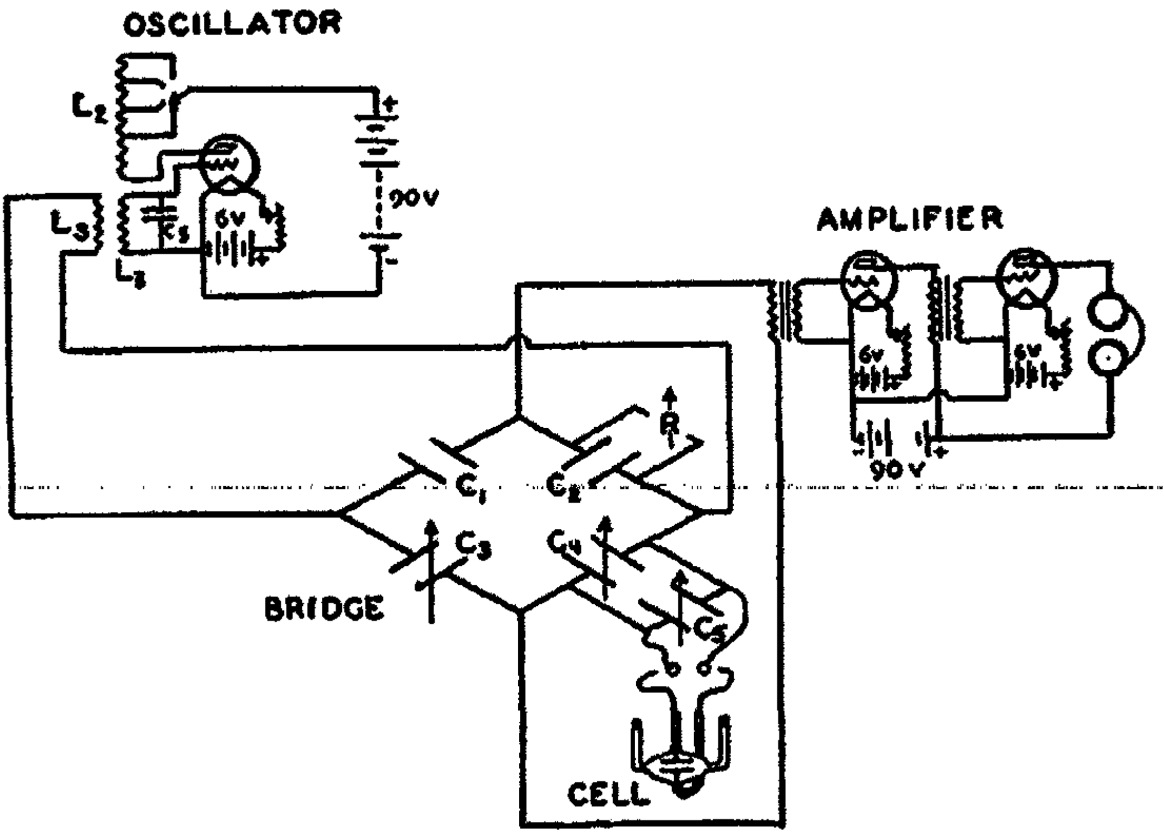

Fig. 1. Capacity bridge set-up

TABLE 1

Dielectric constants of various media

	EXPERIMENTAL D	KNOWN D*
Air (24°C.)		1
Benzene (24°C.)		2.275
Chloroform (24°C.)	5.00 ± 0.05	4.98 ± 0.05
Ethyl bromide (24°C.)	9.80 ± 0.10	9.81 ± 0.05
Water (22°C.)	80.1 ± 0.2	79.2
Monoethyl ether of ethylene glycol (24°C.)	29.6 ± 0.1	

* International Critical Tables.

CONDUCTIVITY MEASUREMENTS

Conductivity measurements were made with a four-dial Leeds and Northrup Wheatstone bridge of the post-office type. It was supplied with alternating current by a vacuum-tube oscillator identical with that used in the previously mentioned capacity bridge except that the condenser C_6 was replaced by one of 0.11μf capacity, thereby lowering the frequency to about 900 and reducing the capacity effect in the bridge. Residual capacity was balanced by a variable condenser placed across one of the resistances in the bridge. The Jones and Josephs method of grounding (6) was used, and the head phones employed two stages of amplification. The conductivity cell consisted of two smooth platinum electrodes approximately 1 cm. in diameter and 1 cm. apart. The measurements were made

TABLE 2

Conductance of silver perchlorate in the monoethyl ether of ethylene glycol

Cell constant = 0.3407; R_0 = 3.66 × 10^6

C	R	R_c	L	Λ
4.5515	85.4	85.4	0.00399	0.876
4.3158	78.4	78.4	0.00435	1.008
3.690	48.9	48.9	0.00098	1.891
3.0757	39.8	39.8	0.00856	2.790
2.2308	38.7	38.7	0.00881	3.95
1.3808	46.1	46.1	0.00739	5.35
0.8961	60.9	60.9	0.00560	6.25
0.4412	99.4	99.4	0.00343	7.77
0.2078	187.2	187.2	0.001821	8.78
0.0978	344.3	344.3	0.000990	10.13
0.04607	645.0	645.0	0.000529	11.50
0.009506	2,434	2,435	0.00001400	14.72
0.002162	8,024	8,041	0.0000424	19.59
0.000536	25,080	25,250	0.00001350	25.15
0.0001132	93,950	96,350	0.00000354	31.25
0.0000346	288,000	313,600	0.000001089	31.42

TABLE 3

Conductance of barium perchlorate in the monoethyl ether of ethylene glycol

Cell constant = 0.3527; R_0 = 3.79 × 10^6

C	R_c	L	Λ
1.2422	118.4	0.00298	2.40
0.930	129.4	0.00272	2.92
0.735	153.0	0.002305	3.06
0.6301	190.0	0.001858	2.95
0.420	305	0.001158	2.75
0.2835	473	0.000746	2.635
0.0749	1,520	0.000232	3.10
0.01980	4,132	0.0000854	4.31
0.00523	10,890	0.0000324	6.20
5.613	323.6	0.001086	0.1935
2.542	130.1	0.00271	1.067
1.112	120.5	0.00293	2.635
0.504	243.2	0.001451	2.880
0.230	575.4	0.000613	2.665
0.0960	1,317	0.000268	2.795
0.0256	3,380	0.0001038	4.05

in a water bath at 25.00° ± 0.03°C. Saturated solutions of the salts were prepared and weaker solutions made by dilution.

TABLE 4

Conductance of lead perchlorate in the monoethyl ether of ethylene glycol

Cell constant = 0.3407; $R_0 = 3.66 \times 10^6$

C	R	R_c	L	Λ
5.7761			0.000914	0.1583
2.4782	85.5	85.5	0.00395	1.610
1.5627	95.1	95.1	0.00358	2.290
1.0341	123.9	123.9	0.002755	2.660
0.6203	208.0	208.0	0.001639	2.640
0.3985	342.0	342.0	0.000996	2.500
0.3270	413.0	413.0	0.000825	2.525
0.2768	491.6	491.6	0.0006935	2.500
0.2405	571.8	571.8	0.0005955	2.48
0.2120	651.4	651.4	0.000523	2.465
0.1900	729.6	729.6	0.000467	2.460
0.00781	9,827	9,823	0.0000347	4.45
0.01523	5,934	5,935	0.0000575	3.75
0.02955	3,541	3,541	0.0000962	3.26
0.05465	2,152	2,152	0.0001587	2.90
0.0944	1,354	1,354	0.0002515	2.665
0.1257	1,027	1,027	0.000332	2.665
1.098	123.3	123.3	0.002880	2.622
0.740	172.3	172.3	0.001975	2.67
0.667	118.2	118.2	0.00181	2.71
0.0001297	189,000	200,000	0.00000170	13.10
0.000381	87,900	90,000	0.00000379	9.95
0.000741	54,180	55,000	0.00000620	8.36
0.001803	27,700	27,900	0.00001222	6.78
0.0000485	389,000	435,000	0.000000785	16.21
0.0000252	638,000	773,000	0.000000441	17.51

TABLE 5

Solubilities of silver, barium, and lead perchlorates in the monoethyl ether of ethylene glycol at 25°C.

	SILVER PERCHLORATE	BARIUM PERCHLORATE	LEAD PERCHLORATE
Solvent density	0.9252	0.9252	0.9252
Solution density	1.688	1.645	1.630
Grams per 100 g. of solvent	127.65	138.20	259.4
Grams per 100 cc. of solution	94.36	95.162	117.29
Grams per 100 cc. of solvent	117.71	127.5	239.27
Normality	4.5515	5.660	5.7733

The results are given in tables 2 to 5 and in figure 2. In these C is the normality, L the specific conductivity of the solution in reciprocal ohms per cubic centimeter, and Λ is the equivalent conductivity calculated by the formula

$$\Lambda = 1000 \frac{L}{C}$$

R_0 is the resistance of the cell filled with pure solvent, R the resistance of the cell filled with the solution, and R_c the corrected resistance, all resistances in ohms. The corrected resistance is obtained by applying the solvent correction (2).

$$\frac{1}{R} = \frac{1}{R_c} + \frac{1}{R_0}$$

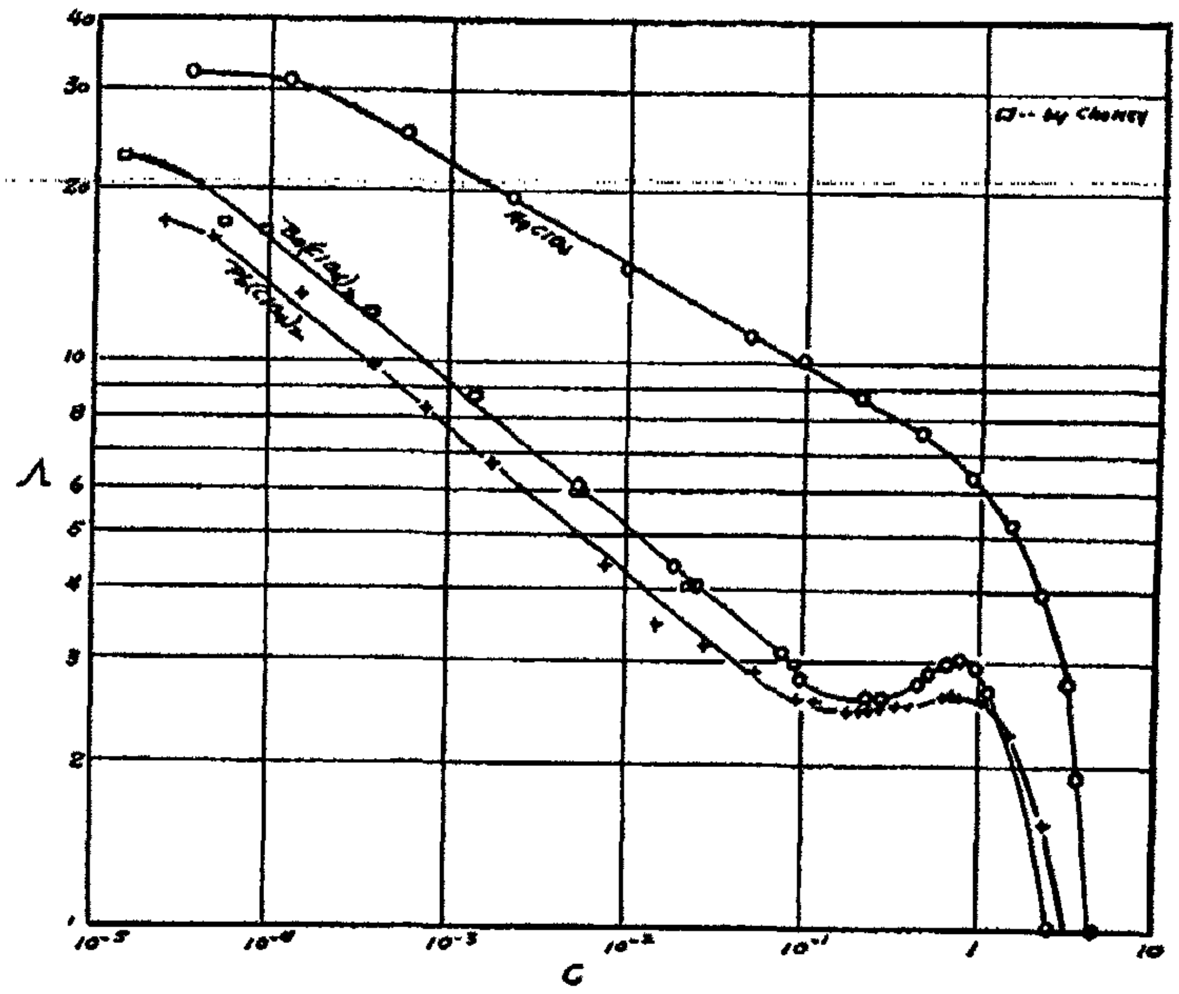

FIG. 2. Conductance curves

Figure 2, a plot of equivalent conductance and normality on log-log paper, shows that over the greater part of the concentration range the values fall in straight lines.

POLARIZATION MEASUREMENTS

Polarization measurements require the use of a reference half-cell electrode, and for non-aqueous studies it seems advisable that this electrode should employ the same solvent as the system studied. A half-cell consisting of a silver wire, the surface freshly deposited from a silver cyanide plating bath, dipped in a 0.1 N solution of silver perchlorate in the monoethyl ether of ethylene glycol was found satisfactory. Measured against a tenth-normal calomel electrode this had a potential of −0.45 volt with respect to the calomel electrode. This corresponds to − 0.78 volt with respect to a normal hydrogen electrode. The potential remained constant for several days. Figure 4 shows that the potential of silver in this solution is independent of the current density.

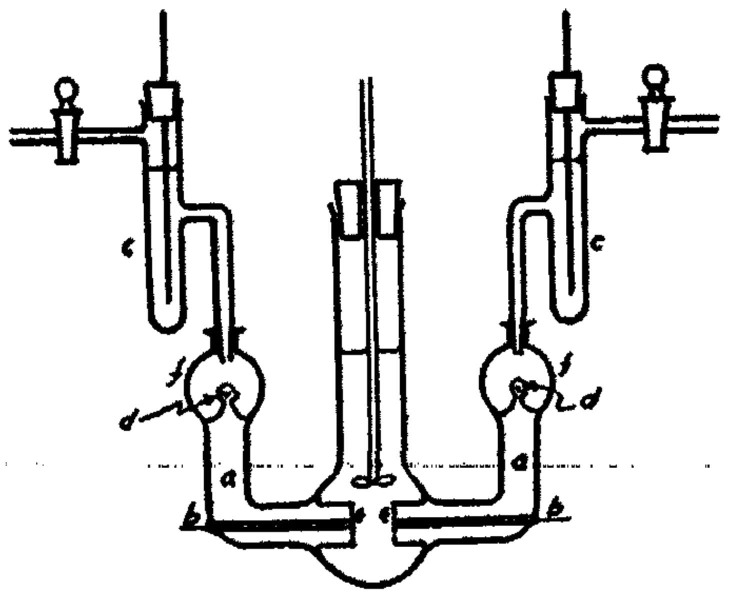

Fig. 3. Polarization cell No. I

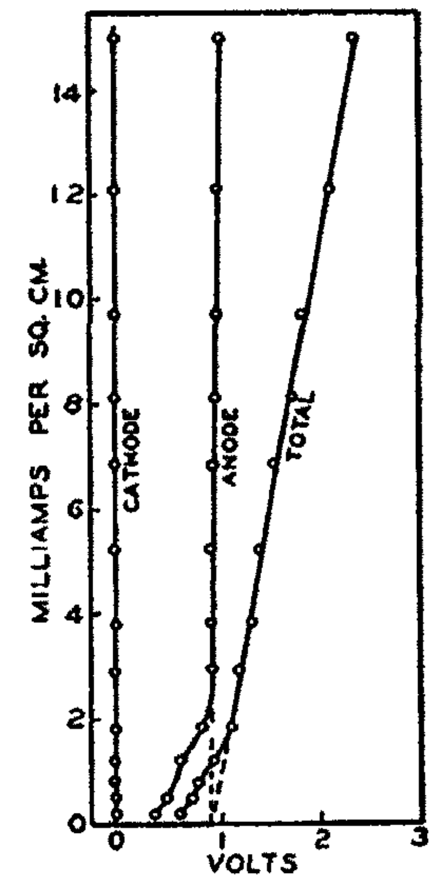

Fig. 4. Polarization curves of 0.1 *N* silver perchlorate

The cell used was similar to that of Müller (7 to 12) except that the electrodes, e of figure 3, were 11 mm. in diameter. Communication between the solution and the half-cell electrodes, c, was made by means of small holes in each of the platinum electrodes, and diffusion was reduced by the constrictions, d, filled with glass wool. A small stirring paddle was placed slightly above the level of the electrodes, for it was found to aid the constancy of the readings. The potential readings were taken after a 2-min. flow of current at the desired intensity. Between each reading the electrolysis was interrupted for 2 min.

TABLE 6

Polarization measurements of 0.1 N silver perchlorate

TOTAL VOLTAGE	CURRENT DENSITY	ANODE POTENTIAL REFERRED TO Ag | 0.1 *N* $AgClO_4$ HALF-CELL	CATHODE POTENTIAL REFERRED TO Ag | 0.1 *N* $AgClO_4$ HALF-CELL
volts	*milliamperes per square centimeter*	*volts*	*volts*
0.61	0.020	0.38	0
0.72	0.050	0.49	0
0.78	0.081	0.63	0
0.92	0.121	0.82	0
1.10	0.183	0.91	0
1.18	0.295	0.91	0
1.30	0.381	0.92	0
1.40	0.520	0.92	0
1.54	0.685	0.93	0
1.73	0.813	0.94	0
1.80	0.870	0.94	0
2.10	1.21	0.97	0
2.33	1.50	0.99	0

TABLE 7

Polarization measurements of 1.0 N silver perchlorate

TOTAL VOLTAGE	CURRENT DENSITY	ANODE POTENTIAL REFERRED TO Ag | 0.1 *N* $AgClO_4$ HALF-CELL	CATHODE POTENTIAL REFERRED TO Ag | 0.1 *N* $AgClO_4$ HALF-CELL
volts	*milliamperes per square centimeter*	*volts*	*volts*
0.53	0.05	0.37	0.04
0.68	0.101	0.60	0.04
0.81	0.186	0.76	0.04
0.90	0.302	0.86	0.04
0.93	0.672	0.88	0.04
1.01	0.91	0.90	0.04
1.10	1.42	0.92	0.04
1.18	2.06	0.96	0.04
1.44	3.23	1.02	0.04
1.60	4.45	1.15	0.04
1.87	6.64	1.16	0.04
2.25	8.26	1.34	0.04
2.50	9.73	1.40	0.04
2.75	12.32	1.52	0.04

Potentials were recorded by means of a vacuum-tube potentiometer as described by Mann and Chaney (1). The leads were so arranged that the potential differences between each electrode and its reference half-cell and also between the two electrodes themselves could be quickly taken.

The electrodeposition of the noble metal silver is illustrated by tables 6 and 7 and figures 4 and 5, which refer to 0.1 and 1.0 *N* silver perchlorate in the monoethyl ether of ethylene glycol, respectively. The anode and cathode potentials are referred to the Ag|0.1 *N* $AgClO_4$ half-cell. Even to the lowest values of current density the cathode potentials remain constant. It is apparent that the ratio of the activity of silver in the 1.0 *N* solution to that in the 0.1 *N* solution for the E.M.F. difference is only 0.04 rather than 0.058 volt. The difference between the anode and cathode potentials as measured by the reference electrodes, 0.90 volt and 0.81 volt for the 0.1 *N* and 1.0 *N* solutions, respectively, is in good agreement with the decomposition voltages obtained by extrapolating the total voltage curves to zero current density. The latter values are 0.90 volt and 0.84 volt and are the voltages across the two cell electrodes. The silver deposited upon the cathode in a smooth even coat.

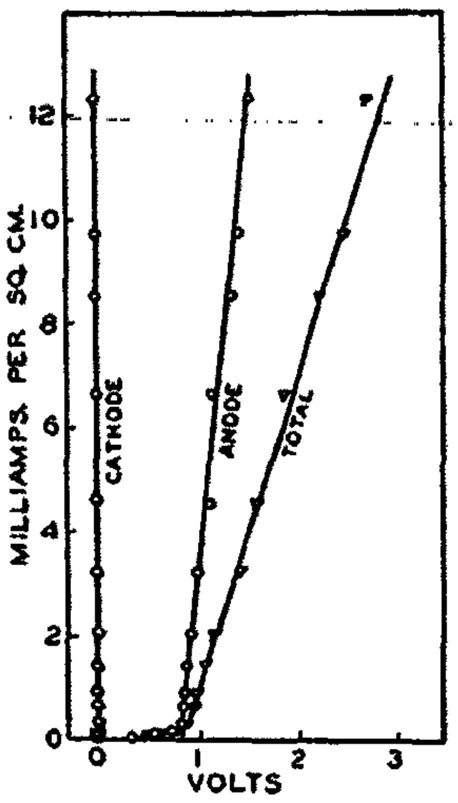

FIG. 5. Polarization curves of 1.0 *N* silver perchlorate

By addition of + 0.78 volt to the cathode potential, the potential can be referred to the hydrogen electrode except for the possible interference of liquid-junction potentials entering into the measurement of the potential of the Ag|0.1 *N* $AgClO_4$ half-cell electrode against the calomel electrode. Adding this value to the potential of silver in 1.0 *N* solution gives 0.82 volt, which is at least in close agreement with the normal potential of silver, 0.80 volt, on the hydrogen scale.

The electrolysis of a 0.5 *N* solution of lead perchlorate is shown by table 8 and figure 6. It proceeded quite similarly to that of silver perchlorate.

TABLE 8

Polarization measurements of 0.5 N lead perchlorate

TOTAL VOLTAGE	CURRENT DENSITY	ANODE POTENTIAL REFERRED TO Ag | 0.1 N $AgClO_4$ HALF-CELL	CATHODE POTENTIAL REFERRED TO Ag | 0.1 N $AgClO_4$ HALF-CELL
volts	*milliamperes per square centimeter*	*volts*	*volts*
0.47		0.19	−0.36
0.61		0.26	−0.38
0.94		0.37	−0.52
1.08		0.41	−0.61
1.28	0.020	0.55	−0.79
1.38	0.040	0.60	−0.79
1.55	0.073	0.76	−0.79
1.66	0.097	0.82	−0.80
1.72	0.109	0.83	−0.79
1.80	0.191	0.81	−0.79
1.85	0.273	0.85	−0.80
1.90	0.387	0.84	−0.79
2.09	0.563	0.85	−0.79
2.38	0.815	0.85	−0.80
2.35	1.08	0.85	−0.80
2.60	1.28	0.90	−0.80
2.76	1.48	0.90	−0.80
	5.16	0.93	−0.80
	9.29	0.94	−0.80

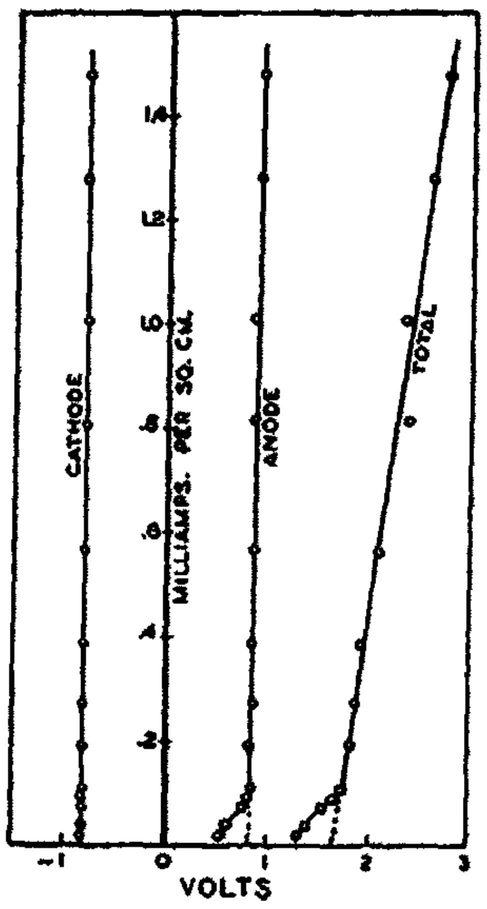

FIG. 6. Polarization curves of lead perchlorate

The sum of the individual electrode potentials agreed quite closely with the decomposition potential of the solution as obtained by extrapolation of the total voltage curve. The lead deposited in a smooth coat and its potential was -0.80 volt referred to the 0.1 N $AgClO_4$–Ag reference electrode. Converting this to the hydrogen scale by adding 0.78 yields a value of -0.02 volt, not greatly less negative than the value $+0.09$ volt for an aqueous solution of 0.5 N activity.

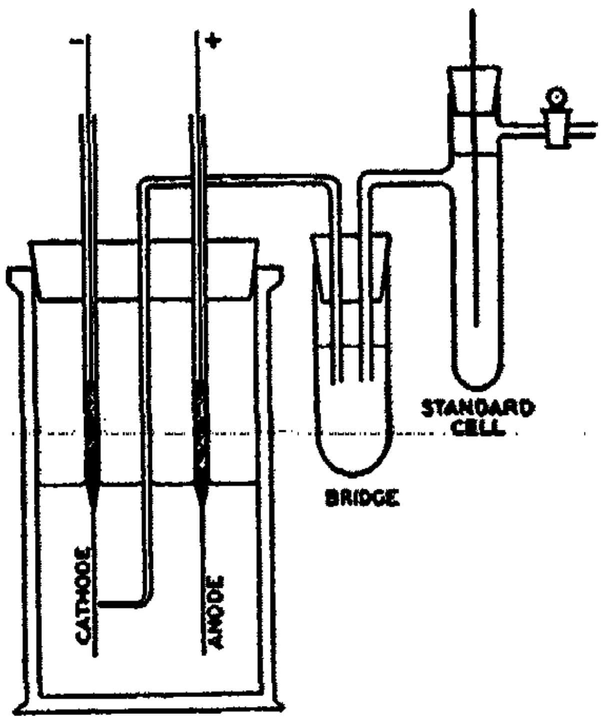

FIG. 7. Polarization cell No. II

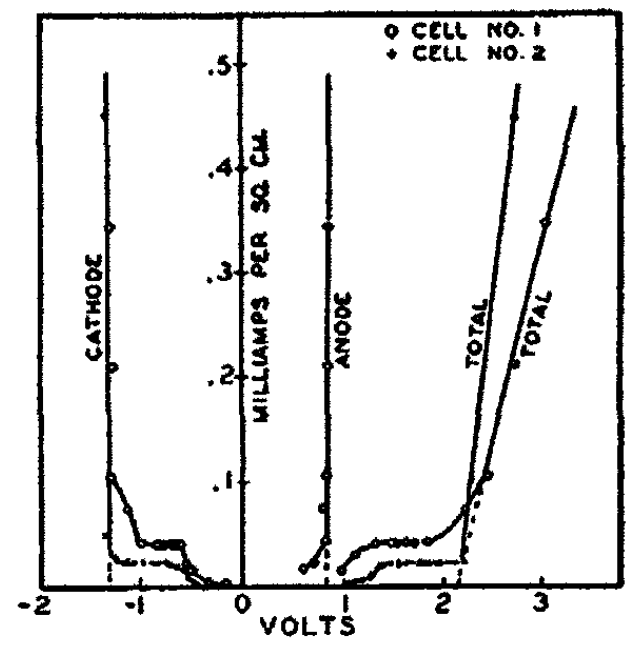

FIG. 8. Polarization curves of zinc perchlorate

The polarization curves for zinc in zinc perchlorate solution are given in table 9 and table 10 and in figure 8. These curves were obtained in two different types of cells. Cell No. I was the one already described. Cell No. II consisted of two platinum electrodes dipping beneath the solution in an open beaker and with the half-cell electrode arm pulled out to a small tip which rested very lightly upon the cathode surface as shown

TABLE 9

Polarization measurements of 0.5 N zinc perchlorate

Cell No. I

TOTAL VOLTAGE	CURRENT DENSITY	ANODE POTENTIAL REFERRED TO Ag | 0.1 N $AgClO_4$ HALF-CELL	CATHODE POTENTIAL REFERRED TO Ag | 0.1 N $AgClO_4$ HALF-CELL
volts	*milliamperes per square centimeter*	*volts*	*volts*
0.68	0.0053		
0.95	0.016	0.58	−0.48
1.10	0.021	0.70	−0.56
1.32	0.042	0.84	−0.63
1.46	0.042	0.84	−0.67
1.53	0.042	0.84	−0.71
1.61	0.042	0.84	−0.80
1.70	0.042	0.84	−0.85
1.82	0.042	0.84	−0.98
2.22	0.074	0.84	−1.12
2.45	0.105	0.83	−1.31
2.73	0.211	0.85	−1.28
3.02	0.348	0.85	−1.32
3.80	2.59	0.88	−1.35

TABLE 10

Polarization measurements of 0.5 N zinc perchlorate

Cell No. II

TOTAL VOLTAGE	CURRENT DENSITY	CATHODE POTENTIAL REFERRED TO Ag | 0.1 N $AgClO_4$ HALF-CELL
volts	*milliamperes per square centimeter*	*volts*
0.02		−0.1
0.162		−0.08
0.323		−0.08
0.485		−0.10
0.625	0.0025	−0.162
0.815	0.0025	−0.335
0.99	0.0037	−0.485
1.265	0.010	−0.550
1.36	0.020	−0.645
1.550	0.0237	−0.760
1.755	0.0237	−0.975
1.965	0.0237	−1.145
2.205	0.0262	−1.320
2.320	0.100	−1.360
2.740	0.45	−1.360
3.03	1.41	−1.360
3.84	4.75	−1.40
4.60	7.50	−1.40

in figure 7. The results from the two different cells were in excellent agreement.

Zinc is a more reactive metal than silver and lead, and the cathode potential curve is of a different nature. The potential does not immediately assume a constant value, but builds up to it as the current density is increased. According to the interpretation of Patten and Mott (13 to 16) and of Müller (7 to 12), the zinc reacts below the threshold value of current density, going into solution as rapidly as it is formed, and no residual amount is deposited. At higher current densities the rate of electrodeposition is greater than the rate of solution and zinc is actually deposited in a visible coat. The potential of the zinc is −1.40 volts referred to the reference electrode used, and this can be converted to −0.62 volt on the hydrogen scale.

TABLE 11

Polarization measurements of 1.0 N barium perchlorate

Platinum cathode

TOTAL VOLTAGE	CURRENT DENSITY	ANODE POTENTIAL REFERRED TO Ag | 0.1 N $AgClO_4$ HALF-CELL	CATHODE POTENTIAL REFERRED TO Ag | 0.1 N $AgClO_4$ HALF-CELL
volts	*milliamperes per square centimeter*	*volts*	*volts*
0.91	0.0051	0.25	−0.63
1.12	0.011	0.32	−0.79
1.28	0.062	0.38	−0.88
1.49	0.123	0.49	−0.94
1.53	0.122	0.51	−1.01
1.85	0.241	0.60	−1.09
2.82	0.88	0.67	−1.34
3.23	1.24	0.68	−1.42
3.57	1.55	0.67	−1.52
4.88	2.62	0.70	−1.74
	3.68	0.70	−1.93

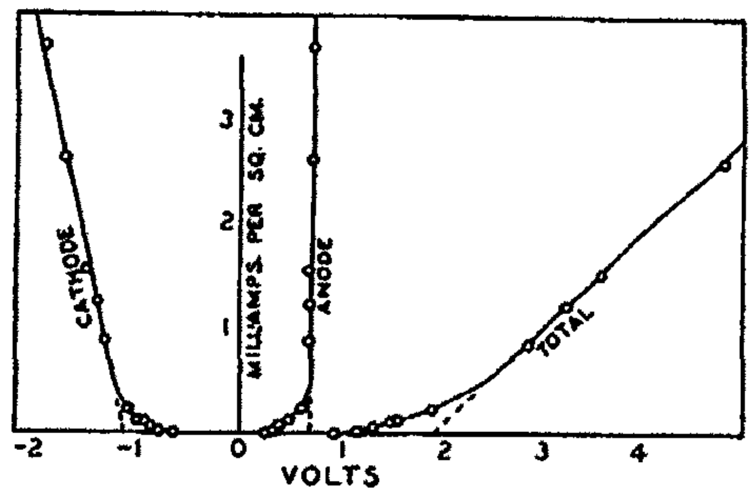

FIG. 9. Polarization curves of barium perchlorate with platinum cathode

The curves for the electrolysis of barium perchlorate between platinum electrodes are different from those of the previous metals. The cathode potential continues to increase with increasing current density, as shown in table 11 and figure 9. The cathode decomposition potential, obtained by extrapolating to zero current density, is only −1.15 volts, and this is much less negative than would be expected for the highly reactive metallic barium.

The potential of metallic barium cannot be measured directly in the solution because its reactivity prevents the keeping of a clean metallic surface. Müller, however, has employed the process of amalgamating reactive metals in order to obtain their potentials, and he identified a deposit as calcium by comparing its potential with that of amalgamated calcium in the same solution (9). In the 1.0 N barium perchlorate solution amalgamated barium was found to have a potential of −2.16 volts with respect to the reference half-cell electrode. This is so much more negative than the decomposition potential of the cathode that there is no possibility that barium was deposited during the electrolysis.

TABLE 12

Polarization measurements of 1.0 N barium perchlorate

Cadmium cathode

TOTAL VOLTAGE	CURRENT DENSITY	ANODE POTENTIAL REFERRED TO Ag | 0.1 N $AgClO_4$ HALF-CELL	CATHODE POTENTIAL REFERRED TO Ag | 0.1 N $AgClO_4$ HALF-CELL
volts	*milliamperes per square centimeter*	*volts*	*volts*
1.25	0.05	0.25	−1.02
1.42	0.09	0.35	−1.13
1.85	0.21	0.57	−1.28
2.20	0.35	0.68	−1.56
2.92	0.47	0.68	−2.03
3.35	0.49	0.68	−2.24
3.90	0.87	0.68	−2.30
4.45	1.35	0.69	−2.28
4.66	1.55	0.70	−2.28
	3.15	0.71	−2.29
	4.05	0.72	−2.30
	4.90	0.73	−2.40
	4.76	0.73	−2.46
	7.26	0.77	−2.48
	16.21	0.77	−2.48
	90.0	0.78	−2.49

The barium solution was electrolyzed using metal cathodes other than platinum. These were obtained by plating the desired metal upon the cell cathode. The cathode potential curves obtained with a copper cathode and with a zinc cathode were rather similar to those obtained with platinum, and the potentials were too positive to indicate the deposition of barium. The results with a cadmium cathode, given in table 12 and figure 10, do indicate the deposition of metallic barium. Above the threshold value of 0.5 milliampere per square centimeter barium is deposited at a potential of −2.28 volts. The favorable influence of the cadmium cathode can be explained by the tendency of barium to form alloys with cadmium, as reported by Gautier (4).

Chemical confirmation of the deposition was poor, for with removable cathodes any attempts to remove the cell liquor resulted in the removal of the deposit as well, and only traces of barium could be reported. But when the cathode was removed quickly and placed in distilled water, small amounts of hydrogen gas could be seen to be evolved.

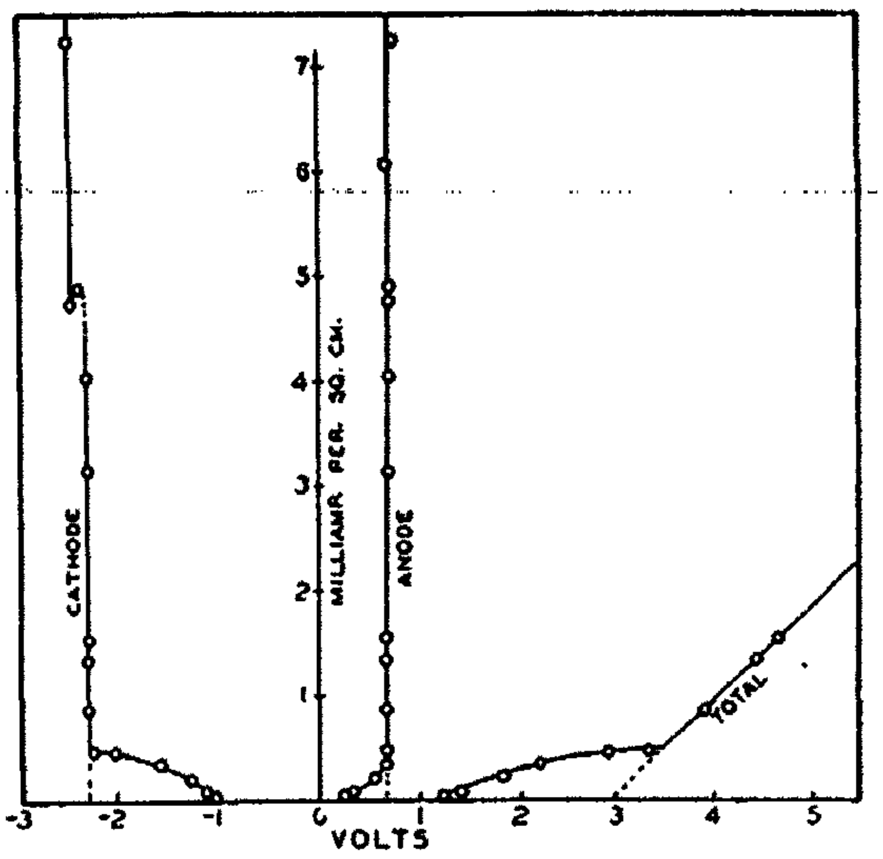

FIG. 10. Polarization curves of barium perchlorate with cadmium cathode

For the deposition of aluminum one would expect copper to be a favorable cathode metal, for several compounds of copper and aluminum have been reported (3). Table 13 and figure 11 show the results of the electrolysis of a 0.5 N solution of aluminum perchlorate prepared as previously described. The irregularity of the curves is similar to that found by Müller for the electrolysis of aluminum iodide in pyridine (9). No cathode potential value is negative enough to indicate the deposition of metallic aluminum. For comparative purposes the potential of aluminum was measured in the same solution. When freshly cleaned and scraped, aluminum had a potential of −0.67 volt with respect to the 0.1 N $AgClO_4$–Ag

TABLE 13

Polarization measurements of 0.5 N aluminum perchlorate

Copper cathode

TOTAL VOLTAGE	CURRENT DENSITY	CATHODE POTENTIAL REFERRED TO Ag | 0.1 N $AgClO_4$ HALF-CELL
volts	*milliamperes per square centimeter*	*volts*
0.47	0.03	−0.26
0.74	0.19	−0.35
0.77	0.25	−0.35
0.88	0.37	−0.47
0.93	0.45	−0.48
1.02	0.61	−0.60
1.06	0.74	−0.65
1.23	1.00	−0.93
1.50	1.30	−0.85
1.85	1.75	−0.80
1.95	1.95	−1.06
2.05	2.20	−1.30
2.12	2.45	−1.20
2.27	2.97	−1.15
2.38	3.85	−0.95
2.63	4.75	−0.95
3.05	5.70	−1.10
3.38	6.25	−0.79
3.85	7.70	−0.80
4.43	9.25	−1.10
4.47	11.60	−0.90

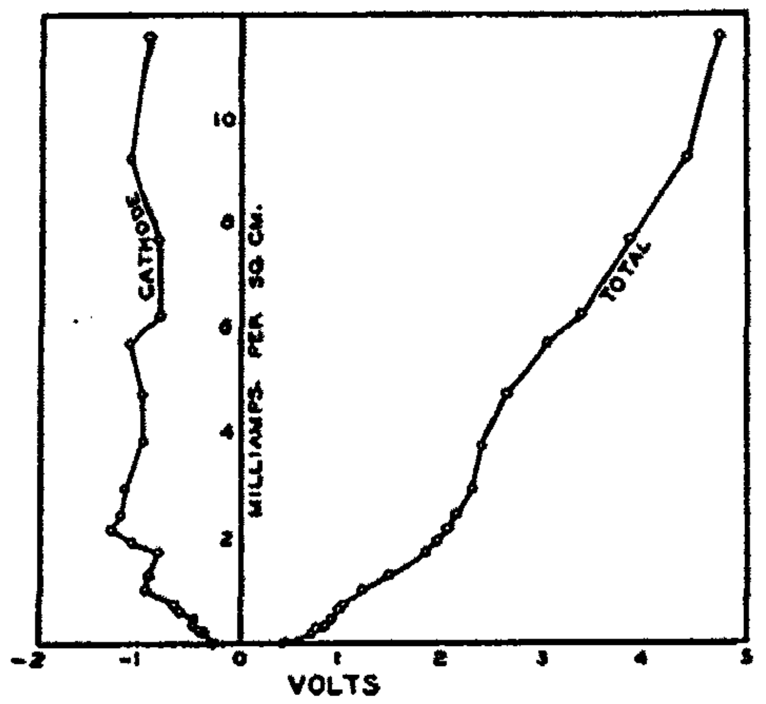

FIG. 11. Polarization curves of aluminum perchlorate

electrode. This value is obviously less negative than the true potential of the metal. Samples amalgamated by rubbing the cleaned surface with mercury had potentials ranging between −1.59 and −1.61 volts. Samples amalgamated by dipping in aqueous mercuric chloride and drying with alcohol and ether gave potentials between −1.83 and −1.94 volts. While these values are not in agreement, they are enough more negative than the cathode potentials to indicate the absence of aluminum deposition during the electrolysis.

CONCLUSION

Both the dielectric constant of the monoethyl ether of ethylene glycol and the conductance of its solutions are between those of methyl and ethyl alcohols. The monoethyl ether of ethylene glycol may be considered as an alcohol of high molecular weight, and as such the high molecular weight does not, in this case, show the usual effect of decreasing conductance.

The polarization curves show that metals even as reactive as barium may be electrodeposited from solutions in the monoethyl ether of ethylene glycol. Although anhydrous solutions of aluminum perchlorate may be prepared in this solvent, the polarization curves show no tendency toward the electrodeposition of aluminum from such solutions.

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NEW BOOKS

Outlines of Theoretical Chemistry. By F. H. GETMAN and FARRINGTON DANIELS. Sixth edition. 662 pp. New York: John Wiley and Sons, 1937. Price: $3.75.

Although a large amount of new material is included in the sixth edition of this well-known textbook of physical chemistry, the length of the book is practically unchanged. This result has been accomplished by means of a marked abbreviation of some of the older material, particularly of those parts which dealt with experimental methods; for example, twenty diagrams of apparatus and their attendant descriptions which were present in the fifth edition are now omitted.

It is interesting to note that the thermodynamic notation of Lewis and Randall has been adopted in the present edition.

The new material which appears in this edition includes such topics as quantum mechanics, the Hund-Mulliken theory, the Heitler-London theory, and the calculation of activation energies. While Dr. Daniels has been very skillful in his brief presentation of these relatively difficult topics, the discussion of them is necessarily purely descriptive. The reviewer is of the opinion that there is some danger that this type of treatment may give the beginning student the impression that physical chemistry, while interesting, is a rather intricate subject full of formulas whose derivations are difficult, of little interest, and certainly none of his concern. To compensate partially for this lack of rigor in the text, a sixteen-page appendix of derivations has been added, ranging in difficulty from the evaluation of van der Waals constants to a discussion of the Debye-Hückel theory. A few minor mistakes, such as the curiously impractical method for collecting radon (page 577), have found their way from the fifth to the sixth edition.

On the whole Dr. Daniels is to be congratulated on a successful revision of a valuable text. The changes will undoubtedly increase the widespread popularity which the book now enjoys.

ROBERT LIVINGSTON.

Die Fluorescenzanalyse in der Mikrochemie. Monographien aus dem Gesamtgebiete der Mikrochemie. By MAX HAITINGER. 192 pp.; 4 fig.; 7 tables. Vienna and Leipzig: Emil Haim and Co., 1937. Price: 8 RM.

The author, who was awarded the Fritz Pregl Prize for his work in fluorescence microscopy, has in this monograph made a worthwhile contribution to the literature of fluorescence analysis. Already many important applications of this comparatively new physicochemical method of analysis have been made in the microchemical field, and doubtless the future will see more extensive development of the technique, especially, it is to be hoped, in the quantitative branch of analysis. The topics treated in the book include: light sources and filters, methods of fluorescence analysis, fluorescence microscopy, fluorometry, applications of fluorescence analysis in chemical investigations (individual tests for many inorganic and organic substances are described), mineralogical applications, trace detection, and micro reactions in animal and vegetable cells. There are more than 800 references (with titles) to the literature.

A number of typographical errors, especially in the spelling of names, were noted. At the bottom of page 52, "Mg-Oxim" is evidently a misprint for "Mg-Oxin."

E. B. SANDELL.

Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. System-Nummer 35: Aluminium. Teil A. Lieferung 5. Legierungen von Aluminium mit Zink bis Uran. 26 x 18 cm.; pp. xvi + 683-886. Berlin: Verlag Chemie, 1937. Price: 24.75 RM.

This section continues the treatment of aluminum alloys, and further parts will follow. It deals with the alloys, simple and mixed, of aluminum with zinc, cadmium, mercury, gallium, indium, thallium, rare-earth metals, titanium, zirconium, hafnium, thorium, germanium, tin, lead, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, and uranium. The treatment is on the usual lines of descriptive text, tables, and diagrams, and a wealth of information is given in an admirably concise form, with full references to the literature. In view of the increasing importance of aluminum alloys, this volume will be especially welcome.

J. R. PARTINGTON.

Magnesium-Legierungen. Patentsammlung geordnet nach Legierungssystem von A. Grützner. Zugleich Anhang zu Magnesium Teil A in Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. 26 x 18 cm.; 192 pp. Berlin: Verlag Chemie, 1937. Price: 15 RM.

This volume consists entirely of tables giving the salient properties and uses of magnesium alloys with references to patents. It includes a large number of alloys of great importance in modern technology and should be invaluable not only to chemists but also to engineers. The plan of the work is clearly described in a short preface, so that the reader will be able to find any particular alloy without difficulty.

J. R. PARTINGTON.

Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. System-Nummer 22: Kalium. Lieferung 3. 26 x 18 cm.; pp. xx + 515-804. Berlin: Verlag Chemie, 1937. Price: 35.25 RM.

This section of the volume on potassium includes compounds with bromine and iodine (including salts of oxyacids), sulfur, selenium, and tellurium (including salts of oxyacids and salts of acids of nitrogen and sulfur). The methods of preparation include technical processes in the case of salts of industrial importance. The properties are given very fully and comprise both physical and chemical properties for the solids and solutions. Among physical properties may be noticed the full discussions of crystal structure and optical properties. The colored forms of the haloid salts formed by radiation, etc., are discussed and the polybromides and polyiodides receive adequate treatment. Systems of salts are treated from the point of view of the phase rule. This volume, it will be seen, contains important and interesting material and the treatment is full and authoritative, recent literature being very satisfactorily covered.

J. R. PARTINGTON.

Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. System-Nummer 27: Magnesium. Teil A. Lieferung 1. 26 x 18 cm.; pp. iii + 156. Berlin: Verlag Chemie, 1937. Price: 18 RM.

This is the first part of the volume on magnesium and deals with the history, occurrence, and preparation (including technical processes) of magnesium. The section on occurrence is very complete on the geological, economic, and geochemical sides, the mineral deposits in the United States receiving very ample treatment. The production of the metal is well described, the electrolysis of the fused chloride, free from water, being the most important method. The utilization of the chlorine evolved in working up oxide or carbonate minerals is mentioned. The technical undertakings in Germany, France, the United States, and England are stated, and attention is directed to the large increase in the production of the metal in a very recent period. The total annual production has been estimated as 25,000 tons in 1935 as compared with 2500 tons in 1929 and 250 tons in 1926. This great increase is due to the increasing use of light alloys containing magnesium. The cells used for the electrolysis of the fused chloride contain a carbon anode and iron cathode, separated by a partition or diaphragm, the exact construction being little known. The electrolysis of the oxide in a bath of molten fluoride is also in use. The separation of the metal in the cell is rather difficult and in the Ashcroft process, used in England, an alloy of lead and magnesium is first obtained and afterwards separated in a second electrolytic cell. The metal may be purified by sublimation.

The information in the volume is very detailed and up-to-date; the literature has been well covered.

J. R. PARTINGTON.

Gmelins Handbuch der anorganischen Chemie. 8 Auflage. Herausgegeben von der Deutschen Chemischen Gesellschaft. System-Nummer 27: Magnesium. Teil A. Lieferung 2. 26 x 18 cm.; pp. vi + 157-372. Berlin: Verlag Chemie, 1937. Price: 25.50 RM.

This section contains the physical properties of the magnesium nucleus (including the isotopes 23, 24, 25, 26, and 27), atom, crystals, and massive metal. They are very exhaustively dealt with, the spectra, magnetism, and electrochemical relations being included. The chemical properties are given in outline, according to the usual plan of the work, and there is a good section on analysis. The preparation of this section has involved the abstraction of a large amount of literature, and very recent papers and monographs are well covered. In view of the increasing use of magnesium in metallurgy, this volume will provide indispensable information for those engaged in technical concerns as well as for the research chemist and analyst. The thorough consideration of the physical chemistry of magnesium is very noteworthy.

J. R. PARTINGTON.

Selected Topics in Colloid Chemistry. By ROSS AIKEN GORTNER. 6 x 9 in.; 169 pp.; 35 fig. Ithaca, N. Y.: Cornell University Press, 1937. Price: $2.50.

"This book covers the content of a series of lectures delivered in the Department of Chemistry of Cornell University during the first semester of the academic year 1935–1936, at which time the author held the George Fisher Baker Non-Resident Lectureship in Chemistry." (p. vii.)

Serving as an introduction to the book is the public lecture on "Scientific Genealogy" presented by the author at the beginning of his lectureship. This is followed by eight chapters grouped under the following headings: "The Beginnings of the Science"; What is "Colloid Chemistry"; "Some Basic Concepts"; "Some Fundamental Properties of Colloid Systems"; "Electrokinetics"; "Surface Tension, Surface Energy, Interfacial Tension, and Molecular Orientation"; "Adsorption"; "The Water Relationship of Bio-Colloids."

The author has treated each topic briefly but systematically, has brought the material up-to-date, and has especially emphasized the application of colloid chemistry to biochemical problems; of particular interest is his able treatment of the controversial subject "bound water." He has included, in condensed and well-oriented form, much of the highly important and extensive work from his own laboratories.

While the material presented is not intended to serve as a text in colloid chemistry, it does furnish an excellent introduction to that subject, and can be recommended to all who are interested in it. It will be of special value to the biochemist, who will find a welcome approach to the realm of colloid chemistry through the medium of examples with which he already has a speaking acquaintance.

F. E. Bartell.

The Chemistry and Technology of Rubber. C. C. Davis, Editor, and J. T. Blake, Assistant Editor. 941 pp. New York: Reinhold Publishing Co., 1937.

This book, which is No. 74 in the series of A.C.S. Monographs, is a collection of twenty-six chapters, each written by one or more authorities in the field. The book is encyclopedic in character; the chapters cover all phases of rubber chemistry and technology from crude rubber to finished products, and from the chemistry of the rubber hydrocarbon through polymerization, vulcanization, accelerators, and autooxidation to synthetic and substitute rubbers. As the book was written by some forty contributors, each one an authority on some phase of the rubber problem, it would be difficult to find a reviewer who was competent to judge accurately the merits of the whole work. This reviewer has accordingly read critically only those chapters which he felt competent to judge (chapters 3, 8, 9, 12, 13, 14, and 20). These seven chapters are distinguished by clarity of presentation, thoroughness of treatment, and unbiased attitude in presenting all the facts and theories, and yet a definite critical faculty is exercised throughout. The material is up-to-date and the bibliographies are extensive. A cursory examination of the other nineteen chapters indicates that these, too, are well written and complete. The whole book is distinguished by a continuity which reflects great credit upon the editor and his assistant. The printing and binding are quite up to the standard for this series of monographs, and there is a section on the literature of the chemistry of rubber, as well as over forty pages of author and subject indexes. Altogether, this is an excellent treatise.

Lee Irvin Smith.

Colorimetric Methods of Analysis, Volume II, Organic and Biological. By Foster D. Snell and Cornelia T. Snell. New York: D. Van Nostrand Co., 1937. Price: $9.50.

Soon after the appearance of the first volume of *Colorimetric Methods of Analysis* dealing with the colorimetry and nephelometry of inorganic substances, this second volume giving similar methods for organic substances was published. Because of the great number of known organic substances, it is not possible to give an exhaustive treatment of all of them. The authors have concentrated mainly on those substances which are of importance from a biological or medical viewpoint. Included are hydrocarbons, alcohols, aldehydes, ketones, acids (aliphatic and carbocyclic) carbohydrates, phenols, proteins, peptides, amines, alkaloids, some nitro compounds, hormones, and vitamins. The last 180 pages are devoted to the determination of color in various technically important liquids.

Physical chemists who in their research need methods for the determination of traces of organic compounds (in photochemistry, in studies of inhibition, etc.) will find the book very helpful. In general, a complete review of the literature is given, followed by the sampling, the procedure, and the selection of proper standards. The compilation given is a valuable addition to the literature on the colorimetry of organic compounds, for which the authors deserve the recognition not only of organic and analytical chemists, but also of workers in the biological and medical fields.

I. M. Kolthoff.

THE HYDRATION AND PHYSICOCHEMICAL PROPERTIES OF PECTIN AND ITS DERIVATIVES

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Although the properties and structure of pectin have been under investigation for many years, no agreement as to the complete structure has yet been reached. It is, however, usually conceded that a polygalacturonic acid is contained in the pectin molecule. According to Ehrlich (2), four galacturonic acid molecules, two of which are methylated, constitute the fundamental unit. Other views are those cf Nanji, Paton, and Ling (8), who look upon pectin as having a ring structure containing four methylated galacturonic acid molecules and one each of galactose and arabinose. Morell, Baur, and Link (7) have concluded that at least eight or ten acid residues are contained in the pectic acid molecule. If the views of Nanji, Paton, and Ling be accepted, the normally acidic nature of pectin sols does not follow unless one assumes partial demethoxylation to have occurred in the preparation of the pectin. Spencer (11) explains this acid condition as being due to preferential adsorption of anions. However, since the methods used in preparation of pectins are such that demethoxylation takes place, it is permissible to assume that all pectins used in the making of jellies may be acidic of themselves.

While the degree of hydration of pectin is usually considered to be one of the factors involved in its jelling, no previous attempts to measure it directly have been made, although qualitative results have been reported (4). In this work, measurements of the hydration in alcohol suspensions were carried out.

It has long been known that the presence of salts is important in the jelling of pectin. Halliday and Bailey (6) showed that the effect of calcium chloride is such that the amount of sugar required to induce jelling is decreased. On the other hand, Spencer (11) finds that in the presence of acids sodium chloride decreases the jelling ability. It is generally agreed that the cation (4) is of more importance in these salt effects, although definite anion effects may be observed under proper conditions (5). Whereas some workers explain the behavior of pectin in the presence of salts as due to sorption effects only (11), others prefer the hypothesis that exchange of cations between the pectin molecule and the salt is involved

(5). Glückmann (5) has prepared and investigated the properties of pectins containing a number of anions in varying proportions.

In the present work an investigation has been made of the acidic character of pectin and of its hydration and sorption characteristics in the acidic and several salt forms.[1] An apple pectin was used. The acidic form was prepared by thoroughly washing the pectin with a 50 per cent alcohol solution containing hydrochloric acid. This treatment removed practically all of the metallic ions. The pectinic acid described is a product of low-temperature acid hydrolysis of pectin and the pectic acid a product of alkaline hydrolysis of pectin. The salt forms were prepared by the neutralization of the acid with the proper base in the presence of buffer salts containing the same cation. These buffer salts were then washed out by thorough extraction with 50 per cent alcohol. The combining weights of the three acids were found to be 848, 425, and 207, respectively, for vacuum-dried pectin, pectinic acid, and pectic acid.

EXPERIMENTAL

The conductance of pectic materials and their salts

Solutions of the materials were prepared by weighing out the proper amounts and dispersing them in conductivity water. Lower concentrations were prepared by dilution. The sodium salts used in these experiments were prepared by addition of the proper amount of sodium hydroxide to the acidic sol. The conductivities of acidic pectin and pectinic acid are given in table 1.

The conductivities of the sodium salts of the two materials are given in table 2.

The observed values of pH were obtained by means of a glass electrode. The calculated values were obtained by computation from the data of tables 1 and 2 and the ionic conductances of sodium and hydrogen. The calculation of the dissociation constant was made on the assumption that the same value obtains for all hydrogens, and, while not constant, it does give an indication of the acid strength of pectin and a pectinic acid. It is interesting to note that the values for the two materials are almost identical.

The conductances of the magnesium salts of the two materials and the calcium salt of the pectin were also determined. These values are given in table 3.

The data are of interest in that dissociation is far from complete even at extremely low concentrations, and may probably be looked upon as explaining, at least in part, the differences noted in the past in the effects of the various cations on the jelling of pectin.

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[1] For nomenclature see A. W. Thomas: Colloid Chemistry, p. 371, McGraw-Hill Book Co., New York (1934).

TABLE 1

Conductivities of acidic pectin and pectinic acid

SUBSTANCE	NORMALITY	EQUIVALENT CONDUCTIVITY	pH		DISSOCIATION CONSTANT $\times 10^4$
			Calculated	Observed	
Pectin	0.00825	64.1	2.87	2.85	2.9
	0.00330	89.3	3.13	3.10	2.3
	0.00132	118.7	3.43	3.38	1.9
	0.000528	138.8		3.71	1.2
	0.0001056	177.8	4.79	4.31	0.45
Pectinic acid	0.00941	61.7	2.81	2.81	2.9
	0.00376	83.9	3.10	3.08	2.4
	0.001505	105.0	3.40	3.38	2.0
	0.000602	123.3	3.60	3.71	0.94
	0.0001204	154.4	4.30	4.30	0.34

TABLE 2

Conductivities of sodium pectin and sodium pectinate

NORMALITY	EQUIVALENT CONDUCTIVITY	
	Sodium pectin	Sodium pectinate
0.0100	59.9	62.2
0.0040	65.1	67.1
0.0016	69.2	70.9
0.00064	72.8	75.3
0.000128	82.1	
0.000256		77.5
0.000041		78.0
0.0000256	73.7	

TABLE 3

Conductances of magnesium pectin, magnesium pectinate, and calcium pectin

NORMALITY	MAGNESIUM PECTIN		MAGNESIUM PECTINATE		CALCIUM PECTIN	
	Conductivity	Per cent dissociation	Conductivity	Per cent dissociation	Conductivity	Per cent dissociation
0.0100	38.4	49	29.1	36	36.7	43
0.0020	46.1	59	33.3	42	45.7	54
0.0004	52.4	67	39.2	49	51.4	60
0.00008	60.5	77	42.2	53	56.9	67

The conclusions from conductivity data were further substantiated by precision measurements[2] of the lowering of freezing point made by the

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[2] All these measurements were made by Dr. Kurt H. Andresen, to whom my best thanks are due.

method of Scatchard (10), and, for the less dilute solutions, by measurements[2] of the lowering of vapor pressure made by the method of Robinson and Sinclair (9). The results were as given in table 4, where g (the osmotic coefficient) $= 1 - j = \theta/\nu\lambda m$, where ν is taken for the purpose of this calculation as 2 for sodium pectinate and as 3 for magnesium pectinate. It will be noted that the results from conductivity and the osmotic data are in close agreement.

Hydration of pectic materials

Experiments with the ultrafiltration method with methyl alcohol and also with sodium chloride as reference substance showed that pectin is hydrated to the extent of only about one-third of its weight of water. The experiments here described were made as follows, without ultrafiltration. Thoroughly dried materials were immersed in alcohol solutions of known concentration and left in contact for about twenty-four hours. Samples of the supernatant liquid were then withdrawn and analyzed for alcohol content. This analysis was made by carefully distilling and then determining the alcohol content by means of a dipping refractometer. In cases where the concentration of the alcohol used was less than 20 per cent, an interferometer was used in analysis. Table 5 gives the data thus obtained. Hydrations are given in per cent of the dry weight of the material.

TABLE 4

Osmotic coefficient of sodium pectinate and magnesium pectinate solutions

SODIUM PECTINATE SOLUTIONS		MAGNESIUM PECTINATE SOLUTIONS	
Normality	Osmotic coefficient g	Normality	Osmotic coefficient g
0.00088	0.9699	0.00417	0.4318
0.00163	0.9281	0.00630	0.3902
0.00241	0.8901		
0.00318	0.8572	0.00981	0.3233*
0.00392	0.8273	0.01209	0.3267*
0.0108	0.7683*		

* By lowering of vapor pressure; all others by freezing point.

The form of the curves in figure 1 indicates that extrapolation to zero alcohol concentration is justified. Such extrapolation leads to the following values for the various materials in pure aqueous solution:

Pectin	25 per cent hydration
Pectic acid	21 per cent hydration
Sodium pectate	38 per cent hydration
Calcium pectate	35 per cent hydration

The tendency for pectin to disperse in solutions of alcohol of low concentration prevents their use with pectin and its salts; however, the similarity in the behavior of pectates and salts of pectin at high concentrations justifies the assumption that the same would hold true throughout. An experiment with 0.1 *N* hydrochloric acid in 40 per cent alcohol gave the

TABLE 5

Hydration of pectic materials

SUBSTANCE	WEIGHT OF SOLUTION PER GRAM OF MATERIAL	INITIAL ALCOHOL CONCENTRATION	FINAL ALCOHOL CONCENTRATION	PER CENT HYDRATION
Acidic pectin	11.58	19.51	19.81	18.3
	12.20	32.77	34.42	23.1
	18.39	41.13	42.07	18.8
	9.81	49.86	51.12	24.8
	12.03	56.77	58.08	25.4
	6.42	60.15	62.42	23.3
	5.55	70.10	72.33	17.1
	5.23	80.43	82.35	12.3
	6.9	95.22	92.52	2.1
Pectic acid	10.0	95.09	96.41	6.8
	10.0	76.61	70.33	17.1
	10.0	71.66	74.47	18.9
	10.0	51.56	52.47	17.0
	10.0	42.14	43.78	19.0
	20.3	23.31	24.31	20.9
	10.0	10.77	11.33	20.3
	15.0	4.939	5.141	21.0
	14.4	1.162	1.206	21.2
Sodium pectate	10.0	76.61	80.03	21.4
	20.0	41.79	43.29	35.0
	21.0	32.52	33.66	35.0
	10.0	23.31	25.14	36.4
Calcium pectate	10.0	95.09	96.26	5.9
	10.0	76.61	80.03	21.4
	10.0	71.66	74.91	22.6
	10.0	51.94	54.76	25.7
	10.0	41.79	44.38	29.1
	10.1	41.79	44.14	26.7
	10.0	23.31	24.96	32.6
	10.0	10.77	11.50	32.7
	10.2	4.939	5.375	34.0
	10.2	1.162	1.273	37.0
Magnesium pectate	10.0	20.58	22.12	37.1

same hydration value for hydration of acidic pectin as the control in which water was used.

Table 6 summarizes the data for a number of materials. In this case all hydration values are for approximately 50 per cent alcohol, and so do not represent the hydrations at zero concentration of the reference substance.

In general the pectates appear to be slightly less hydrated than the salts of pectin or of pectinic acid. Also, the acids are in all cases definitely less hydrated than are the salts, and the calcium salts are less hydrated than either the sodium or the magnesium salts, the latter being hydrated to the same extent within the limits of error. One may conclude then that the degree of hydration in a pectin jelly will be dependent upon pH and upon the other cations present in the jelly. The degree of hydration appears to be dependent upon the degree of hydration of the cation and may also be correlated roughly with the degree of dissociation of the salt as previously described.

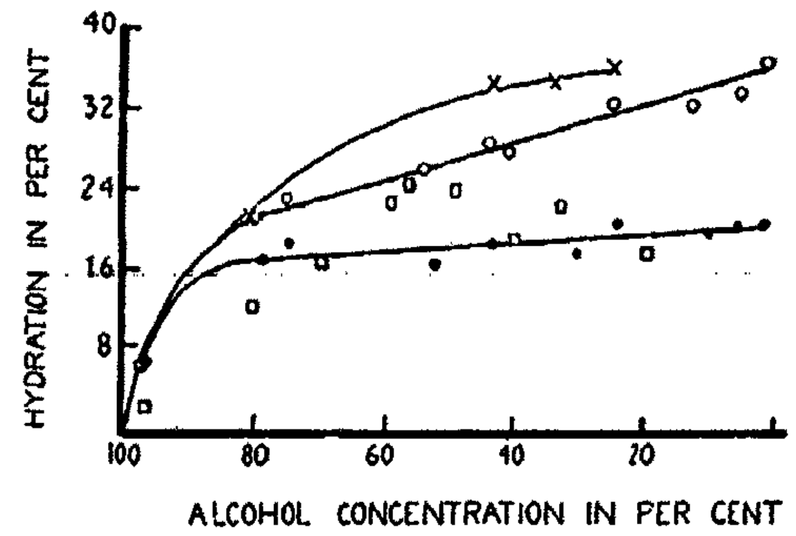

FIG. 1. Hydration of pectin and its derivatives. ☐, pectin; ●, pectic acid; ×, sodium pectate; ○, calcium pectate.

TABLE 6

Hydration of the acids and their salts in 50 per cent alcohol

	PER CENT HYDRATION OF			
	Acid	Sodium salt	Magnesium salt	Calcium salt
Pectin	25	33	33	
Pectinic acid	26	34	37	30
Pectic acid	19	33	33	27

Sorption of potassium iodate by pectic materials

Sorption experiments were carried out by addition of dried materials to solutions of iodates, both in water and in alcohol solutions. Analyses of the supernatant liquid were then made to determine the amount of sorption which had taken place. Necessarily, conditions used were at all times such that dispersion of the material did not take place to any appreciable extent. The nature of these materials under such conditions of nondispersion must be similar to that of permutites. They are, therefore, subject to so-called exchange adsorption, which is merely the exchange of cations between the salt present and the colloidal material. Molecular sorption may also take place, and it is this type of sorption with which the following experiments are concerned. Specifically, the effect of various cations in both the sorbent and sorbate was investigated.

TABLE 7

Relative sorptive powers of pectic materials for potassium iodate

SUBSTANCE	SOLUTION USED								
	30 per cent alcohol			1.0 N sodium chloride			Water		
	Normality of KIO_3								
	0.04	0.01	0.0025	0.2	0.02	0.002	0.2	0.01	0.002
Pectic acid	32.6	18.9	25.7	8.8	16.1	52.9		3.2	20.6
Magnesium pectate	29.1	28.7	30.6	1.2	5.2	19.8	2.0	4.6	15.9
Sodium pectate	3.9	1.3	0.6	−0.6	3.2	8.6			

TABLE 8

Per cent sorption of iodates by pectates

CATION	0.04 N IODATE	0.01 N IODATE	0.0025 N IODATE
Potassium	2.4	0.4	2.0
Sodium	3.9	1.0	1.3
Magnesium	35.8	31.5	33.8
Hydrogen	9.1	8.4	8.6

The data in table 7 were obtained by keeping the materials in contact with the solutions for eleven days with constant shaking. In all cases 14 g. of solution per gram of pectin was used. The iodate concentrations given are initial concentrations, and sorptive powers are expressed as the percentage of the iodate sorbed, without allowance for hydration.

A similar series of experiments was run in which each pectic material was allowed to remain in contact with the corresponding iodate in 30 per cent alcohol solution for a week with constant shaking. The results were as given in table 8.

It is apparent from the data in tables 7 and 8 that the effects of the ions on adsorption of iodate are quite marked. The potassium and sodium salts do not sorb nearly as much of the potassium iodate as do the acid and the magnesium salt. The sorption is much greater from sodium chloride than from water solution when pectic acid is the sorbent, but it is not much different when magnesium pectate is used. This at first sight appears to be in disagreement with the fact that hydrogen ions and magnesium ions are about equally effective in sorption from alcohol solution, but it is explainable on the basis of greater displacement of magnesium than of hydrogen from the pectic molecule by the relatively ineffective sodium ion. Actually such a difference exists even in the sorption from alcohol solution, and the magnesium ion is considerably more effective in promoting sorption than is the hydrogen ion, as shown by table 8, where sorbent and sorbate contain the same cation. That the exchange of magnesium and sodium does not take place to a very great extent, however, follows from the fact that magnesium pectate is insoluble in water. The greater acid strength of iodic acid than of pectic acid precludes any very great exchange of potassium and hydrogen in the case of potassium iodate and pectic acid.

TABLE 9

The effect of total electrolyte concentration on the progress of adsorption

PER CENT SORPTION FROM WATER SOLUTIONS			PER CENT SORPTION FROM 1.0 N SODIUM CHLORIDE		
Initial KIO_3	Final KIO_3	Sorption	Initial KIO_3	Final KIO_3	Sorption
per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
0.0687	0.0685		0.0591	0.0481	18.6
0.137	0.140		0.261	0.234	10.4
0.279	0.283		1.044	0.960	8.1
0.591	0.588		4.427	4.103	7.3
1.208	1.183	2.1			
1.991	1.922	3.5			
4.485	4.278	4.6			

TABLE 10

Rate of sorption of potassium iodate on magnesium pectate

	WATER SOLUTIONS				1.0 N SODIUM CHLORIDE SOLUTIONS			
Time..............	0	10 min.	4 hr.	24 hr.	0	10 min.	4 hr.	24 hr.
Per cent KIO_3.....	0.0409	0.0426	0.0419	0.0405	0.0381	0.0377	0.0374	0.0364
Per cent sorbed....		−3.5	−2.4	1.0		1.1	1.8	4.4

The effect of total electrolyte concentration on the progress of adsorption is shown in the data in table 9, which were obtained in experiments in which overnight contact between solution and sorbent was allowed.

The marked difference at low concentrations is certainly to be attributed to electrical effects, and in the above data is due both to a difference in the manner in which sorption progresses and to the lack of equilibrium at the low concentrations. It can be shown that in the presence of small electrolyte concentrations an initial negative sorption takes place, which later becomes positive in many cases, whereas in the presence of a greater amount of electrolyte to suppress the Donnan effect, the sorption is at once positive. The data in table 10 serve to illustrate this point.

Sorption is greater at high than at low concentrations in the case of sodium pectate sorbing iodate from alcohol solutions (see table 7). In general, the sorption from alcohol solutions is abnormal in that it does not follow the adsorption isotherm, and the per cent sorption may be greater at high than at low concentrations.

Since pectin itself is readily dispersible, an extensive comparison of its sorptive properties with those of pectic acid could not be carried out; however, a comparison of sorption from alcohol solutions was made.

TABLE 11

Sorption of potassium iodate from 40 per cent alcohol solution

SORBENT	PER CENT OF IODATE SORBED	
	Initial KIO_3 concentration 0.467 per cent; 3 days shaking	Initial KIO_3 concentration 0.058 per cent; 7 days shaking
Pectin	45.2	19.0
Pectinic acid	29.7	28.7
Pectic acid	32.7	15.6
Sodium pectin	Dispersed	Dispersed
Sodium pectinate	10.9	10.5
Sodium pectate	9.2	3.1
Magnesium pectin	25.9	27.0
Magnesium pectinate	37.3	39.6
Magnesium pectate	47.2	45.6

One may conclude that qualitatively the same effects of cations are to be found with pectin and pectinic acid and their salts as with pectic acid. Insufficient data are obtainable to determine the quantitative relationships precisely, but the data do show that the effects vary in magnitude with the various materials under the conditions of this experiment.

GENERAL DISCUSSION

The conductivity data reported substantiate the views held by those who consider pectin to be acidic of itself, and are in agreement with the facts as regards the effect of acidity in pectin jellies. These data show pectin to be a weak acid, but very definitely stronger than acetic acid. The contention of Glückmann to the effect that the acidic pectin is freed from its salts in pectin jellies is justified, although in practice jellies are not always of sufficiently low pH to cause complete conversion. The fact that the sodium salt is highly dissociated, the salts of divalent metals are considerably less dissociated, and the acid still less is in agreement with the reported facts (11, 6, 3) that sodium salts hinder jelling while calcium chloride promotes it and that acids are particularly effective in causing jelling in the presence of an organic substance such as sucrose.

The data on hydration show that, as Spencer postulates, the addition of acid to pectin decreases the hydration, since the acidic pectin set free is less hydrated than the salt. On the other hand, the postulate that the effect of sugar is one of dehydration of the pectin micelles does not appear to follow, for although a very slight change in hydration occurs with change in alcohol concentration, the great differences which may be obtained in jelling ability with small changes in concentration of the organic precipitant seem not to be accounted for by dehydration.

That sorption effects are of only minor importance seems to be indicated by the fact that the effect of acidity is mostly one of pH (12). Differences due to the anion present in the acid have been observed (5, 1). A further indication is the fact that, according to the data here presented, sorption is most marked when hydrogen or a divalent metal is present in the pectin molecule, and almost negligible in the case of monovalent metals. Yet anion adsorption should tend to stabilize the pectin, and so this stabilizing effect is greatest, but still overshadowed, in the presence of cations which promote jelling.

In short, pectin is a self-stabilized colloid, its charge resulting from the ionization of the pectic molecule itself. In the form of its highly ionized sodium salt, the charge is great and the stability is accordingly greater than in the case of the less ionized calcium salt. In the acid the ionization is still less and consequently the charge is smaller. An added stabilizing effect is that due to sorption of anions, but this effect appears to be a minor one under ordinary conditions. Its magnitude is dependent upon the anion itself and upon the cations present. The degree of hydration is in the same order as the degree of dissociation in the case of the acid and the calcium and sodium salts; however, the magnesium salt is less dissociated but just as highly hydrated as the sodium salt. The main differences between salts of monovalent and divalent metals are due to unequal dissociation, and differences between salts of ions of the same valence are probably attributable to differences in hydration which affect stability.

SUMMARY

The hydration of pectin and of a number of its derivatives has been measured by the method of a reference substance in water and in aqueous alcohol, in agreement with results by ultrafiltration. It is found that the

hydrate water amounts to 0.25, 0.21, 0.38, and 0.35 g. of water to 1 g. of pectin, pectic acid, sodium pectate, and calcium pectate, respectively. That of pectinic acid resembles pectin; the three sodium and the three magnesium derivatives are somewhat more hydrated.

The sorption of potassium iodate by these materials has been studied.

Pectin and pectinic acid are weak acids, definitely stronger than acetic acid. The sodium salts are moderately strong electrolytes, but the magnesium and calcium salts are far from completely dissociated, even in *N*/10,000 solution.

Conclusions are drawn as to the colloid nature of pectin and its derivatives.

Our sincere thanks are due to Professor James W. McBain, under whose supervision this work was carried out.

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THE FREE ENERGY OF FORMATION OF ETHYL PROPIONATE

Equilibrium in the Gaseous State[1]

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INTRODUCTION

In this investigation a determination of the standard free energy of formation of ethyl propionate has been made, using the method employed by Essex and Clark (2) for the determination of the standard free energy of formation of ethyl acetate. The standard free energy change of the reaction

$$C_2H_5COOH + C_2H_5OH \rightleftarrows C_2H_5COOC_2H_5 + H_2O$$

has been calculated at several temperatures from carefully determined values of the equilibrium constant of the reaction in the gaseous state, which, together with data already available in the literature, leads to an evaluation of the standard free energy of formation of ethyl propionate. Silica gel was the catalyst used for this esterification reaction.

EXPERIMENTAL

A. Preparation of pure reagents

Commercial ethyl alcohol was purified by the same process used by Essex and Clark (2), and only that fraction distilling over within 0.1°C. was accepted for use in this investigation. This fraction was distilled directly into a bottle containing twice-distilled water, thus giving a dilution of alcohol which could be kept in a state of constant composition more easily than the undiluted alcohol. Its specific gravity at 20°C. compared to water at 4°C. was 0.81006, corresponding to 92.916 per cent alcohol.

The propionic acid used was a "C.P." product from the Eastman Kodak Company, and was further purified by fractionation. The fraction used had a boiling point range of 141.1°C.–141.5°C., and a specific gravity of 0.99534 at 20°C. compared to water at 4°C. It was standardized by titra-

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[1] Submitted by Marjorie Sandholzer to the Faculty of Syracuse University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, May, 1936.

tion with the standard barium hydroxide solution which gave a value of 99.88 per cent propionic acid.

The ethyl propionate was also a "C.P." product from the Eastman Kodak Company and was further purified by fractionation. The fraction used had a boiling point range of 98.9°C.–99.3°C., and a specific gravity of 0.8907 at 20°C. compared to water at 4°C. It was standardized by hydrolysis with the standard barium hydroxide solution, which gave a value of 99.72 per cent ethyl propionate.

Barium hydroxide was used to follow the progress of the esterification reaction. It was standardized by weight titration, first against succinic acid, and finally against a sample of pure benzoic acid from the Bureau of Standards.

Twice-distilled water was used in the experimental work.

The silica gel used was the commercial product from the Silica Gel Corporation of Baltimore, Maryland.

B. Apparatus and procedure

The apparatus was that used by Essex and Clark (2), with the exception of an improved automatic temperature control consisting of a mercury regulator which kept the temperature constant to within 0.4°C. maximum difference.

Equilibrium was determined by the same dynamic method used by Essex and Clark, and the equilibrium product was analyzed by the same method of weight titration against standard barium hydroxide solution.

C. Preliminary experiments

Preliminary experiments were run to determine the stability of the system relative to heat, and the approximate equilibrium position. A small test apparatus was set up and mixtures of the reactants were passed over the catalyst at several temperatures. The absence of uncondensed gases in the product and a negative test for aldehydes were accepted as sufficient evidence of the absence of decomposition reactions. There were no uncondensed gases produced up to a temperature of 225°C. The ammoniacal silver oxide test for aldehydes was applied both to the pure reagents and to the condensates from the final runs. In no case was an appreciable amount of aldehyde shown.

It became evident from the preliminary experiments that the equilibrium mixture produced by the action of 1 mole of acid on 1 mole of alcohol is not miscible, since the condensate formed two liquid layers. With initial mixtures sufficiently rich in water, however, homogeneous equilibrium mixtures are obtained. The equilibrium mixtures must be homogeneous as in the final and accurate runs, initial mixtures approximating the equilibrium mixtures must be used, and these initial mixtures must, evidently, be homogeneous. The mixture which proved most satisfactory was that which would be produced at equilibrium by the action of 100 moles of water upon 1 mole of ester.

Some preliminary tests were carried out to determine the error involved in titrating propionic acid in the presence of ethyl propionate. Duplicate samples of the acid were titrated with barium hydroxide, using phenolphthalein as the indicator, with and without the addition of ethyl propionate. No appreciable error was found in titrating the acid in the presence of the ester, provided an excess of the base was avoided and care was exercised in recognizing the first permanent end point.

Before the final runs were made, the reaction vessel and catalyst were thoroughly cleaned by treatment with oxygen as described by Essex and Clark (2).

THE EQUILIBRIUM MEASUREMENTS

The equilibrium was determined at three temperatures, namely, 155°C., 170°C., and 200°C. At each temperature, after an approximate determination of the equilibrium position by preliminary experiments, carefully controlled runs were made with (*a*) a reaction mixture richer in acid and alcohol than the equilibrium mixture, (*b*) a reaction mixture richer in ester and water than the equilibrium mixture, and (*c*) a reaction mixture having exactly the equilibrium concentrations as calculated from the average composition of the products of the runs (a) and (b). A single run, richer in ester and water than the equilibrium mixture, was made at the additional temperature of 184.7°C. Each reaction mixture was made up in proportions which would be reached at some stage in the reaction

$$C_2H_5COOH + C_2H_5OH \rightleftarrows C_2H_5COOC_2H_5 + H_2O$$

if the initial mixture contained ester and water alone in the proportion of 100 moles of water to 1 mole of ester. Since the proportions of the acid, alcohol, and ester compared to the water in the reaction mixtures were always small, and since they are quite volatile, it did not seem accurate enough to make up the mixtures by weighing out the required amount of each constituent into an open container (the method used by Essex and Clark). Therefore the required amount of each of these volatile constituents was weighed out in a tared glass bulb drawn down to a capillary and thus readily sealed off after the sample had been introduced. These bulbs were filled by immersing them in a bottle of the liquid and reducing the pressure on the surface by means of a suction pump. The air contained in the bulb bubbled out and when the pressure on the surface of the liquid was again increased, the liquid was forced into the bulb. This process was repeated until the bulb was filled as completely as desired. These sealed bulbs containing the acid, alcohol, and ester were placed in a

TABLE 1

Results of experiments

Reaction mixture ratios: C_2H_5COOH, 0.707 mole; C_2H_5OH, 0.707 mole; $C_2H_5COOC_2H_5$, 0.293 mole; H_2O, 99.293 moles. Temperature, 155°C. Weight per cent of acid in the reaction mixture, 2.75

DURATION OF RUN	WEIGHT OF PRODUCT COLLECTED	WEIGHT OF BASE (AQ.) REQUIRED TO NEUTRALIZE PRODUCT	WEIGHT PER CENT OF ACID IN PRODUCT
minutes	*grams*	*grams*	
45	7.3573	8.9121	3.113
50	11.3196	13.7994	3.133
70	7.9887	9.6797	3.114
35	8.4006	10.1685	3.111
35	7.5830	9.2675	3.141
60	9.3314	11.4210	3.146
45	11.9357	14.4266	3.106
45	11.2228	13.5442	3.102
60	8.0933	9.7627	3.100
90	9.4104	11.4498	3.127
45	8.4683	10.4224	3.163
65	14.6363	17.7385	3.115
Average			3.123

$K_a\left(K_a = \frac{a_{(\text{ester})}\,a_{(\text{water})}}{a_{(\text{acid})}\,a_{(\text{alcohol})}}\right)$ for average = 30.67

TABLE 2

Summary of results

TEMPERATURE	WEIGHT PER CENT OF ACID IN REACTION MIXTURE	AVERAGE WEIGHT OF ACID IN PRODUCT	K_a
°C.			
155	2.75	3.123	30.67
	3.11	3.133	30.09
	3.60	3.104	31.80
170	2.75	3.205	25.90
	3.21	3.187	26.89
	3.21	3.190	26.71
	3.60	3.209	25.67
184.7	3.21	3.260	22.96
200	3.21	3.322	19.90
	3.32	3.313	20.32
	3.60	3.324	19.78

glass-stoppered bottle into which had already been weighed the required amount of water. Since the bulbs were blown of very thin glass, a vigorous shaking of the bottle was sufficient to shatter them and produce a complete mixture of the reaction constituents.

Runs were made over a considerable range of rates of flow with each reaction mixture at each temperature. The results of the run at 155°C. from the ester-rich side are presented in detail in table 1. Independence of the per cent of acid in the product on the rate of flow is further evidence of the absence of side or consecutive reactions. The results of the runs at all four of the temperatures used are summarized in table 2.

The probable error in the determination of the per cent of acid at each temperature was calculated by the method of least squares, using at each temperature all the determined values of acid percentages in the products after constancy in composition was attained. Each run consisted of a considerable number of these determined values of acid percentages, as shown in table 1.

TABLE 3

Summary of the equilibrium determinations

TEMPERATURE	AVERAGE PER CENT OF ACID IN PRODUCTS	PROBABLE ERROR IN DATA OF COLUMN 2	AVERAGE VALUES OF K_a
°*C.*			
155	3.122	0.00269	30.85
170	3.200	0.00279	26.29
184.7	3.260	0.00452	22.96
200	3.320	0.00151	20.00

The results of all the equilibrium determinations have been summarized in table 3.

CALCULATIONS

A. Molal composition of the equilibrium mixture

1. The number of moles of each constituent

At the temperatures at which measurements were made, no products were detected other than those entering into the reaction

$$C_2H_5COOH(g) + C_2H_5OH(g) \rightleftarrows C_2H_5COOC_2H_5(g) + H_2O(g)$$

The molal composition of the gaseous mixture leaving the reaction tube was calculated from the composition of the entering mixture and the acid in the product.

For example, in one experiment at 155°C., the mixture entering the reaction tube contained 2.75 per cent of propionic acid, corresponding to the following number of formula weights of each constituent per 100 g.

of the mixture: acid, 0.03714; alcohol, 0.03714; ester, 0.01539; water, 5.216.

This mixture was passed over the heated catalyst. The final product, after constancy in the acid percentage had been reached, analyzed 3.123 per cent propionic acid. This shows a shift of the equilibrium in the direction of acid and alcohol formation, and corresponds to an increase of 0.005037 formula weights of acid and of alcohol per 100 g., and a like decrease in the number of formula weights of ester and water. Therefore, in this final product there were 0.04218 formula weights of acid and alcohol, 0.01035 formula weight of ester, and 5.211 formula weights of water. For alcohol, ester, and water, the formula weights are the number of moles; these are listed in table 6 in the columns headed n_3, n_4, and n_5, respectively.

The work of Miss Klein (8) on the association and fugacity of gaseous propionic acid indicates that even at a temperature of 184°C. and a pressure of 140 mm. propionic acid exists partly as double molecules. At lower temperatures even greater complexity is shown.

The association constant of the reaction

$$2C_2H_5COOH(g) \rightleftarrows (C_2H_5COOH)_2(g)$$

is given by the relation

$$K_z = \frac{P_{(C_2H_5COOH)_2}}{P^2_{(C_2H_5COOH)}} \tag{1}$$

where $P_{(C_2H_5COOH)_2}$ is the partial pressure of the double molecules of propionic acid, and $P_{(C_2H_5COOH)}$ is the partial pressure of the single molecules.

The number of moles of C_2H_5COOH (n_1), and of $(C_2H_5COOH)_2$ (n_2) per 100 g. of our reaction product may be calculated from this K_z and the number of moles of alcohol (n_3), of ethyl propionate (n_4), of water (n_5), and the number of formula weights of propionic acid (w). The partial pressures of $(C_2H_5COOH)_2$ and C_2H_5COOH in our products are given respectively by the equations

$$P_{(C_2H_5COOH)_2} = \frac{n_2}{n_1 + n_2 + n_3 + n_4 + n_5} \times 1 \tag{2}$$

and

$$P_{(C_2H_5COOH)} = \frac{n_1}{n_1 + n_2 + n_3 + n_4 + n_5} \times 1 \tag{3}$$

1 being the total pressure in atmospheres of these experiments. That is, each partial pressure is the product of the mole fraction and the total pressure. Substituting these values into equation 1,

$$K_z = \frac{n_2(n_1 + n_2 + n_3 + n_4 + n_5)}{n_1^2} \tag{4}$$

If G is the grams of propionic acid in the equilibrium products, then

$$G = 74.05n_1 + 148.10n_2$$

and

$$w = \frac{G}{74.05} = n_1 + 2n_2$$

or

$$n_2 = \frac{w - n_1}{2} \tag{5}$$

Upon substituting the value of n_2 (equation 5) into equation 4

$$K_x = \frac{\frac{w - n_1}{2} \cdot \left(n_1 + \frac{w - n_1}{2} + n_3 + n_4 + n_6\right)}{n_1^2}$$

from which

$$n_1 = \pm\sqrt{\frac{2w}{4K_x + 1}\left(\frac{w}{2} + n_3 + n_4 + n_6\right) + \left(\frac{n_3 + n_4 + n_6}{4K_x + 1}\right)^2} - \frac{n_3 + n_4 + n_6}{4K_x + 1} \tag{6}$$

In order that n_1 be positive, the sign preceding the square root must be positive. This expression (equation 6) may be used to find the number of single moles of propionic acid (n_1) in the equilibrium mixture from its percentage composition. The number of double moles of propionic acid (n_2) may be obtained by substituting the numerical value of n_1 into equation 5.

2. Evaluation of K_x at the temperatures of the experiments

The K_x values of table 4 were taken from the work of Miss Klein (8). From these values, K_x is given as a function of temperature by the relation (throughout this paper, $\ln = \log_e$, while $\log = \log_{10}$)

$$\log K_x = \frac{5615.87}{T} + 14.1416 \log T - 50.47295 \tag{7}$$

Substituting for T the desired temperature and solving for K_x, the results of table 5 were computed.

The values of K_x, n_1 (calculated from equation 6), n_2 (calculated from equation 5), n_3, n_4, and n_6 are listed in table 6.

B. Activities of the constituents of the mixture at equilibrium

For the esterification reaction under consideration the activity equilibrium constant K_a is

$$K_a = \frac{a_4 \times a_6}{a_1 \times a_3} \tag{8}$$

in which a_1, a_3, etc., are the activities of the acid, alcohol, ester, and water, respectively, in the equilibrium mixture.

At the low total pressure of these experiments, namely 1 atm., and the low partial pressures of the several constituents of the resulting mixture at equilibrium, it is justifiable to substitute for the activities of the alcohol, ester, and water in the gaseous mixture their mole fractions, and equation 8 becomes

TABLE 4

Values of K_x at the three different temperatures

T	372.1°	412.1°	457.1°
K_x	9.390	1.364	0.269

TABLE 5

Values of K_x at the temperatures of the experiments

T	428.1°	443.1°	457.8°	473.1°
K_x	0.7236	0.4235	0.2633	0.1681

TABLE 6

Composition of the equilibrium mixtures in moles

T IN °K.	K_x	w	n_1	n_2	n_3	n_4	n_5
428.1	0.7236	0.04218	0.04170	0.000237	0.04218	0.01035	5.211
		0.04192	0.04146	0.000234	0.04192	0.01061	5.211
		0.04231	0.04184	0.000239	0.04230	0.01022	5.211
443.1	0.4235	0.04334	0.04306	0.000140	0.04334	0.00919	5.210
		0.04328	0.04299	0.000145	0.04328	0.00925	5.210
		0.04304	0.04275	0.000145	0.04303	0.00949	5.210
		0.04308	0.04279	0.000145	0.04307	0.00945	5.210
457.8	0.2633	0.04402	0.04383	0.000095	0.04402	0.00850	5.209
473.1	0.1681	0.04486	0.04474	0.000060	0.04486	0.00767	5.208
		0.04489	0.04476	0.000065	0.04489	0.00764	5.208
		0.04474	0.04461	0.000065	0.04475	0.00779	5.208

$$K_a = \frac{N_4 \times N_5}{a_1 \times N_3} \tag{9}$$

The results of several investigators support this assumption. The experimental data used by Gibson and Sosnick (5) for mixtures of ethylene and argon indicate practical identity of fugacity and mole fraction at 1 atm. pressure, and the assumption is further justified by the experimental results obtained by Lurie and Gillespie (11) for mixtures of ammonia and nitrogen. Of more particular application, moreover, are the results of Essex and Kelly (3) for mixtures of alcohol and water which well support such an assumption. These mole fractions are

$$N_3 = \frac{n_3}{n_1 + n_2 + n_3 + n_4 + n_5}$$

$$N_4 = \frac{n_4}{n_1 + n_2 + n_3 + n_4 + n_5} \quad \text{etc.}$$

Since the gas mixture is justifiably assumed to be very nearly ideal, the partial pressure due to single molecules of propionic acid may be substituted for its fugacity or activity. This partial pressure or fugacity of the propionic acid in the equilibrium mixture may be calculated from the following relation,

$$P_1 = f = \frac{\sqrt{1 + 4KP} - 1}{2K} \tag{10}$$

In this equation K is the quantity previously indicated by K_x. The fugacity of the propionic acid gas may be calculated by substituting for K the association constant of propionic acid at the temperature of the experiment, and for P the partial pressure of the propionic acid gas, which is equal to the sum of the partial pressures of the single and double molecules, and given by the expression,

$$P_{(\text{acid})} = \frac{n_1 + n_2}{n_1 + n_2 + n_3 + n_4 + n_5} \times 1 \tag{11}$$

The values of $P_{(\text{acid})}$ and K_x of table 7, when substituted into equation 10, give the values for the fugacity of propionic acid, $f_{(\text{acid})}$, listed in this same table.

C. Equilibrium constant and standard free energy of the gaseous reaction. Heat of gaseous reaction

At any temperature, the standard free energy change, ΔF^0, of a reaction is related to the activity equilibrium constant by the equation

$$\Delta F^0 = -RT \ln K_a \tag{12}$$

By substituting the numerical values of K_a and the corresponding temperatures, the values of ΔF^0 listed in table 7 were calculated. The maximum variation in the ΔF^0 values calculated from the different K_a values given at each temperature is 1.6 per cent.

Expressing ΔF^0 as a function of temperature by means of

$$\Delta F^0 = \Delta H_0 - \Delta\Gamma_0 T \ln T + IT \tag{13}$$

and solving three simultaneous equations involving the values of ΔF^0 from the experimentally determined equilibrium constants, the following equation was obtained

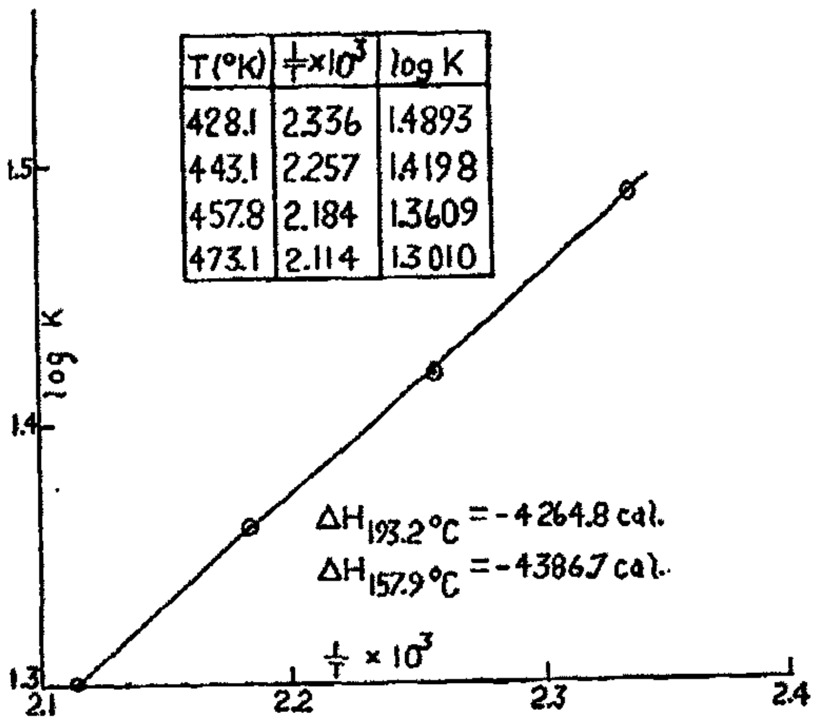
$$\Delta F^0 = -8381.03 - 10.0076T \ln T + 73.4090\,T \qquad (14)$$

From equation 14, $\Delta F^0_{298.1}$ equals −3497.8 cal., or K_a equals 365.3.

TABLE 7

Activity data and standard free energies of the gaseous reactions

T IN °K.	K_x	$P_{(acid)}$	$f_{(acid)}$	N_3	N_4	N_5	K_a	AVERAGE K_a	ΔF^0 FROM K_a
428.1	0.7236	0.007905	0.007863	0.007950	0.001951	0.9822	30.65	30.85	−2919.2
		0.007859	0.007815	0.007902	0.002000	0.9822	31.81		
		0.007932	0.007884	0.007973	0.001926	0.9822	30.09		
443.1	0.4235	0.008142	0.008115	0.008169	0.001732	0.9820	25.66	26.29	−2880.5
		0.008130	0.008103	0.008157	0.001743	0.9820	25.90		
		0.008085	0.008058	0.008111	0.001789	0.9820	26.88		
		0.008093	0.008065	0.008118	0.001781	0.9820	26.71		
457.8	0.2633	0.008279	0.008260	0.008297	0.001603	0.9818	22.96	22.96	−2852.6
473.1	0.1681	0.008444	0.008432	0.008456	0.001445	0.9817	19.90	20.00	−2818.3
		0.008449	0.008440	0.008461	0.001440	0.9817	19.79		
		0.008421	0.008409	0.008436	0.001468	0.9817	20.32		



T(°K)	$\frac{1}{T}\times 10^3$	log K
428.1	2.336	1.4893
443.1	2.257	1.4198
457.8	2.184	1.3609
473.1	2.114	1.3010

FIG. 1. Curve showing change of K_a with temperature

The heat of the reaction, ΔH, may be calculated by plotting $R \ln K_a$ against $1/T$. This has been done in the curve of figure 1. The individual points fall upon a curve which is very nearly a straight line, showing that the heat of the reaction is practically independent of the temperature.

The negative values of the slope of the curve (ΔH) at two different temperatures are listed.

Temperature, °C.	193.2	157.9
ΔH in calories	−4264.8	−4386.8

On substituting the previously determined values of ΔH_0 and $\Delta\Gamma_0$ into the integrated form of Kirchoff's equation

$$\Delta H(298.1°, g) = -5397.76 \text{ cal.}$$

D. Standard free energy change on vaporization of the liquid constituents. Heats of vaporization

The vapor pressure data of table 8 are taken from the International Critical Tables (6). From each vapor pressure the standard free energy change on vaporization was calculated from the relation

$$\Delta F^0 = -RT \ln P$$

TABLE 8

Vapor pressure data

T	VAPOR PRESSURE FOR ALCOHOL	VAPOR PRESSURE FOR ETHYL PROPIONATE
°*K.*	*mm.*	*mm.*
293.1	43.9	27.75
303.1	78.8	47.75
313.1	135.3	77.9

From the three values of ΔF^0 obtained in this manner for the vaporization of each liquid, the constants ΔH_0, $\Delta\Gamma_0$, and I were found by solving three equations of the form

$$\Delta F^0 = \Delta H_0 - \Delta\Gamma_0 T \ln T + IT \qquad (15)$$

for the unknowns. The standard free energy change on vaporization at 298.1°K. was then calculated from equation 15, and the heat of vaporization at the same temperature was calculated from the constants ΔH_0 and $\Delta\Gamma_0$ and the equation

$$\Delta H = \Delta H_0 + \Delta\Gamma_0 T$$

For alcohol, the values of the constants are: $\Delta H_0 = 14{,}359.88$; $\Delta\Gamma_0 = -13.5044$; and $I = -120.049$; and for the reaction

$$C_2H_5OH(l) \rightleftarrows C_2H_5OH(g)$$

$\Delta F^0_{(298.1)} = 1513.31$ cal. and $\Delta H_{(298.1)} = 10{,}334.22$ cal. For ethyl propionate the values of the constants are: $\Delta H_0 = 20{,}230.64$; $\Delta\Gamma_0 = -35.7028$; and $I = -265.288$; and for the reaction

$$C_2H_5COOC_2H_5(l) \rightleftarrows C_2H_5COOC_2H_5(g)$$

$\Delta F^0_{(298.1)} = 1796.93$ cal., and $\Delta H_{(298.1)} = 19{,}166.34$ cal. For the reaction

$$H_2O(l) \rightleftarrows H_2O(g)$$

the standard free energy change and heat of vaporization were taken directly from the International Critical Tables and are: $\Delta F^0_{(298.1)} = 2053$ cal. and $\Delta H_{(298.1)} = 10{,}450$ cal.

Saturated propionic acid vapor is highly associated at 298.1°K. Therefore its vapor pressure cannot be substituted for its activity nor can its fugacity be calculated by equation 10, which holds only for those conditions under which the gas consists only of single and double molecules. Essex and Clark used the following indirect method of arriving at the standard free energy change on vaporization of acetic acid at 298.1°K. First, the fugacity of the saturated vapor at each of three different temperatures for which data were available in the literature was calculated. This was done by determining the fugacity at some low pressure at each temperature by use of equation 10, and then calculating the fugacity at the saturation pressure from the relation

$$\log f_{P_2} = \frac{A}{2.303\,RT} + \log f_{P_1} \tag{16}$$

in which f_{P_2} is the fugacity at the saturation pressure of the temperature T, f_{P_1} is the fugacity at the lower pressure (calculated by equation 10), and A is the area under the P–V curve from P_1 to P_2. From the value of the fugacity of the saturated vapor, the standard free energy change on vaporization at each temperature was obtained from the relation

$$\Delta F^0 = -RT \ln f$$

From the ΔF^0 values at three different temperatures the constants in the relation

$$\Delta F^0 = \Delta H_0 - \Delta \Gamma_0 T \ln T + IT$$

were evaluated, and then it was solved for $T = 298.1$°K.

The same procedure was followed in finding the standard free energy change on vaporization at 298.1°K. for propionic acid in this investigation. However, since the data available were inadequate for these calculations, it was necessary to extend them by some further experimental measurements. Miss Klein's (8) α–P curve $\left(\alpha = \frac{RT}{P} - V\right)$ for propionic acid at 99°C. covers a pressure range from 84 mm. to 135.2 mm., and that at 139°C. covers a range from 111.7 mm. to 525.3 mm. Using the method of Blackman (1), P–V measurements were made at each of these temperatures to extend these α–P curves up to the respective saturation pressures (173.4 mm. at 99°C., and 738.3 mm. at 139°C.). The 2.5 per cent to 3.0

per cent accuracy attained in these measurements was considered quite sufficient for the purpose of this calculation, since a slight error in the extension of the curve would make little difference in the total value of the area under the curve, which is itself a relatively small factor in equation 16. The α–P curve for a third temperature, 117°C., was also obtained by making experimental P–V measurements at the higher pressures up to the saturation pressure of 345.3 mm., and by calculating the molal volumes at the lower pressures from the relation

$$V = \frac{RT}{2P} + \frac{1}{2}\left(\frac{1}{4KP + 1}\right)^{\frac{1}{2}} \times \frac{RT}{P}$$

This relation should hold accurately at low pressures where only single and double molecules exist and where the gas laws hold accurately.

TABLE 9

Fugacities of propionic acid at saturation pressures

T	P_1	P_2	K_x	A	P_1	P_2
°K.	*atm.*	*atm.*		*liter-atm.*		
372.1	0.1779	0.2282	9.390	2.7537	0.0942	0.1104
390.1	0.1316	0.4543	3.685	9.4979	0.0969	0.2487
412.1	0.6579	0.9714	1.364	3.4346	0.4140	0.5523

From the α–P curve and the fugacity at some low pressure (calculated by equation 10) the fugacity at the saturation pressure was calculated at each of the three temperatures, 99°C., 117°C., and 139°C., by the relation

$$\ln f_2 - \ln f_1 = \ln P_2 - \ln P_1 - \frac{1}{RT}\int_{P_1}^{P_2} \alpha\, dP$$

where

$$\alpha = \frac{RT}{P} - V$$

and V is the molal volume at the temperature T. The data and results of these calculations appear in table 9, where A is the area under the α–P curve from P_1 to P_2, or the quantity

$$\int_{P_1}^{P_2} \alpha dP$$

By the procedure Essex and Clark used in their calculations on acetic acid, the following standard free energy changes on vaporization of propionic acid at the three different temperatures were obtained: $\Delta F^0_{372.1} = 1630.8174$; $\Delta F^0_{390.1} = 1079.4960$; and $\Delta F^0_{412.1} = 486.5631$. From these the constants in the following equation were evaluated

$$\Delta F^0 = 40{,}691.434 + 72.5895T \ln T - 534.720T$$

from which, for the reaction

$$C_2H_5COOH(l) \rightleftarrows C_2H_5COOH(g)$$

$\Delta F^0_{298.1} = 4599.79$ cal. and $\Delta H_{298.1} = 19{,}052.50$ cal.

E. Standard free energy change of the liquid reaction. Free energy of formation of ethyl propionate

1. Standard free energy change of the liquid reaction

By combining algebraically the vaporization equation of each pure constituent and the esterification reaction in the gaseous state, the standard free energy change for the esterification reaction in the liquid state may be calculated.

$$\begin{aligned}
C_2H_5COOH(g) + C_2H_5OH(g) &= C_2H_5COOC_2H_5(g) \\
&\quad + H_2O(g) & \Delta F^0_{298.1} &= -3497.8 \text{ cal.} \\
C_2H_5OH(l) &= C_2H_5OH(g) & \Delta F^0_{298.1} &= 1513.3 \text{ cal.} \\
C_2H_5COOH(l) &= C_2H_5COOH(g) & \Delta F^0_{298.1} &= 4599.8 \text{ cal.} \\
C_2H_5COOC_2H_5(g) &= C_2H_5COOC_2H_5(l) & \Delta F^0_{298.1} &= -1796.9 \text{ cal.} \\
H_2O(g) &= H_2O(l) & \Delta F^0_{298.1} &= -2053.0 \text{ cal.} \\
\hline
C_2H_5OH(l) + C_2H_5COOH(l) &= C_2H_5COOC_2H_5(l) \\
&\quad + H_2O(l) & \Delta F^0_{298.1} &= -1234.6 \text{ cal.}
\end{aligned}$$

or $K_{a(298.1,\ l)}8.03$.

2. Free energy of formation of ethyl propionate

From heat capacity measurements at low temperatures, Parks and his coworkers (12) have computed, with the aid of the third law of thermodynamics, the standard free energy of formation of ethyl alcohol to be $-42{,}200$ cal. From the results of similar computations for several acids they suggest the equation

$$\Delta F^0_{298} = -96{,}000 + 1080n$$

for obtaining the molal free energy of formation in the liquid state of a normal, saturated, aliphatic acid containing n carbon atoms. From this equation, $\Delta F^0_{298} = -92{,}760$ cal. for propionic acid.

The standard free energy of formation of water has been calculated by Lewis and Randall (10) and found to be $-56{,}560$ cal. at 298.1°K.

Using these values, the standard free energy of formation of ethyl propionate was calculated to be $-79{,}634.6$ cal. at 298.1°K.

F. Heat of the liquid reaction

The heat of the reaction in the liquid state was obtained at 298.1°K. from the heats of vaporization of the various constituents as previously calculated, and the ΔH for the reaction taking place in the gaseous state. Combining these algebraically

$$\begin{aligned}
C_2H_5COOH(g) + C_2H_5OH(g) &= C_2H_5COOC_2H_5(g) \\
&\quad + H_2O(g) \quad \Delta H_{298.1} = -5{,}397.8 \text{ cal.} \\
C_2H_5COOH(l) &= C_2H_5COOH(g) \quad \Delta H_{298.1} = 19{,}052.5 \text{ cal.} \\
C_2H_5OH(l) &= C_2H_5OH(g) \quad \Delta H_{298.1} = 10{,}334.2 \text{ cal.} \\
C_2H_5COOC_2H_5(g) &= C_2H_5COOC_2H_5(l) \\
&\quad \Delta H_{298.1} = -19{,}166.3 \text{ cal.} \\
H_2O(g) &= H_2O(l) \quad \Delta H_{298.1} = -10{,}450.0 \text{ cal.} \\
\hline
C_2H_5COOH(l) + C_2H_5OH(l) &= C_2H_5COOC_2H_5(l) \\
&\quad + H_2O(l) \quad \Delta H_{298.1} = -5{,}627.4 \text{ cal.}
\end{aligned}$$

Kharasch (7) made a general and critical review of the data to be found in the literature for heats of combustion. By using the data of his choice the heat of the esterification reaction in the liquid state was calculated as follows:

$$\begin{aligned}
C_2H_5OH + 3O_2 &= 2CO_2 + 3H_2O & \Delta H &= -326{,}660 \text{ cal.} \\
C_2H_5COOH + 3\tfrac{1}{2}O_2 &= 2CO_2 + 3H_2O & \Delta H &= -367{,}200 \text{ cal.} \\
5CO_2 + 5H_2O &= C_2H_5COOC_2H_5 + 6\tfrac{1}{2}O_2 & \Delta H &= 690{,}800 \text{ cal.} \\
\hline
C_2H_5OH + C_2H_5COOH &= C_2H_5COOC_2H_5 + H_2O & \Delta H &= -3{,}060 \text{ cal.} \\
& & &\text{at } 298.1^\circ\text{K.}
\end{aligned}$$

Kharasch estimated that the figures to be found in the literature for the heats of combustion may be in error by 1.0 to 1.5 per cent. It is to be noted that the value of the heat of the esterification reaction calculated from the heats of combustion of the several constituents of the reaction agrees with the heat of the reaction calculated from the equilibrium constants determined in this work, within the 1.0 per cent error involved in the heat of combustion data.

G. Entropy of ethyl propionate

Because of the 1 per cent error that may exist in the determined value of the heat of combustion of ethyl propionate, the entropy of ethyl propionate calculated by means of the equation

$$\Delta F^0 = \Delta H - T\Delta S^0$$

can be considered as no more than an approximation. Using −121,950 cal. as the heat of formation of ethyl propionate

$$\Delta S^0_{298.1} = -141.95 \text{ cal.}$$

and

$$S_{298.1} = 70.04$$

DISCUSSION

It is believed that the heat of this reaction calculated from the temperature coefficient of the free energy change is considerably more accurate than that calculated from the data on heats of combustion. It is significant to note that for the esterification of acetic acid and ethyl alcohol studied by Essex and Clark, the more accurate combustion data for alcohol now available (13) give a heat of reaction much closer to the value they determined. Thus, ΔH for the liquid reaction as determined by Essex and Clark is 4795 cal.; from combustion data available at the time of their work it is 1630 cal.; using the more accurate combustion data for alcohol now available it is 3520 cal.

Moreover, the free energy change for this esterification reaction determined by this method should exceed appreciably in accuracy values which may be obtained, when all the data are available, from the entropies or free energies of the reactants and resultants, for the following reasons:

(1) Kürti (9) and Giauque (4), who have attained very low temperatures by means of the demagnetization of paramagnetic substances, have obtained a C_p-T curve at low temperatures for $Gd_2(SO_4)_3 \cdot 8H_2O$ which is very different from the curve obtained by extrapolation using the Debye formula. Hence it appears that entropy values calculated by use of the area under such extrapolated curves may be appreciably in error.

(2) In getting the free energy of formation of each compound from the relation

$$\Delta F = \Delta H - T\Delta S$$

ΔF is the difference between two quantities which are often of comparable magnitude, resulting in a large percentage error in ΔF.

(3) In obtaining the free energy change for the reaction from the relation

$$\Delta F = (\Delta F_3 + \Delta F_4) - (\Delta F_1 + \Delta F_2)$$

ΔF is again the difference between two quantities of comparable magnitude for reactions which reach an easily measurable equilibrium, and is therefore subject to a large percentage error. On the other hand, this same situation must make for a small percentage error in the value of the free energy of any one of the reactants or resultants obtained from a determined value of the free energy change of the reaction by use of the above relation.

SUMMARY

1. Equilibrium has been reached in the gaseous phase for the system propionic acid, ethyl alcohol, ethyl propionate, and water, approaching it by a dynamic method from both sides at three temperatures, 428.1°K., 443.1°K., and 473.1°K.

2. The activity ratio K_a has been calculated by means of the gaseous state equilibria to be:

T, °K	298.1	298.1	428.1	443.1	473.1
State	Liquid	Gas	Gas	Gas	Gas
K_a	8.03	365.3	30.85	26.29	20.00

3. The standard free energy changes for the esterification reaction calculated from the determined activity ratios are:

T, °K	298.1	298.1	428.1	443.1	473.1
State	Liquid	Gas	Gas	Gas	Gas
ΔF^0, cal	−1234.6	−3497.8	−2919.2	−2880.5	−2818.3

The standard free energy of formation of ethyl propionate in the liquid state at 298.1°K. is calculated to be −79,634.6 calories.

4. From the curve for the change of K_a with temperature, the heat of the esterification reaction has been calculated for the gaseous state at 431.0°K. and 466.3°K. For 298.1°K. it was calculated from Kirchoff's equation for the gaseous state, and from the vapor pressure and heat of the gaseous reaction for the liquid state.

T, °K	298.1	298.1	431.0	466.3
State	Liquid	Gas	Gas	Gas
ΔH, cal	−5627.4	−5397.8	−4386.7	−4264.8

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THE THERMAL CHEMISTRY OF *d*-GLUCOSE AND OTHER GLUCOSE SUGARS IN SODIUM HYDROXIDE SOLUTIONS

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A great many methods of studying the behavior of sugars in solutions have been used by students of sugar chemistry. A very complete catalogue and bibliography of such techniques has but recently been published (13). The authors wish to suggest in this paper still another plan of following the changes of sugars in solution.

Some work on the thermal properties of glucose and its derivatives, reported previously (1), gives values for the heats of solution (9, 14), and some earlier workers (2, 4) attempted to measure the heat of mutarotation of glucose. Evans and students (6) have varied the concentration of alkali used and the temperature of the reaction in an effort to interpret the mechanism of such reactions. In this study the concentration of the alkali in which the sugar was dissolved was varied, and the quantity of heat evolved was measured for each variation.

METHOD, APPARATUS, AND SUGARS USED

The measurements here reported were made in an adiabatic calorimeter in a manner much as previously described (11, 6). However, instead of placing water in the Dewar flask, sodium hydroxide solution of the proper concentration was placed in it. The reciprocating stirrer used did not appreciably agitate the surface of the solution, consequently the air present in the solution was scarcely more than that which entered by diffusion. As the concentration of the alkali solution became greater, a heat of stirring was noted. Proper corrections were applied, in such cases, to the temperature data for this energy. At the higher concentrations some heat was evolved after the principal evolution of heat had stopped. It was not difficult to determine the point of inflection between the temperature-time curve of this second evolution of heat and the temperature-time curve resulting from the first introduction of the sugar. Such point of inflection was always considered the end of the reaction, thermally speaking. The average times of reaction for the sugars were as follows: *d*-glucose, 38 min.; *α*-*d*-glucose, 30 min.; *β*-*d*-glucose, 33 min.; and *α*-methyl-*d*-glucoside, 29 min., although six of the twelve experiments with this glucoside were of only 10 min. duration.

The *d*-glucose, *β*-*d*-glucose, and *α*-methyl-*d*-glucoside were prepared and had the properties previously described (9). The *α*-*d*-glucose had a rotation of $[\alpha]_D^{20^\circ} = +110.1$ and was prepared by the method of Hudson and Dale (12). (Throughout this paper wherever the term "*d*-glucose" is used the equilibrium mixture with $[\alpha]_D^{20^\circ} = 52.5$ is meant.) The sodium hydroxide solutions were prepared from Mallinckrodt's C.P. quality stick sodium hydroxide in carbonate-free water.

TABLE 1

Heat of reaction of crystalline d-glucose with sodium hydroxide at 25.2° ± 0.3°C.

EXPERIMENT NO.	ALKALI NORMALITY	Δt	W_1 WEIGHT OF SUGAR SAMPLE	W_2 WEIGHT OF ALKALI SOLUTION	CALCULATED HEAT OF REACTION	AVERAGE HEAT OF REACTION	ALKALI ABSORBED PER MOLE OF SUGAR	HEAT OF NEUTRALIZATION OF ABSORBED ALKALI
	N	*°C.*	*grams*	*grams*	*Cal. per mole*	*Cal. per mole*	*moles*	*Cal. per mole*
90	0.483	0.0673	3.76	997	6.14	6.15	0.055	0.7
91	0.483	0.0629	3.47	986	6.16			
92	0.996	0.0732	3.29	1013	6.65	6.61	0.295	4.1
93	0.996	0.0478	2.28	1021	6.57			
94	1.988	0.0746	3.26	1039	7.06	7.03	0.558	7.7
95	1.988	0.0801	3.55	1037	6.99			
96	3.054	0.0725	3.14	1094	7.28	7.27	1.242	17.0
97	3.054	0.0493	2.12	1089	7.26			
98	4.635	0.0517	2.15	1146	8.07	8.06	1.134	15.6
105	4.635	0.0428	1.57	1099	8.03			
137	6.229	0.0330	1.09	1188	8.95	8.99	0.990	13.6
128	6.229	0.0322	1.05	1190	9.02			

EXPERIMENTAL

The heat capacity of the calorimeter vessel (10) was 123.3 cal. This value was checked by an alternative method, using the heat of neutralization of sodium hydroxide by hydrochloric acid at 25°C. (16). The heat of reaction is defined in kilogram-calories per mole of sugar. It is calculated as the total heat of the reaction corrected for heat of solution (9, 10) of the sugar under test.

The heats of reaction of *d*-glucose with sodium hydroxide solutions of varying concentration are given in table 1. After a determination for each alkali concentration a measured volume of the alkali–sugar solution was titrated against standard hydrochloric acid for alkali absorption. In the last column of the table the heat of neutralization of the alkali so absorbed per mole of sugar is listed, using 13,721 gram-cal. per mole as the heat of formation of water from its ions (17).

TABLE 2

Heat of reaction of α-d-glucose with sodium hydroxide at 25.1° ± 0.3°C.

EXPERIMENT NO.	ALKALI NORMALITY	Δt	W_1 WEIGHT OF SUGAR SAMPLE	W_2 WEIGHT OF ALKALI SOLUTION	CALCULATED HEAT OF REACTION	AVERAGE HEAT OF REACTION	ALKALI ABSORBED PER MOLE OF SUGAR	HEAT OF NEUTRALIZATION OF ABSORBED ALKALI
	N	°C.	*grams*	*grams*	*Cal. per mole*	*Cal. per mole*	*moles*	*Cal. per mole*
133	0.247	0.0477	3.21	994	5.47	5.49	0.072	0.99
134	0.247	0.0468	3.11	995	5.51			
26	0.523	0.0488	2.20	1010	6.56	6.48	0.216	2.96
25	0.523	0.0497	2.35	1010	6.48			
24	0.523	0.0444	2.15	1010	6.41			
22	1.039	0.0474	2.50	1032	6.66	6.67	0.378	5.18
21	1.039	0.0407	2.15	1027	6.68			
20	2.124	0.0451	2.34	1067	6.93	6.91	0.648	8.91
19	2.124	0.0500	2.25	1071	6.95			
18	2.124	0.0551	2.52	1069	6.86			
16	3.145	0.0490	2.22	1105	7.01	6.99	1.368	18.77
15	3.145	0.0474	2.17	1111	6.97			
14	4.691	0.0496	2.19	1158	7.22	7.23	1.008	13.82
13	4.691	0.0513	2.22	1137	7.24			
12	4.691	0.0510	2.18	1114	7.22			
11	6.045	0.0471	2.28	1188	7.42	7.44	0.738	10.12
10	6.045	0.0613	2.28	1026	7.47			
9	6.045	0.0597	2.38	1093	7.42			
7	7.550	0.0621	2.07	1147	8.34	8.40	0.738	10.12
6	7.550	0.0600	2.06	1203	8.41			
5	7.550	0.0555	1.95	1231	8.39			

TABLE 3

Heat of reaction of β-d-glucose with sodium hydroxide at 25.1° ± 0.3°C.

EXPERIMENT NO.	ALKALI NORMALITY	Δt	W_3 WEIGHT OF SUGAR SAMPLE	W_2 WEIGHT OF ALKALI SOLUTION	CALCULATED HEAT OF REACTION	AVERAGE HEAT OF REACTION	ALKALI ABSORBED PER MOLE OF SUGAR	HEAT OF NEUTRALIZATION OF ABSORBED ALKALI
	N	*°C.*	*grams*	*grams*	*Cal. per mole*	*Cal. per mole*	*moles*	*Cal. per mole*
135	0.247	0.0584	2.61	996	5.47	5.47	0.072	0.99
136	0.247	0.0692	3.11	997	5.46			
27	0.523	0.0518	2.14	1010	6.52	6.46	0.216	2.96
28	0.523	0.0513	2.04	1005	6.39			
29	0.523	0.0476	2.03	1008	6.48			
30	1.039	0.0547	2.09	1026	6.65	6.65	0.486	6.67
31	1.039	0.0528	2.11	1025	6.65			
33	2.124	0.0649	2.20	1064	6.88	6.87	0.594	8.15
34	2.124	0.0641	2.19	1071	6.86			
35	3.145	0.0591	2.01	1110	7.01	6.99	1.224	16.74
36	3.145	0.0592	2.03	1110	6.97			
37	4.691	0.0658	2.22	1160	7.19	7.19	0.990	13.58
38	4.691	0.0683	2.30	1155	7.19			
39	6.045	0.0630	2.09	1195	7.38	7.39	0.810	11.11
40	6.045	0.0635	2.11	1195	7.40			
131	7.542	0.0693	2.01	1218	8.36	8.32	0.550	7.54
132	7.542	0.0626	1.84	1221	8.28			

TABLE 4

Heat of reaction of α-methyl-d-glucoside with sodium hydroxide at 25.2° ± 0.3°C.

EXPERIMENT NO.	ALKALI NORMALITY	Δt	W_3 WEIGHT OF SUGAR SAMPLE	W_2 WEIGHT OF ALKALI SOLUTION	CALCULATED HEAT OF REACTION	AVERAGE HEAT OF REACTION	ALKALI ABSORBED PER MOLE OF SUGAR
	N	*°C.*	*grams*	*grams*	*Cal. per mole*	*Cal. per mole*	*moles*
55	0.525	0.0072	2.64	961	1.17	1.17	None
56	0.525	0.0074	2.76	962	1.16		
53	1.039	0.0126	2.51	1021	1.67	1.68	None
54	1.039	0.0129	2.53	1009	1.68		
57	2.124	0.0201	2.42	1035	2.35	2.35	None
58	2.124	0.0203	2.45	1044	2.35		
59	3.145	0.0219	2.47	1097	2.52	2.53	None
60	3.145	0.0234	2.62	1097	2.54		
61	4.692	0.0245	2.55	1131	2.72	2.72	None
62	4.692	0.0252	2.66	1159	2.72		
63	6.045	0.0294	2.47	1148	3.22	3.22	None
64	6.045	0.0318	2.67	1148	3.22		

Tables 1 to 4 give the following data: the normality of the alkali; Δt, the change in temperature; W_s, the weight of the sugar sample; W_a, the weight of alkali solution used; the calculated heat of reaction; the average heat of reaction; the moles of alkali absorbed per mole of sugar; and the heat of neutralization of the absorbed alkali per mole of sugar.

DISCUSSION

The quantity of sodium hydroxide absorbed in each experiment was determined in an effort to account for the heat evolved in the reaction. A study of tables 1, 2, and 3 and figure 1 suggests three energy factors operating in these experiments: one, which is exothermic, in the absorption or neutralization of the sodium hydroxide; another which, at lower alkali concentrations, is of sufficient exothermic magnitude to add to the heat of neutralization of the alkali; and a third, evident above 2 *N* alkali concentration, which is sufficiently endothermic to render the heat of reaction less than the heat of neutralization. Another indication of the character of the changes in the sugar at higher alkali concentrations is the drop in alkali absorption above 3 *N* concentration. One interpretation of this drop may be that it is due to a decrease in the amount of hydrogen-ion-yielding products formed in the alkali–sugar reactions.

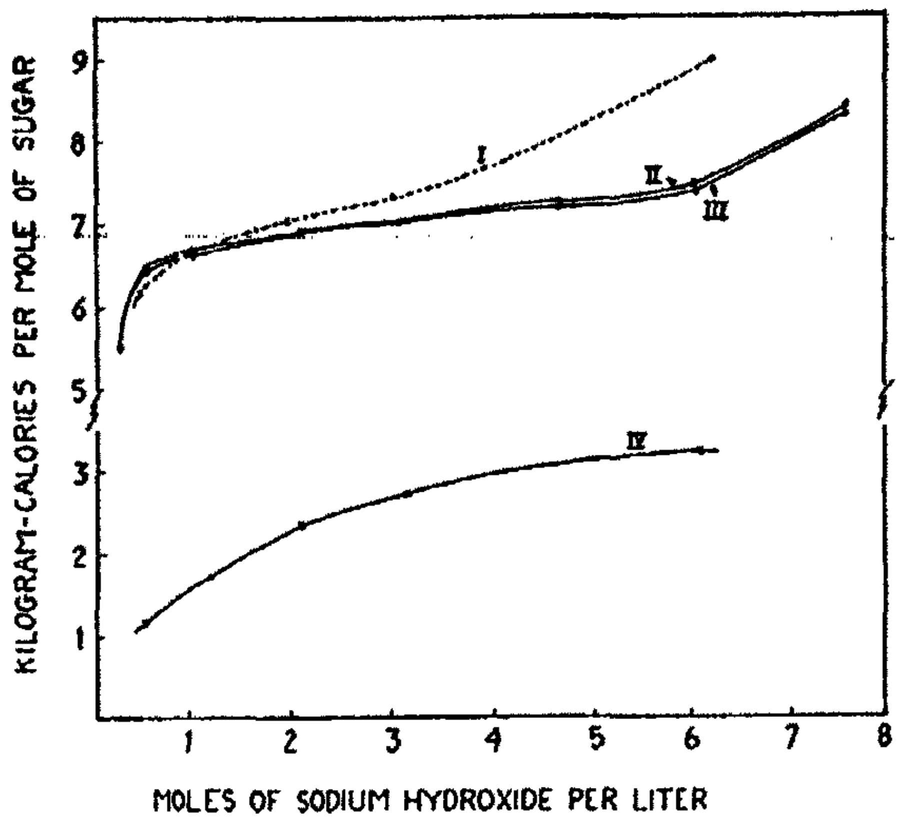

FIG. 1. Summary of the heats of reaction curves. I, crystalline *d*-glucose; II, crystalline α-*d*-glucose; III, crystalline β-*d*-glucose; IV, crystalline α-methyl-*d*-glucoside.

The work of Shaffer, Urban, and Williams (20, 21) quite definitely shows *d*-glucose as a source of hydrogen ions in water solutions. Their work also states that α-methyl-*d*-glucoside exhibits no acidity (21), just as table 4 indicates no alkali absorption. It is not possible to use their data in checking this work, however, since their lowest concentration of sugar was 0.1 *M*, while the highest concentration used here was 0.017 *M*.

The increased heat of reaction with increased alkalinity for the first three sugars studied may, in part at least, be attributed to the following factors: (*1*) greater interconversion of the de Bruyn and van Ekenstein type at higher alkalinity (5), and (*2*) the increased tendency to form products of the saccharinic acid type at the higher alkalinities with the resulting greater heat of neutralization of the hydrogen ion.

In relation to the first of the above suggestions, the heats of reaction of *d*-mannose ($[\alpha]_{D}^{20°} = -14.3$) and *d*-fructose ($[\alpha]_{D}^{20°} = -91.7$) with 3 *N* to 6 *N* sodium hydroxide solutions have been found (18) to be 1.14 ± 0.16 Cal. per mole and 3.19 ± 1.06 Cal. per mole, respectively, greater than that of *d*-glucose ($[\alpha]_{D}^{20°} = 52.5$) under the same conditions. An examination of the papers of de Bruyn and van Ekenstein (5) indicates a larger conversion of *d*-glucose to *d*-mannose and *d*-fructose at higher concentrations of the alkali. The application of this fact to this study would seem justifiable.

The increased heat of reaction of α-methyl-*d*-glucoside with increased alkalinity may not be accounted for as above. The fact that its rather constant heat of reaction is less than that of *d*-glucose, α-*d*-glucose, and β-*d*-glucose may be attributed to its negligible formation of hydrogen ions. It would seem that the acidity found by Shaffer, Urban, and Williams must be due largely to the first carbon atom of the sugar molecule, since the methyl group has so completely depleted such ionization.

The heat of reaction of α-*d*-glucose (in table 2) is an average of 0.03 Cal. per mole more than that of β-*d*-glucose (table 3). While this difference is not significantly greater than the experimental error of these measurements, it is a difference which, if found at all, always shows a greater heat of reaction for α-*d*-glucose.

Recent investigations indicate that there is a measurable heat of mutarotation of β-*d*-glucose to α-*d*-glucose. Isbell and Pigman (13) report the specific rotation for *d*-glucose in water solution to be $[\alpha]_{D}^{20°} = 52.7$ and $[\alpha]_{D}^{0.2°} = 52.1$. This would indicate that there is a heat of mutarotation of 0.06 Cal. per mole absorbed by the β-form in changing to the α-form Sturtevant (19), by direct calorimetric measurement, gives the heat of mutarotation for α-*d*-glucose, in 5×10^{-5} *N* hydrochloric acid, as 0.16 Cal. per mole. While these values do not agree quantitatively, they do support each other as to the existence and the sign, i.e., direction of absorption, of this energy factor. In an analysis of heats of reaction in this investigation this factor should be considered.

The foregoing interpretation does not account for the difference in the heats of the reaction of *d*-glucose as compared with those of α-*d*-glucose and β-*d*-glucose. If *d*-glucose, as has been generally considered, is purely an equilibrium mixture of the α- and β-*d*-glucoses, then there is no reason to expect any difference between energies of reactions for any two of these sugars. But the findings of this research do not present such an identity. The authors consider this failure of their data to support such an identity to warrant doubt that *d*-glucose is as simple as a two-component system. In a previous communication (9) they pointed out that the heat of solution for crystalline *d*-glucose ($[\alpha]_D^{20°} = 52.5$) does not duplicate the heat of solution of the generally accepted 2:1 mixture of β-*d*-glucose with α-*d*-glucose. They submit these two independent sets of data as warrant for more than a passing interest in the statement (15): "we must suppose that the proportion of furanose sugar is by no means negligible even in solutions from which only alpha and beta pyranose sugars can be separated by crystallization."

Changes due to oxidations, other than autoöxidation, are not considered of importance in these experiments for two reasons: first, the duration, 30 min. more or less, of the individual runs at the highest alkalinity, 6 *N*, is known (3) to destroy less than 0.5 per cent of the sugar even if air is bubbled continuously through the solution. This per cent would obviously be much less at lower concentrations and would probably, in no case, be that great, since air by diffusion into the solution would be much less than if it were forced through, as was the case in Boschult's work. Second, the bromine oxidation rate of β-*d*-glucose is about thirty times that of α-*d*-glucose (13). The authors, in this research, found no appreciable difference in the reaction rates for these two sugars. This means that if there is any oxidation in these reactions its effect is entirely masked by other factors. They recognize that oxidations by air (3) or copper acetate (7) are much less rapid than by bromine (13), which would, in turn, minimize the energy contribution of this factor in these experiments.

SUMMARY

1. Heats of reaction with sodium hydroxide, at six or more different alkali concentrations, have been determined for *d*-glucose, α-*d*-glucose, β-*d*-glucose, and α-methyl-*d*-glucoside.

2. Heats of reaction for all four sugars increase with increased alkali concentration.

3. Heats of reaction for α-*d*-glucose are consistently, though only slightly, higher than those for β-*d*-glucose.

4. Heats of reaction for *d*-glucose at alkali concentrations above 2 *N* are increasingly greater with increasing alkali concentration than those of α-*d*-glucose and β-*d*-glucose.

5. The heats of reaction for α-methyl-*d*-glucose for all concentrations of the alkali above 0.5 *N* are 4.52 ± 0.42 Cal. per mole less than the corresponding heats of reaction of the α- and β-*d*-glucoses.

6. Salt formation with the alkali seems to be the major source of the heat measured.

7. Increased heat of reaction with increased alkali concentration is attributed to influence of alkali upon the de Bruyn–van Ekenstein interconversion of *d*-glucose, *α*-*d*-glucose, and *β*-*d*-glucose.

8. The departure of the heats of reaction for *d*-glucose from those of the *α*- and *β*-*d*-glucoses is considered possible evidence for other components than the *α*- and *β*-*d*-glucoses in crystalline *d*-glucose.

9. The adiabatic calorimeter is recommended for use along with the polarimeter, the dilatometer, and the refractometer in the study of sugar solutions and their reactions.

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ALKALI ADSORPTION BY SYNTHETIC RESINS

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In spite of the great industrial importance and common use of the phenol-formaldehyde resins, it was not until 1935 that attention was drawn to their adsorptive properties and possible use as water softeners (1). This appears somewhat surprising, since it might be expected that some, at least, of the phenolic hydroxyl groups will remain active after condensation, serving as active centers for adsorption. Thus, although attention had been called to the amphoteric properties of phenol-formaldehyde resins (9), and Shono (11) had examined the behavior of metallic salts reacting with phenolic resins to give colored products, the first systematic adsorption experiments were made by Adams and Holmes (1), using a flow method. The solution under examination was allowed to pass down a column packed with the resin, and, although difficulties due to channelling made the results only semiquantitative in nature, strong selective adsorption in acid solution was shown by catechol, resorcinol, quinol, pyrogallol, and catechin resins and general adsorption by phloroglucinol and quebracho tannin resins. In alkaline solution marked adsorption of cations occurred, varying considerably with the nature of the phenol present. Amine-formaldehyde resins showed adsorption in acid solution. Ellis (4) has stated that a wide variety of phenols of high molecular weight and of natural origin may be condensed with formaldehyde to give products which will remove cations from dilute aqueous solution. Complete removal of dissolved salts, therefore, may be accomplished by treatment with a phenolic resin to remove cations followed by an amine-aldehyde resin to remove anions (1). Since many of the resins can be produced at economical prices, their application to water treatment is obvious and appears to have commercial possibilities. The present investigation was an attempt to elucidate the mechanism of the adsorption process and the relation of the molecular structure of the resins to their adsorptive power. For this purpose the adsorption and rates of adsorption of calcium hydroxide and three other bases by simple mono-, di-, and tri-hydroxy phenol resins were measured. The results should be

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of value in the study of resins made from more complex, naturally occurring phenols, which are of greater utility in commercial water softening.

PROCEDURE

A. *Preparation of resins*

Two parts[2] of phenol, 20 parts of water, and 4 parts of formalin (40 per cent) were heated to boiling and 1 part of concentrated hydrochloric acid in 2 parts of water was added. The resin separated almost immediately and was filtered and washed, first with boiling water, then with aqueous calcium hydroxide solution until the filtrate became colorless. The resin was regenerated by washing several times with 5 per cent hydrochloric acid, followed by water, alcohol and ether. After drying at 100°C. it was crushed and graded through 48 mesh on to 200 mesh.

In most preparations the resin was precipitated on 2 parts of kieselguhr, added to the mixture before the catalyst. Subsequent procedure was the same as for the pure resin, but analyses were made for water and organic content. The presence of kieselguhr resulted in a smaller loss in fines on grading the resin.

B. *Adsorption measurements*

A known quantity of resin was weighed out into a bottle and a known amount of standard calcium hydroxide or other solution added. After agitation for a measured time on a rotary shaker at room temperature (25° ± 2°C.), the solution was filtered and analyzed. Blanks were run to determine any adsorption by the kieselguhr. This was small, of the order of 0.012 g. of calcium per gram of kieselguhr. This was allowed for when calculating the amount of adsorption. Results were reproducible, within 3 per cent, on different samples of a resin as well as on the same sample and are expressed as millimoles per gram of resin in all cases.

VARIATION OF ADSORPTION WITH ALKALINITY

Adams and Holmes (1) found that the simple phenolic resins did not appear to adsorb cations from neutral solution. Phenol, quinol, catechol, and resorcinol resins behaved similarly with calcium sulfate solution. Even after agitation for three months the adsorption by catechol resin from 0.01 *M* calcium sulfate was only 0.15 millimole per gram of resin.

RATE OF ADSORPTION

Adsorption is relatively slow, apparently becoming almost complete after about seven days, but probably proceeding very slowly over a period of months. In figure 1 are represented the results obtained for various

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[2] All parts are parts by weight.

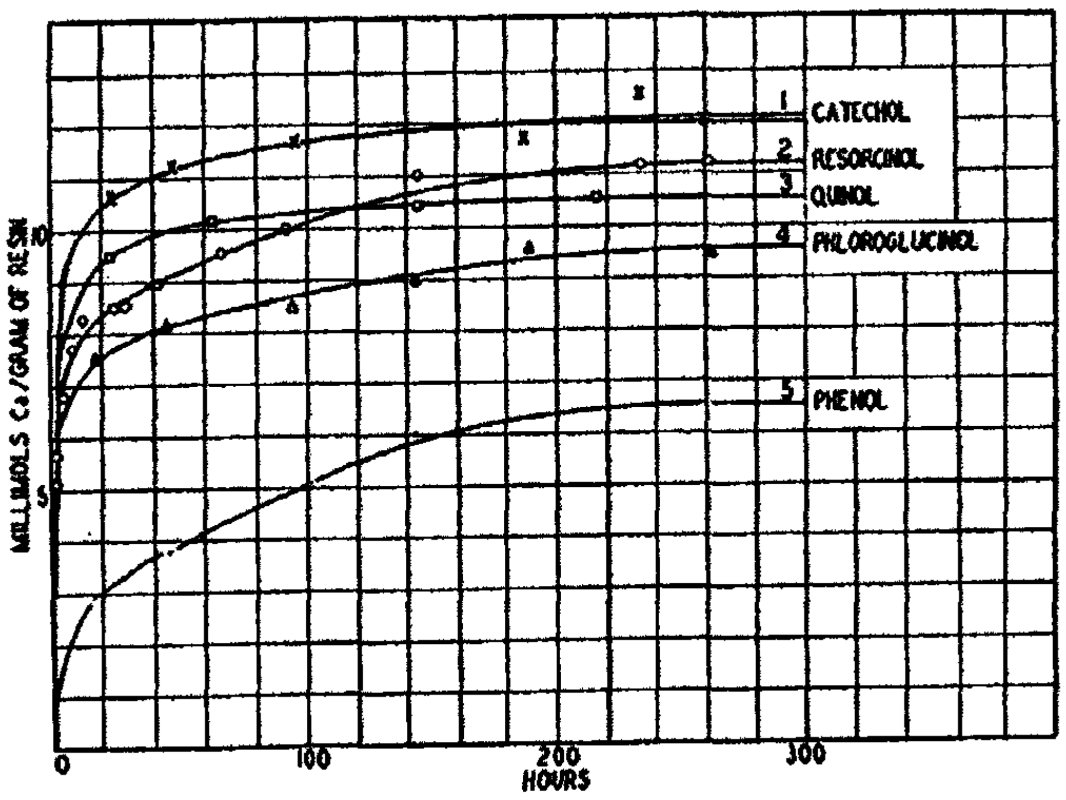


FIG. 1. Rate of adsorption of calcium hydroxide by various resins

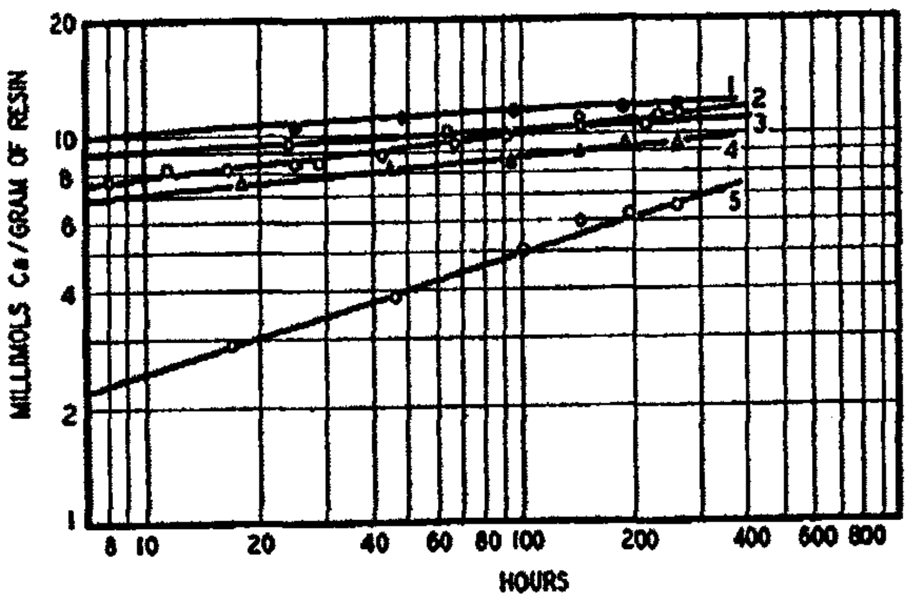


FIG. 2. Adsorption of calcium hydroxide by various resins

TABLE 1

Rates of adsorption by different resins

RESIN	k	n	EQUILIBRIUM ADSORPTION
			millimoles per gram of resin
Resorcinol	11.8	0.12	11.2
Quinol	17.0	0.042	10.5
Catechol	18.1	0.054	12.1
Phloroglucinol A	12.0	0.081	9.6
Phloroglucinol B	10.8	0.068	7.9
Phenol	2.7	0.29	6.25(approx.)

resins and calcium hydroxide solution. In all these experiments a quantity of sorbent, corresponding to 0.27 g. of resin after correcting for the kieselguhr content, and 500 cc. of 0.0198 *N* calcium hydroxide were taken. The curves, as seen from figure 2, can be represented by an equation of the usual type (6)

$$x/m = kt^n$$

where x/m is the adsorption in millimoles of calcium per gram of resin, t is the time of adsorption, and k and n are constants. The values of the constants k and n and the equilibrium adsorptions (i.e., the adsorptions at infinite time read from figure 1) for the various resins are tabulated in table 1. Results obtained for a resorcinol resin (table 2) appear to indicate that slow adsorption does occur even after three hundred hours. The equilibrium adsorption value is raised somewhat and is independent of concentration.

TABLE 2

Adsorption of calcium hydroxide by a resorcinol resin

0.5175 g. of resin (0.270 g. of organic content) agitated with 500 cc. of calcium hydroxide solution for three months

INITIAL CONCENTRATION OF CALCIUM HYDROXIDE	FINAL CONCENTRATION OF CALCIUM HYDROXIDE	x/m
millimoles of Ca *per liter*	*millimoles of* Ca *per liter*	
99.0	26.2	13.5
148.5	74.5	13.7
198.0	125.0	13.6

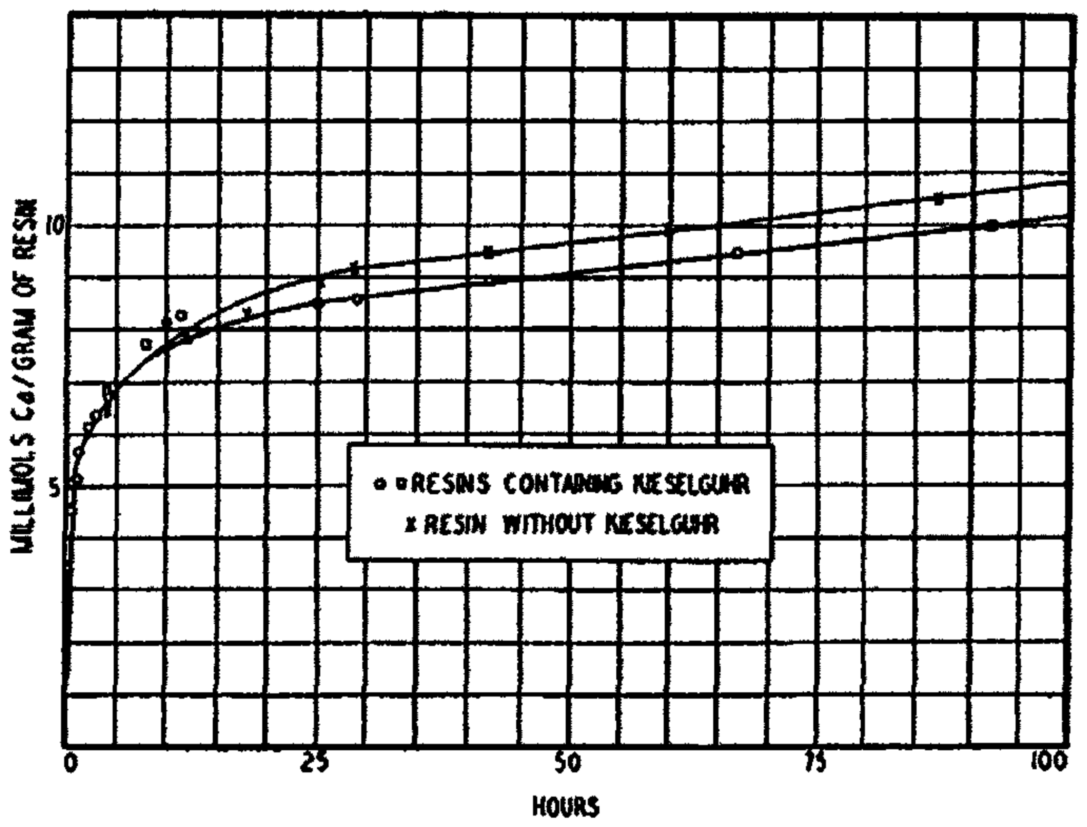


FIG. 3. Adsorption of calcium hydroxide by resins with and without kieselguhr

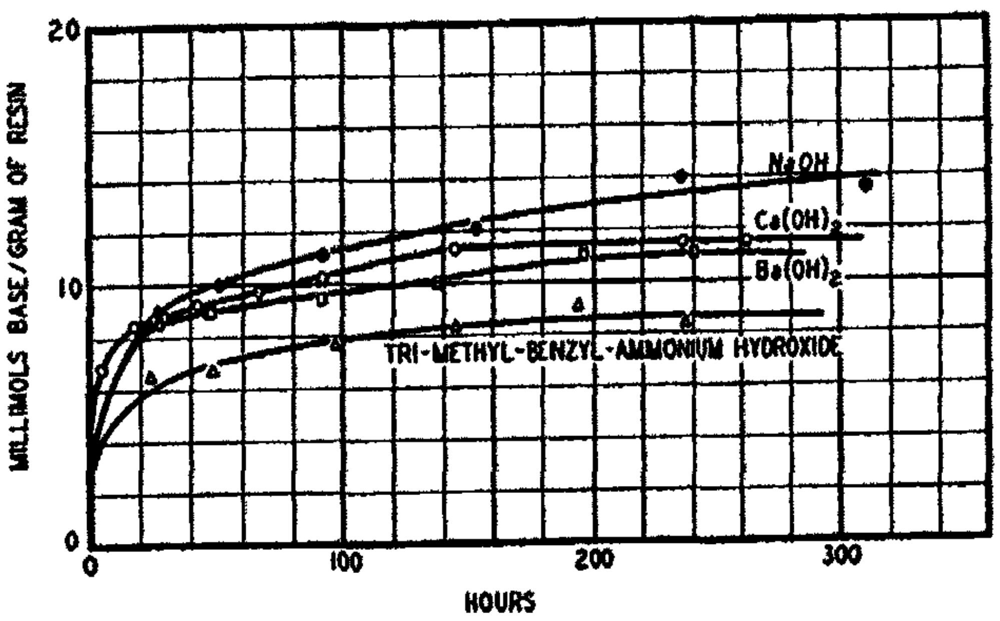


FIG. 4. Adsorption of calcium, barium, sodium, and trimethylbenzylammonium hydroxides on a resorcinol resin containing kieselguhr

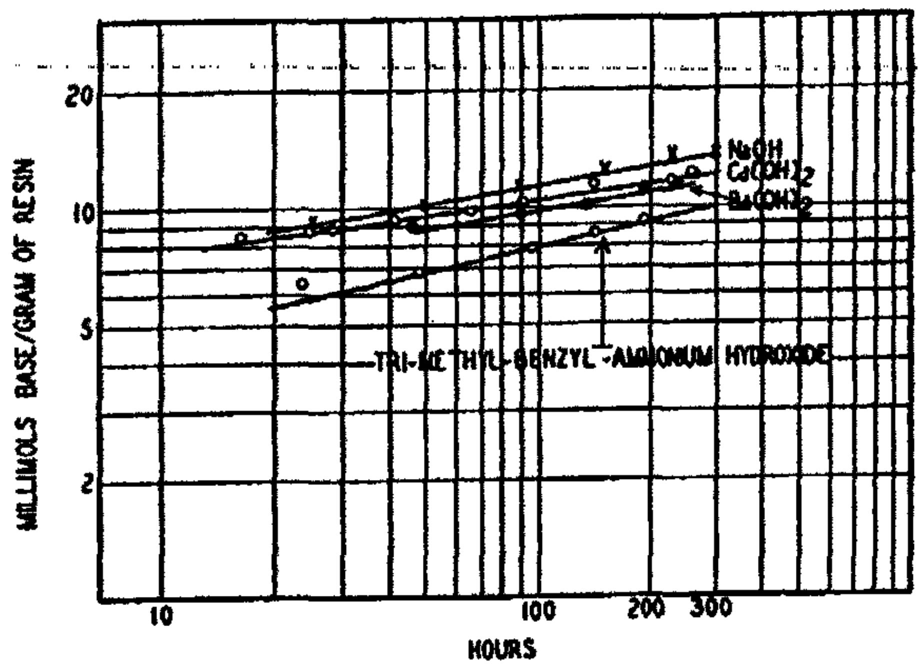


FIG. 5. Adsorption of calcium, barium, sodium, and trimethylbenzylammonium hydroxides on a resorcinol resin containing kieselguhr

TABLE 3

Adsorption of different bases by a resorcinol resin containing kieselguhr

BASE	k	n RATES OF ADSORPTION OF DIFFERENT BASES	n DIAMETER OF ION IN ÅNGSTRÖM UNITS (13)	EQUILIBRIUM ADSORPTION
				millimoles per gram
Calcium	11.9	0.12	1.02	11.5
Barium	9.17	0.16	1.37	11.3
Sodium	5.09	0.17	0.98	14.0
Trimethylbenzylammonium hydroxide	2.92	0.21	9.0*	8.6

* Estimated.

It is surprising to find that incorporation of kieselguhr by direct formation of the resin on it has little effect on the rate of adsorption or the final value attained. Thus, up to about twenty-five hours the curves in figure 3 for resins, with and without kieselguhr, appear to be identical. Above this point they run parallel with a spread of roughly 5 per cent. This may be compared with the finding of Bhatnagar, Hapur, and Puri (2) that different modes of activation had little or no effect on the adsorptive properties of a resorcinol-formaldehyde resin.

A series of experiments were also made with calcium, barium, sodium, and trimethylbenzylammonium hydroxides on a resorcinol resin containing kieselguhr. As before, 500 cc. of 0.0198 *N* base with 0.27 g. of resin (after correcting for kieselguhr content) was used. The results are shown in figures 4 and 5 and are summarized in table 3.

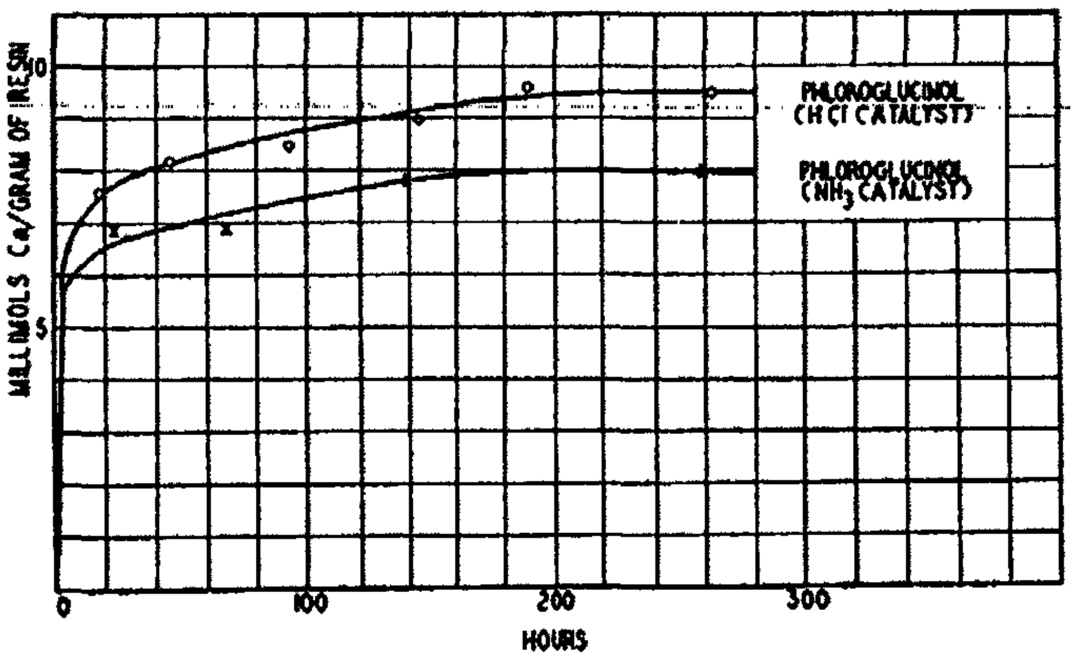


Fig. 6. Adsorption of calcium hydroxide by phloroglucinol resins

EFFECT OF CATALYST ON ADSORPTIVE POWER

The equilibrium adsorption found above for the phloroglucinol resin, in contrast to the results of Adams and Holmes (1), is considerably lower than the equilibrium values for the dihydroxy resins. For this reason samples of the resin were prepared, using different catalysts and conditions. It was found that a phloroglucinol resin prepared using ammonia as catalyst had an even lower adsorptive power than the acid-catalyzed resin (figure 6).

ADSORPTION ISOTHERMS

Bhatnagar, Hapur, and Puri (2) determined the adsorption isotherms of a number of substances on resins of this type. The values they found for a resorcinol resin, apparently prepared by the same method, are, however, very much lower than those found in the present investigation. For adsorption from 0.1 *N* sodium hydroxide solution their adsorption maximum was approximately 5 millimoles per gram of resin as compared with 14.0 in the present experiments. This may possibly be due to differences in the resins or to insufficient time being allowed by them for their solution to come to equilibrium. Thus they state "the systems were agitated for half an hour and allowed to remain until equilibrium was attained." Their values, in fact, check roughly with those interpolated at two hours from the present rate curves (figure 4). In figure 7 are plotted "adsorption isotherms" of resorcinol and catechol resins in calcium hydroxide solution, determined after agitation for one day and seven days, respectively. Points for a resorcinol resin after three months' stirring are also shown. Hence for short times of agitation typical adsorption isotherms are obtained (figure 8), but for long times a curve indicative of chemical combination is observed. The isotherms resemble those for calcium hydroxide and silica gel (7), where there is undoubtedly chemical combination to give calcium silicate.

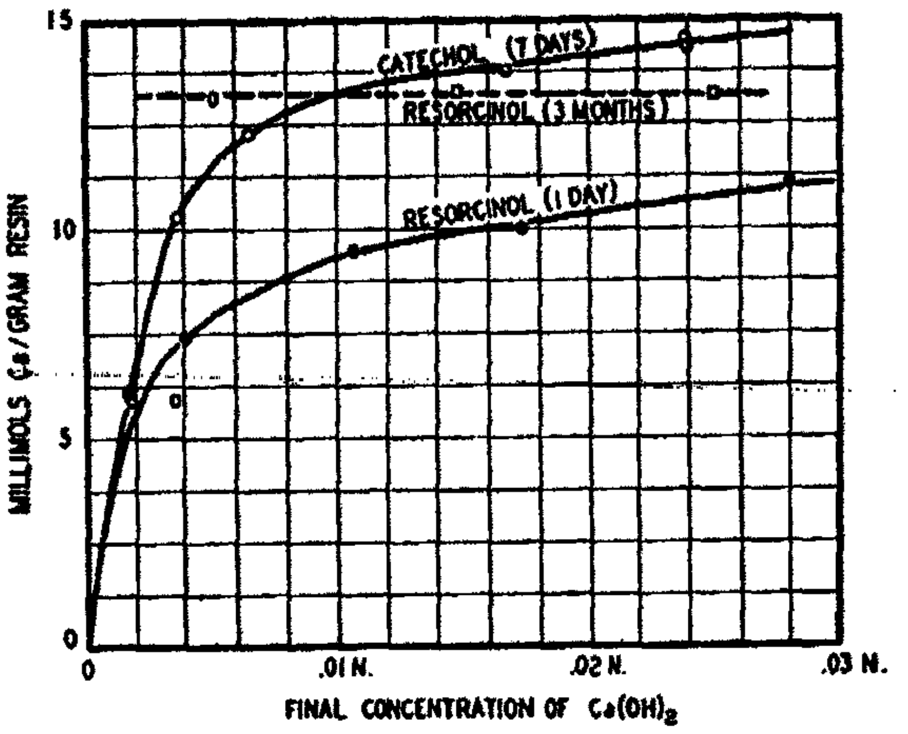


FIG. 7. Adsorption of calcium hydroxide by resorcinol and catechol resins

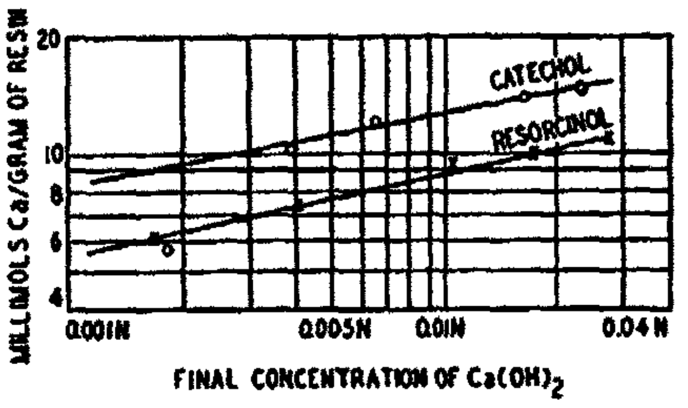


FIG. 8. Adsorption of calcium hydroxide by catechol and resorcinol resins during short times of agitation

INTERPRETATION AND DISCUSSION OF RESULTS

Adsorption of cations in any appreciable quantity is peculiar to the phenol-formaldehyde resins; natural resins and glyptal, vinyl, and ketone-formaldehyde resins show inappreciable adsorption (1). Hence adsorption would seem to be bound up with the phenolic hydroxyl groups and might be expected to be chemical in nature. The present work supports this view.

There is now considerable evidence (7, 10, 8) for the following mode of formation of phenol-formaldehyde resins:

$$R{-}OH + CH_2O \rightarrow HO{-}R'{-}CH_2OH$$

or

$$R{-}OH + nCH_2O \rightarrow HO{-}R^x{-}(CH_2OH)x$$

$$HO{-}R'{-}CH_2OH + R{-}OH \rightarrow HO{-}R'{-}CH_2{-}R'{-}OH + H_2O$$

$$\Big\downarrow{\scriptstyle CH_2O}$$

$$HO{-}R'{-}CH_2{-}R''(OH)CH_2OH$$

$$\Big\downarrow{\scriptstyle ROH}$$

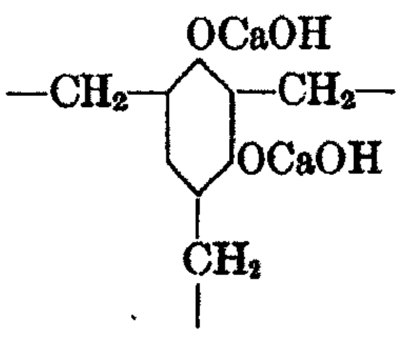
$$HO{-}R'{-}CH_2{-}R''(OH){-}CH_2{-}R'{-}OH$$

$$\Big\downarrow$$

$$HO{-}R'{-}CH_2{-}(R''(OH){-}CH_2)_n{-}R'{-}OH$$

The linear condensation products may further give complex three-dimensional structures by the formation of cross links (4), but in both linear and three-dimensional polymers the phenolic hydroxyl groups are not involved.

Formation of cross links leads to modification of the physical properties of resins, which become harder and more insoluble. Insoluble resins are always formed in the presence of alkaline catalysts although acid catalysts, in the absence of excess formaldehyde, produce soluble Novolak resins, which can only be converted into the insoluble form with excess formaldehyde (6, 1). The resins under investigation are of the insoluble, cross-linked type, excess formaldehyde always being used in their preparation. It is interesting to compare the adsorptions obtained with the values which might be expected on the basis of the above structure, assuming chemical combination to occur between the hydroxide and the base. Taking the basic unit of the dihydroxy phenol resin as $C_6H(OH)_2(CH_2)_{3/2}$, its molecular weight will be 128, there being two hydroxyl groups per unit. Steric considerations indicate that the most probable compound would be



giving a saturation adsorption of 15.5 millimoles of calcium per gram of resin.[3] The corresponding figures for mono- and tri-hydroxy phenol resins are 8.9 and 20.8 millimoles per gram, respectively. For a monobasic hydroxide and a dihydroxy phenol resin the saturation adsorption would similarly be 15.5. Tables 1, 2, and 3 show that the resins, with the exception of the phloroglucinol resin, which will be discussed later, approach these maxima. This confirms the predominantly chemical character of the adsorption.

Viewing the adsorption as a chemical reaction, it is necessary to explain the different equilibrium adsorptions obtained for the various resins. Table 3 and figure 4 would also seem to indicate that the size of the adsorbed ion is important, the equilibrium adsorptions being in inverse order to the ionic diameters. This suggests steric hindrance as a factor; different resins may contain hydroxyl groups of varying degrees of accessibility. Again, the calcium ions as they become adsorbed on the resin may affect accessibility of the remaining hydroxyl groups. Models of the resins were constructed; they indicated that the hydroxyl groups in the catechol resin, being in the ortho position, have a tendency to fall into more accessible positions; the links between the benzene rings are on the opposite side to the groups active in adsorption. On the other hand, resorcinol, having a point between the hydroxyl groups at which linkage can occur, forms a structure in which the possibility of shielding the hydroxyl groups is much more likely.

Consideration of figure 7 shows that at seven days the catechol resin possesses higher adsorption values at all concentrations than the resorcinol resin at three months. Furthermore the adsorption measured, 14.5 millimoles per gram, is 94 per cent of the theoretical adsorption maximum.

There remains the anomaly of the phloroglucinol resin, with an adsorption maximum of 19.2 compared to 41.7 theoretically required. This may be attributed, partially at least, to a high degree of polymerization. In phloroglucinol the 2-, 4-, and 6-positions are free, each one allowing substitution in the position ortho to two hydroxyl groups, so that it might be expected that polymerization would occur to a higher degree than in the mono- and di-hydroxy phenols. When the maximum number of cross links are formed the resin offers the maximum steric hindrance to the reaction of the hydroxyl groups; thus a hardened phenol-formaldehyde resin of the Bakelite type does not adsorb cations. Such a pronounced cross-linkage effect would account for the low maximum of the phloroglucinol resin.[4] A more active catalyst in the resinification might be

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[3] If there were two —CH_2 links per benzene ring, the adsorption maximum would be 33. These figures might be lowered somewhat if some calcium atoms were able to satisfy two hydroxyl groups simultaneously.

[4] The difference might also be accounted for by resinification occurring through the hydroxyl groups, but this appears unlikely (7, 10, 8).

expected to increase the number of cross linkages and hence decrease the adsorptive power of the resin. A resin prepared with ammonia, known to be a very active catalyst (polymerization takes place at room temperature instead of in a boiling solution as with other catalysts), gave a lower adsorption maximum than the acid catalyst resin (figure 6). This observation, that the total possible adsorption is dependent upon the degree of polymerization, is of considerable importance from the commercial standpoint.

The negligible effect of kieselguhr on the rate of adsorption might well be explained by the fact that the amount of kieselguhr employed, 50 per cent by weight, corresponds to only 28 per cent by volume; a larger difference might be detected by the use of a considerably higher volume per cent of kieselguhr. However if, in keeping with the above discussion, it is assumed that the number of available interior hydroxyl groups rather than the number of surface hydroxyl groups govern adsorption, an explanation is at once obvious.

Non-adsorption of calcium sulfate by the resins, the unique behavior of phenolic resins compared with the glyptal, vinylite, and other resins, the results of the adsorption experiments at three months, and the general character of the curves all make it difficult to describe the adsorption as other than chemical. Indeed, the present data can all be explained as a consequence of chemical interaction between the base and the phenolic hydroxyl groups, varying in accessibility in each resin and from resin to resin. Accessibility of these groups, as shown by the amount of base adsorbed, is governed by the structure of the phenol concerned and by the degree of polymerization of the resin.

SUMMARY

The rates of adsorption of calcium hydroxide by some simple mono-, di-, and tri-hydroxy phenol-formaldehyde resins have been determined. The results obtained can be explained on the basis of chemical reaction of the calcium hydroxide with phenolic hydroxyl groups of various degrees of accessibility rather than as a pure adsorption phenomenon.

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STUDIES ON THE LYOTROPIC SERIES. I

THE ADSORPTION OF SALTS ON METHYLCELLULOSE

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I. THE LYOTROPIC SERIES

With many phenomena which are influenced by the presence of salts, it is found that if the ions are arranged in the order of their efficiency, they fall into a definite series called the lyotropic series. As examples of such phenomena may be cited the decrease of solubility of gases in liquids on the addition of salts (22), the influence of salts on the solubility, precipitation, or dispersion of hydrophilic colloids (14, 20, 6), the influence of salts on the temperature of the reversible sol-gel transformation and on the swelling pressure of gels (5a). The order of the ions in the lyotropic series is usually CNS^-, I^-, NO_3^-, NO_2^-, Br^-, Cl^-, acetate, tartrate, SO_4^{--} for the more common anions, and Li^+, Na^+, K^+ for the univalent cations. Slight variations in this order are often encountered.

It was suggested by Hofmeister that the phenomena are due to the dehydrating action of the ions ("salting out") and their individual affinity for the water molecules, whereby there is a competition between the dissolved molecules or colloidal particles and the ions for the solvent (water). The decrease of the solubility of gases in water caused by the addition of salts may be explained on this assumption. All salts decrease the solubility of inert gases and they act according to the series

$$I^- < Br^- < NO_3^- < Cl^- < SO_4^{--}$$

the weakly hydrated I^- causing the smallest, the strongly hydrated SO_4^{--} the largest, depression of the solubility. The explanation would be that the ions with a high energy of hydration, e.g. SO_4^{--}, decrease the hydration of the dissolved molecules more than the ions with a small energy of hydration, e.g., I^- and presumably CNS^-.

Hofmeister's assumptions contain some features which are characteristic of Debye's theory of the effect of ions on the electric field of the solvent, particularly in the case when the solvent is composed of two kinds of molecules. The bearing of this theory on the problem of the lyotropic action will be discussed in the conclusion.

The action of ions on the solubility and flocculation of hydrophilic colloids cannot be explained on the basis of Hofmeister's simple assumptions. Some salts decrease the solubility of a hydrophilic colloid, whereas others increase it. Generally, it may be assumed that in the case of non-charged or isoelectric hydrophilic colloids flocculation is accompanied by a decrease in the hydration of the particles, and dispersion, or increase of solubility, by an increase. On the basis of Hofmeister's theory only a flocculating and not a dispersing action of ions would be plausible. The dispersing action of weakly hydrated ions such as I^- and CNS^- cannot be explained by this theory.

The same difficulty exists with regard to the reversible sol-gel transformation. In the system gelatin-water, which forms a reversible gel on cooling, SO_4^{--} raises the "melting point" of the gel whereas I^- and CNS^- lower it. In this system the series is (20)

$$SO_4^{--} > \text{acetate} > Cl^- > NO_3^- > Br^- > I^-$$

In the system methylcellulose-water, which forms a reversible gel on heating, SO_4^{--} and acetate lower the "melting point," whereas I^- and especially CNS^- raise it, the series being (9, 10)

$$SO_4^{--} > \text{tartrate} > \text{acetate} > Cl^- > Br^- > NO_3^- > I^- > CNS^-$$

In both systems the ions at the beginning of the series have solidifying, i.e., presumably dehydrating, action, whereas the ions at the end of the series have liquefying properties and their action is presumably accompanied by an increase of the particle hydration. In this case also, it can be visualized that, according to Hofmeister, ions with a strong energy of hydration, e.g. SO_4^{--}, exert a solidifying influence by their dehydrating action on the particle, but it is not understandable how the weakly hydrated ions CNS^- and I^- can exert liquefying influence. At most it might be expected that they do not influence the solubility or the melting point at all.

I. R. Katz and F. W. Muschter (15) point out that the phenomena in such cases must be the result of more than a salting-out effect. They suggest that an adsorption of ions by the colloidal particles occurs and that the ions at the end of the series, like CNS^- and I^-, are more strongly adsorbed because of their smaller affinity for the solvent than the ions at the beginning of the series, like SO_4^{--}, the latter presumably being either adsorbed very weakly or not at all, because of its strong affinity for water. Thus the weakly hydrated ions CNS^- and I^- increase the hydration of the particles moderately because they carry water molecules with them when adsorbed, whereas SO_4^{--}, although strongly hydrated, does not increase the hydration of the particles because its adsorption is presumably weak. In other words, there is a superposition of the salting-out effect by an adsorption effect, the former prevailing with the strongly hydrated ions at the beginning of the series, the latter with the weakly hydrated ions at the end. It is significant that in such phenomena where no adsorption or interaction is likely to occur, e.g., the solubility of inert gases, the addition of salts always causes a decrease of solubility, the salting-out effect operating exclusively. On the other hand in such cases where, according to previous experience, adsorption or chemical interaction is possible, e.g., phenomena where interfaces or colloidal molecules with polar groups are involved, the weakly hydrated ions produce an increase of solubility. Here mainly the adsorption effect is operating.

In a recent paper Freundlich and Gordon (5a) suggest that even the lyotropic influence of ions on a complex phenomenon like the swelling pressure of isinglass, CNS^-, I^-, and NO_3^- having an increasing action, SO_4^{--} a decreasing action, may be explained on similar assumptions.

The different magnitudes of adsorption of different ions may be explained on the assumption that these ions have different affinities for the water dipoles. These affinities may be estimated by the energy of hydration which, for univalent atomic ions, generally increases with decreasing atomic diameter (2, 1, 5). For the halide ions the following values have been obtained: Cl^-, 84; Br^-, 73; I^-, 64 kg-cal., the order agreeing well with the order in the lyotropic series. It can be seen from the measurements of Osaka (18) that the adsorption of potassium chloride, bromide, and iodide on a comparatively inert adsorbent, like charcoal, is determined by the energy of hydration of these ions, the strongest adsorption being exhibited by iodide, which has the smallest energy of hydration, whereas chloride, which has the highest energy of hydration, shows the weakest adsorption.

Unfortunately the energy of hydration is known in a few cases only. In others the magnitude of the hydration itself may be taken as a rough estimate of the affinity between the ions and the water molecules, although it must be remembered that the methods for its determination are still open to controversy.

The magnitude of the adsorption of ions by hydrophilic colloidal particles, however, depends not only on the affinity of the former for water but also on their affinity for the particles, probably owing to the van der Waals attraction between the ions and the polar groups of the particle. The latter may be specific in many cases and depends on the chemical nature of the respective groups. This may cause deviations from the lyotropic series, as usually observed. Such deviations have in fact been frequently found.

In higher concentrations association of ions to molecules occurs, these frequently forming addition compounds with water, e.g., aquo-acids, aquo-bases (16). As a result of this the lyotropic series at higher concentrations may differ from that in dilate solutions. This too has been observed experimentally, e.g., in the system gelatin-water (20).

II. ADSORPTION ON HYDROPHILIC SUBSTANCES

In adsorption processes on hydrophilic colloidal particles, the adsorption of the water molecules, i.e., the hydration, must be taken into account.

It has become customary to determine the adsorption (a) of a solute on an adsorbent from the concentration before (c) and after (c') the process:

$$a = \frac{c - c'}{w} \tag{1}$$

where w is the weight of the adsorbent. In this case it is assumed that no adsorption of the solvent occurs, so that $c - c'$ is positive, if a is greater than zero. If the other extreme is considered, namely that no solute is adsorbed, but that an adsorption of solvent takes place ("solvation"), its molecules in the adsorption layer not being able to act as solvent, c' will be greater than c, and a, which in this case may be called "apparent adsorption," will be negative. In general, both phenomena—adsorption of solute and of solvent—occur with hydrophilic substances. If the former is only slight, the apparent adsorption a, as calculated by equation 1, will be negative. If it increases, a passes from negative values to zero and eventually to positive values, when it outweighs the adsorption of the solvent.

In order to judge the validity of the explanations given for the mechanism of the lyotropic series, it is necessary to obtain more accurate data on the adsorption of salts by lyophilic colloids than have been available up to now. The adsorption of several salts on proteins in solution was measured by Pauli and Matula (21), Northrop and Kunitz (17), and Heymann and Oppenheimer (12), but the investigations were mainly concerned with heavy metal salts. Of the alkali salts only the adsorption of potassium chloride and potassium sulfate on gelatin was determined by conductimetric and potentiometric methods (19, 4), the former showing positive, the latter negative, apparent adsorption. Northrop and Kunitz' measurements of the membrane equilibrium give effects which, in the case of alkali salts, hardly exceed the experimental error. J. A. van der Hoeve (13) measured the adsorption of alkali salts on potato starch and found the series

$$SO_4^{--} < Cl^- < I^- < CNS^-$$

SO_4^{--} showing negative, CNS^- positive apparent adsorption.

A systematic investigation of the adsorption of various salts on hydrophilic colloidal particles in systems where the lyotropic series is well known with regard to various properties, such as gelatin, agar, methylcellulose, has not yet been carried out.

It is the purpose of this and the following investigations to close this gap.

The system methylcellulose-water is one of the few systems showing reversible gel formation on heating. At low concentrations, where no gel formation occurs, the dissolved substance is precipitated on heating. The methylcellulose gel consists most probably of a fibrous network of particles which are insoluble above 50-55°C. (9). For this reason the adsorption of potassium salts on methylcellulose was investigated at 59°C.

III. THE ADSORPTION OF VARIOUS SALTS ON METHYLCELLULOSE

A. Experimental

In adsorption experiments at an elevated temperature care has to be taken to avoid evaporation losses during filtration of the solution from the methylcellulose with which it has come into equilibrium. To this end special adsorption vessels were devised (figure 1). These were made of Pyrex, except for the tap and central tube which were of soda glass. After equilibrium between the solutions and methylcellulose had been attained, the solutions were filtered by connecting the upper end of the tube through a filter medium to a vacuum pipet, the connections being made with rubber pressure tubing. A rapid, and quite efficient, filter was found to be a wad of glass wool packed into a short piece of glass tubing, constricted in the middle.

FIG. 1. The adsorption vessel

The adsorption vessels containing the solution and the methylcellulose were placed in an electric thermostat which was maintained at 59.3°C. ± 0.1° by means of a toluene-mercury electric regulator.

Preliminary experiments showed that the methylcellulose, which was identical with that used by E. Heymann (9), contained a soluble chloride impurity. In order to purify the methylcellulose, it was boiled with successive large quantities (about 3 to 4 liters) of water, being filtered and washed with boiling distilled water between each such treatment.

This was done four to five times and yielded a product which was sufficiently free from soluble impurities. Immediately after the last washing, the methylcellulose was placed in an electric oven at 105–110°C. to dry. The methylcellulose used in the adsorption experiments was recovered, washed well with hot water, and then purified as above.

To facilitate ease of manipulation of the methylcellulose in the actual adsorption experiments, it was in all cases made into small pellets, using a tablet press. These were dried in an electric oven for at least eighteen hours at 105–110°C., after which time they were constant in weight.

The salts used in the adsorption experiments were potassium thiocyanate, potassium bromide, potassium acetate, potassium chloride, potassium sulfate, potassium nitrate, and potassium iodide of "A.R." (B.D.H.) quality.

The adsorption vessel containing 40 ml. of the solution was hung in the thermostat until the solution had reached the thermostat temperature (at least twenty minutes). Then 3 g. of the dry methylcellulose was added. On shaking the pellets broke into a loose mass. The solutions were left in contact with the methylcellulose for at least two days, to attain equilibrium. (In no case was the adsorption found to be appreciably different when solutions of the same concentration were left over longer periods.) Without removing the adsorption vessels from the thermostat, the solutions were then filtered, cooled, and transferred to Jena bottles to await analysis. Usually about 20 ml. of solution was recovered. Adsorption experiments for each concentration were done in duplicate.

Potassium thiocyanate and potassium bromide were analyzed by the Volhard method. Potassium iodide was determined by the same method, with the modifications recommended by Treadwell-Hall (23) to prevent adsorption of potassium iodide by the precipitated silver iodide. Potassium chloride was analyzed by Mohr's method. Copper sulfate was determined by the iodometric method.

Since the convenient methods of estimating sulfate are not very accurate, the potassium sulfate solutions were estimated by evaporating a known weight to dryness in a porcelain crucible, and then heating the potassium sulfate crystals to constant weight in an electric muffle at 610°C.

The potassium nitrate and potassium acetate solutions were converted to potassium sulfate according to the method given by Treadwell-Hall.

These last-mentioned gravimetric methods have the complication that a correction must be made for the weight of the remaining impurities dissolved from the methylcellulose. This was done by evaporating to dryness the filtrates from the experiments with distilled water and methylcellulose, sulfating them, and heating in the muffle to constant weight.

Preliminary experiments showed that the adsorption effects would probably be very small, producing a change in concentration of 1 to 2 per cent at most. Hence it was decided to supplement the ordinary chemical analysis of the solutions before and after adsorption, by first measuring their conductivities. Since we are dealing with strong electrolytes, we may assume that the equivalent conductivity does not change appreciably in the small concentration range of ± 1 to 2 per cent, and therefore the

TABLE 1

Apparent adsorption of salts by methylcellulose

SALT	(1) APPROXIMATE CONCENTRATION	(2) CONCENTRATION IN MOLES PER LITER	(3)	(4) IMPURITY CORRECTION	(5) CORRECTED CONCENTRATION DIFFERENCE	(6) CORRECTED CONCENTRATION DIFFERENCE IN MILLIMOLES PER LITER	(7) PERCENTAGE APPARENT ADSORPTION
		Before adsorption	After adsorption				
KCNS	*M*/10	0.1052	0.1050		+0.0002	+0.2	+0.2
	M/5	0.1925	0.1925		0.0000	0	0
	M/2	0.5130	0.5098		+0.0032	+3.2	+0.6
	M/1	1.035	1.031		+0.0040	+4.0	+0.4
KI	*M*/10	0.0987	0.0989		−0.0002	−0.2	−0.2
	M/5	0.2000	0.2003		−0.0003	−0.3	−0.2
	M/2	0.4991	0.5002		−0.0011	−1.1	−0.2
KBr	*M*/10	0.1001	0.1012		−0.0011	−1.1	−1.1
	M/3	0.3333	0.3368		−0.0035	−3.5	−1.0
	M/1	1.0010	1.0110		−0.0100	−10.0	−1.0
$KOOC\cdot CH_3$	*M*/5	0.2335	0.2365	0.0003	−0.0026	−2.6	−1.1
	M/2	0.5348	0.5411	0.0003	−0.0060	−6.0	−1.1
	M/1	0.9920	1.0038	0.0003	−0.0115	−11.5	−1.2
KNO_3	*M*/5	0.1998	0.2030	0.0003	−0.0029	−2.9	−1.4
	M/2	0.5012	0.5072	0.0006	−0.0054	−5.4	−1.1
KCl	*M*/10	0.1006	0.1021		−0.0015	−1.5	−1.5
	M/2	0.5004	0.5076		−0.0072	−7.2	−1.4
	M/1	1.0010	1.0110		−0.0100	−10.0	−1.0
K_2SO_4	*M*/10	0.1012	0.1033	0.0002	−0.0019	−1.9	−1.9
	M/4	0.2501	0.2549	0.0002	−0.0046	−4.6	−1.9
	M/2	0.5013	0.5089	0.0002	−0.0074	−7.4	−1.5
$CuSO_4$	*M*/10	0.0981	0.0995		−0.0014	−1.4	−1.4

specific conductivities of the solutions are directly proportional to their concentrations.

The conductivity cell used was of the pipet type, made of Jena glass, and of capacity about 16 ml. The cell constant was 0.4063 at 14.20°C. When in use the lower end of the cell was blocked by a piece of rubber tubing sealed with a glass rod.

The interferometer could not be used to measure adsorption, because traces of methylcellulose are soluble in water even at 59°C.

B. Results

In table 1 apparent adsorption is calculated from the results of chemical analysis. Usually, it is expressed as in equation 1

$$a = \frac{c - c'}{w}$$

TABLE 2

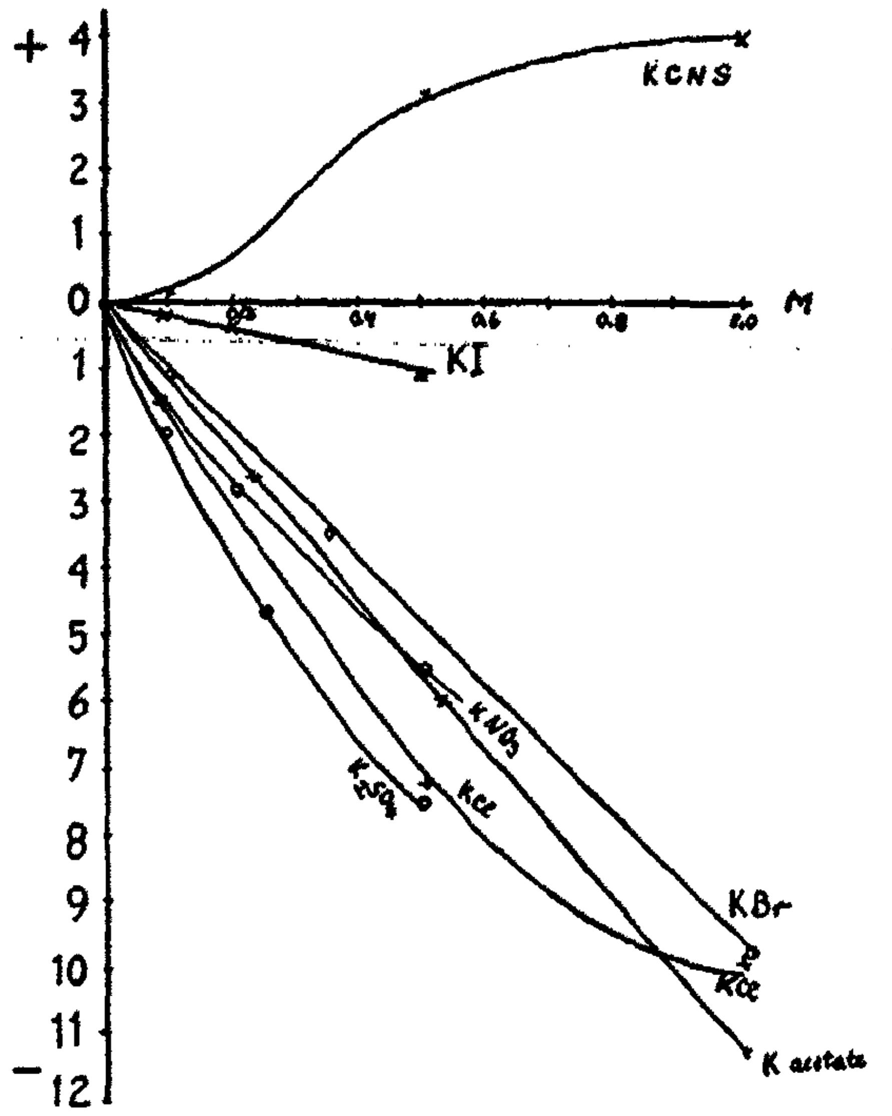
Apparent adsorption of salts by methylcellulose, calculated from the conductivity measurements

SALT	CONCENTRATION BEFORE ADSORPTION	SPECIFIC CONDUCTIVITY BEFORE ADSORPTION	SPECIFIC CONDUCTIVITY AFTER ADSORPTION	CORRECTION FOR IMPURITIES	CORRECTED DIFFERENCE OF CONDUCTIVITY	PERCENTAGE CHANGE OF CONDUCTIVITY	TEMPERATURE OF CONDUCTIVITY MEASUREMENT
	equivalents per liter	*ohm*$^{-1}$ × *10*^{2}	*ohm*$^{-1}$ × *10*^{2}	*ohm*$^{-1}$ × *10*^{2}	*ohm*$^{-1}$ × *10*^{2}		°*C.*
KCNS	0.1049	1.002	1.005	0.003	0.000	0	14.20
	0.1925	1.776	1.783	0.003	−0.004	−0.2	
KI	0.0987	1.293	1.297	0.003	−0.001	0	24.25
	0.1998	2.507	2.509	0.003	−0.001	0	
KNO_3	0.1000	1.184	1.198	0.005	−0.010	−0.8	24.25
	0.2000	2.222	2.248	0.005	−0.021	−1.0	
KCl	0.1000	1.029	1.047	0.003	−0.015	−1.5	14.20
	0.2000	1.977	2.007	0.003	−0.027	−1.3	
K_2SO_4	0.1000	1.034	1.055	0.005	−0.016	−1.6	22.30
	0.2000	1.906	1.941	0.005	−0.030	−1.6	

In this case, however, since the same weight of methylcellulose (3 g.) was in each case added to the same volume (40 ml.) of solution, apparent adsorption was simply expressed as

$$a = c - c' \tag{2}$$

where c is the concentration before and c' the concentration after adsorption ("equilibrium concentration"). Column 6 contains this difference in concentration in millimoles per liter. Column 7 is the percentage change of concentration during adsorption per initial concentration, i.e., $\frac{c - c'}{c} \cdot 100$ ("percentage apparent adsorption"). The second and third columns give c and c′. All concentrations are expressed as moles per liter. The fourth column gives the correction for impurity (i) for those ions which have been determined gravimetrically. This correction must be subtracted from the figures in column 3 to give the true concentrations of those salts concerned. In column 5 (c — c′ — i) is tabulated as "corrected concentration difference"). It has to be remembered, however, that the percentage apparent adsorption is a difference of two concentrations which are not very different. Hence the average error may amount to ± 0.1 to 0.2 unit on the figure obtained.



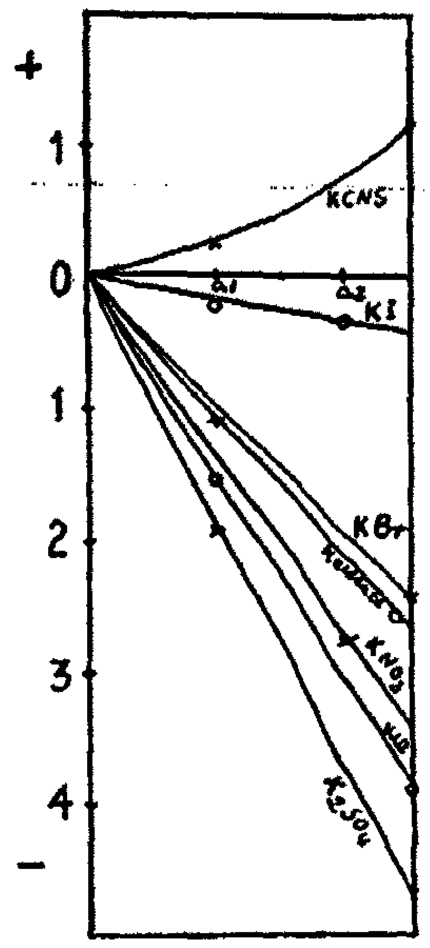


FIG. 2 FIG. 3

FIG. 2. Plot of apparent adsorption ($a = c - c'$) against the equilibrium concentration c'

FIG. 3. Plot of apparent adsorption ($a = c - c'$) against the equilibrium concentration c' at lower concentrations

In table 2 apparent adsorption is calculated from the conductivity measurements as percentage change in specific conductivity (κ). Since for strong electrolytes and small changes of concentration (c)

$$\kappa \sim \text{prop. } c$$

the percentage change in specific conductivity should be approximately equal to the percentage apparent adsorption in table 1.

However, the correction due to the small conductivity of traces of dissolved methylcellulose and impurities is about six to ten times as large as the correction for the gravimetric analysis, whereas in the titrimetric analysis there is no such correction. Consequently accuracy of the value of the percentage apparent adsorption as calculated from the conductivity measurements is much less than that calculated from chemical analysis. For this reason the conductivity results will be merely regarded as confirmatory. A comparison between table 1 and table 2 shows that the values from the conductivity method are slightly less numerically than those obtained by chemical analysis.

In figures 2 and 3 the apparent adsorption $a = c - c'$ is plotted against the equilibrium concentration c'. Only potassium thiocyanate shows positive apparent adsorption, and for potassium iodide apparent adsorption is approximately zero, whereas all the other salts are strongly negatively adsorbed. The difference between the values for apparent adsorption for these other salts is not very marked in concentrated solutions, some of the curves overlapping at higher concentrations (cf. section I). The individual character of the ions is more clearly shown at lower concentrations (figure 3). Potassium sulfate shows the strongest negative apparent adsorption. Then follow potassium chloride and potassium nitrate, which are about equal, and then potassium acetate and potassium bromide. The values for this group of ions from Br^- to SO_4^{--} are, however, not very much different, whereas the values for I^- and CNS^- (zero or positive apparent adsorption) stand far apart from all other ions.

Measurements of the pH of the solutions were made in some cases before and after adsorption. No evidence of an appreciable hydrolytic adsorption was obtained.

IV. THE INFLUENCE OF SALTS ON THE SOLUBILITY OF METHYLCELLULOSE IN WATER

It was decided that an investigation of the influence of salts on the solubility of methylcellulose would prove a useful addition to the results obtained by E. Heymann (9) on the coagulating action of various salts and on their influence on the temperature of the sol–gel transformation.

A few preliminary data were derived from the adsorption experiments where it was shown that the solubility of methylcellulose in water at 59.3°C. is so slight that the accuracy of the determination of adsorption was not affected.

Although the absolute values given in table 3 are small, it can be seen that sulfate has a decreasing, iodide an increasing, effect on the solubility.

It is known that there is an immense increase in the solubility of methylcellulose with decreasing temperature, probably owing to the formation of an oxonium hydroxide. Solubility measurements in water and in salt solutions were therefore carried out at room temperature.

The methylcellulose used in these experiments was not the same as that used for the adsorption experiments, but was material not quite as soluble in water, obtained from the I. G. Farbenindustrie. It was purified by boiling and washing with distilled water. The solubility of this methylcellulose in solutions of the same concentration of various potassium salts was investigated. The concentrations were 1 *M* potassium thiocyanate, 1 *M* potassium iodide, 1 *M* potassium nitrate, 1 *M* and 0.5 *M* potassium chloride, and 0.5 *M* potassium sulfate (1 *M* solution not being obtainable at ordinary temperatures).

TABLE 3

Solubility of methylcellulose at 59.8°C.

SOLVENT	METHYLCELLULOSE	PER CENT OF THE SOLID PHASE DISSOLVED
	grams per 100 ml.	*per cent*
Potassium sulfate (*M*/5)	0.015	0.20
Water	0.028	0.37
Potassium iodide (*M*/5)	0.032	0.43

TABLE 4

Solubility of methylcellulose in salt solutions at room temperature

SALT	CONCENTRATION OF SALT	CONCENTRATION OF METHYLCELLULOSE
Potassium thiocyanate	1*M*	2.9
Potassium iodide	1*M*	2.8
Distilled water		1.85
Potassium nitrate	1*M*	0.70
Potassium chloride	1*M*	0.24
Potassium chloride	0.5*M*	0.60
Potassium sulfate	0.5*M*	0.23

Ten grams of methylcellulose was packed into each of seven 250-ml. bottles, and 100.0 ml. of the various solutions added, the bottles then being agitated on a mechanical shaker for three days. It was observed that the potassium thiocyanate and potassium iodide solutions were characterized by producing a marked dispersive effect. The supernatant liquid was then filtered through glass wool filters into pipets. Duplicate samples of each filtrate were evaporated to dryness and heated to constant weight in an air oven at 110°C.

In table 4 the concentration of the methylcellulose is expressed as grams of methylcellulose per 100 grams of solution.[1]

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[1] It might have been more reasonable to express the concentration not as grams per 100 grams of solution but as the molar fraction. In this case it would have been necessary to introduce an arbitrary molecular weight for the methylcellulose. The

It can be seen from this table that potassium nitrate, potassium chloride, and potassium sulfate depress the solubility of methylcellulose in water, the order being $SO_4^{--} > Cl^- > NO_3^-$, whereas potassium iodide and potassium thiocyanate increase it. In addition these two last-mentioned ions have a dispersing effect on that part of the methylcellulose which is not being dissolved.

V. DISCUSSION AND CONCLUSIONS

A. The presumable true adsorption

We have seen in section III that the apparent adsorption of potassium thiocyanate is slightly positive and that of potassium iodide about zero, whereas all the other ions show negative apparent adsorption. The order is:

$$CNS^- > I^- > Br^- = \text{acetate} > NO_3^- = Cl^- > SO_4^{--}$$

with a distinct separation between the CNS^-–I^- group and the other ions. The differences between the ions from Br^- to SO_4^{--} are noticeable, but comparatively small, and they become less significant at higher concentrations.

The fact that the apparent adsorption of potassium iodide is zero cannot be explained on the assumption that no adsorption of iodide occurs, because negative apparent adsorption is found with the ions from Br^- to SO_4^{--}, i.e., water molecules are adsorbed by the methylcellulose particles from a solution containing salt. Consequently the zero apparent adsorption of iodide has to be interpreted on the assumption that iodide is adsorbed as well as water, i.e., that the true adsorption of iodide is positive. Thus thiocyanate shows a still stronger positive true adsorption, since even the apparent adsorption of this salt is positive.

It should be remembered that zero apparent adsorption means that the solute as well as the water is adsorbed in such an amount that the initial concentration remains unchanged. This does not mean, however, that solute molecules and water molecules are adsorbed in equal numbers. Suppose that the apparent adsorption of a 1 per cent molar solution (molar fraction 0.01) is zero. In this case, assuming that both solute molecules and water molecules are being removed from the solution, the ratio of each kind of molecule removed must be one of solute to one hundred of water. In the case of negative apparent adsorption this ratio is still greater. Only in the case of a molar fraction 0.5 are equal numbers of solution molecules and solvent molecules removed, when the apparent adsorption is zero; in all other cases the ratio may be calculated from the

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solubility of methylcellulose in the various salt solutions shows such large differences, however, that the order of salts would not be changed if the concentrations were expressed as molar fractions.

molar fraction (cf. Heymann and Boye (11)). There is no difficulty in extending these considerations to ionized solutes.

The negative *apparent* adsorption of sulfate, which shows the highest value of negative adsorption, can mean that either water is being adsorbed and no solute, or both are adsorbed but the adsorption of the water is so much larger than that of the sulfate that the total concentration is increased. Since the negative apparent adsorption of the ions from Cl^- to Br^- is slightly smaller than that of sulfate, their true adsorption must be slightly higher. However, the fact that the negative adsorptions of all ions from Br^- to SO_4^{--} differ but little suggests that in all these cases the true adsorption is either zero or very small, and that only iodide and thiocyanate show an appreciable positive true adsorption.

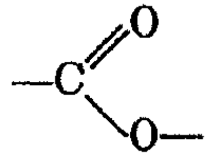
B. The hydration of methylcellulose

Assuming that the true adsorption of sulfate is zero, the hydration of the methylcellulose can be calculated from the negative adsorption, since the increase in concentration of the solute during this process will be due to the fact that the adsorbed water molecules responsible for the hydration of the methylcellulose can no longer act as a solvent for the electrolyte. From the values for $M/10$ and $M/4$ solutions (1.9 per cent adsorption for 3 g. of methylcellulose in 40 ml. of solution), the hydration of methylcellulose in the presence of $M/10$ potassium sulfate at 59°C. is 0.25 g. of water per gram of methylcellulose; in salt-free water it may be higher. The corresponding value for gelatin is about 0.30 to 0.50 g. per gram of gelatin, according to the method employed. This hydration value for methylcellulose constitutes a minimum value for the hydration. If a slightly positive true adsorption of sulfate be assumed, the hydration value would be higher. It should be remembered that the experiments have been carried out at 59°C., hence the hydration of the methylcellulose in the water-insoluble (gel) state is obtained. It may be assumed from measurements of the volume expansion during the sol–gel transformation (Heymann (9)), that the hydration of the methylcellulose in the water-soluble (sol) state at ordinary temperature is several per cent higher.

C. The interpretation of the lyotropic action and the theories of Hofmeister, Debye, and Katz

The ions at the end of the lyotropic series, CNS^- and I^-, which raise the temperature of the sol–gel transformation and increase the solubility of methylcellulose, i.e., which have liquefying properties, show a true adsorption which is much stronger than that of all the other ions. This fact constitutes a strong support for Katz' (15) theory of lyotropic action. Most probably the liquefying properties of CNS^- and I^- are due to adsorption, whereby these ions, although weakly hydrated, increase the hydration of the colloid, because they carry water molecules with them when adsorbed. On the other hand the experiments show that the true adsorption of all other ions from Br^- to SO_4^{--} is either zero or very small. Consequently no such increase of hydration of the methylcellulose particles can be caused by them. On the contrary they will probably decrease the hydration as a consequence of their affinity for the water molecules, in accordance with Hofmeister's original assumption. The result must be a salting-out effect. In fact, the temperature of the sol-gel transformation of the methylcellulose is lowered (solidifying action) and the solubility in water is strongly depressed in the presence of these ions, the strongly hydrated sulfate having the strongest depressing action. Then follow the more weakly hydrated chloride and then bromide, the energy of hydration of which is still smaller.

Thus the assumption that the lyotropic action is due to (*1*) a salting-out effect which causes solidification and (*2*) an adsorption effect which causes liquefaction seems to be in accordance with the experimental results, the first effect operating mainly in the case of the ions at the beginning and the second mainly with those at the end of the lyotropic series.

If the order of the members of the series for the adsorption is compared with that for other phenomena, e.g., precipitation and sol-gel transformation, an irregularity in the position of the acetate is noticed. This ion would be expected to be between chloride and sulfate, whereas it shows about the same apparent adsorption as bromide. This may be due to the fact that the  $-C{\overset{O}{\diagup}}\!\!{\underset{O-}{\diagdown}}$ dipole of this organic ion has a special affinity for polar groups of the methylcellulose, causing a stronger positive true adsorption than that expected from analogy to other phenomena (cf. section I).

Since the adsorption effect (and its mechanism) has been fully discussed in section I, it needs no further explanation. A few more words, however, seem to be necessary about the salting-out effect. The competition between ions and colloidal molecules for the water molecules is difficult to visualize, since the water molecules are present in very great excess. A theory of the salting out and the salting in of ordinary molecules in binary liquid mixtures has been proposed by Debye (3), who considered the effect of ions on a solvent which is composed of two kinds of molecules. If the solute decreases the dielectric constant of the solvent, the former will be salted out; if it increases the dielectric constant, it will be salted in. This prediction from Debye's theory has been established experimentally for aqueous solutions of acetone and hydrogen cyanide by P. Gross and his coworkers (7). The effect is due to a separation, the concentration of the stronger polar molecules being higher in the immediate neighborhood of the ions, whereas that of the less polar molecules is higher at a distance from the ions. This assumption is clearly related to the conception of solvated ions. It is, however, doubtful whether Debye's theory in its original form can explain the lyotropic action even in ordinary solutions. It is true that effects of different magnitude have to be expected for different ions according to their diameter, but it is doubtful, as P. M. Gross (8) has pointed out, whether the theory can explain that the same solute is salted in by some electrolytes, whereas it is salted out by others. Moreover, Debye himself remarks that the electric effect may be only part of the whole and that interaction between the solute and the ion may be important. Besides the latter, the attraction between the molecules of the solute and those of the solvent is not accounted for in Debye's theory.

In the case of solute molecules of colloidal size the departure of the experimental conditions from the idealized assumptions is still greater. It is doubtful, for instance, whether it depends on the dipolar moment of the whole solute molecule or on that of individual groups, whether the solute or the water is more strongly attracted by the ions. Neither the dielectric constant of methylcellulose solutions nor the dipolar moment of this solute has yet been measured. We are at present engaged in measurements of the adsorption of electrolytes on gelatin, in which case the dielectric properties are better known. If the water is the component of higher polarity, an increase of concentration of water dipoles round the ions may be visualized. In the opposite case, however, the assumption of an ion surrounded by colloidal molecules much larger than the ion itself presents considerable difficulties. One would, in this case, rather assume ions surrounding the colloidal molecule. However, even if Debye's theory can be adapted to colloidal systems, it seems highly improbable that the very marked liquefying effects of ions like iodide and thiocyanate can be explained without assuming an interaction between the colloidal molecules and these ions. This assumption seems to be well supported by the adsorption effects found in this investigation.

SUMMARY

1. The adsorption of various salts in aqueous solution on methylcellulose at 60°C. has been investigated. The apparent adsorption is positive for potassium thiocyanate, almost zero for potassium iodide, and negative for all the other salts investigated, the order being potassium bromide, potassium acetate, potassium nitrate, potassium chloride and potassium sulfate, the last showing the strongest negative adsorption. The true adsorption of CNS^- and I^- is considerable, while that of the other ions, in particular of SO_4^{--}, is either zero or very small.

2. From the negative adsorption of potassium sulfate the minimum

hydration of methylcellulose in the insoluble (gel) state has been calculated as 0.25 g. per gram of methylcellulose.

3. The solubility of methylcellulose in water is increased by potassium thiocyanate and potassium iodide and decreased by the other salts, the order being $K_2SO_4 > KCl > KNO_3$. The behavior is analogous to the action of salts on the sol-gel transformation.

4. The results mentioned in paragraphs 1 to 3 show that Katz' theory, assuming a salting-out effect for the strongly hydrated ions and an adsorption effect for the weakly hydrated ones, is a satisfactory basis for the explanation of the lyotropic action. Debye's theory on similar effects for solutes of low molecular weight has also been discussed.

It gives us much pleasure to thank Professor E. J. Hartung for his interest and for providing us with excellent facilities for work in the laboratory.

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MELTING TEMPERATURES OF COMPOUNDS ADSORBED ON SILICA GEL[1]

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INTRODUCTION

One would expect that the capillary forces believed to be responsible for the adsorption of vapors by silica gel would cause a change in the melting temperature of the adsorbed substance. There is already some evidence for this phenomenon in the behavior of the vapor pressure of adsorbed substances at temperatures below their normal melting points. Coolidge (1) found that the vapor pressure isotherms of benzene on charcoal at temperatures below its normal melting point are curves similar to those at higher temperatures. Furthermore, while the latter curves ran asymptotic to the vapor pressure of normal liquid benzene, the former met at a definite angle with the vapor pressure of solid benzene at the same temperature. This lack of phase continuity between adsorbed and solid benzene was still in evidence at a temperature as low as 40°C. below the normal melting point. Patrick and Land (3) measured the adsorption of iodine on silica gel above and below its normal melting point and interpreted their results as indicating a lowering of the melting point of the adsorbed iodine.

Jones and Gortner (2) have measured the freezing temperatures of water on silica gel with a dilatometer. In these experiments the gel and water were covered with toluene and the volume changes on cooling were noted. The thermal contraction of ice, water, and gel were negligible and that of the toluene present was known. The remaining change was attributed to the expansion of water on freezing. Hence the amount of water frozen at each temperature was calculated. They found that as the temperature was lowered more water continued to freeze, and that even at −48°C. there was still 33 g. of unfrozen water per 100 g. of activated gel. They also found a hysteresis effect in that at a given temperature during cooling there was more unfrozen water than at the same temperature during heating. In repeated experiments the same results were

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[1] This paper is based on a dissertation submitted by W. A. Kemper to the Board of University Studies of the Johns Hopkins University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1934.

obtained on heating, only if the cooling had terminated at the same temperature.

Experiments were run with three different concentrations of *gel in water*, but in each case the quantity of water was in excess of that required to saturate the gel. Since this excess froze near 0°C., at lower temperatures there remained saturated gels, all containing the same amount of unfrozen water. Moreover, the results for the amount of unfrozen water at the various temperatures were calculated *per gram of total water present.* However, if the amount of unfrozen water *per gram of dry gel* had been tabulated instead, the results of all three experiments would have been seen to be nearly identical.

The dilatometric method raises two questions. First, what is the effect of immersing the system in toluene? Since the water–toluene interfacial tension is only half that of water–air, larger effects would be expected from capillary forces in the absence of toluene. Secondly, can density changes caused by the negative pressures from these capillary forces be neglected? These negative pressures are greatest on the last-remaining unfrozen water.

Swain and Porter (8) measured the specific heats of argon and hydrogen absorbed on charcoal from 6–50°K. without finding any breaks indicating a sudden change of phase. The specific heats were observed to be less than that of either the solid or the liquid form of these respective elements.

In the present paper a calorimetric method was used to detect any heats of transition attending melting. Specific heats were measured by the Andrews calibrated heat conduction method (5), which is both rapid and continuous. Since it is continuous no intervals are omitted in which a change of phase could escape detection.

APPARATUS AND PROCEDURES

The apparatus is shown in figure 1. The heat is supplied to the calorimeter across an oxygen-filled space separating the calorimeter from an electrically heated, concentric, heavy copper cylinder. The same temperature head is always maintained from the cylinder to the calorimeter, hence the rate of heat transfer to the calorimeter at a given temperature is always the same. Measurements are made of the time required for the temperature of the calorimeter to be raised through successive increments. Two runs with different amounts of a substance of known specific heat give the rate of heat input and the specific heat of the empty calorimeter as functions of the temperature. These functions are used to translate heating times into specific heats of the contents of the calorimeter.

The temperature head and temperature of the calorimeter can were measured by calibrated copper–constantan thermocouples (6) in conjunction with either a White double potentiometer or two type K potentiometers. D'Arsonval galvanometers were used, giving a scale sensitivity of 1.3 to 2.0 mm. per microvolt.

The heat was distributed in the calorimeter can by thirty-four radial fins of 2-mm. brush copper. During a run the temperature at the center of the calorimeter was only 1.5°C. less than at the wall.

An improvement in the apparatus was made by grounding the outer cylinder. This led stray voltages off the thermocouples and the anomalous results previously found (5) at 0°C., where the thermocouple voltage changes sign, were not experienced. Another modification was the chromium plating of the outside of the calorimeter and of the inside of its containing cylinder.

Identical preparations were made for each run. The calorimeter can and the space between the can and the outer cylinder were rinsed three times with boiling acetone, then dried by heating in a current of dry oxygen. The calorimeter was then filled and sealed, and the space between the cylinders was swept with oxygen for another half-hour before cooling to the starting temperature. It is essential that the rubber tubing on the inlet oxygen line does not give off condensable vapors. It was found economical to cool first with half a pound of solid carbon dioxide before adding liquid oxygen. When cooling was completed, the inlet oxygen valve was closed and a large heating current was applied until the 1000 microvolt head was obtained. Then, while this temperature head was carefully maintained by manipulation of the vernier adjustment of a series resistance, the times required for each increase of 100 microvolts in the temperature of the calorimeter can were measured with stop watches.

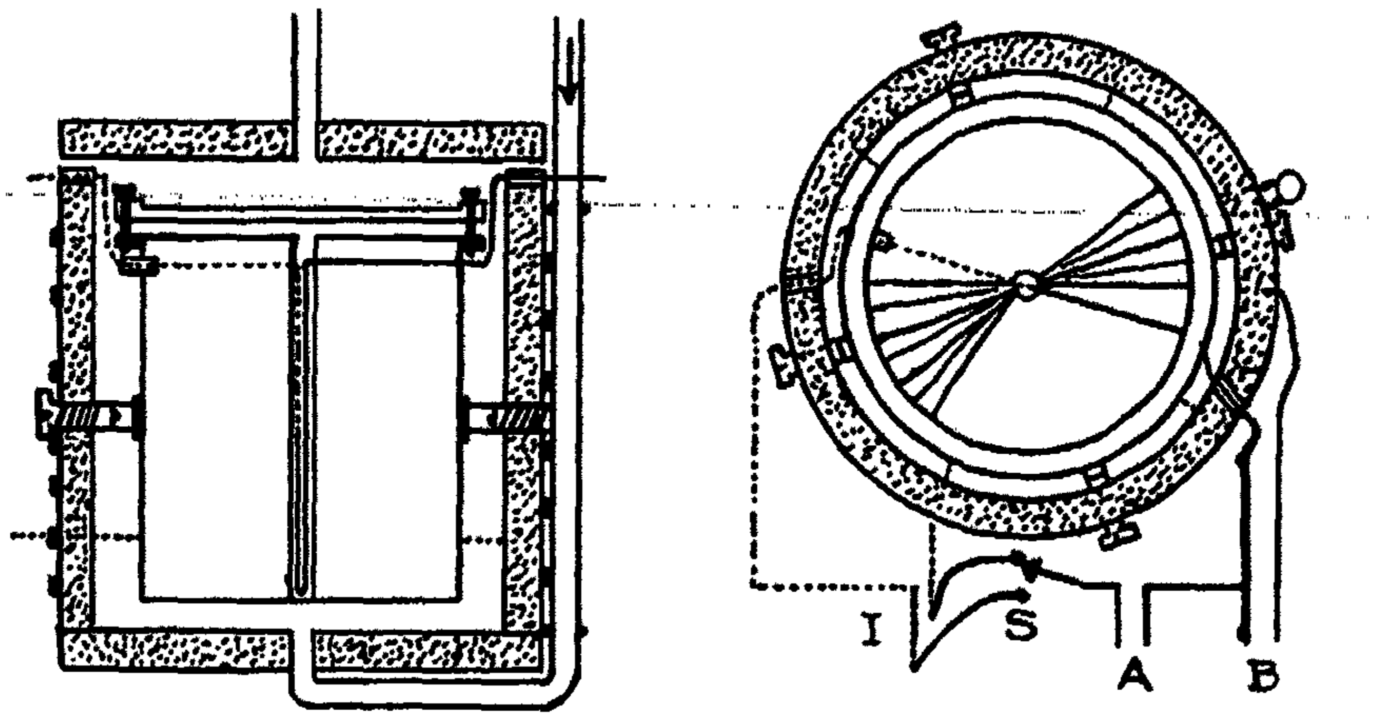

Fig. 1. Vertical cross section of the calorimeter and view from above. I, ice junctions; A, leads to potentiometer indicating temperature at center with knife switch S in upper position and of the wall when in lower position; B, leads to potentiometer for average temperature head. (½ actual size.)

Naphthalene was used as the empirical standard for the calibration.

Wherever available Southard's values (7) for its specific heat were used. Two sets of runs with 22.4 and 71.62 g. of naphthalene gave the rate of heat transfer to the calorimeter and the heat capacity of the empty calorimeter as functions of the temperature.

Silica gel from the Silica Gel Corporation of America was purified by digestion in nitric acid on a steam bath for several days. It was then thoroughly rinsed many times with distilled water during several weeks and finally dried in an oven at 110°C.

The gel was activated by heating for about eight hours at 360°C. in a stream of dried air. The weight of water per unit weight of anhydrous gel was then 3.25 per cent. In this paper the term "activated gel" will represent gel of this water content.

TABLE 1

Amounts of gel and sorbate in experiments

EXPERIMENTS	FIGURES	SILICA GEL	SORBATE	WEIGHT OF SORBATE
		grams		*grams*
52	2	73.63	Naphthalene	35.96
37, 38, 39, 40, 42, 43	8	48.75	Naphthalene	22.9
57	4	69.22	*p*-Nitrotoluene	39.26
35	3	52.1	Water	30.1
44 to 48	7	53.3	Water	26.9
19	5, 10	86.6	Benzene	41.8
21 to 24	6	81.3	Benzene	33.2
16	10	82.7	Benzene	25.7
14	10	83.2		0

The sorption was carried out by mixing gel and sorbate in a heated glass-stoppered bottle on a shaking machine for about twelve hours. The shaking was continued until the gel cooled to room temperature. With naphthalene 70°C. was sufficient for rapid adsorption. A higher temperature resulted in a grey discoloration.

OBSERVATIONS

In figures 2, 3, 4, and 5 (see table 1), the observed times of heating are plotted for typical experiments with silica gel and naphthalene, water, *p*-nitrotoluene, and benzene, respectively. In these experiments a little more of the sorbate was present than was necessary to saturate the gel. The melting of this excess can be seen at the indicated normal melting points. There was also a large heat capacity for the system over a wide temperature interval at a lower temperature. This is taken as evidence of the melting of the adsorbed phase. The actual values for the heat capacity of the adsorbed substance, which are calculated later in this paper, are consistent with this interpretation.

The curves in figures 6, 7, and 8 (see table 1) demonstrate a hysteresis phenomenon. The results were dependent, in the manner shown, upon the lowest temperature to which the system had been cooled previously.

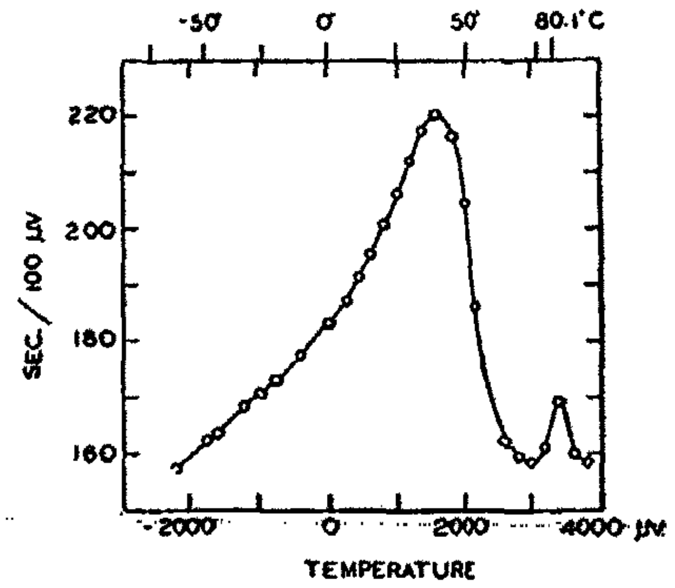

FIG. 2

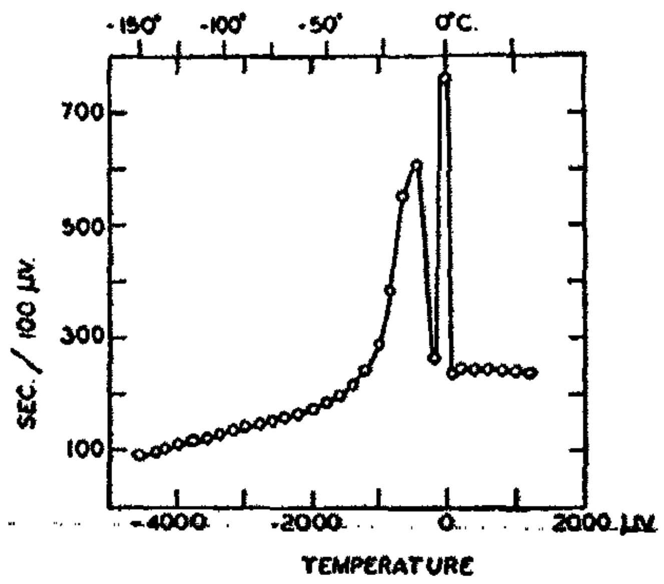

FIG. 3

FIG. 2. Observed heating times for gel saturated with naphthalene and a little excess naphthalene, experiment 52

FIG. 3. Observed heating times for gel saturated with water and a little excess water, experiment 35

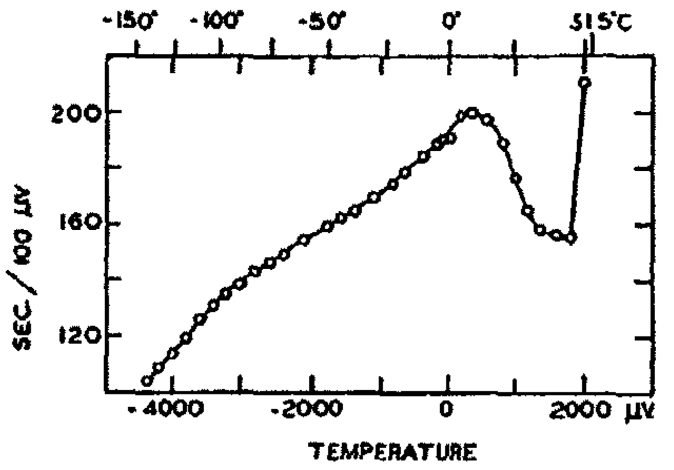

FIG. 4

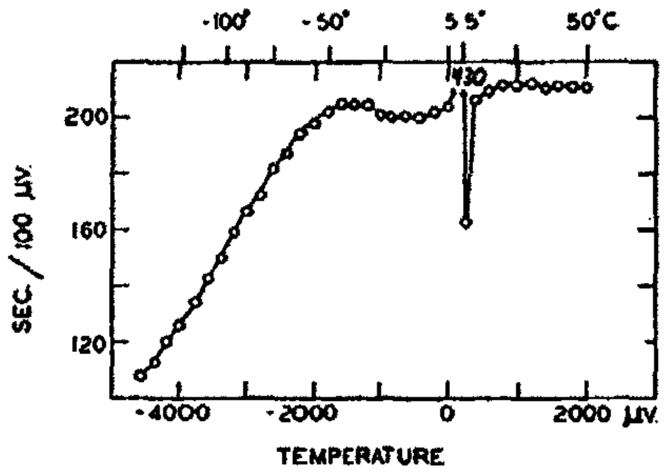

FIG. 5

FIG. 4. Observed heating times for gel saturated with *p*-nitrotoluene and a little excess *p*-nitrotoluene, experiment 57

FIG. 5. Observed heating times for gel saturated with benzene and a little excess benzene, experiment 19

However they were quite reproducible when starting from the same low temperature, and, as far as could be determined, were independent of the rate of cooling or heating.

Figure 9 illustrates how hysteresis in the melting of the adsorbed material could bring about these effects. The slopes of the curves of figure 9,

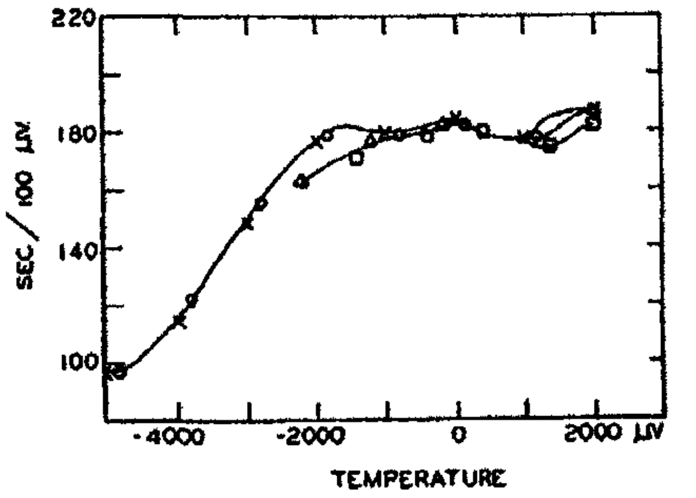

FIG. 6

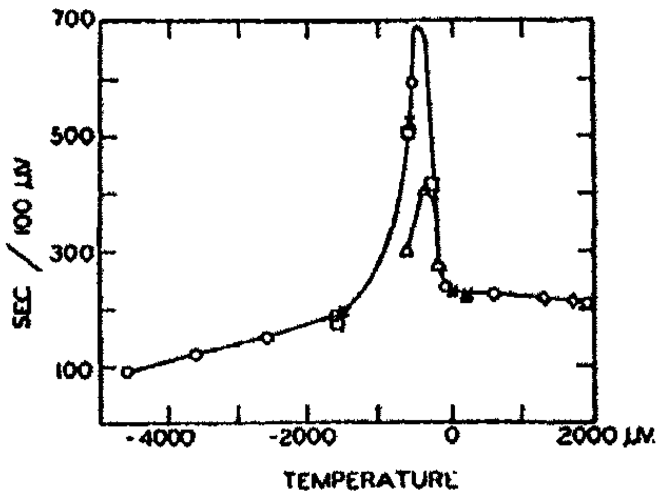

FIG. 7

FIG. 6. Observed heating times for gel nearly saturated with benzene.[2,3] ×, experiment 21, cooled to liquid air temperature; ○, experiment 22, cooled to liquid air temperature slowly, between ±3.5°C. for 48 hr., at carbon dioxide temperature for 18 hr.; □, experiment 23, cooled to carbon dioxide temperature; △, experiment 24, cooled to carbon dioxide temperature.

FIG. 7. Observed heating times for gel nearly saturated with water.[2] ○, experiment 44, cooled to liquid air temperature; ×, experiment 45, cooled to carbon dioxide temperature; □, experiment 48, cooled to carbon dioxide temperature, experiment interrupted at −780 microvolts and held between −780 and −730 microvolts for 3.5 hr.; △, experiment 46, cooled to −20°C.; ◇, experiment 47, started from room temperature.

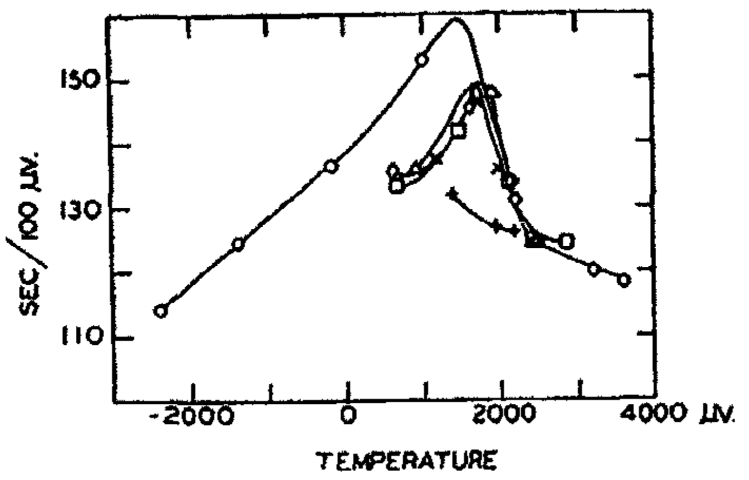

FIG. 8

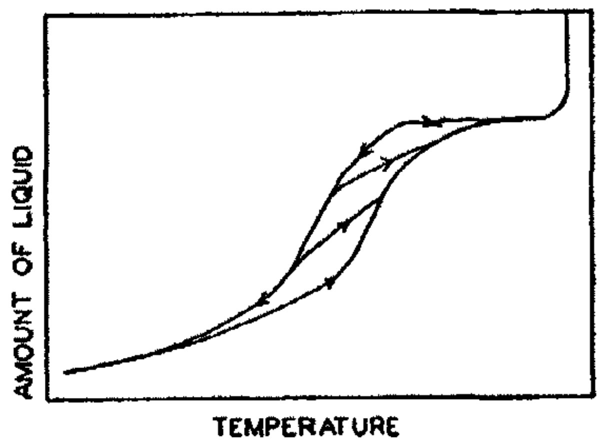

FIG. 9

FIG. 8. Observed heating times for gel nearly saturated with naphthalene.[2] ○, experiment 37, cooled to −89°C.; △, experiment 42, cooled to 2.5°C. rapidly; □, experiment 39, cooled to 5°C. slowly; ◇, experiment 40, cooled to 5°C.; ×, experiment 43, cooled to 5°C., then heated to 15°C. at 2.5 times the usual rate, before taking readings; +, experiment 38, started at room temperature.

FIG. 9. Hypothetical curve, showing hysteresis in amount of liquid in gel

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[2] In order to simplify the curves only every fifth point and the last point were plotted.

[3] The differences in experiments 21, 22, and 23 at the high-temperature end of the curves were due to different rates of evaporation of benzene from the calorimeter, which was not sealed vapor-tight. Because of previous loss, the vapor pressure of benzene was less in the following run.

which represent the amount melting per degree rise in temperature, are similar to the curves in figures 7 and 8. This is the same as the hysteresis in adsorption and desorption measurements with the amount of melt corresponding to the amount adsorbed.

Figure 10 shows typical curves obtained with different concentrations of sorbate. The high values at the low-temperature end of the curves are the result of a complication. The lid of the calorimeter did not seal on tight, and, during cooling, oxygen from between the cylinders was adsorbed on the gel in some experiments. During the measurements the heat of desorption caused these high values. It is apparent that this effect diminishes with increasing concentration of sorbate and is absent with saturated gels.

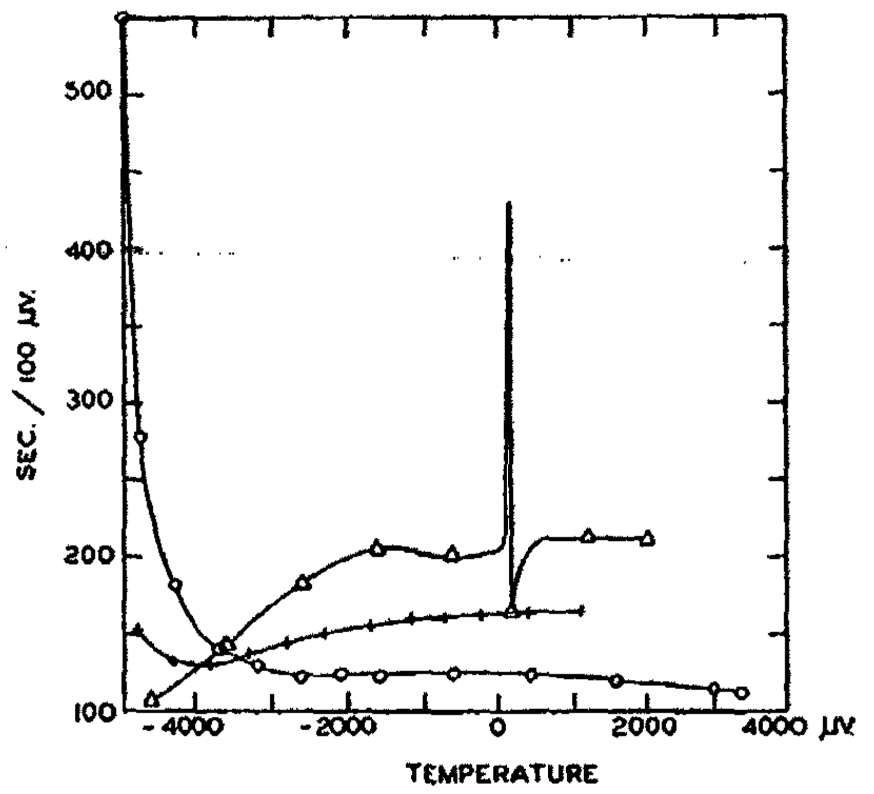

FIG. 10. Observed heating times for silica gel with various amounts of benzene, showing desorption of oxygen.[3] ○, experiment 14, activated gel; +, experiment 16, gel with 31 per cent benzene; △, experiment 19, gel saturated with benzene and some excess.

TREATMENT OF OBSERVATIONS

The heat capacities were calculated from the times of heating. The heat capacity of the sorbate was obtained by subtracting from the heat capacity of the gel and sorbate that of the gel present.

The heat capacity of activated silica gel, as measured in experiment 14, is given in the third column of table 2. However, because of the desorption of oxygen, only those values above 0°C. were used in the calculations of the heat capacity of the sorbate. Below 0°C. estimated values, shown in the last column, were used instead. These were the sum of the heat capacity of silica as measured in this apparatus and that of 3.25 per cent ice as given in the International Critical Tables. The heat capacity of silica was the average of two runs (Nos. 9 and 10, table 2) with 167 g. and 205 g. of Merck's C.P. sea sand. The average difference between 9 and 10 was 0.85 per cent, and their mean averages were 3.3 per cent higher than the values of Simon (4).

Values for the difference in the heat capacity of the sorbate in its adsorbed and normal state are recorded in table 3 and some are shown in figure 11.[4] The values are for the amount of sorbate associated with 100 g. of activated gel, rather than per gram of sorbate, in order that the contributions of the various portions of the sorbate under different capillary forces may be additive instead of averaged, and that the results may be independent of the amount of excess sorbate which has normal heat capacity.

TABLE 2

Specific heats used in calculations

Values are given in calories per degree per 100 grams

TEMPERATURE	HEAT CAPACITY OF SILICA	HEAT CAPACITY OF ACTIVATED SILICA GEL	
	Average of runs 9 and 10	As measured in experiment 14	Estimated
°*k*.			
126	5.45	48.6	8.8
147	6.08	30.2	10.7
167	6.82	23.0	12.0
184	7.47	20.1	13.1
201	8.01	18.4	14.1
217	8.44	17.8	14.8
232	8.92	17.5	15.7
246	9.38	17.3	16.6
260	9.83	18.2	17.4
273	10.27	18.9	18.3
286	10.65	19.2	
299	11.00	19.8	
311	11.28	20.1	
323	11.56	20.5	
334	11.80	20.8	
346	12.03	21.3	

Table 3 shows that at temperatures below its normal melting point the heat capacity of the sorbate is in excess of its normal heat capacity. If the sorbate is condensed in capillaries in the gel, then the difference is accounted for as follows: (*1*) by the heat of fusion of sorbate melting at

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[4] See also figures 3 to 6 of the second paper on this subject (J. Phys. Chem. **42**, 381 (1938)).

lower temperatures; (*2*) by the heat of wetting of the gel by the melt; (*3*) by the heat of compression due to diminishing surface forces; and (*4*) by the difference between the specific heat of the melt and that of the normal solid. The difference increases with rising temperature to a maximum below the normal melting point. At this temperature presumably most of the sorbate is now melted. At the normal melting point the heat of fusion of only the excess sorbate is observed.

These values are given in the last row (opposite "n.m.p."). Above the normal melting point, the differences are small. They are partly due to vaporization of the sorbate from the calorimeter, which absorbs heat. Such loss also makes the estimate of the amount of sorbate in ensuing runs too high. For this reason the results for benzene are not in as good agreement as those for the less volatile sorbates. It is to be noted that these differences are especially small in comparison with the total measured heat capacity of the systems, which, for example, for experiment 44 at 286°K., is 70.2 cal. per degree.

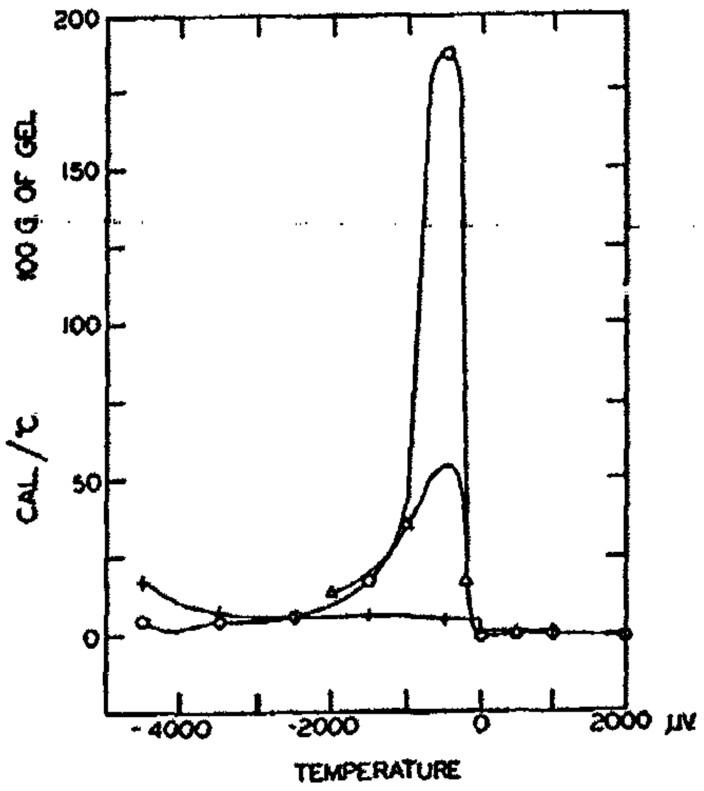

FIG. 11. Heat capacity of adsorbed water in excess of normal heat capacity of water. +, experiment 36, gel 7.1 per cent saturated; △, experiment 51, gel 37.4 per cent saturated; ○, experiment 44, gel 91.4 per cent saturated.

Figure 11 indicates how the results depend upon the composition of the gel-sorbate system. In experiment 36 the gel was 7 per cent saturated with water. Since the surface forces on this small amount of sorbate would be large, it would be expected to be liquid over most of the interval shown. The result then would be the difference in heat capacity of supercooled water and ice. At low temperatures the values are high because of the desorption of oxygen. The results for the 37 per cent saturated

TABLE 3

Heat capacity of substances on silica gel less their normal heat capacity

	BENZENE			WATER							NAPHTHALENE		*p*-NITROTOLUENE*
Experiment	17	21	19	36	51	44	45	48	35	49	50	52	57
Moles per 100 g. of gel	0.542	0.544	0.618	0.217	1.145	2.8	2.8	2.8	3.21	5.36	0.367	0.378	0.413
°K.	CALORIES PER DEGREE PER AMOUNT OF SORBATE ASSOCIATED WITH 100 G. OF ACTIVATED GEL												
126	4.3			17.1		3.7							
147	2.6	2.9	2.8	9.2		2.1			2.8				2.8
167	3.7	2.6	1.6	7.1		3.7			3.3				1.3
184	4.5	3.3	2.8	5.8		5.1			5.1				2.0
201	5.5	4.4	4.0	5.4		6.5			6.5				1.6
217	5.6	4.5	5.0	5.0	13.0	9.2			9.7	7.7	4.8	4.0	1.4
232	4.7	3.5	5.4	5.7	19.3	16.5	15.7	16.0	18.6	16.8	3.6	3.4	1.4
246	2.7	1.2	4.6	4.6	35.5	42.9	41.1	41.5	34.8	41.1	3.5	3.4	1.5
260	1.5	0.3	2.0	4.5	54.2	185.8	160.1	174.4	157.4	153.7	4.1	3.9	2.6
268			2.5	4.2	17.0	43.5	30.8	38.0	35.5	37.3			4.5
273	0.9	−0.2	0.2	0.7‡	0.7‡	−0.8‡	−1.3‡	−5.9‡	1.7‡		5.6	5.1	7.1
281													9.5
286	−0.3	−2.3		0.8	0.2	−0.3	−2.6	−5.7	2.9	−2.5	7.6	7.4	9.3
299	−1.0	−2.4	−0.3	1.3	0.1	−0.4				−3.4	11.5	11.4	3.4
311	1.4	0.5	1.2			−0.6					16.0	15.9	2.7
323	3.7	1.8	1.7			−0.9					10.4	12.3	16.4
334											0.4	1.4	
346												−1.4	
n.m.p.§	−1283	−1290	−1350†	−312	−1645	−4022	−4022	−4022	−4340†	−4460†	−1648	−1700†	

* Normal specific heat (estimated as the mean molecular specific heat of *p*-dinitrobenzene and *p*-xylene) = 12.60 + 0.0991*T* cal. per mole degree.

† Excess sorbate melting. These differences indicate gel capacity to be 0.57 mole of benzene in experiment 19, 3.02 moles of water in experiment 35, 3.11 moles of water in experiment 49, and 0.378 mole of naphthalene in experiment 52.

‡ Heat capacity of sorbate less specific heat of *liquid* water.

§ Normal melting point.

gel are close to those for the 92 per cent saturated gel for an interval, but reach a maximum at a temperature 3°C. lower. Other experiments shown in table 3 indicate that the results are independent of any excess sorbate present. Because of the presence of this frozen excess sorbate, it is unlikely that the remaining sorbate could have supercooled.

CONCLUSION

Substances adsorbed on silica gel melt at temperatures below those at which they would melt in their normal state. Fusion begins at a very low temperature, but the melting temperature rises as increasing amount of melt is formed on the gel. Also, the amount melting increases with the temperature until nearly all the sorbate has melted. In the case of saturated gels this maximum melting occurs with benzene 44°C. below its normal melting point, with water 12°C. below, with naphthalene 40°C. below, and with *p*-nitrotoluene 41°C. below. The amount melting per degree is a reproducible function of the temperature, independent of the rate of cooling or heating, provided the experiments start from the same low temperature. Otherwise there is hysteresis, wherein the amount of solid phase at a given temperature is greater in the experiment starting at the lower temperature.

This is all in accord with the expected behavior of substances condensed in fine capillaries. The negative pressure on the condensed liquid, resulting from surface forces, reduces the escaping tendency of this phase, and a lower temperature is necessary for equilibrium with a solid phase not acted on by surface forces.

SUMMARY

1. The Andrews calibrated heat conduction method was used to measure the heat capacity of substances adsorbed on silica gel. Water, naphthalene, benzene, and *p*-nitrotoluene were investigated in various concentrations.

2. Results from typical experiments for the difference in heat capacity of the adsorbed and normal states of the amount of sorbate associated with 100 g. of activated gel were tabulated. Expressed in this manner, the results were independent of the amount of excess sorbate and over a limited temperature range were independent of concentration for unsaturated gels.

3. Only material in excess of that which saturates the gel melts at its normal melting point. Melting of the adsorbed phase is indicated at lower temperatures by its abnormally large heat capacity. This increment is largest at -12°C. with water, and with the other sorbates at temperatures about 40°C. lower than their normal melting points.

4. These heat capacities were quite reproducible and independent of

the rate of cooling or heating, if started from the same lowest temperature. If previously cooled to a lower temperature, the system had greater heat capacity over certain temperature intervals.

5. The heat of desorption of oxygen was apparent in some experiments. On pure silica gel it was observed up to 240°K. But the larger the amount of sorbate on the gel, the smaller was the capacity of the gel for oxygen.

6. The lowered melting points of the substances adsorbed on silica gel are in agreement with the theory that they are condensed in the capillary voids of the gel and that the forces arising from the highly concave surface of the liquid sorbate are responsible for the lowered escaping tendency of this phase.

We are much indebted to Dr. D. H. Andrews for the apparatus and technique which he has developed and made available for these experiments. Also we wish to acknowledge the generous assistance of Dr. S. Goldheim and Dr. V. Deitz in the laboratory, and of Dr. N. Hackerman in the preparation of this report.

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THE EFFECT OF SURFACE FORCES ON MELTING[1]

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The preceding paper (5) described calorimetric observations from which the lowered melting temperatures of certain substances adsorbed on silica gel were inferred. In this paper calculations are made of the melting temperatures to be expected if capillary condensation is the cause of adsorption, and the calculations are compared with the calorimetric observations of the preceding paper.

MELTING TEMPERATURES OF ADSORBED SUBSTANCES

It is well known (1) that certain adsorbents are supposed to have capillaries in which vapors condense to liquids, and that the vapor pressure of the condensate increases as the capillaries fill and the stress arising from surface forces decreases. The temperature at which this condensate will freeze depends upon how the solid forms. There are several conceivable ways in which the solid might form, each affecting the stresses on the two phases and consequently the freezing temperature, differently. The solid may form on the walls, narrowing the capillaries. It may form entirely within the body of the liquid, causing but little change in the surface of the liquid. Or, it may form by a process of evaporation and sublimation entirely outside the liquid. In this case the vapor pressure of the liquid remaining would be that of the same amount of liquid with no solid present. The stresses on the solid formed would also be different in these cases. In the last case, the vapor pressure of the small solid particles might be increased by a surface tension of the solid, if such a force exists.

It will here be assumed that: (*1*) *the stress on the unfrozen sorbate is independent of the amount of frozen sorbate present*,[2] and (*2*) *the frozen sorbate is not under any stress from surface forces.* The melting temperature will then be calculated as the temperature at which adsorbed liquid and normal solid have the same vapor pressure.

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[1] This article is based on a dissertation submitted by W. A. Kemper to the Board of University Studies of the Johns Hopkins University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1934.

[2] In this paper the assumptions made are printed in italics.

The vapor pressure of the adsorbed liquid, p, is estimated by the Patrick isotherm (6)

$$X_l v_l = k\left(\frac{p\sigma}{\bar{p}}\right)^n \tag{a}$$

In this, in accord with assumption 1, X_l, the amount of melt on the gel, is used in place of the total amount of sorbate, customarily used in the equation at temperatures above the melting point of the sorbate. v_l, σ, and $\bar{p}$ are the specific volume, the surface tension, and the normal vapor pressure of liquid sorbate at the temperature concerned. The subscript l denotes a property of the liquid state and the overrule ($^-$) refers to the value for the unadsorbed or normal state. k and n are constants which characterize the adsorbent. This equation with the same values of k and n gives the vapor pressure isotherm at any temperature and, with the exception of water, for any sorbate.

The normal vapor pressure of liquid, $\bar{p}$, at temperature T, in terms of its value $\bar{p}_m$ at the normal melting point, is given by the Clapeyron equation

$$\ln \frac{\bar{p}}{\bar{p}_m} = \int_{T_m}^{T} \frac{H_g - H_l}{RT^2}\,\mathrm{d}T$$

where H_g and H_l are the heat content of vapor and liquid and R is the gas constant.

With this value of $\bar{p}$, equation a becomes

$$\ln \frac{p}{\bar{p}_m} = \frac{1}{n} \ln \frac{X_l v_l}{k\sigma^n} + \int_{T_m}^{T} \frac{H_g - H_l}{RT^2}\,\mathrm{d}T \tag{b}$$

The vapor pressure of solid at the temperature T, in terms of its value at the normal melting point, T_m, also $\bar{p}_m$, is

$$\ln \frac{\bar{p}_s}{\bar{p}_m} = \int_{T_m}^{T} \frac{H_g - H_s}{RT^2}\,\mathrm{d}T \tag{c}$$

Equating p and p_s from equations b and c, one obtains the melting temperature, T, corresponding to the amount of melt, X_l:

$$\frac{1}{n} \ln \frac{X_l v_l}{k\sigma^n} = \int_{T_m}^{T} \frac{H_l - H_s}{RT^2}\,\mathrm{d}T$$

or

$$\frac{R}{n} \ln \frac{X_l v_l}{k\sigma^n} = \frac{\bar{H}_f}{T_m} - \frac{\bar{H}_f}{T} + \int_{T_m}^{T} \frac{1}{T^2} \int_{T_m}^{T} (C_{pl} - C_{ps})\,\mathrm{d}T^2 \tag{d}$$

where C_{pl} and C_{ps} are the specific heats of liquid and solid sorbate and H_f is the heat of fusion at the normal melting point.

An approximate equation, which neglects the change in the heat of fusion with temperature, is

$$\frac{RT}{n\bar{H}_f} \ln \frac{X_l v_l}{k\sigma^n} = \frac{T - T_m}{T_m} \tag{d'}$$

With these equations (d or d'), when k and n are known for the adsorbent, one can calculate X_l, the amount of sorbate that can exist as liquid at temperature T. Any sorbate in excess of this is solid. This temperature is termed the melting temperature corresponding to the amount of melted sorbate, X_l.

Calculations of this function, X_l, were made for the four compounds studied in the preceding paper (5). The values of k and n were those which best fitted a set of adsorption isotherms for benzene and water which were obtained in the laboratories of the Silica Gel Corporation on a gel of the same type as ours (7). The similarity of the two gels was verified by comparing their water content when activated, a definite characteristic of a gel. Our activated gel contained 0.0325 g. of water per gram of silica as compared to 0.0324 g. of water per gram of silica reported for the gel from which the adsorption data were obtained.

The following are the resulting values:

$$\log X_l v_l = 1.13 + 0.46 \log \frac{p\sigma}{\bar{p}}$$

for organic sorbates, and

$$\log X_l v_l = -0.145 + 1.05 \log \frac{p\sigma}{\bar{p}}$$

for water where X_l is grams of water (above 3.24 per cent) per 100 grams of activated gel.

The specific heat of *p*-nitrotoluene, which has not been reported, was estimated as the mean of the molar specific heats of *p*-xylene and *p*-dinitrobenzene. The values obtained were $C_{ps} = 12.6 + 0.0991T$ and $C_{pl} = 21.17 + 0.085T$ cal. per °C. mole.

The other data for the calculations were obtained from accredited sources.

The actual values of X_l were not calculated from the observations in the previous report. However, the values of X_l, calculated from equation d, are shown in figure 1. Since the amount melting increases with temperature until melting is complete, the observed temperature of maximum melting can be compared with calculations of the temperature at which the sorbate would be completely melted. The temperature at which the heat capacity was a maximum was taken as the temperature of maximum melting. Values of X_l equal to the total amount of sorbate present in these experiments are indicated on the curves by the horizontal lines. A comparison of these two is given in table 1.

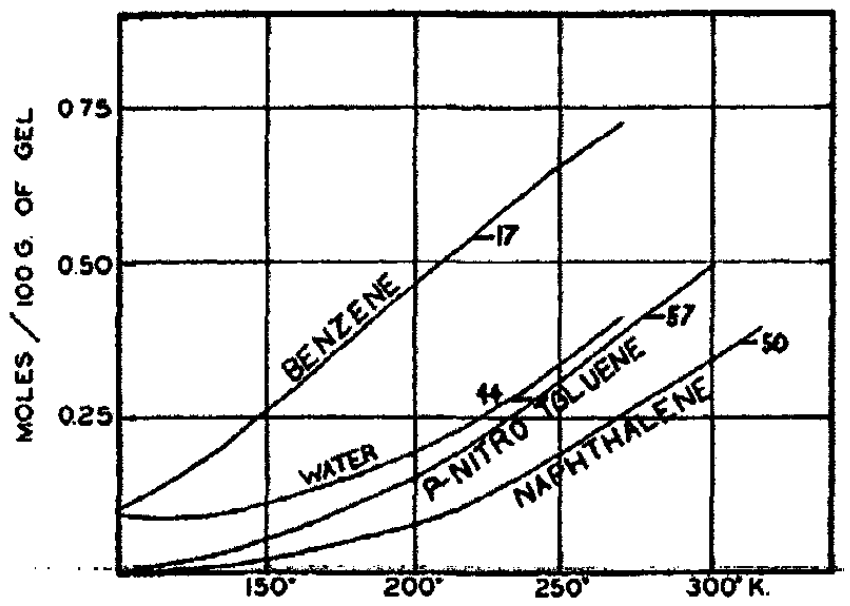

FIG. 1. Calculated amount of unfrozen sorbate. Numbered horizontal line indicates total sorbate present in the experiment indicated

TABLE 1

Comparison of observed temperature of maximum melting with calculated temperature at which the sorbate would be completely melted

SUBSTANCE	EXPERIMENT NO.	CALCULATED TEMPERATURE AT WHICH MELTING IS COMPLETE	OBSERVED TEMPERATURE OF MAXIMUM HEAT CAPACITY
		°*K.*	°*K.*
Benzene	17	219	229
Water	44	231	260
Naphthalene	50	307	313
p-Nitrotoluene	57	278	283

The observed temperatures are not as low as the calculated values. The discrepancy is believed to be due to a hysteresis. The difference is largest in the case of water, and water is known to show more hysteresis than other sorbates.

CALCULATIONS OF THE APPARENT HEAT CAPACITY OF THE ADSORBED PHASE

In the previous paper (5) values were obtained for the difference in apparent heat capacity of the adsorbed phase and normal solid sorbate. If the theory of capillarity is correct, this difference consists of the following terms:

(1) $(C_{pl} - C_{ps})X_l$, the difference in heat capacity of adsorbed liquid and normal solid times the amount of adsorbed liquid.

(2) $(H_l - H_s)\dfrac{dX_l}{dT}$, the heat of fusion times the amount of melting per degree increase in temperature.

(3) $X_l\left(\dfrac{\partial H_l}{\partial P}\right)\dfrac{dP_l}{dT}$, the heat of compression for the change in pressure accompanying one degree rise in temperature.

(4) $-H_\omega \dfrac{d\omega}{dT}$, minus the heat of wetting per unit area times the amount of surface newly wetted by melt per degree rise in temperature.

(5) $\omega \dfrac{dH_\omega}{dT}$, the heat capacity of the surface layer.

The evaluation of each of these terms for the amount of sorbate contained on 100 g. of silica gel follows. In the calculations the *change in density of adsorbed liquid with pressure will be neglected.*

The heat capacity of a liquid is independent of pressure, if *thermal expansion is assumed to be linear.* For

$$\frac{\partial C_{pl}}{\partial P} = T\frac{\partial^2 v_l}{\partial T^2} = 0$$

Hence the first term is

$$(\bar{C}_{pl} - \bar{C}_{ps})X_l \tag{1}$$

The amount melting per degree is obtained from the derivative of equation d with respect to temperature, σ being represented by $A + BT$ and $\dfrac{1}{v_l}\dfrac{\partial v_l}{\partial T}$ by E, the coefficient of cubical expansion. The expression is

$$\frac{dX_l}{dT} = \frac{nX_l}{RT^2}\left[\bar{H}_f + \int_{T_m}^{T}(C_{pl} - C_{ps})\,dT + \frac{BRT^2}{A + BT}\right] - EX_l \tag{e}$$

The heat of fusion is

$$H_l - H_s = \bar{H}_f + \int_{T_m}^{T}(C_{pl} - C_{ps})\,dT + \int_0^{P_l}\left(\frac{\partial H_l}{\partial P}\right)_T dP_l$$

where P_l is the hydrostatic pressure on the adsorbed liquid.

The value of the last term, the heat of expansion, is obtained from the equation of state:

$$\left(\frac{\partial H_l}{\partial P}\right)_T = v_l - T\left(\frac{\partial v_l}{\partial T}\right)_P$$

The second term of this is neglected so that

$$\int_0^{P_l}\left(\frac{\partial H_l}{\partial P}\right)_T dP_l = v_l P_l$$

In order to change from the auxiliary function P_l to T the following procedure can be used: P_l is related to the vapor pressure of the liquid by the equation for the vapor pressure of a liquid under hydrostatic pressure,

$$RT \ln p/\bar{p} = v_l P_l$$

Then, using the value of $p/\bar{p}$ from equation a, one obtains

$$v_l P_l = \frac{RT}{n} \ln \frac{X_l v_l}{k\sigma^n}$$

Finally by means of equation d the value of $v_l P_l$ is found in terms of T.

$$v_l P_l = \frac{\bar{H}_f T}{T_m} - \bar{H}_f + T \int_{T_m}^{T} \frac{1}{T^2} \int_{T_m}^{T} (C_{pl} - C_{ps})\, \mathrm{d}T^2 \qquad \text{(f)}$$

This is a fundamental equation and also could have been obtained from

$$v_l \mathrm{d}P_l = \frac{H_l - H_s}{T} \mathrm{d}T$$

which results from equating

$$\mathrm{d}F_l = \mathrm{d}F_s$$

where F denotes free energy.

Using equation f, and simplifying, one then obtains for the heat of fusion,

$$H_l - H_s = \frac{\bar{H}_f T}{T_m} + T \int_{T_m}^{T} \frac{C_{pl} - C_{ps}}{T} \mathrm{d}T \qquad \text{(g)}$$

The second term of the heat capacity, $(H_l - H_s)\frac{\mathrm{d}X_l}{\mathrm{d}T}$, can now be obtained by multiplying equations e and g.

As the amount of liquid is increased by melting, the negative pressure decreases and the liquid is subject to compression. The increase of pressure on the liquid with temperature is found by taking the derivative of equation f with respect to temperature. When v_l is represented by $v_l = v_{l_0}(1 + E\Delta T)$, the equation of state becomes

$$\left(\frac{\partial H_l}{\partial P}\right)_T = \frac{1 + ET_0}{1 + E\Delta T} v_l$$

(This coefficient of v_l is small and was neglected above in calculating the correction to the heat of fusion for the expansion of newly melted liquid.) The heat of compression is then

$$X_l \frac{\mathrm{d}P_l}{\mathrm{d}T}\left(\frac{\partial H_l}{\partial P}\right)_T = X_l \frac{1 - ET_0}{1 + E\Delta T}\left[\left(\frac{\bar{H}_f}{T_m} - \frac{\bar{H}_f}{T} + \int_{T_m}^{T} \frac{1}{T^2} \int_{T_m}^{T} (C_{pl} - C_{ps})\, \mathrm{d}T^2\right)\right.$$
$$\left.\left(\frac{1 - ET_0}{1 + E\Delta T}\right) + \frac{\bar{H}_f}{T} + \frac{1}{T} \int_{T_m}^{T} (C_{pl} - C_{ps})\, \mathrm{d}T\right] \qquad (3)$$

The heat content per unit area of surface,

$$H_\omega = \sigma - T\frac{\mathrm{d}\sigma}{\mathrm{d}T} = A$$

where A was defined by $\sigma = A + BT$.

Activated silica gel is assumed to be covered with a monomolecular film of water. As melted sorbate fills the capillaries, this water-air interface is replaced by a water-sorbate interface. The heat evolved will be the heat content of the water-air interface less that of the water-sorbate interface. By Antonow's rule (2), which is valid if the molecules of the second liquid are not oriented at the water interface, this difference is equal to the heat content of the sorbate-air interface, which is A times the area.

The change in area of surface, ω, is calculated by considering a differential element of the capillary as a cylinder. The element of volume is $\pi r^2 \mathrm{d}h$ and the element of area is $2\pi r \mathrm{d}h$. Hence

$$\frac{\mathrm{d}\omega}{v_l \mathrm{d}X_l} = \frac{2}{r}$$

and since

$$P_l = -\frac{2\sigma}{r}$$

$$\frac{\mathrm{d}\omega}{\mathrm{d}T} = -\frac{v_l P_l}{\sigma}\frac{\mathrm{d}X_l}{\mathrm{d}T}$$

Using the value of $v_l p_l$ from equation f, one obtains for the fourth term,

$$H_\omega \frac{\mathrm{d}\omega}{\mathrm{d}T} = \frac{AT}{A + BT}\left[\frac{\bar{H}_f}{T_m} - \frac{\bar{H}_f}{T} + \int_{T_m}^{T} (C_{pl} - C_{ps})\,\mathrm{d}T^2\right]\frac{\mathrm{d}X_l}{\mathrm{d}T} \qquad (4)$$

Since the heat content of the surface,

$$H_\omega = \sigma - T\frac{\mathrm{d}\sigma}{\mathrm{d}T} = A$$

and A is independent of the temperature,

$$\omega\frac{\mathrm{d}H_\omega}{\mathrm{d}T} = 0 \qquad (5)$$

The sum of the above five terms represents, on the basis of the assumptions that have been made, the apparent heat capacity of the adsorbed substance in excess of its heat capacity in its normal solid state, if capillarity is the cause of its adsorption.

Calculation of all of these quantities for the four substances reported in

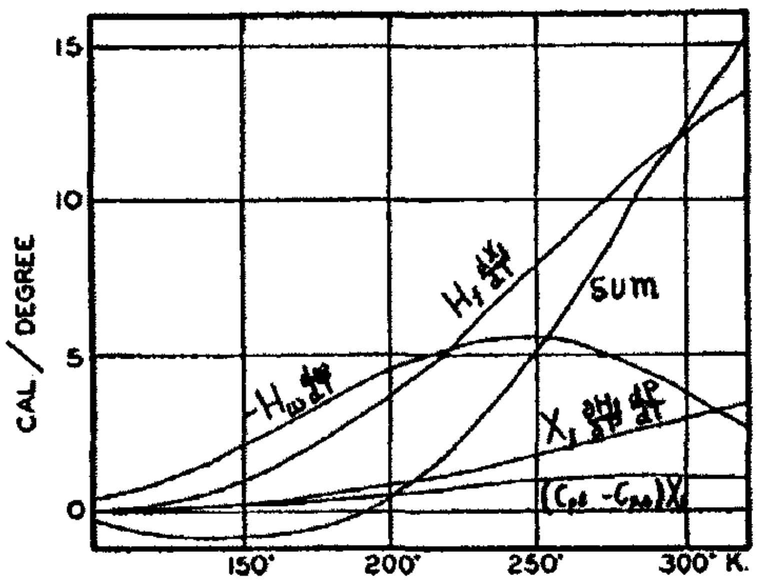

FIG. 2. Calculated component parts of extra heat capacity of naphthalene associated with 100 g. of activated gel

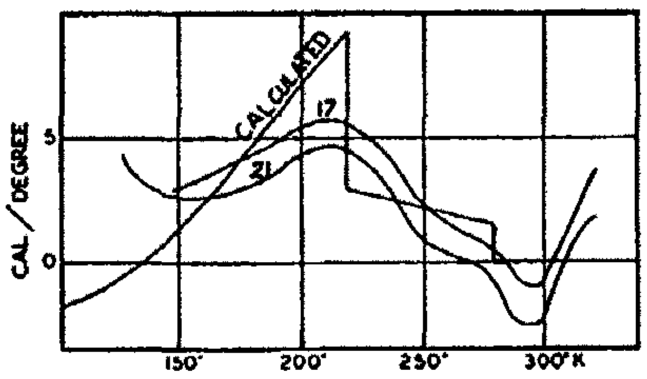

FIG. 3

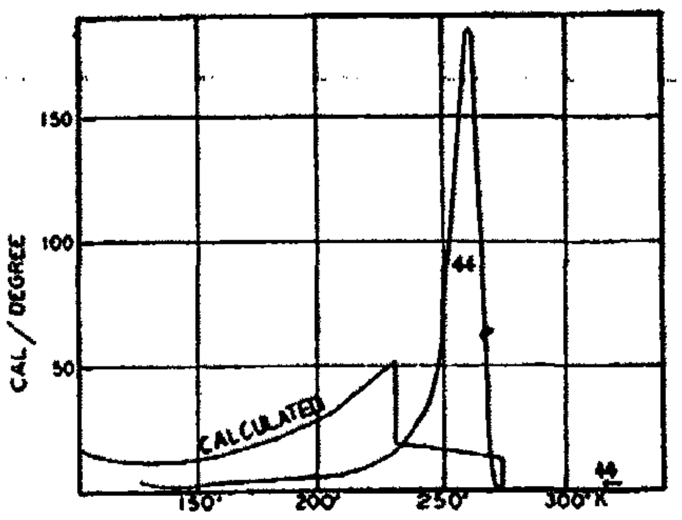

FIG. 4

FIG. 3. Additional heat capacity of benzene adsorbed on 100 g. of gel
FIG. 4. Additional heat capacity of water adsorbed on 100 g. of gel

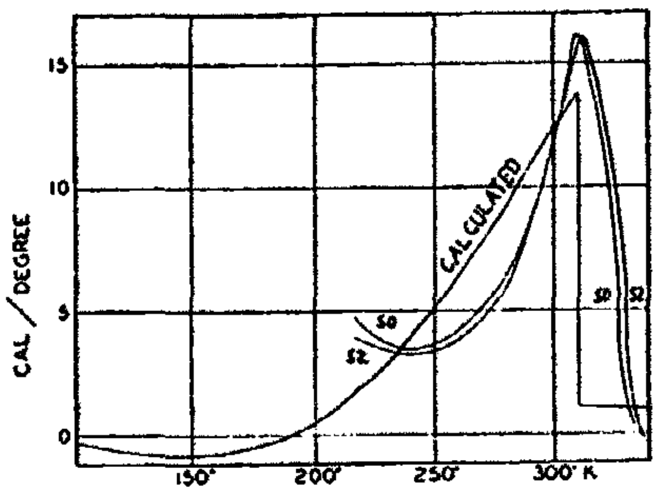

FIG. 5

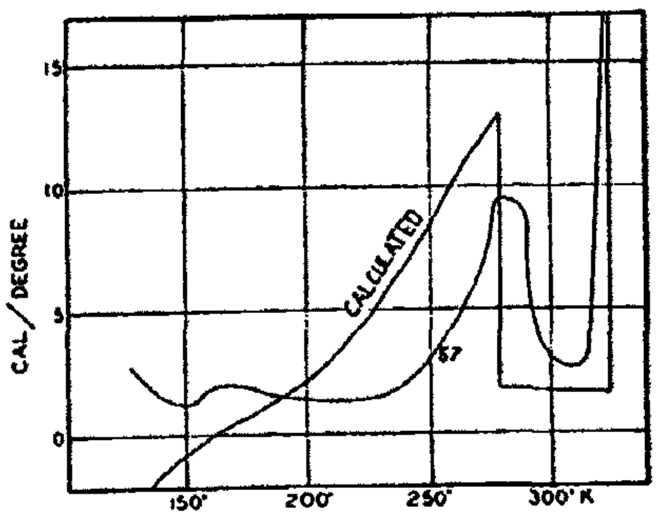

FIG. 6

FIG. 5. Additional heat capacity of naphthalene adsorbed on 100 g. of gel
FIG. 6. Additional heat capacity of *p*-nitrotoluene adsorbed on 100 g. of gel

the previous paper has been made. Figure 2 shows the calculated increase in heat capacity of adsorbed naphthalene and the components from which it was evaluated. Figures 3 to 6 show the calculated and observed values for the increase in heat capacity of benzene, water, naphthalene, and *p*-nitrotoluene when adsorbed on the gel.

The observed values lie on the high temperature side of the calculated values, and once more the poorest agreement found is in the case of water. The hysteresis would cause the values observed on heating to lag behind those calculated for equilibrium conditions.

DISCUSSION

One might suppose that the small size of the solid particles would have some effect on the melting point. Meissner (4) observed a melting-point lowering of a fraction of a degree with crystals 0.8 μ thick. However, Meissner's experiments and most of the theoretical treatments have been concerned with a situation in which the particles were within the melt. In the present experiments the simplifying assumption has been made that the solid has normal vapor pressure. Kubelka (3), who discussed various theoretical equations, proposed a similar simplification for sorbates in silica gel or charcoal. He derived an approximate equation for the melting-point lowering as a function of the radius of the capillaries, in which he assumes that the heat of fusion is constant with the temperature.

In this paper we have calculated the temperature at which normal solid is in equilibrium with an adsorbed phase, which follows the Patrick isotherm modified for a supercooled liquid. It is, of course, possible that the use of some other isotherm equation based upon some other theory of adsorption might give equally good results. However, the assumptions made contain intrinsically a good deal of the idea of capillarity. To this extent, accordingly, such agreement as exists between the calculations of the present paper and the calorimetric observations lends some support to the theory of capillary condensation. A closer agreement could not be expected without eliminating the hysteresis phenomenon.

SUMMARY

1. The Patrick equation for adsorption was extended below the normal melting point of the sorbate by using as values for normal vapor pressure, surface tension, and specific volume, those of supercooled liquid sorbate.
2. A general equation was obtained for the melting temperature of substances condensed in porous adsorbents.
3. Calculations were made of the melting temperatures of the four substances adsorbed on silica gel reported in the previous paper (5). The calculations used only two constants characterizing the gel, k and n of the Patrick equation. The values employed for these were obtained from

a study of adsorption isotherms of benzene and water on this gel at higher temperatures. The temperatures at which the last portions of the sorbates were calculated to have melted averaged only 14°C. lower than the temperatures at which the maxima in the heat capacities of the systems had been observed. It is believed that the calculated temperatures are lower because of hysteresis.

4. Further equations were derived from the various terms which compose the difference between heat capacity of the sorbate in the adsorbed state and in its normal solid state.

5. The results of these calculations were compared with the observations reported in the previous paper (5).

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ELECTROKINETIC ASPECTS OF SURFACE CHEMISTRY. IV

THE RATIO OF ELECTROÖSMOSIS TO ELECTROPHORESIS

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Abramson (1), Daniel (6), Dummett and Bowden (7), and Bull (5) have found that the electrophoretic mobility, *v*, of inert particles coated with protein is the same as the electroösmotic mobility, *u*, of the solution past the wall of the electrophoresis cell when it, too, is coated with the same protein. White, Monaghan, and Urban (15, 16) have agreed that the ratio *R* (where $R = u/v$) is equal to unity in the presence of salts when a concentration of gelatin of about 0.01 per cent or more is present, but they contend that in the absence of added salt *R* assumes values between 2 and 2.3. Moyer and Abramson (13) investigated this reported value of *R*, using concentrations of gelatin down to 0.02 per cent at specific conductances of about 4×10^{-6} ohm^{-1}-cm.$^{-1}$, yet were unable to detect a significant rise of the ratio from unity. Recently, however, White and Fourt (14) have again reported divergent ratios and maintain that the difference between the results of Moyer and Abramson and those of White, Monaghan, and Urban, in the absence of added salt, is due to the higher gelatin concentration used by Moyer and Abramson. It was claimed that, although the coating was complete in all concentrations of gelatin employed, the effect of "an increase in gelatin concentration, as of increasing electrolyte concentration, is to bring the ratio to unity".

As proof of complete coating of the cell and particles, the identity of their isoelectric points was presented. Abramson (2) has pointed out that identity of isoelectric points is a necessary but not a sufficient condition to establish identity of surfaces. (See in particular experiments performed by the writer (10) with aluminum oxide particles coated with egg albumin.) For their experiments Abramson and Moyer and Abramson have always been careful to place both the cell and the particles in strong (1 per cent) gelatin solutions until coating is established, and then to dilute the solutions to the gelatin concentration desired, using this device in order to have a *low* conductance with a *complete* film.

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[1] John D. Jones Scholar at the Biological Laboratory, Cold Spring Harbor, New York, during the summer of 1937.

On the other hand, White *et al.* have contended that merely placing wall and particles in contact with 0.01 per cent gelatin solutions is sufficient to coat the surfaces completely and that the high values for the ratio are due to other causes. Willey and Hazel (17) have recently investigated the problem, using particles of colloidal ferric oxide in gelatin solutions. By exposing the particles and cell walls to dilute gelatin solutions, they concluded that to get identical surfaces, other than at the isoelectric point and in the absence of added salts, about 0.2 per cent gelatin was required. Below this concentration divergent values for u and v were reported. Addition of salts brought the ratio to $R = 1.0$. Further details are presented in their paper. Similar results have been reported by van Gils (8) who states, however, that complete coating is attained first at a concentration of 0.05 per cent gelatin in the absence of salts.

In the experiments now to be presented, quartz particles were placed in 1 per cent solutions of electrodialyzed "Silver Label" gelatin (manufactured by the American Carbon Works) for fifteen minutes. They were then centrifuged and the supernatant liquid removed. Some of the sediment was diluted to 0.001 per cent nominal concentration of gelatin. Meanwhile an Abramson horizontal microelectrophoresis cell (a modification of a cell described by Northrop and Kunitz but constructed of one piece of glass)[2] (2, 9) was also filled with some of the original gelatin solution. After the lapse of time, the excess gelatin was removed from the cell by repeated rinsing (at least four times) with distilled water. Precaution was taken to coat the walls of all measuring vessels with gelatin in the same way. The suspension was then introduced into the cell and measurements performed by our usual methods (9, 13).

Figure 1 shows the observed mobility, V, of these particles at various depths, X, from the top of the cell. The specific conductances of these solutions of 0.001 per cent gelatin were about 4×10^{-6} ohm^{-1}-cm^{-1}. The smooth, unbroken curve has been drawn from the usual parabolic equation (13), assuming $R = 1.0$. The two upper curves (dashed) have been calculated, taking $R = 1.5$ and $R = 2.0$. Other experiments in which Pyrex glass was used instead of quartz gave the same results. Under our conditions, it seems that the ratio is very near unity.

These experiments indicate that once the surfaces are coated, they retain their coating even after great dilution of the gelatin. It appears probable that the exposure of particles to initially dilute gelatin solutions in distilled water may not produce a complete, uniform film. The ratio of unity hardly permits one to draw conclusions (17) as to the value of the constant

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[2] This cell has a rectangular cross section, with non-polarizable electrodes, and has been shown to yield data which check quantitatively with results obtained from measurements in U-tubes (3, 4, 9). White *et al.* and Willey and Hazel used cells for which, as yet, no comparisons of this character seem to have been presented.

of proportionality in the Helmholtz-Smoluchowski equations of electroosmosis and electrophoresis, except that it is the same in both equations when the coated surfaces of the particle and the wall are exposed to identical conditions. The agreement between mobilities of certain dissolved and adsorbed proteins suggests that these adsorbed proteins confer their own effective radii on the particle and the wall surfaces (2, 11, 13). Hence the constant might assume varying values, depending on the ionic strength and effective radius (12), yet under any given conditions the proportionality constant would be the same for both wall and particle, when completely coated, and the ratio would remain at $R = 1.0$. Gelatin is

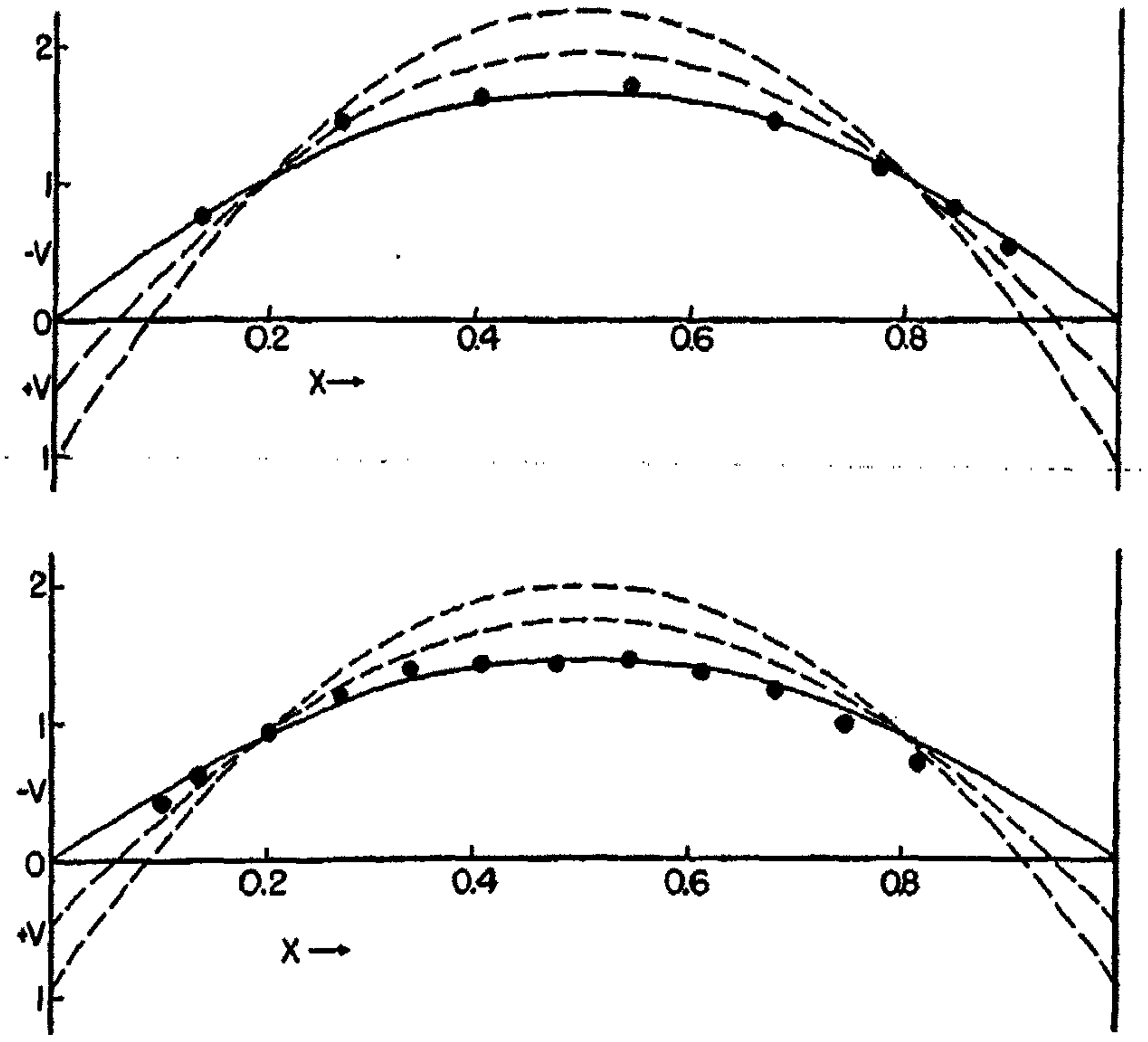

FIG. 1. The mobility, V, of gelatin-coated particles at various levels, x, of a microelectrophoresis cell. Both experiments were performed at a final gelatin concentration of 1:100,000 without added salt, and at a specific conductance of about 4×10^{-6} ohm^{-1}-cm^{-1}. The smooth, unbroken curve (lowest) has been calculated, assuming $R = 1.0$. The two upper curves (dashed) have been calculated, taking $R = 1.5$ and $R = 2.0$. It is evident that, within the limits of error, the experimental points fit the curve for $R = 1.0$, indicating that electrophoresis and electroösmosis are equal. The mobilities given in each figure have been reduced to unit field strength.

a protein of non-uniform particle size. In certain cases this might hinder the attainment of identity of surfaces (by adsorption of slightly different components by wall and particle), yet for systems where $R = 1.0$ the surfaces under comparison have probably adsorbed the same component (or mixture of components). Hence under these conditions r would be the mean radius and κr would be statistically the same for both wall and particle.

SUMMARY

The ratio of electroösmotic to electrophoretic mobility of gelatin-coated surfaces is very near unity, even in gelatin solutions as dilute as 0.001 per cent and in the absence of added salt, if care is taken to insure a complete coating.

ADDENDUM

While this paper was in press, White and Fourt published their complete results (J. Phys. Chem. **42**, 29 (1938)). Two of their undialyzed gelatin preparations (Eastman and Coignet) gave high ratios at low concentrations in distilled water *but Agfa gelatin yielded ratios of 1.00, even at 0.01 per cent gelatin in distilled water.* This contradiction to be observed in their own data makes it necessary to scrutinize their experimental method for its precision. White and Fourt report that initial exposure of the wall of the cell to 1 per cent gelatin solutions, and subsequent dilution, failed to reduce the high ratios, but no measurements appear to be presented in which both wall and particles were initially exposed to this concentration, as in our experiments. They mention the ratio of 1.11 obtained by Moyer and Abramson with 0.02 per cent Agfa gelatin in distilled water. That this is not significantly higher than 1.0 is shown by our control experiment (13) in $M/100$ potassium chloride with 0.2 per cent gelatin for which the ratio was 1.07.

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THE DETERMINATION OF MOLAR WEIGHTS OF VAPORS NEAR THE BOILING POINT

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INTRODUCTION

Molecular weights have been determined by a great variety of methods. One of the oldest of these is the determination of the vapor density of the substance and the subsequent calculation of the molecular weight from this. Measurements of vapor density permit not only the calculation of molecular weights, but also the study of heats of vaporization and of the departure of the behavior of the vapor from the perfect gas law.

From a consideration of the perfect gas law it is clear that in order to determine the molecular weight of a vapor it is necessary to know four quantities: namely, mass, volume, temperature, and pressure.

The most famous method, and the one used more than any other for the determination of vapor densities, is that devised by Victor Meyer (4) in 1876. The most important improvements attempted on this method were those of Weiser (6) and MacInnes and Kreiling (3). Other well-known methods of determining vapor densities are those of Lunsen, Gay-Lussac, and Hofmann.

In 1933 Cady devised the most precise and rapid method ever developed for the determination of molar weights from vapor densities. This method is an application of the Westphal balance to vapors. In 1936 Rankin (5) modified Cady's method so that it was possible to determine the vapor densities of substances over a range of temperature, thus enabling one to approach the vapor density of the substance at the boiling point very closely. The apparatus was so constructed that data could be obtained making it possible to correct for any adsorption that might be in evidence as the boiling point of the liquid was approached.

The well-known method of Dumas is often used in measuring vapor densities. Cady proposed the modification of the Dumas method in such a manner as to eliminate the errors possible when weighing a vessel of large surface. The apparatus described in this paper not only eliminates this error but also enables one to determine vapor densities of substances close to their boiling points.

APPARATUS

The apparatus used in measuring the volume and mass of the vapor being studied is shown in figure 1. The volumetric flask F was calibrated after the stopcocks 2 and 3 had been sealed onto the vessel; these two stopcocks were of capillary tubing.

All of the external glass tubing, starting at the distilling flask and ending at the condenser, was wrapped with resistance wire and heated with a current of about 1 ampere while making determinations. This was done to prevent condensation of the vapors in the tubes before they reached the condenser or weighing bottle.

The weighing bottle, not shown in figure 1, was connected at B by a ground-glass joint. The weighing vessel consisted of a tube 10 mm. in diameter and 75 mm. long. Both openings were at the top, one tube extending about 65 mm. down inside the vessel. This tube had a glass-wool plug in a constriction at the lower end. Each of the entry tubes was connected to a small stopcock, one of the stopcocks being sealed to a ground-glass joint so that the weighing vessel could be attached to the main apparatus at B. A counterpoise was used that had the same shape and nearly the same volume as the weighing vessel.

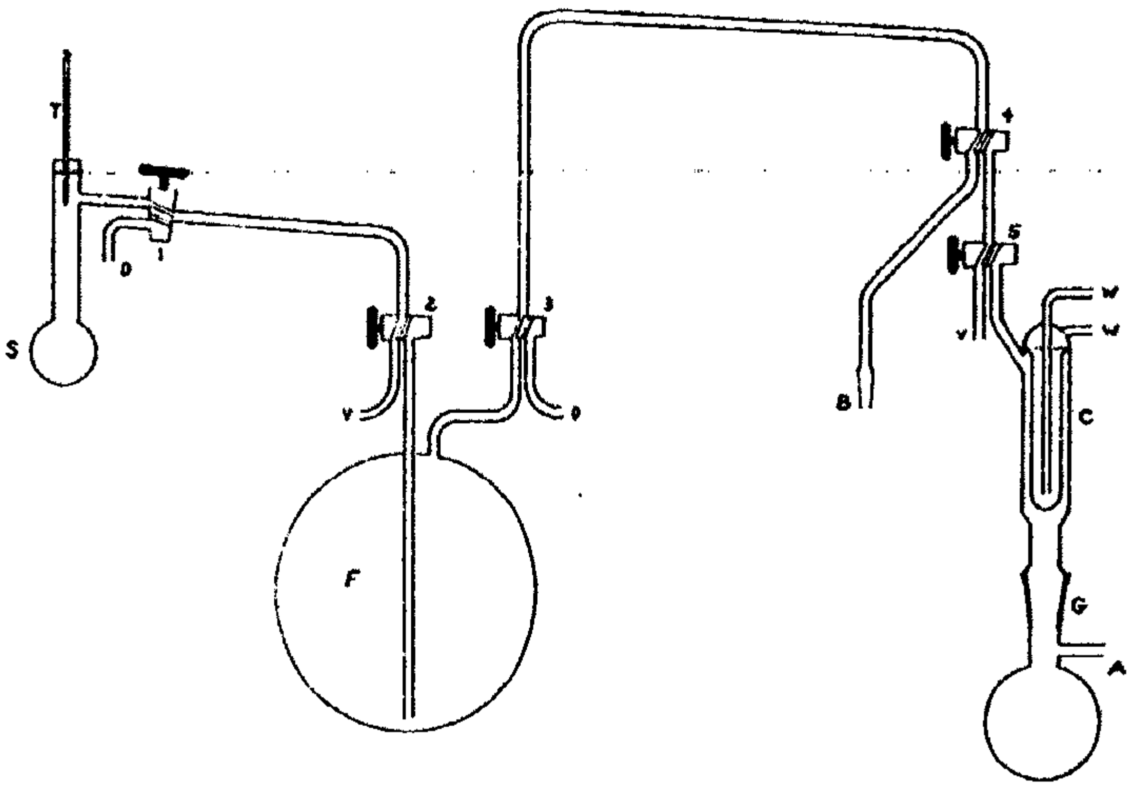

Fig. 1. Apparatus used in measuring the volume and mass of the vapor

The apparatus used in controlling the pressure is shown in figures 2 and 3. The apparatus shown in figure 2 operates on the principle that the flask packed in ice will always bring the trapped air to the same volume. Hence the external pressure will always have to be the same at R in order to close the tungsten-mercury contact in the capillary tube.

Figure 3 shows the artificial atmosphere which was used to maintain a constant pressure on the volumetric apparatus.

The principle on which this apparatus works is as follows: Compressed air is admitted at C by means of a constant-pressure reducing valve set at a pressure of 10 lb. The magnetic valve G being open, as is the stopcock V when the air is turned on, the air passes over into the bottle B and there builds up pressure until contact is made by the mercury contact in the pressurestat shown in figure 2. This contact closes the solenoid circuit and the magnetically operated ground valve G is drawn into place and closed. V is then closed, and the two needle valves N are adjusted until the amount of air leaving the valve connected to the large bottle is slightly greater than the amount getting through G when it is closed; thus the pressure falls and the contact is broken in the pressurestat. This opens the valve G, and more air now goes through the needle valve above G than can escape through the other needle valve; hence the pressure builds up until contact is made in the pressurestat, again closing G. When G is closed the air escapes through the mercury bubbler M.

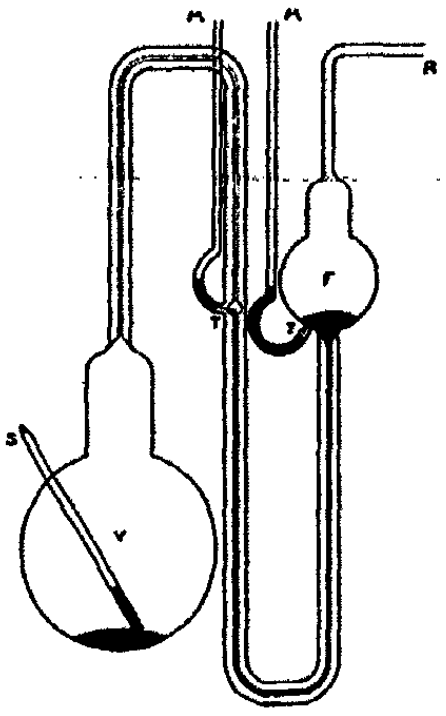

Fig. 2

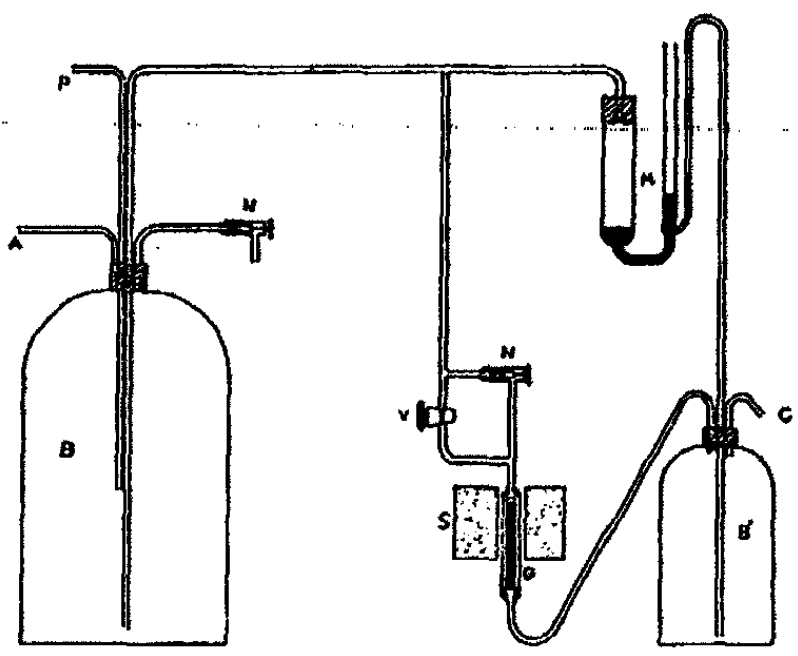

Fig. 3

Fig. 2. Apparatus used in controlling the pressure
Fig. 3. Artificial atmosphere used to maintain a constant pressure on the volumetric apparatus

Since the solenoid is connected to 110 volts D.C., an amplifier and relay are used to prevent sparking of the mercury contact in the pressurestat. The relay used was one that closed on 12 milliamperes and opened cleanly on 3 milliamperes or less.

The volumetric apparatus was maintained at a constant temperature by having the volumetric flask immersed in mineral oil contained in a vessel insulated with rock wool. The heater in this bath was controlled by a mercury regulator which operated a relay connected to an amplifier.

The pressurestat was calibrated by hooking it up to the artificial atmosphere, which in turn was connected to a precision barometer. The pressurestat was packed in ice and the difference in levels of the barometer was read with a cathetometer. It was found that, with the contact in the pressurestat making and breaking at five-second intervals, no movement of the mercury levels was visible through the cathetometer; this indicated that the apparatus was maintaining the pressure constant to 0.02 mm. The pressure maintained was 760.44 mm.

The principle involved in making a vapor density determination with the apparatus described is very simple. It merely involves getting a known volume of vapor under known conditions of temperature and pressure and then condensing this vapor into a weighing bottle and weighing it.

After the vapor has been brought to constant conditions in the volumetric apparatus the flask is cut off from the rest of the system by closing stopcocks 2 and 3. The connecting tubes are cleaned out by drawing dry air through them. The air is dried by passing it through a calcium chloride tube and then through a spiral containing a filter immersed in liquid air. The weighing bottle is immersed in liquid air, and the vapor in the volumetric flask is drawn over into the weighing bottle and frozen out by the liquid air. The weighing bottle is then weighed, and the four quantities necessary for the calculation of the vapor density are then available.

PURIFICATION OF MATERIALS

The authors were very fortunate in having very pure liquids at hand with which to work. All of the alcohols which were used in the vapor density measurements had been purified by Mr. Morgan Rarick of the Department of Chemistry, University of Kansas.

These alcohols had been purified chiefly by fractional distillation and fractional freezing. Their purity was checked by determining their physical constants and also by the use of Cady's vapor density machine, which is a sensitive device for the determination of the purity of liquids.

The deuterium oxide used was obtained from the Stuart Chemical Co., San Francisco, and was listed as 99.9+ per cent D_2O; its density at 25°C. was 1.1079 g. per cubic centimeter.

METHOD OF CALCULATION

The calculation of molar weights from the data obtained is accomplished by a transposition of the well-known perfect gas equation:

$$M = \frac{mRT}{PV}$$

The author concludes that the results calculated from the data taken may be taken as accurate to 0.03 of a molar weight unit for the alcohols and 0.05 of a molar weight unit for water and deuterium oxide. These figures were obtained from a consideration of the following facts: the temperature may be taken as accurate to 0.1°C., the pressure is known to 0.02 mm., the volume to 0.01 cc., and the mass to one part in two thousand in the case of the smallest amount of liquid weighed.

TABLE 1

Molar weights of alcohols, water, and deuterium oxide

TEMPERATURE	VOLUME	MASS	MOLAR WEIGHT
Data for methyl alcohol, formula weight 32.03, b.p. 64.5°C.			
°C.	cc.	grams	
66.2	512.15	0.6214	33.76
70.2	512.17	0.6101	33.54
75.1	512.20	0.5986	33.38
80.2	512.23	0.5858	33.14
85.3	512.25	0.5737	32.92
Data for ethyl alcohol, formula weight 46.05, b.p. 78.5°C.			
82.0	512.23	0.8423	47.89
86.0	512.25	0.8308	47.77
90.0	512.27	0.8190	47.61
95.0	512.30	0.8051	47.44
100.0	512.33	0.7916	47.28
Data for *n*-propyl alcohol, formula weight 60.06, b.p. 97.8°C.			
100.1	512.33	1.0590	63.27
104.0	512.35	1.0440	63.02
107.9	512.37	1.0296	62.80
113.0	512.40	1.0125	62.57
118.0	512.42	0.9956	62.32
Data for isopropyl alcohol, formula weight 60.06, b.p. 82.3°C.			
83.9	512.24	1.1037	63.09
86.3	512.26	1.0927	62.88
90.0	512.27	1.0777	62.67
95.1	512.30	1.0594	62.44
102.0	512.35	1.0364	62.23
Data for *n*-butyl alcohol, formula weight 74.08, b.p. 117.7°C.			
°C.	cc.	grams	
120.1	512.43	1.2607	79.34
122.0	512.44	1.2501	79.09
126.1	512.46	1.2241	78.21
131.1	512.49	1.1932	77.18
136.0	512.52	1.1646	76.24
Data for water, formula weight 18.016, b.p. 100.0°C.			
101.9	512.34	0.3102	18.62
104.0	512.35	0.3085	18.62
108.0	512.37	0.3050	18.61
112.0	512.39	0.3016	18.59
117.0	512.41	0.2974	18.57
122.0	512.44	0.2935	18.56
132.0	512.49	0.2849	18.47
Data for deuterium oxide, formula weight 20.032, b.p. 101.4°C.			
104.0	512.35	0.3440	20.77
106.0	512.36	0.3415	20.72
109.8	512.38	0.3365	20.62
115.0	512.40	0.3319	20.61
123.4	512.45	0.3234	20.52

DATA

In all of the cases reported the mass recorded in table 1 is the average of at least three trials. The pressure was the same during all runs and

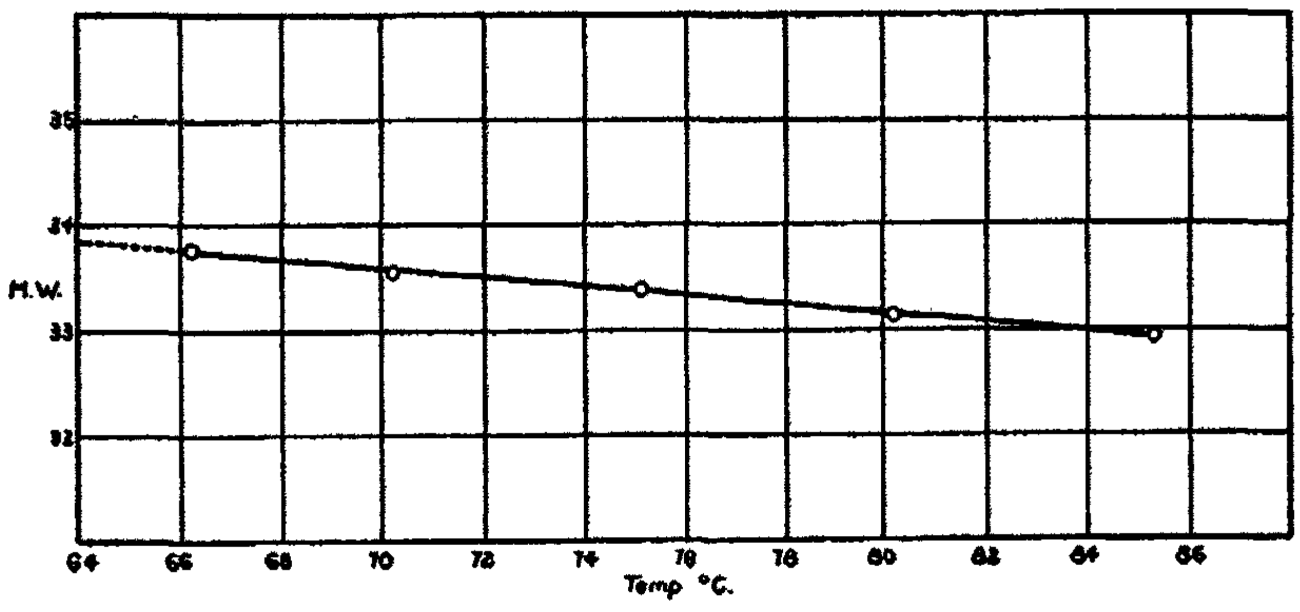

FIG. 4. Plot of data for methyl alcohol

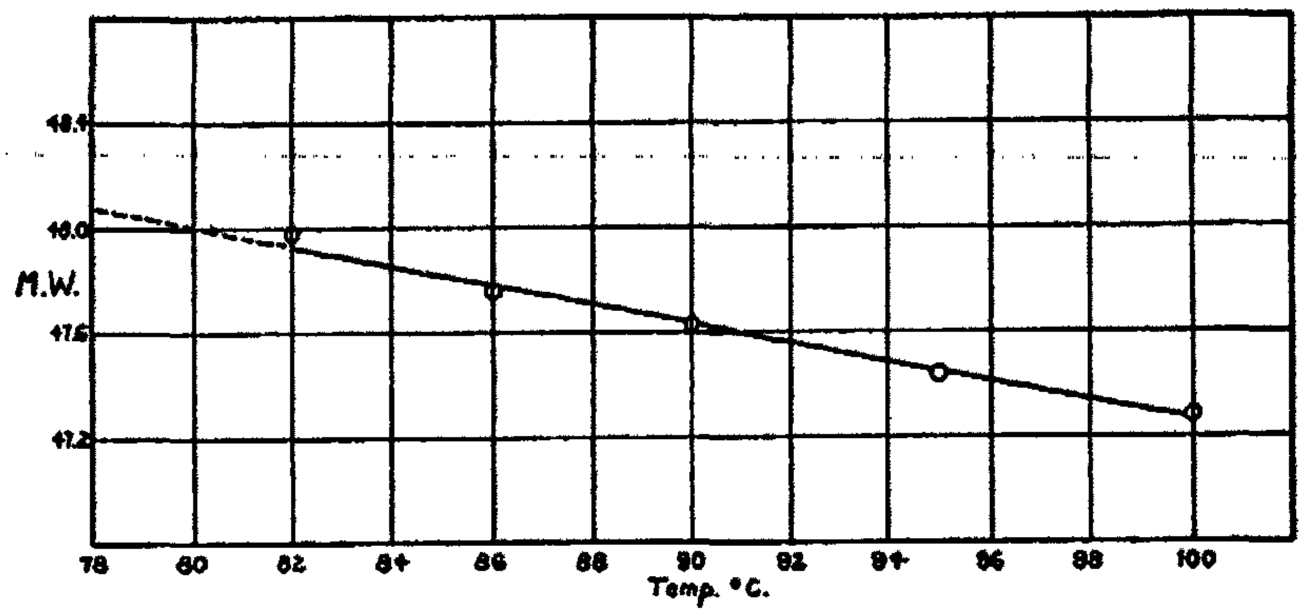

FIG. 5. Plot of data for ethyl alcohol

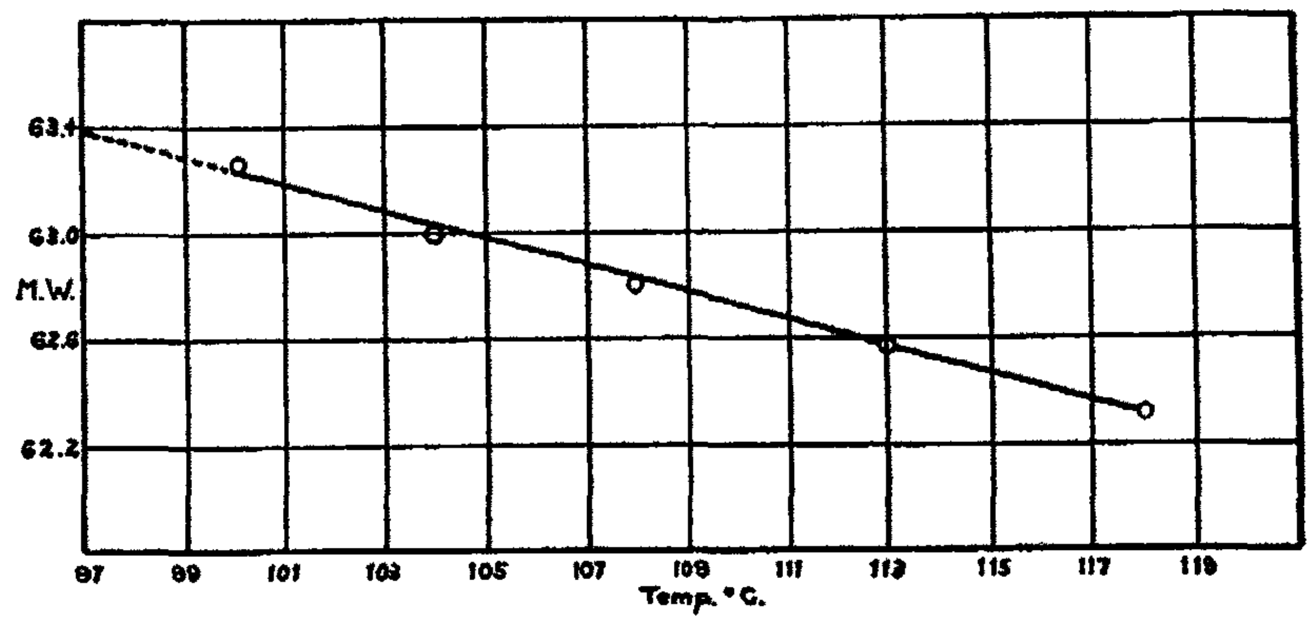

FIG. 6. Plot of data for *n*-propyl alcohol

was 1.0006 atm. The volumes recorded are those calculated from the calibration volume by use of the cubical coefficient of expansion of Pyrex.

The data of table 1 are shown in a graphical manner in figures 4 to 10.

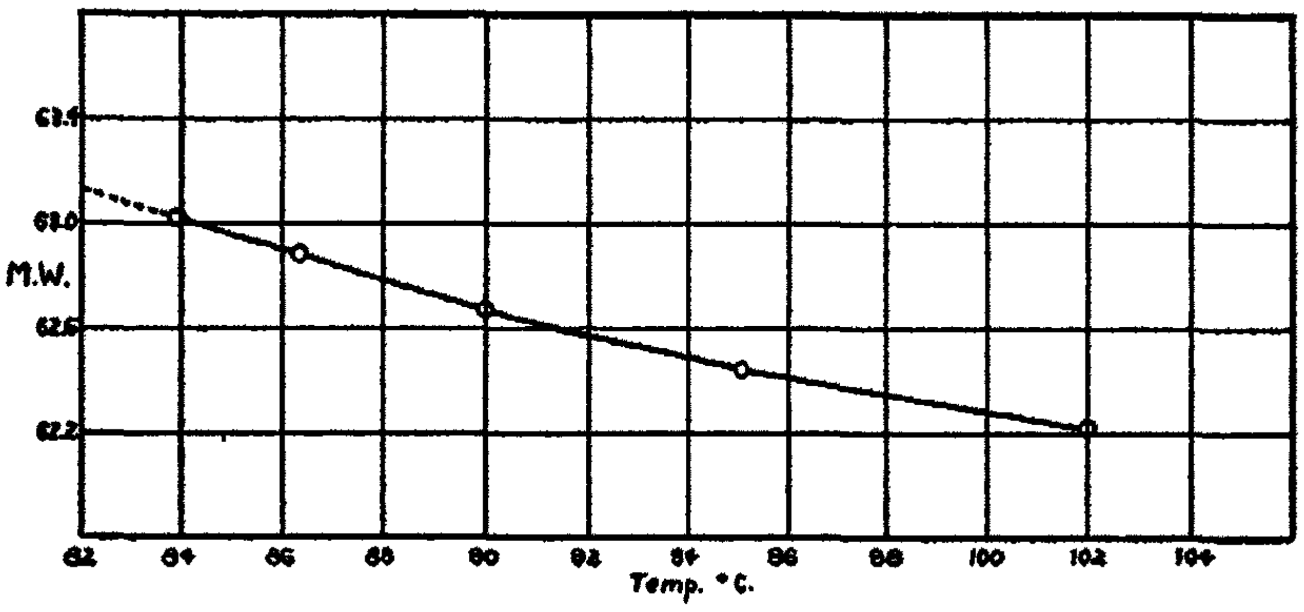

Fig. 7. Plot of data for isopropyl alcohol

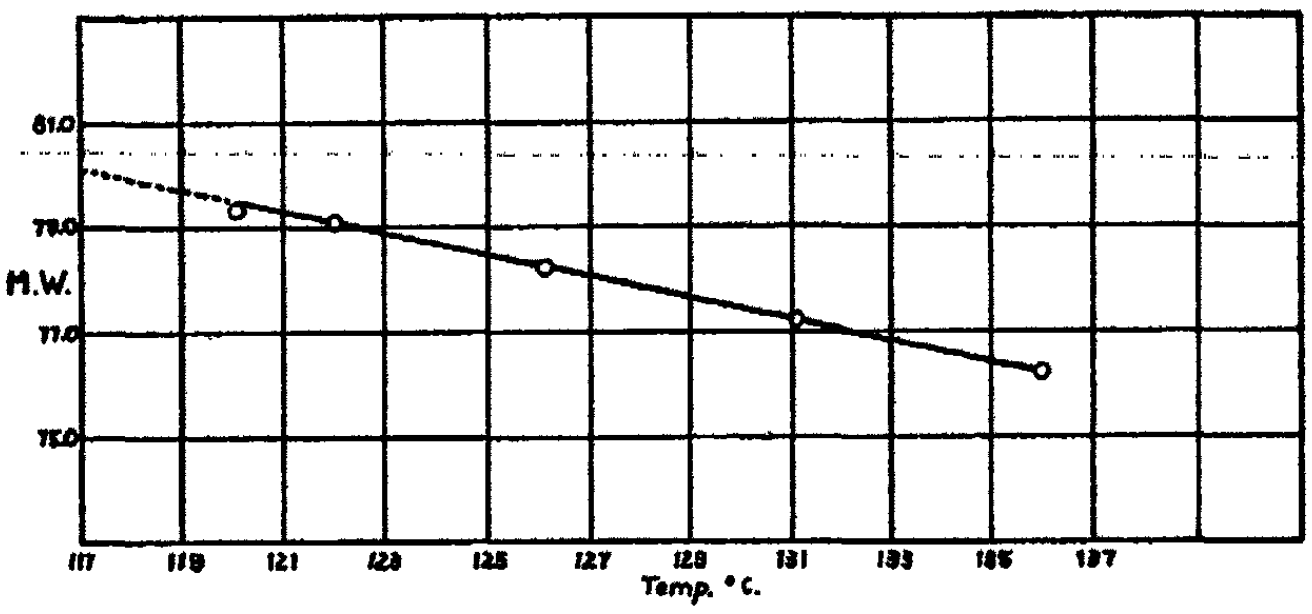

Fig. 8. Plot of data for *n*-butyl alcohol

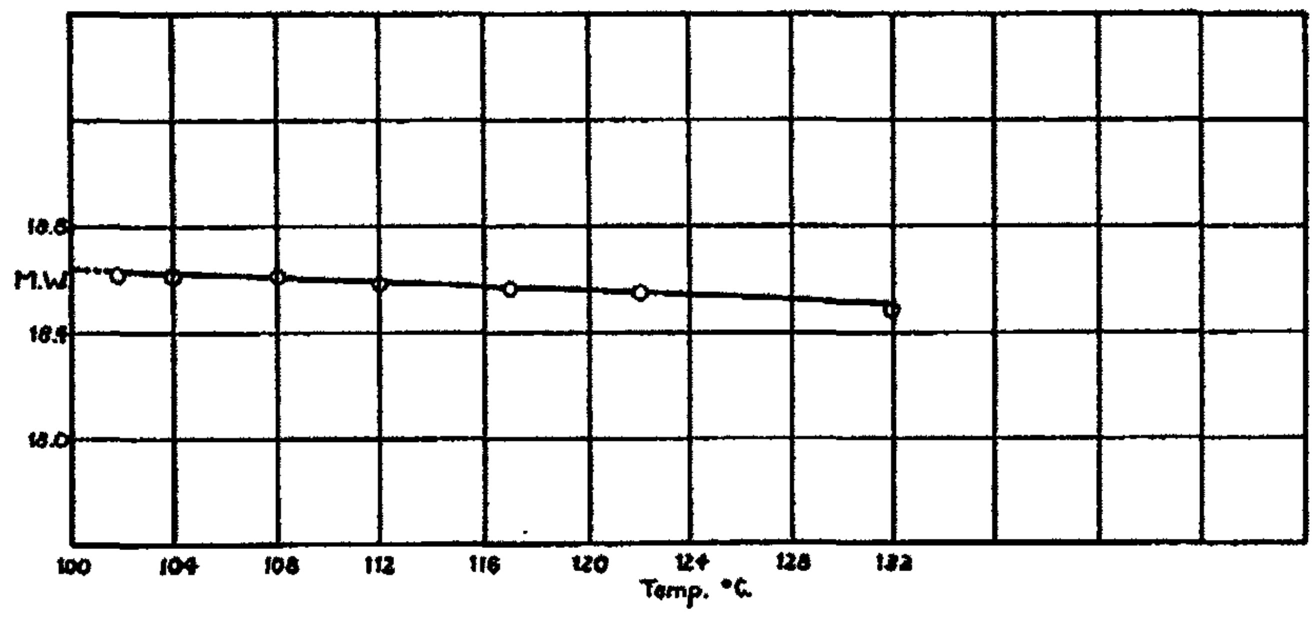

Fig. 9. Plot of data for water

In all cases the calculated molar weights are plotted as a function of temperature and are extrapolated back to the boiling point of the liquid in question. This extrapolation should be quite accurate, as Rankin (5) showed in his work that if the molar weights close to the boiling point were corrected for adsorption on the glass, the curves continued as a straight-line function of temperature. His data also showed that adsorption had no effect on the molar weights until the vapor was down to within 2° of the boiling point, in the case of the alcohols and water.

Table 2 shows the molar weights extrapolated to the boiling points of the liquids.

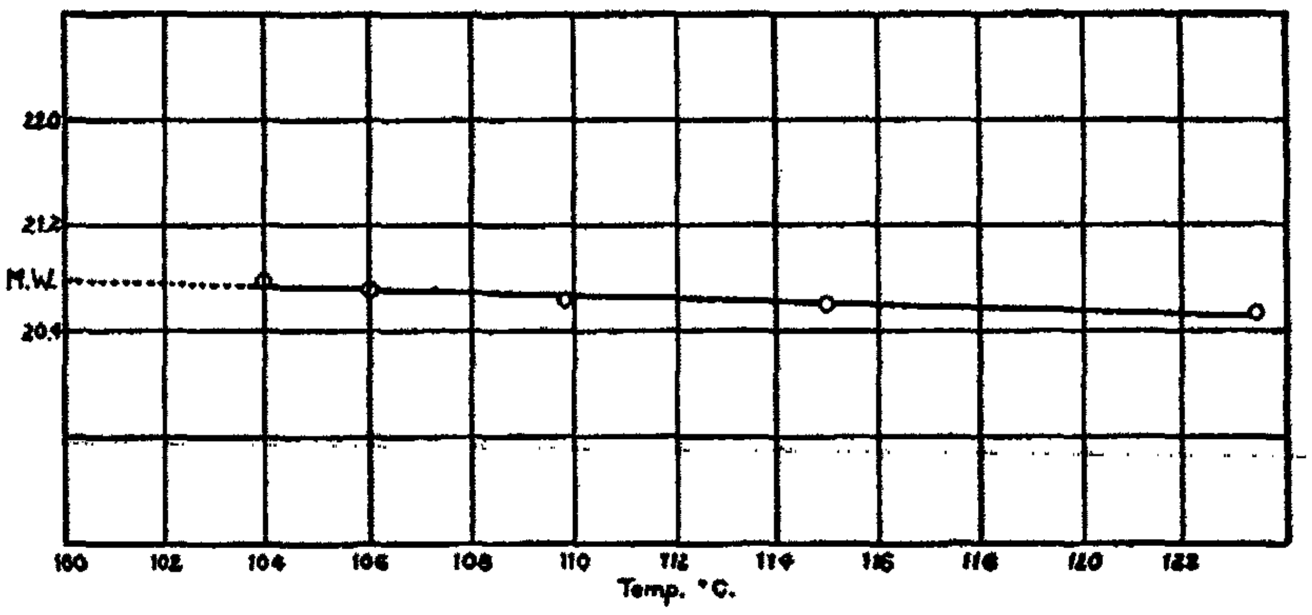

FIG. 10. Plot of data for deuterium oxide

TABLE 2

Molar weights extrapolated to the boiling points of the liquids

SUBSTANCE	FORMULA WEIGHT	EXTRAPOLATED MOLAR WEIGHT	DIFFERENCE	BOILING POINT
				°C.
Methyl alcohol	32.03	33.82	1.79	64.5
Ethyl alcohol	46.05	48.07	2.02	78.3
n-Propyl alcohol	60.06	63.34	3.28	97.8
Isopropyl alcohol	60.06	63.12	3.06	82.3
n-Butyl alcohol	74.08	79.95	5.87	117.7
Water	18.02	18.64	0.62	100.0
Deuterium oxide	20.03	20.78	0.75	101.4

DISCUSSION

A consideration of the data and curves indicates that when the molar weights of extremely pure liquids are plotted against temperature, the values of molar weights seem to fall in an almost linear manner with increasing temperature.

It should be remembered that the temperature ranges studied were only about 30° at the most. It is evident that the relationship between molar weight and temperature must change from this straight-line function as the temperature is increased more and more. The rate of change of molar weight with temperature must decrease until a temperature is reached at which the molar weight becomes equal to the formula weight.

A survey of the data presented shows clearly that the molar weights of the liquids at their boiling points are invariably higher than the formula weights of the liquids. It should be remembered that these molar weights were calculated using the perfect gas equation, and hence they would be expected to differ from the formula weights.

Two explanations of these differences are possible. Either the vapors are "associated," i.e., have double or triple molecules present, or else the individual molecules have stronger forces acting between them than predicted by the gas laws. Both of the above assumptions will give an apparent explanation of the experimental results, because it may be assumed that an increase in temperature would increase the degree of dissociation of the polymolecules and hence give smaller apparent molar weights with increasing temperature. On the other hand, it might be assumed that an increase in temperature increases the kinetic energy of the individual molecules and hence increases the distance between them, this leading to smaller apparent molar weights as the temperature increases.

Bose (1) has made calculations concerning the association of water vapor under its own vapor pressure. At a temperature of 100.0°C. he calculated a degree of dissociation equal to 0.911, assuming that the water vapor was a mixture of single and double molecules. Using the same equation used by Bose the writer obtained a degree of dissociation of double molecules of water at the boiling point and under a pressure of 1.0006 atm. equal to 0.933. A similar calculation made for deuterium oxide yields a value of 0.928. From this result it might be assumed that the attractive forces are slightly greater between the deuterium oxide molecules than between those of water.

It is interesting to note that van der Waals equation

$$(p + a/v^2)\,(v - b) = RT$$

does not correctly express the P–V relationships of water vapor at its boiling point under a pressure of 1.0006 atm. The constants a and b are evidently much too small for these conditions.

New constants have been calculated for the equation, using our vapor density data. The authors found that the value of a obtained was about five times as large as that given in the Landolt-Börnstein Tables, while the value of b was about twice as large as the value ordinarily used.

It has been previously mentioned that values of molar weights at the boiling point would be useful in calculating heats of vaporization.

The Clapeyron equation shown below is not easy to integrate, because V

and v are functions of pressure and temperature while l is a function of temperature also.

$$\frac{dP}{dT} = \frac{(l \times M.W.)}{T(V - v)}$$

The above equation is usually integrated after making several simplifying assumptions, such as setting v equal to zero as v is very small compared to V, and taking V as equal to RT/P. The latter assumption is perfectly correct if the molar volume is defined as RT/P, which is precisely what is done in calculating the molar weights at the boiling point, i.e., the molar weight is defined as the weight of the substance that occupies a volume RT/P cubic centimeters. After making these assumptions the equation may be integrated if it is assumed that l is independent of temperature, and takes the following form

TABLE 3

Latent heats of vaporization per gram

SUBSTANCE	l (CALCULATED)	l (FROM INTERNATIONAL CRITICAL TABLES)
	cal. per gram	*cal. per gram*
Methyl alcohol	270.3	262.8
Ethyl alcohol	207.2	204
n-Propyl alcohol	164.5	162.5
Isopropyl alcohol	156.1	159
n-Butyl alcohol	139.5	141
Water	530.1	539.55

$$\ln P = -(l \times M.W.)/RT + \text{constant}$$

This equation omits the molar volume of the liquid at the boiling point and hence is not an exact equation.

Rankin (5) has shown that it is possible to integrate the Clapeyron equation without omitting the molar volume of the liquid, and that the equation obtained is too complex and awkward to be used for the calculation of heats of vaporization.

Going back to the differential form of the equation it may be seen that the desired calculations cannot be made from values of P and T alone, but that there must also be a knowledge of dP/dT. The method of obtaining dP/dT values by plotting P against T and determining the slope by means of a tangentimeter has been suggested by Latshaw (2), but it has been found very difficult to get accurate values by this method. It has been found that more accurate values may be obtained by the use of an analytical method.

Rankin (5) has shown that the equation

$$\frac{dP}{dT} = \frac{LP}{RT^2}$$

obtained from the Clapeyron equation by neglecting the molar volume of the liquid is valid for this type of work, since L may be established from vapor pressure data.

It is not necessary actually to calculate dP/dT because it may be shown that the true molar heat of vaporization, L', is related to the arbitrary constant, L, by the equation,

$$L' = \frac{L(V - v)}{V}$$

In using this equation it should be remembered that the molar volume of the vapor at the boiling point has been previously defined as RT/P cubic centimeters. L, as shown above, may be determined from vapor pressure data, and v may usually be found in orthobaric density tables.

In order to obtain l, L' must be divided by the molar weight of the substance at its boiling point, as found experimentally.

Table 3 contains the latent heats of vaporization per gram as calculated by the method shown above. The values given in the International Critical Tables are also given for comparison.

An inspection of table 3 shows that the values of l calculated as described above agree fairly well with those given in the International Critical Tables. With the exception of the value of l calculated for water the authors feel that the values reported here are more accurate than any previously reported. The relatively low value of l calculated for water is indeed puzzling, and the authors have no explanation to offer.

SUMMARY

1. The Dumas method of determining molar weights from vapor density measurements has been improved upon so that molar weights may be determined at the boiling point.

2. The molar weights of water, deuterium oxide, and several aliphatic alcohols have been determined at their boiling points.

3. The heats of vaporization of the above substances have been determined by use of the molar weights at the boiling points and of vapor pressure data.

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MOBILITY STUDIES WITH COLLOIDAL SILICIC ACID[1]

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The mutual reactions of colloids attending the mixing of systems of opposite sign have been investigated by electrokinetic methods (1, 2, 3, 7). Of these, the method employing the ultramicroscope offers a distinct advantage, since mobilities of mixed systems can be observed throughout the concentration range including the flocculation zone. Accordingly, it is possible to study the mutual coagulation process as well as the mutual effects produced by varying concentrations of components in stable mixtures. In the latter case information can be obtained relating to the change in stability of the components and, in a restricted sense, to changes in the state of the particles, e.g., whether the components are completely independent, or combined (owing to capillary-active properties), or partially combined and partially free (7).

Weiser and Chapman (9) are of the opinion that the mutual coagulation process may be determined by a number of factors: namely, electrical neutralization, mutual adsorption of the particles, interaction between stabilizing ions, and the presence of excess electrolyte in the sols. These same factors probably influence the state of the particles in stable mixed systems. On the other hand, exponents of a chemical mechanism explain mutual coagulation as a result of a reaction between the stabilizing electrolytes. Thus Thomas and Johnson (8) found for the undialyzed system ferric oxide–silicic acid that coagulation was at an optimum where the concentrations of sodium hydroxide and hydrochloric acid were equivalent.

Hazel and McQueen (3) investigated the electrophoretic behavior of mixtures obtained from a number of oppositely charged sols and, although no silicic acid sols were employed, they were led to a mechanism for mutual coagulation that supported Weiser's conclusions. Furthermore, it was observed in the coagulation zones and in the stable regions on either side that the particles of the mixed systems possessed a single mean velocity

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[1] This research was supported by a Grant-in-Aid from the Graduate School of the University of Wisconsin.

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value, indicating that the oppositely charged components had completely combined with each other.

The present study is concerned with the electrophoretic properties of silica sols and of mixtures of silica sols with colloidal ferric oxide and aluminum oxide. These systems, in various states, comprise the major part of the inorganic fraction of soil colloids.

PREPARATION OF SOLS

The silica sol used in the present investigation was prepared by Graham's method. The aluminum oxide sol was made by small additions of $N/20$ hydrochloric acid to the precipitated oxide with alternate boiling. The iron oxide sol was prepared by hydrolysis of ferric chloride in boiling water. All of the sols were dialyzed for one week in collodion sacs. Data on the sols are given in table 1.

TABLE 1

Data on the sols

SOL	TEMPERATURE OF DIALYSIS	pH OF DIALYSATE	CHLORIDE TEST	CONCENTRATION (STOCK)
	°C.			*grams per liter*
Silica	22–25	4.75	Trace	10.0
Aluminum oxide	22–25	6.5	Trace	2.3
Ferric oxide	70–90	5.5	Trace	1.9

EXPERIMENTAL

Electrophoretic measurements were carried out by an ultramicroscopic method previously described (5). A velocity-depth curve was constructed, and the value for the true mobility obtained from the area under the curve was found to agree with that observed at the calibrated 0.147 level. In ascertaining the mean velocity values, ten readings were taken in alternate directions of the time required for a particle to traverse 200 μ under a potential gradient of 8.0 volts per centimeter. The distance between the electrodes was 11.75 cm.

Hydrogen-ion activities were determined with a glass electrode.

The "visibility" of the particles varied considerably with the three colloids. Thus the particles of the silica sol were poorly resolvable, while those of the aluminum oxide sol appeared very distinct.

RESULTS

The effect of hydrogen-ion activity on the mobilities of colloidal silica and of aluminum oxide are shown in figure 1. Adjustments of pH were made with hydrochloric acid or with sodium hydroxide. The concentration of silica in this experiment was 1.00 g. per liter, and that of aluminum oxide was 0.23 g. per liter. Data for a purified, naturally occurring, hydrogen-saturated aluminum bentonite are also included for comparison. These are shown as black dots in figure 1. The bentonite had a silica–alumina ratio of about four to one, and its concentration was 0.024 g. per liter. The silica and bentonite curves are characterized by the fact that neither is recharged at the higher acidities, resembling arsenic trisulfide in this respect (3).

The aluminum oxide curve is similar in form to that obtained with iron oxide (5) under like conditions.

In table 2 are shown mobility data for colloidal silica with electrolytes. The potential of the particles is decreased markedly by small additions of electrolytes, and the valency effect conforms to that usually found for negative colloids. It is noteworthy, however, that the negative character of the sol seems to be permanent, as is evidenced in the behavior with aluminum chloride.

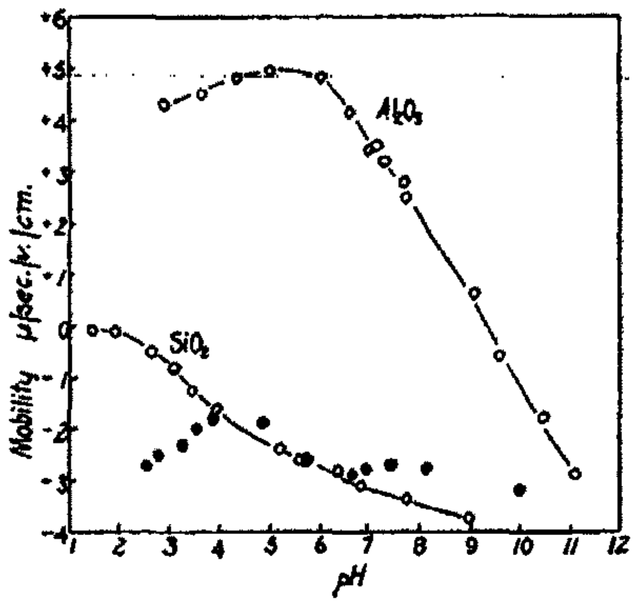

FIG. 1. The effect of hydrogen-ion activity on the mobilities of colloidal silica and aluminum oxide

The effect of electrolytes of different valence types on the mobilities of the aluminum oxide and ferric oxide sols that were used in later experiments with mixed systems was found to be quite normal and is not reported here.

Data are given in table 3 for systems obtained by mixing colloidal silica and alumina in the proportions indicated. Table 4 gives similar data for colloidal silica–ferric oxide mixtures.

The mobilities in tables 3 and 4 are plotted in figure 2.

The sols employed in these experiments, when diluted to the concentrations used in preparing the mixtures, all had a pH of close to 5.1. They were well dialyzed, which cut down the presence of free electrolytes to a minimum.

It is to be noted, from figure 2, that aluminum oxide is much more effective in discharging silica than is ferric oxide. Thus when alumina, which had the higher electrokinetic potential, is present to the extent of 17 per cent the mixture is isoelectric, whereas more than 70 per cent of ferric oxide is required to produce the same result. It is not probable that this

TABLE 2

Mobility data for colloidal silica with electrolytes

ELECTROLYTE CONCENTRATION IN MILLIMOLES PER LITER	MOBILITY IN μ PER SECOND PER VOLT PER CENTIMETER	
	NaCl	KCl
0	−2.3	−2.3
2	1.6	1.4
4	1.0	0.9
8	0.7	0.7
16	0.5	0.4
	$CaCl_2$	$BaCl_2$
0	−2.3	−2.3
0.16	1.2	1.1
0.4	1.0	0.8
1.4	0.8	0.7
5.0	0.5	0.4
	$AlCl_3$	
0	−2.3	
0.02	2.1	
0.04	1.5	
0.1	0.7	
0.3	*ca.* 0.1 (coagulated)	
0.6	0.0 (coagulated)	

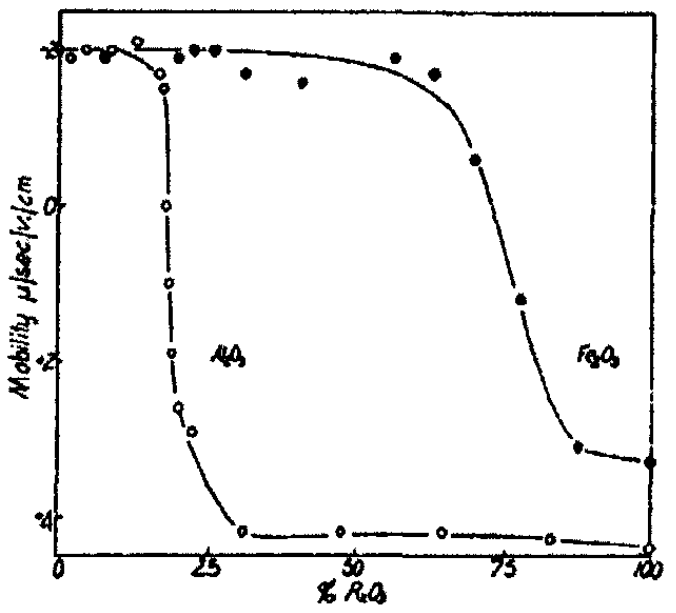

FIG. 2. Mobilities for systems obtained (*a*) by mixing colloidal silica and alumina and (*b*) by mixing colloidal silica and ferric oxide.

wide difference in effectiveness can be accounted for on the basis of a chemical mechanism of reaction between stabilizing ions, because this would necessitate postulating a marked difference in solubility of the silicates.

TABLE 3

Data for systems obtained by mixing colloidal silica and alumina

PER CENT OF Al_2O_3	MOLECULAR RATIO OF SiO_2 TO Al_2O_3	MOBILITY IN μ PER SECOND PER VOLT PER CENTIMETER		REMARKS	
0		−2.0		Few particles "visible"	
1.9	88.7	1.9		Number of "visible" particles increasing	
4.5	35.5	2.0			
8.7	17.7	2.0		Number of "visible" particles decreasing	Coagulation
12.6	11.8	2.1			Coagulation
16.1	8.9	1.7			Coagulation
16.8	8.5	1.5			Coagulation
17.4	8.1	±0.0			Coagulation
18.1	7.7	+1.0			Coagulation
18.7	7.4	+1.9	+4.3*		Coagulation
20.0	6.8	+2.6	+4.5*	"Visible" particles increasing in number	Coagulation
22.3	5.9	+2.9	+4.5*		Coagulation
31.0	3.8	+4.2	+1.8*		
47.4	1.9	+4.2	+2.0*		
64.3	0.94	+4.2	+2.8*		
81.8	0.38	+4.3			
100		+4.4			

* Two sets of velocity values.

TABLE 4

Data for systems obtained by mixing colloidal silica and ferric oxide

PER CENT OF Fe_2O_3	MOLECULAR RATIO OF SiO_2 TO Fe_2O_3	MOBILITY IN μ PER SECOND PER VOLT PER CENTIMETER		REMARKS
0		−2.0		
7.5	33.1	1.9		
19.5	11.0	1.9		
22.0	9.5	2.0		Coagulation
25.3	7.9	2.0		Coagulation
31.1	5.9	1.7		Coagulation
40.4	4.0	1.6		Coagulation
57.5	2.0	1.9		Coagulation
62.9	1.6	1.7		Coagulation
69.3	1.2	0.6		Coagulation
77.2	0.8	+1.2		Coagulation
87.1	0.4	+3.1	+1.4*	
100		+3.3		

* Two sets of velocity values.

DISCUSSION

It was observed in the present study that the particles of colloidal silicic acid were poorly "visible" in the ultramicroscope. This was to be expected from the well-known fact that silica sols are heavily hydrated. As in the case with gelatin (6) the "visibility" of the particles was enhanced by addition of a hydrophobic colloid up to a certain limit and, similarly, small additions of oppositely charged hydrophobic colloids were without effect on the mobility of the silica particles. This behavior is in marked contrast to that obtained when two oppositely charged hydrophobic colloids are mixed (3).

An inspection of the data in table 3 shows that coagulation began before the particles in the mixed system had experienced any apparent diminution in mobility. These data cannot be used, however, either against or to support the idea of a critical potential. Addition of aluminum oxide up to a silica-alumina ratio of 11.8 did not reduce the mobility of the stable colloid particles, but it did reduce the number of these stable particles. The mobility of the large flocs could not be obtained with accuracy.

The state of the system was definitely heterogeneous throughout the concentration ranges where coagulation took place (except possibly at zero mobility) and where two mean sets of mobilities were observed. The experimental evidence further suggests that the components were present as (*1*) adsorption complexes and, depending upon which was in excess, as (*2*) free alumina or free silica. The results with the colloidal silica–iron oxide mixture were analogous to those obtained with silica–aluminum oxide mixtures.

SUMMARY

1. An electrokinetic study of colloidal silicic acid has been made with the aid of an ultramicroscope.
2. The effect of electrolytes, pH, and of colloids of opposite sign on the mobility has been investigated.

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ON THE KINETICS OF TYROSINE DESTRUCTION AND DOPA FORMATION BY ULTRA-VIOLET RAYS

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One of the products produced when *l*-tyrosine is destroyed by ultra-violet radiant energy is dopa (3,4-dihydroxyphenylalanine) (2). In the experiments described in this paper, tyrosine and dopa have been determined by methods previously reported by the author (1). The only significant modification in the analytical procedure consisted in the use of a compensation cup[1] in the dopa determinations. This was necessary because the irradiated solutions developed a brown color. This color was precipitated by the reagents used in determining tyrosine, and did not interfere with the determination of this compound.

A Victor therapy quartz-mercury arc (air-cooled)[2] was used as a source of ultra-violet radiant energy. This instrument, as used, operated with a voltage drop of 65 to 70 volts across the quartz-mercury tube. All solutions were irradiated at a distance of 30 cm. from the light source. In a preliminary experiment 20 cc. of tyrosine solution, containing 22.1 micromoles of tyrosine, was placed in a test tube. The tube was loosely stoppered and immersed in a boiling water bath for 6 hours. Since no dopa was formed by this procedure, the solutions exposed to the lamp were not cooled. In general, the temperature of the solutions undergoing irradiation quickly rose to about 48-50°C. and remained practically unchanged until the lamp was turned off.

The kinetics of the reactions were investigated by placing 20-cc. portions (containing 22.1 micromoles of tyrosine in distilled water) of tyrosine solution in well-corked clear quartz test tubes (25-cc. capacity) and exposing these solutions to the radiant energy for varying lengths of time.

KINETICS OF TYROSINE DESTRUCTION

The results of tyrosine analyses are given in table 1. *T* represents micromoles of tyrosine present in the 20 cc. of solution, *t* represents time, and

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[1] For a description of the use of the compensation cup see J. F. McClendon (A Manual of Biochemistry, p. 305. John Wiley and Sons, New York (1934)).

[2] This lamp was made available to the author through the courtesy of Dr. W. K. Stenström and the University of Minnesota Hospitals.

D represents micromoles of dopa present in 20 cc. of solution. If log T is plotted graphically as a function of t, a straight line results. The differential equation relating T and t is thus

$$-\frac{dT}{dt} = k_1 T_1$$

in which k_1 is the velocity constant of the reaction (t is measured in hours). The integrated form of this expression is

$$T = T_0 e^{-k_1 t}$$

where T_0 refers to the amount of tyrosine initially present in 20 cc. of solution. The value of k_1, calculated from the data, is 0.071. Calculated values of tyrosine are given in table 1.

TABLE 1

Destruction of tyrosine and formation of dopa by ultra-violet rays.

t	T (ANALYTICAL)	T (CALCULATED)	D (ANALYTICAL)	D (CALCULATED)
hours	*micromoles in 20 cc.*	*micromoles in 20 cc.*	*micromoles in 20 cc.*	*micromoles in 20 cc.*
0	22.1			
1	20.1	20.1	0.4	0.5
2	19.4	19.2	0.7	0.7
3	18.1	17.9	1.2	1.2
4	16.4	16.6	1.9	1.6
6	14.4	14.5	2.2	2.1
12	8.8	9.4	2.6	2.5
15.8	7.2	7.2	2.8	2.8

The above equations indicate that the destruction of tyrosine in these experiments occurred as a first-order reaction. Verification of this conclusion was obtained by irradiating tyrosine solutions of different initial concentrations for 4 hours. The results are given in table 2. These data indicate that the fraction of tyrosine still present in a given time interval was independent of the initial concentration, a necessary condition of first-order reactions.

The absorption spectrum of tyrosine in aqueous solution is given in the International Critical Tables (3). The molecular extinction coefficients of tyrosine vary from about 5900 at 2800 A. U. to about 1000 at 2460 A. U. McAlister's (4) data indicate that there are four strong mercury emission bands in this region: at 2804, 2652, 2536, and 2483 A. U., respectively. The emission bands at 2967 A. U. and 3022 A. U. are relatively of much less importance, because the molecular extinction coefficients of tyrosine at these wave lengths are relatively low. Calculations using these figures show that practically all the radiant energy between 2460 A. U. and 2800 A. U. is absorbed by the tyrosine solutions undergoing irradiation. This fact suggests that the mechanism of tyrosine destruction may be of the type indicated by the following equations, in which X represents an active intermediate:

$$\mathrm{T} + h\nu \rightarrow \mathrm{X} \tag{1}$$

$$\mathrm{X} \rightarrow \mathrm{T} \tag{2}$$

$$\mathrm{X} + \mathrm{T} \rightarrow \mathrm{D} + \text{other products} \tag{3}$$

If reaction 2 is rapid as compared with reaction 3, this series of reactions would result in a first-order destruction of tyrosine. In the above argument it is tacitly assumed that an unlimited supply of oxygen is available, a condition which is met by the experimental procedure, since a large excess of oxygen is always present. No tyrosine is destroyed in a 4-hour period when tyrosine solutions are irradiated *in vacuo.*

TABLE 2

Destruction of tyrosine in a 4-hour period

T_0	T	$\frac{T}{T_0}$
micromoles in 20 cc.	*micromoles in 20 cc.*	
5.5	4.1	0.75
11.1	8.3	0.75
22.1	16.4	0.74

KINETICS OF DOPA FORMATION

The rate of dopa formation should be given by the equation

$$\frac{\mathrm{d}D}{\mathrm{d}t} = a\frac{\mathrm{d}T}{\mathrm{d}t}$$

where D refers to the micromoles of dopa formed in the irradiated solution, and where a is a constant. If a is 1, each molecule of tyrosine which is destroyed results in the formation of a molecule of dopa; if a is less than 1, it represents the fraction of destroyed tyrosine molecules which form dopa.

One isolated experiment which illustrates that dopa is destroyed by the radiant energy was performed. Twenty cubic centimeters of dopa solution (containing 5.07 micromoles of dopa) was exposed to the lamp for 4.5 hours. Analysis showed that 29 per cent of the dopa had been destroyed. No tyrosine had been formed. If it is assumed that the destruction of dopa is a first-order reaction,

$$-\frac{\mathrm{d}D}{\mathrm{d}t} = k_1D$$

where D represents micromoles of dopa present at time t, and k_2 is the velocity constant.

If the above assumptions are made, the rate of change of dopa in irradiated tyrosine solutions is given by the expression,

$$\frac{dD}{dt} = ak_1T - k_2D$$

Integrating this expression,

$$D = \frac{k_1}{k_2 - k_1} aT_0[e^{-k_1t} - e^{-k_2t}]$$

The only unknowns in this equation are a and k_2. If data are taken from several points on the dopa-time curve, and the resulting equations are solved for a and k_2, the following expression results:

$$D = \frac{0.071}{0.074 - 0.071} \frac{T_0}{3} [e^{-0.071t} - e^{-0.074t}]$$

This equation appears to approximate the experimental data fairly well. Calculated and analytical values for dopa are compared in table 1. This equation can be interpreted to indicate that one-third of the tyrosine molecules which are destroyed are converted to dopa; and that the destruction of dopa is of the first order, the velocity constant having a value of 0.074.

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METALLIC COUPLES. II

CONCERNING THE PREPARATION OF ALUMINA HYDROSOLS[1, 2]

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INTRODUCTION

The author has recently pointed out (35) that practically pure alcoholic alumina jellies can be prepared by a modification of the Kutzelnigg-Wagner reaction (32). Kutzelnigg and Wagner allowed a 2 per cent copper chloride solution in 95 per cent ethyl alcohol to act on metallic aluminum in order to produce an alcoholic alumina gel. Analysis showed the final transparent product to be free from copper ion but to contain a high percentage of chloride ion. The modified method, described by the present author (35), produced gels apparently free from both of these ions. Further studies have indicated that an extension of the modified method can be used to prepare reasonably pure colloidal alumina.

The purpose of the present note is to describe a simple method of preparing large quantities of apparently unprotected, but remarkably stable, alumina hydrosols. Preliminary work on other than the aluminum-copper couple is described, and a mechanism for the reaction is proposed. Data for rate of settling of alumina hydrosols are given.

ALCOHOL-ACTIVATED ALUMINUM-COPPER COUPLE

The Kutzelnigg-Wagner reaction (32) was allowed to proceed for several days. The copper-coated aluminum sheet was then removed, washed thoroughly in alcohol, and placed in distilled water. After several days an alumina hydrosol-producing couple was obtained. The first portion of the hydrosol was discarded, as it contained some copper, and fresh water was added. As the hydrosol concentration became of sufficient strength for whatever purpose it was intended, it was filtered through fine-pored filter paper into a steamed flask or stock bottle.[3] More distilled

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[1] Metallic Couples. I. Über kolloides Kupfer und alkoholisches Aluminiumoxyd Gel. Kolloid-Z. [3] 77, 310-12 (1937).

[2] The experimental work described in this paper was carried out in the Chemical Laboratories of the University of Michigan, Ann Arbor, Michigan, 1932-36.

[3] Since the hydrosol appears to be very sensitive to traces of electrolytes, care should be taken to steam all containers, if flocculation is to be avoided.

water was added to the couple each time. In this manner, with occasional stirring, such couples continued to produce the hydrosol until virtually all of the metallic aluminum was used up. The resulting hydrosols were neutral to litmus. Hydrosols containing up to 1 g. of Al_2O_3 per liter have been prepared.

REACTIONS OF OTHER METALLIC COUPLES

Table 1 summarizes data relative to the physical character of the alumina produced by several metallic couples in various media. The couples were made as follows: Sheets of 99.5 aluminum (ca. 2 in. x 1 in.) were cleaned in 5 per cent caustic, thoroughly rinsed with distilled water, and air-dried. Into each of the designated salt solutions (ca. 2 per cent) a sheet of this aluminum was then immersed for approximately one minute. After washing and air-drying, they were placed in about 50 cc. of the reaction medium and left undisturbed until the character of the product was apparent. In general, this period did not exceed two weeks.

TABLE 1

Physical character of alumina from several metallic couples

METALLIC COUPLE	METHOD OF PREPARING COUPLE: ALUMINUM SHEET IN	FORM OF PRODUCT IN GIVEN MEDIA		
		Distilled H_2O	0.02 *N* $AlCl_3$	95 per cent ethyl alcohol
Al-Hg	Aqueous $HgCl_2$	Fibrous	Hydrosol	Flocculent
Al-Cd I	Aqueous acidic $CdCl_2$		Flocculent	
Al-Cd II	Alcoholic $CdCl_2$	Trace of hydrosol	Trace of hydrosol	
Al-Cu I	Aqueous $CuCl_2$	Fine, flocculent	Hydrosol	Gel
Al-Cu II	Alcoholic $CuCl_2$	Hydrosol	Hydrosol	Gel
Al-Cu III	$CuAl_2$ intermetallic compound	Gelatinous	Flocculent	Trace of gel; coarse black precipitate
Al-Fe I	Aqueous acidic $FeCl_3$	Coarse, flocculent	Fibrous	Gel
Al-Fe II	Alcoholic $FeCl_3$	Trace of hydrosol	Hydrosol	Gel
Al-Ni I	Aqueous ammoniacal $NiCl_2$	Hydrosol formed slowly	Hydrosol formed slowly	Trace of gel
Al-Ni II	Alcoholic $NiCl_2$	Hydrosol	Hydrosol	Gel

Besides the couples listed in table 1, a preliminary investigation was made on couples of aluminum with tin, zinc, cobalt, lead, and silver. Of these only the aluminum-cobalt couple appeared to produce hydrosols in pure water.

From table 1 it is apparent that the manner of preparing the couple is of more than minor importance. The particle size of the deposited metal, the porosity of the coating, and the activity of the deposited metal are evidently functions of the deposition medium. Factors such as the concentration of the depositing solutions and the effect of the temperature of deposition and of reaction, of the pH of the depositing solutions, of the thickness of the metallic coating, and of colloids were not investigated. In the opinion of the author, these factors have an important bearing on the decomposition of water by metallic couples.

We note that in contrast to the well-known aluminum-mercury couple (6, 49), which ordinarily produces with water a flocculent, fibrous alumina (39, 50), and evidently produces true sols (41) only in the presence of stabilizing ions, the alcohol-activated aluminum-copper couple generates a remarkably stable, apparently unprotected hydrosol. Experiments performed with an aluminum-copper couple which had been generated in an aqueous cupric chloride solution invariably resulted in the formation of flocculent alumina, incapable of more than transitory suspension in the absence of stabilizing ions. Mabb (33) has recently discussed certain reactions of the aluminum-copper couple.

The results of the interaction of various metals, including aluminum and copper, with anhydrous ethyl alcohol, gasoline, and mixtures of these two liquids, have recently been reported by Zdarsky (51). This investigator states that ethyl alcohol which contains moisture will give a soft jelly with aluminum. The author has been unable to produce either hydrosols or gels by the action of either water or alcohol on aluminum alone. Apparently a coupled reaction is necessary (35). On the other hand, Bouchet (2) states that he has produced blue sols by allowing natural waters to react on pure zinc. It is possible that certain ions in the waters stabilized the corrosion product produced by the salts present in the waters.

SETTLING EXPERIMENTS WITH ALUMINA HYDROSOL

An attempt was made to determine the rate of settling, if any, of the hydrosol particles resulting from the interaction of the alcohol-activated aluminum-copper couple. The hydrosol used in these experiments contained 0.22 g. of Al_2O_3 per liter.[4] Tubes of various diameters, ranging from 0.5 to 2.0 cm., were used. Evidently tube length is of more importance than tube diameter.

Some gradient settling took place and was noticeable after several weeks. No visible boundaries resulted, however, until after about three months, though a trace of sediment was apparent at the bottom of the settling tubes before this time. At the end of about six months sharp boundary effects became visible. By the proper adjustment of a light

[4] Value obtained from calcining residue from given sol volume.

TABLE 2

Rate of settling of hydrosol particles from typical alcohol-activated aluminum-copper couple

Height of column = 31.5 cm.; diameter of tube = 1.05 cm.

AFTER 2500 HOURS			AFTER 3000 HOURS			AFTER 3500 HOURS			AFTER 4000 HOURS			AFTER 4500 HOURS			AFTER 5000 HOURS		
Boundary	Length of zone	Volume of zone	Boundary	Length of zone	Volume of zone	Boundary	Length of zone	Volume of zone	Boundary	Length of zone	Volume of zone	Boundary	Length of zone	Volume of zone	Boundary	Length of zone	Volume of zone
cm.	*cm.*	*cc.*	*cm.*	*cm.*	*cc.*	*cm.*	*cm.*	*cc.*	*cm.*	*cm.*	*cc.*	*cm.*	*cm.*	*cc.*	*cm.*	*cm.*	*cc.*
			3.0	3.0	2.6	4.4	4.4	3.8	5.1	5.1	4.4	5.2	5.2	4.5	5.2	5.2	4.5
5.3	5.3	4.5	8.1	5.1	4.4	10.9	6.5	5.6	11.8	6.7	5.8	12.0	6.8	5.9	12.2	7.0	6.0
			9.8	1.7	1.5	12.7	1.8	1.6	14.5	2.7	2.3						
10.4	5.1	4.4				14.5	1.8	1.5	16.0	1.5	1.3	16.4	4.4	3.8	16.4	4.2	3.7
			14.9	5.1	4.4	19.1	4.6	4.0	21.7	5.7	4.9	22.4	6.0	5.2	22.5	6.1	5.2
			19.3	4.4	3.8	23.0	3.9	3.3	25.5	3.8	3.3						
31.4	21.0	18.1	31.4	12.1	10.4	31.3	8.3	7.2	31.2	5.7	5.0	31.2	18.8	16.3	31.2	18.7	16.2
31.5	0.1	0.1	31.5	0.1	0.1	31.5	0.2	0.1	31.5	0.3	0.3	31.5	0.3	0.3	31.5	0.3	0.3
	solid			solid			solid			solid			solid			solid	

source, these boundaries could be read to within 2 mm. Representative results are recorded in table 2.

It will be seen that at first a few fairly sharp boundaries appear, that after about a thousand hours more the number has increased, and that as equilibrium is approached, several of the boundaries tend to disappear. It would be interesting to carry out similar experiments in tubes of the same diameter but of various lengths, in analogy to The Svedberg's experiments with the centrifuge.

The figures do not readily lend themselves to quantitative calculations of particle size, since no attempt was made to measure the concentration of alumina in each of the zones. Visual observation indicated that there were more particles of an intermediate size than either very small particles or very large particles. In short, the distribution was what might be expected.

Pavlov (42) has recently discussed the mechanism of coagulation. The Smoluchowski theory (43) of liquid envelopes and mutual attractions and repulsions has been further developed. It is difficult to apply the theory of velocity of coagulation to a distribution type of normal settling. One would have to assume a slow but continuous coagulation of hydrosol particles, and hence the absence of an apparent equilibrium stratification, such as was actually obtained.

DISCUSSION OF RESULTS

From a consideration of the action of water on an active metallic couple we would infer that a distribution of particle sizes would be expected. We may tentatively consider the hydrosol particles to result from the action of one or both of two series of processes. Firstly, electrochemical reaction may produce aluminum ions, which migrate into the solution before forming aluminum oxide molecules. These oxide molecules then agglomerate sufficiently to produce a range of colloidal-sized particles in agreement with experiment. The second mechanism would also begin as an electrochemical reaction, with the production of films of oxide, impermeable to aluminum ions; these films would then disrupt, under the influence of growth and pressure of generated hydrogen gas, to produce a gradation of colloidal sizes in harmony with the actual figures.

The latter mechanism seems more in keeping with experiments on aluminum-mercury couples, where the formation of films is obvious, as well as with the fact that particle sizes range from the colloidal to the macroscopic. On the other hand, the first mechanism would more adequately account for the stability of the sols, since ionic aluminum is known to peptize the fibrous alumina ordinarily produced by aluminum-mercury couples (38, 41). It is possible that alcohol-activated aluminum-copper couples produce hydrosols in pure water because of stabilization by an ethylate.

It remains to consider the individual couples. Table 3 lists the normal electrode (single) potentials and the relative hydrogen overvoltages of some of the metals investigated. The E.M.F. of a metal indicates its replacement or deposition ability; any metal will tend to replace any metal below it in the E.M.F. series. Likewise, the total E.M.F. of a cell is equal to the difference between the single electrode potentials of the electrodes. For example, the aluminum-copper couple will have an E.M.F. of 1.63 volts; the aluminum-nickel couple will have an E.M.F. of 1.06 volts.

The hydrogen overvoltages are a function of the position in the periodic arrangement of the elements, dependent upon the group. Oliverio and Belfiori (40), after investigating the decomposition of water by metals and metallic couples, conclude that this decomposition depends more on the overvoltage of the more noble metal of the couple with respect to hydrogen than on the position in the E.M.F. series. They found, for instance, that from the metals which follow zinc in the E.M.F. series only couples containing iron decompose water. These workers also investigated the effect of temperature on the decomposition of water by zinc-nickel couples, the decomposition increasing with rise in temperature.

TABLE 3

Single potentials and relative hydrogen overvoltages of several metals

METAL	NORMAL ELECTRODE POTENTIALS	METAL	RELATIVE HYDROGEN OVERVOLTAGES
	volts		*volts*
Al	+1.28	Zn	0.72
Zn	0.76	Hg	0.70
Fe	0.44	Cd	0.66
Cd	0.40	Al	0.50
Co	0.29	Sn	0.45
Ni	0.22	Pb	0.42
Sn	0.14	Cu	0.34
Pb	0.12	Ag	0.30
H	0.00	Fe	0.27
Cu	−0.35	Co	0.26
Hg	−0.80	Ni	0.24
Ag	−0.80		

Superficial considerations make it at once apparent that the heredity of the created couple, particularly the interagent of its formation, and the environment of the acting couple, especially the nature of the medium in which it generates the product, have also a major responsibility in determining the physical, and often the chemical, properties of the product.

This conclusion is sensibly identical with that previously advanced by the author in connection with studies on the physical character of iodine and insoluble iodides precipitated in various media (34, 36, 37). It is notable that somewhat similar summarizations have been made as follows: (*a*) *concerning the genesis of somatoidal* aluminum oxide (25, 26, 27), basic aluminum sulfate (8, 9, 10), calcium carbonate (21, 22, 23, 24), iodides (30), and electrolytic deposits and corrosion products (28, 29) by Kohlschütter and his students; (*b*) regarding "memory"[6] (12, 14, 15, 18), interaction (11, 13, 17, 19, 20, 31), and sorption (7, 16) by solid substances, especially active oxides by Hüttig and his coworkers; (*c*) respecting crystal polymorphism (1, 3, 4, 5) by Buerger; and (*d*) pertaining to spatially influenced origin and growth of various substances (44, 45, 46, 47, 48) by Urazovskii and fellow workers.

We are once more forced to the conclusion that the vectorial properties attending a given substance, by virtue of the mode of its formation, are largely responsible for the subsequent characterizations which that substance displays during the course of its chemical history. A detailed discussion of the importance of vectorialism as related to the physical and chemical character of a product and to the growth of crystals in general will be discussed in a different connection.

SUMMARY

A simple method of preparing large quantities of alumina hydrosols, apparently in the absence of stabilizing ions, has been described. It has been shown that alcohol-activated aluminum-copper couples produce sols which settle to an apparent equilibrium stratification after a period of about 5000 hours.

Preliminary experiments on other than the aluminum-copper couple have been described. A mechanism for the reaction of metallic couples with water has been proposed.

It is concluded that the vectorial properties attending a given substance, by virtue of the mode of its formation, are largely responsible for the subsequent characterizations which that substance displays during the course of its chemical history.

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THE RÔLE OF ADSORPTION IN THE COAGULATION OF SOLS BY ELECTROLYTES[1]

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The stability of sols of the hydrophobic type results from the adsorption of "potential-determining" ions (2) on the surface of highly dispersed particles. The adsorbed, potential-determining ions constitute the inner portion of a double layer, the outer portion of which is a diffuse layer of so-called counter ions. To illustrate: in the positively charged hydrous oxide sols prepared from the metallic chlorides by condensation methods, the inner portion of the double layer consists of the respective metallic ions and hydrogen, and the outer diffuse portion consists of the counter chloride ions. Similarly, in negative sols of the so-called "acidoid type," such as arsenic trisulfide, copper ferrocyanide, and silver iodide peptized by the respective acids, the anions of the acids are the potential-determining ions and hydrogen ions are the counter ions.

The coagulation of sols of the above-mentioned type by electrolytes results from the lowering of the electrokinetic or ζ-potential of the particles, which, in turn, is caused by contraction of the double layer or, if preferred, by compression of the outer layer surrounding the dispersed particles. This change in the double layer which reduces the ζ-potential has been attributed by the authors to adsorption of ions opposite in charge to the potential-determining ions which constitute the inner portion of the double layer. Since the adsorption of the added coagulation ions is greater than that of the counter ions of the diffuse outer layer, because of either the nature or the concentration of the added ions, the outer layer is compressed or the thickness of the double layer is reduced, thereby lowering the ζ-potential and reducing the stability of the sol. The adsorption, at least up to the coagulation point, is an exchange adsorption process in which the coagulating ions are in exchange with the counter ions of the diffuse outer layer. Some of the counter ions are held so strongly (adsorbed) by the attractive force of the inner layer that they are not a part of the intermicellar solution and therefore cannot be detected by potentiometric or electrometric methods in the original sol.

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The adsorption of the coagulating ions displaces these counter ions from the innermost portion of the outer layer and the displaced ions may be estimated subsequently in the intermicellar solution. The changes which are assumed to take place on adding coagulating electrolytes stepwise to sols (*titrations of sols*) are illustrated in figures 1 and 2.

Figure 1 gives the results of titrating two different hydrous oxide sols with potassium sulfate (8, 9, 10, 11). It will be noted that the coagulating sulfate ion is adsorbed almost completely up to the precipitation value (indicated by an arrow), above which the adsorption curve is similar to that of the usual adsorption isotherm. The curve for the displacement of chloride from the innermost portion of the double layer falls well below that of the adsorption curve, since a part of the adsorbed sulfate ions replace the counter chloride ions which are so far out in the diffuse layer that they are a part of the intermicellar solution of the original sol. Figure 2 (12, 13, 14) gives the results of titrating two sols of the acidoid

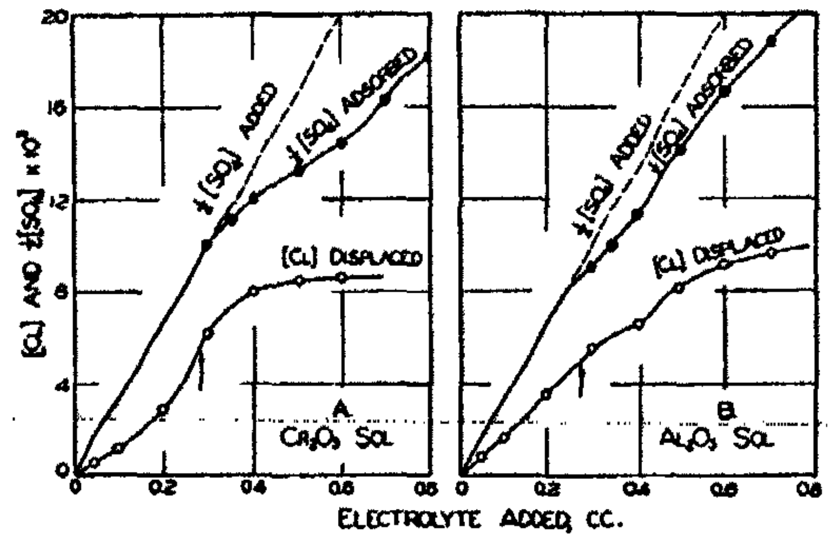

FIG. 1. Simultaneous displacement of chloride ion and adsorption of sulfate ion on titrating hydrous oxide sols with potassium sulfate.

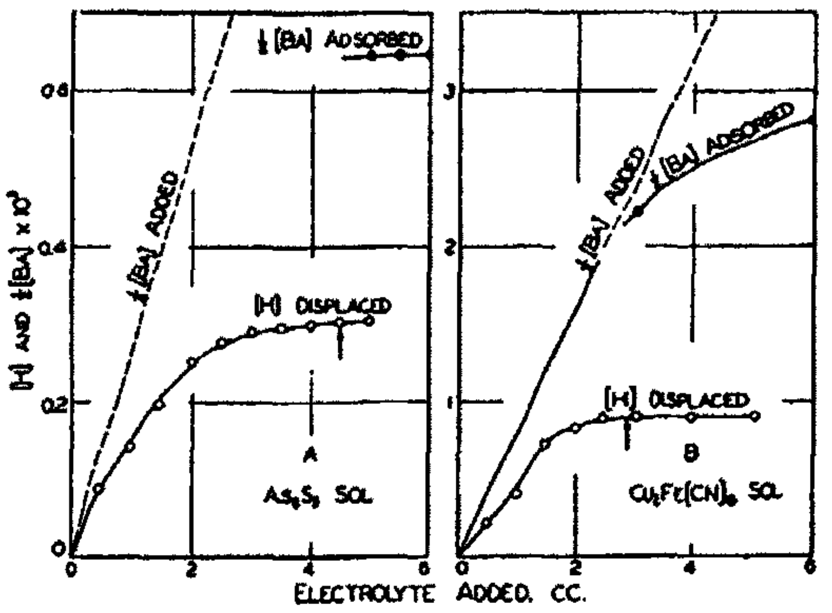

FIG. 2. Simultaneous displacement of hydrogen ion and adsorption of barium ion on titrating "acidoid" sols with barium chloride.

type with barium chloride. In these systems barium ions are adsorbed in exchange with hydrogen ions in the diffuse outer layer. The adsorbed barium ions displace hydrogen ions from the innermost portion of the outer layer, as shown in the curves for hydrogen displacement. Again, the adsorption of barium is much greater than the displacement of hydrogen, since a large part of the hydrogen replaced by barium in the outer layer was in the intermicellar solution originally. Unlike the behavior of the hydrous oxide sols shown graphically in figure 1, the displacement of counter ions from the innermost portion of the outer layer of the acidoid sols is practically complete at the precipitation concentration. The adsorption is also about complete at the precipitation value for arsenic trisulfide sol, whereas the adsorption has not attained its maximum value at the point of coagulation of the more highly gelatinous copper ferrocyanide sol.

Similar titration studies by Verwey and Kruyt (5, 6) on silver iodide sol led to conclusions somewhat different from the above. In the sol employed hydriodic acid was the stabilizing electrolyte; hence it was a sol of the acidoid type like arsenic trisulfide and copper ferrocyanide. With the aged sols used by Verwey and Kruyt, the titration procedure was more complicated and less exact than with the sols employed by the authors. In the first place, the particle charge was much smaller in the iodide sols and the concentration of counter hydrogen ions was much smaller than in arsenic trisulfide and copper ferrocyanide sols of similar concentrations. Moreover practically all the counter ions were measurable potentiometrically in the original silver iodide sol; hence the amount of hydrogen displaced on adding electrolytes was inappreciable. The measurement of hydrogen ion exchanged for the added cation had to be determined in the ultrafiltrate after the addition of the coagulating electrolyte. This introduced errors which may be more or less serious depending on the conditions (4).

The procedure of Verwey and Kruyt was as follows: 15 to 25-cc. portions of sol were weighed in glass-stoppered flasks and varying amounts of electrolyte were added, followed by reweighing. After twenty-four hours the uncoagulated samples were ultrafiltered; the coagulated ones were centrifuged and the supernatant solution decanted. The exchanged hydrogen ion was determined colorimetrically or with the glass electrode. Since nearly all the hydrogen ions were in the intermicellar solution, the exchanged hydrogen may serve as an indirect measure of the amount of cation adsorbed. The adsorption of uranium and cerium was estimated colorimetrically. The results of some observations with a few different sols are shown graphically in figure 3.

From the form of the curves in figure 3, it appears that in certain instances the precipitation value (indicated by an arrow) occurs near the point of maximum adsorption, in accordance with the authors' observations with arsenic trisulfide sol shown in figure 2. In other instances, however, the maximum adsorption by silver iodide appears to fall well below the precipitation concentration. From these and other observations Verwey and Kruyt conclude that adsorption is neither a necessary nor a sufficient cause of potential reduction at the surface of the particles; instead the potential reduction may result from compression of the outer layer without adsorption of the precipitating ions. In opposition to this point of view, all the observations of the authors indicate that the contraction of the double layer or the compression of the outer layer necessary to lower the potential to the coagulation point is the result of adsorption of the precipitating ions.

Since it is not obvious to us how one can have a stable coagulum if the precipitating ions are not carried down (adsorbed) by the agglomerated

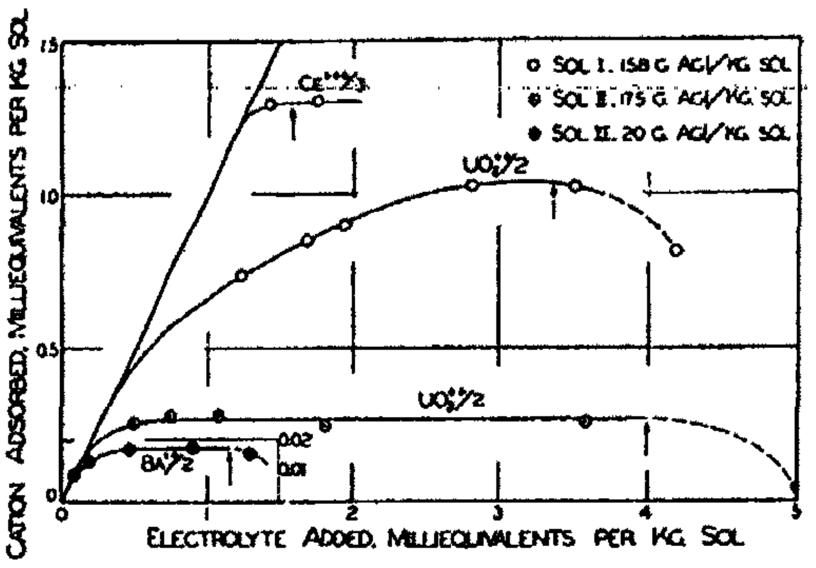

FIG. 3. Adsorption of cations on titrating silver iodide sols with electrolytes (after Verwey and Kruyt).

particles, some of the observations of Verwey and Kruyt would seem to call for special consideration. As already pointed out, the behavior of sol I (figure 3) with certain cations, e.g., UO_2^{++} and Ce^{+++}, is similar in all essential respects to that of the acidoid arsenic trisulfide (figure 2) and sulfur sols with various cations. The barium adsorption estimated indirectly from pH measurements on the ultrafiltrate from sol III (figure 3) can be disregarded, since the change in hydrogen-ion concentration is too small to measure accurately. The behavior of sol II with UO_2^{++} cannot be disposed of in this way. But the fact that the adsorption of UO_2^{++} and Ce^{+++} reaches a maximum near the coagulation point of the respective ions for sol I, whereas the adsorption of UO_2^{++} appears to attain a maximum value well below the coagulation concentration of sol II, calls for an explanation. One possibility is that the stability of sol II results in part from the presence of a stabilizing impurity derived from the membrane used in the dialysis. If such contamination is ruled out, another possibility is that the size distribution of the particles in sol II is quite different from that in sol I. If most of sol II is coagulated at low concentrations but the last trace only at relatively high concentrations (taken as the precipitation value), and if sol I does not exhibit such marked stepwise coagulation, the difference in the behavior of the two sols toward UO_2^{++} may be accounted for. The following experiments indicate that the usual definition of the precipitation value for sols that are quite polydisperse may be unsatisfactory, provided the precipitation value is compared with some other property of the system.

THE STEPWISE COAGULATION OF POLYDISPERSE SOLS

Silver iodide sols

Concentrated silver iodide sols were prepared as follows: Solutions of silver nitrate and hydrogen iodide were made up approximately 0.20 and 0.22 *N*, respectively, and titrated against each other by neutralizing the acid with excess calcium carbonate and taking the end point with potassium chromate as indicator. The required amounts of the two solutions cooled to 0°C. were mixed in a quick-mixing apparatus to give about 500 cc. of a sol containing 100 millimoles of silver iodide per liter with 10 per cent excess of the stabilizing iodide ion. The resulting sol was transferred to an electrodialysis apparatus and electrodialyzed for forty-eight hours at 700 volts and 10 to 20 milliamperes. The dialysis membranes were of Cellophane which had been previously soaked in 63 per cent zinc chloride (3) and thoroughly washed. After the dialysis the relatively pure sol was evaporated at room temperature to 100 cc. by passing a current of cleaned, dried air over it. The resulting preparation was quite stable, had a pH value of 3.5 to 3.7, and contained approximately 60 g. of silver iodide per liter. Several portions prepared simultaneously were mixed to give the sol used in the subsequent precipitation experiments. Two preparations made at different times were employed.

In the precipitation experiments 15 cc. of sol and 5 cc. of electrolyte of the concentration desired were mixed in a small, all-glass, quick-mixing apparatus. The resulting mixture was transferred to a Pyrex test tube and allowed to stand for eighteen hours, after which it was shaken again for ten seconds to break up a kind of gel-like structure which may form during slow coagulation (7). At the end of twenty-four hours, a 5-cc. sample was pipetted from the top of the solution and analyzed for silver iodide. This was accomplished by coagulating the sol with barium chloride, filtering through a Gooch crucible, washing with 0.25 per cent nitric acid until the washings gave no precipitate with sulfuric acid, drying overnight at 110°C., and weighing. Experiments were carried out with the chlorides of potassium, barium, calcium, and aluminum and with lanthanum nitrate and calcium sulfate. Some typical results given in figures 4 and 5 show that (a) the polydisperse sols undergo stepwise coagulation, (b) most of the sol is coagulated in a rather narrow range, and (c) the usual precipitation value, i.e., the point of complete coagulation, indicated by an arrow, may be a concentration 50 to 100 per cent above the concentration required to precipitate 95 per cent of the sol.

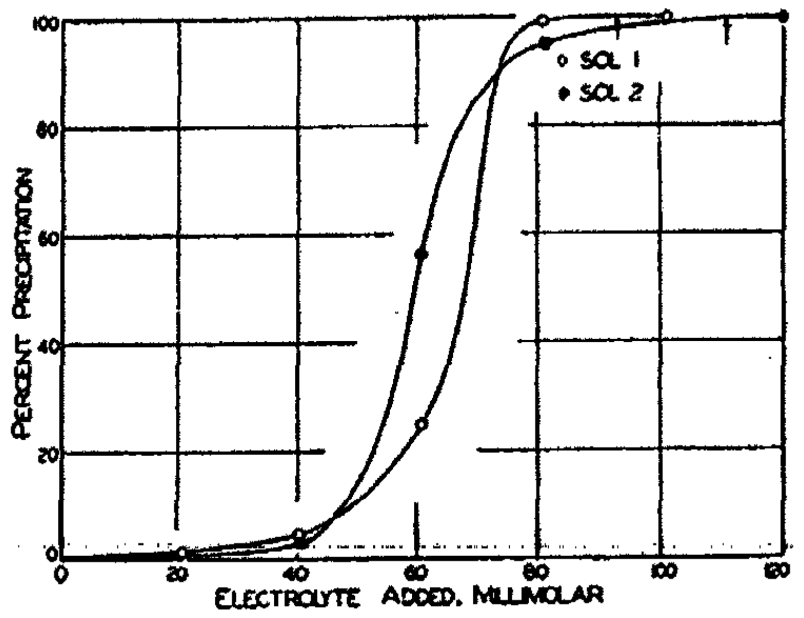

FIG. 4. The stepwise coagulation of silver iodide sols with potassium chloride. Arrows indicate the points of complete coagulation.

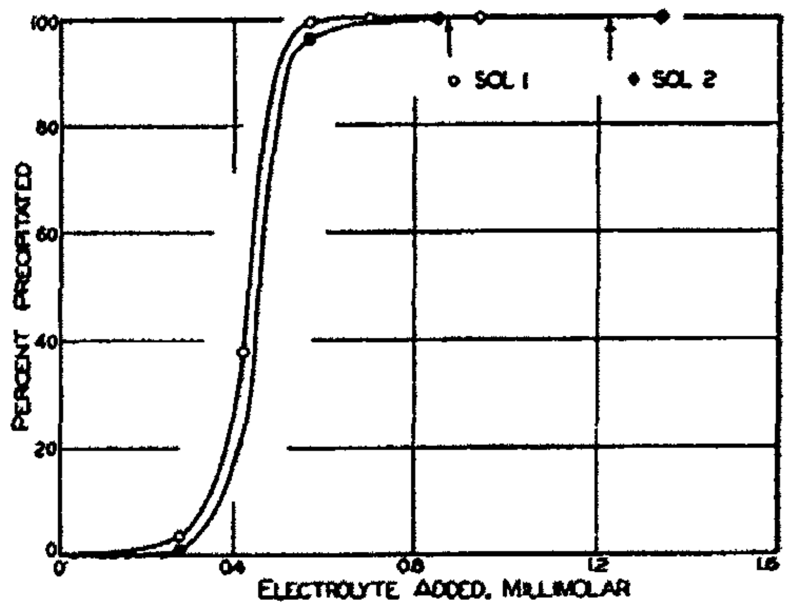

FIG. 5. The stepwise coagulation of silver iodide sols with barium chloride. Arrows indicate the points of complete coagulation.

Arsenic trisulfide sols

Two sols were prepared by two different methods of procedure. The first method, described by Freundlich and Nathansohn (1), is as follows: To 100 cc. of a saturated solution of arsenic trioxide was added 100 cc. of a solution of hydrogen sulfide containing 1 cc. of a saturated solution of the gas. The resulting yellowish mixture was diluted to 1 liter with hydrogen sulfide water ten times as strong as the above. The mixture was then saturated with hydrogen sulfide gas, after which the excess was washed out with a current of hydrogen. By adding very dilute hydrogen sulfide at the start, nuclei are formed throughout the solution; this favors the formation of a monodisperse sol. The concentration was 2.51 g. of arsenic trisulfide per liter.

A second sol of similar concentration was prepared by conducting hydrogen sulfide into 100 cc. of saturated arsenic trioxide, diluting to 1 liter, saturating with hydrogen sulfide, and washing out the excess with a current of hydrogen. This procedure would tend to give a more polydisperse sol than Freundlich and Nathansohn's method.

The precipitation experiments were carried out in much the same way as with the silver iodide sol, except that 20 cc. of the sol was mixed with 5 cc. of electrolyte, and after twenty-four hours a 10-cc. sample was taken for analysis. The results with potassium chloride as precipitating electrolyte are shown graphically in figure 6. The experiments show that Freundlich and Nathansohn's sol is less polydisperse than that formed by conducting hydrogen sulfide directly into saturated arsenious oxide solution. The point of complete precipitation (precipitation value) of the Freundlich and Nathansohn sol is but 20 per cent above the point where 95 per cent of the sol is coagulated, whereas the precipitation value of the more polydisperse sol is 40 per cent above the concentration required to coagulate 95 per cent of the sol.

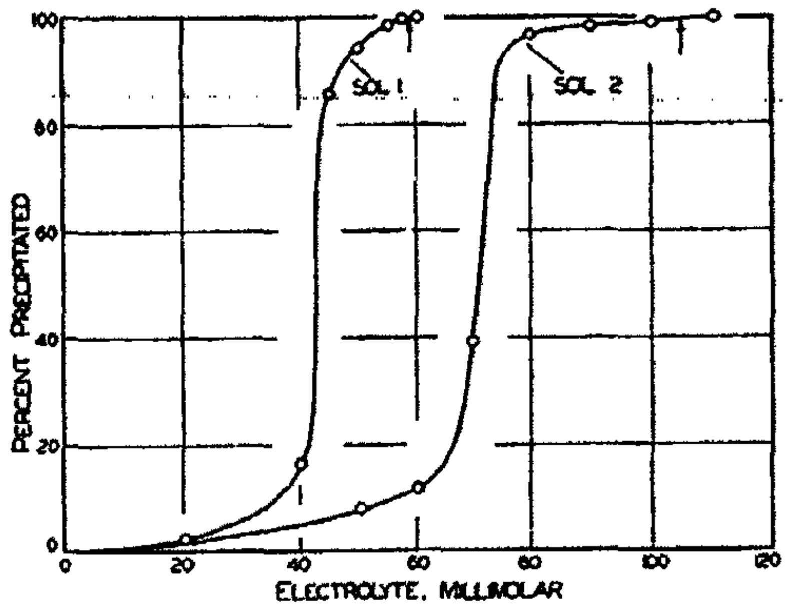

FIG. 6. The stepwise coagulation of arsenic trisulfide sols with potassium chloride. Arrows indicate the points of complete coagulation.

The precipitation value of an electrolyte for a sol is ordinarily taken as that concentration which will cause complete coagulation in a definite time. It is apparent from the above experiments that for polydisperse sols the precipitation value, as defined above, may fall well above the concentration required to precipitate most of the sol. It would seem to be permissible to compare the precipitation values of various electrolytes for a given polydisperse sol among themselves. But if the point of complete coagulation is well above the concentration required for precipitating a large percentage of the sol, the point of maximum adsorption may fall well below the precipitation value as usually defined. This may be in part responsible for Kruyt and Verwey's observation that the precipitation value for certain silver iodide sols falls well above the point of maximum adsorption of the precipitating ion.

SUMMARY AND CONCLUSIONS

1. The coagulation of hydrophobic sols by electrolytes results from the lowering of the electrokinetic or ζ-potential of the particle which, in turn, is caused by contraction of the double layer or, if preferred, by compression of the outer layer surrounding the dispersed particles. This change in the double layer, which reduces the ζ-potential, is attributed to adsorption of precipitating ions opposite in charge to the potential-determining ions which constitute the inner portion of the double layer.

2. In the coagulation of sols of the hydrous oxides of iron, aluminum, and chromium, and of the "acidoid" sols of arsenic trisulfide, sulfur, and copper ferrocyanide, practically complete coagulation by electrolytes takes place at or below the point of maximum adsorption of the precipitation ion.

3. With certain sols of silver iodide Verwey and Kruyt observed that the precipitation value of certain electrolytes was well above the point of maximum adsorption. From these and other observations it was concluded that adsorption is neither a necessary nor a sufficient cause of potential reduction at the surface of the particle.

4. An attempt has been made to account for the apparently anomalous behavior of certain silver iodide sols as observed by Verwey and Kruyt.

5. For highly polydisperse sols the concentration of electrolyte required for complete coagulation in a given time (the precipitation value) may fall well above the concentration necessary to precipitate a large percentage of the sol.

6. If the point of complete coagulation in a polydisperse silver iodide sol is well above the concentration required for precipitating a large percentage of the sol, the point of maximum adsorption may fall well below the precipitation value as usually defined. It is suggested that this may account, in part, for Kruyt and Verwey's observation noted in paragraph 3 above.

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THE SYSTEM NICKEL SULFATE–SULFURIC ACID–WATER AT 25°C. AND 0°C.

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The system nickel sulfate–sulfuric acid–water has been studied by Montemartini and Losana (1), who give data for the 12.5°C. isotherm. Rohmer (2) has investigated this system at 25°C. and 50°C., and gives data for the various transition points of the hydrates of nickel sulfate. This study was undertaken with the purpose of obtaining the complete isotherms for this system at 25°C. and 0°C.

EXPERIMENTAL PROCEDURE

A series of solutions containing approximately 100 cc. of varying concentrations of sulfuric acid were saturated with nickel sulfate. For the lower acid concentrations the solutions were saturated with the hexahydrate, and in the higher acid concentrations the solutions were saturated with anhydrous nickel sulfate. For the 25°C. isotherm these solutions were placed in a constant-temperature water bath. For the 0°C. isotherm the bottles were placed in a large container packed with finely divided ice. The temperature range varied from approximately 0°C. to 0.2°C.

The bottles were shaken by hand at least three times a day and allowed to remain in the bath for four weeks. The solutions were then allowed to settle and samples of the clear liquid were taken for analysis. Solid phases were removed for analysis by means of a glass spoon, as much of the liquid phase as possible being allowed to drain off.

Nickel was determined gravimetrically by the usual dimethylglyoxime method, and sulfate was determined by precipitation with barium chloride. The nickel was calculated to nickel sulfate, and the excess sulfate was calculated to sulfuric acid. Water was determined by difference.

The composition of the solid phases in equilibrium with the various solutions was determined graphically by means of intersecting tie-lines.

The analyses of the liquid and solid phases are given in weight per cent of $NiSO_4$, H_2SO_4, and H_2O.

RESULTS AND DISCUSSION

The data for the 25°C. isotherm are given in table 1 and the results are plotted in figure 1. Data for the 0°C. isotherm are given in table 2 and plotted in figure 2.

TABLE 1

25°C. isotherm

LIQUID PHASE			WET RESIDUES			COMPOSITION OF SOLID PHASE
$NiSO_4$	H_2SO_4	H_2O	$NiSO_4$	H_2SO_4	H_2O	
weight per cent	*weight per cent*	*weight per cent*	*weight per cent*	*weight per cent*	*weight per cent*	
28.13		71.87				$NiSO_4 \cdot 7H_2O$
27.34	1.79	70.87	48.07	0.63	51.30	
27.16	3.86	68.98	53.32	0.23	46.45	
26.15	4.92	68.93	53.62	0.85	45.53	$NiSO_4 \cdot 6H_2O$
23.71	6.85	69.44	52.60	1.27	46.13	
22.26	7.93	69.81	57.02	0.47	42.51	
16.51	16.52	66.97				
15.64	19.34	65.02				
11.23	34.48	54.29	55.95	1.96	42.09	
10.56	44.68	44.76	55.63	2.14	42.23	
12.80	45.12	42.08	57.84	9.55	32.61	$NiSO_4 \cdot 6H_2O$ and $NiSO_4 \cdot H_2O$
9.65	48.46	41.89	68.74	12.63	18.63	$NiSO_4 \cdot H_2O$
4.59	58.53	36.88	73.36	11.40	15.24	
2.67	63.73	33.60				
0.23	72.38	27.39				
0.15	84.52	15.33	43.40	44.27	12.33	
0.12	91.38	8.50	26.02	64.36	9.62	
0.11	93.74	6.15	24.20	71.29	4.51	$NiSO_4$
0.08	96.80	3.12	21.58	76.14	2.28	

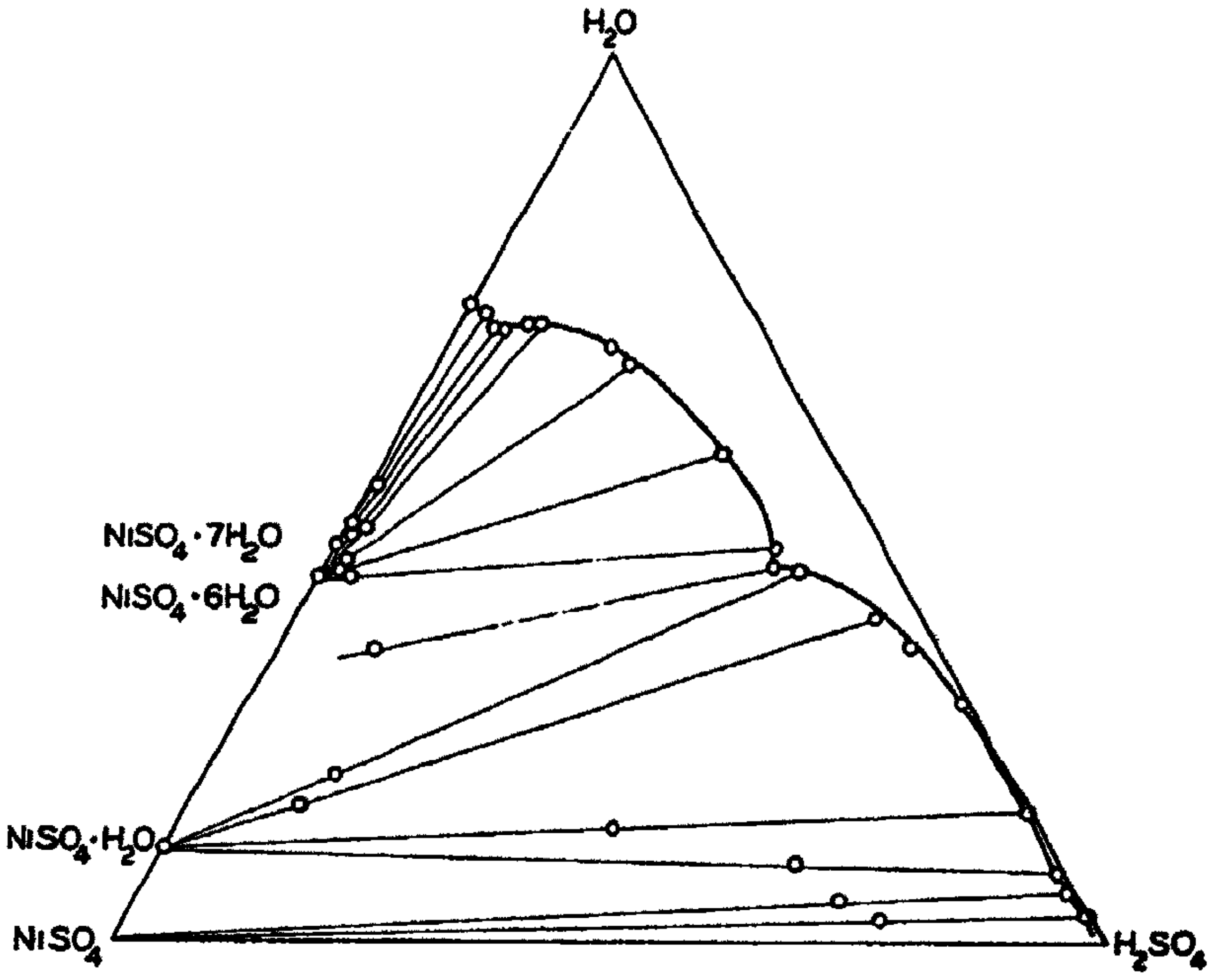

FIG. 1. Plot of the data for the 25°C. isotherm

TABLE 2

0°C. isotherm

LIQUID PHASE			WET RESIDUES			COMPOSITION OF SOLID PHASE
$NiSO_4$	H_2SO_4	H_2O	$NiSO_4$	H_2SO_4	H_2O	
weight per cent	*weight per cent*	*weight per cent*	*weight per cent*	*weight per cent*	*weight per cent*	
21.17		78.83				$NiSO_4 \cdot 7H_2O$
19.22	2.63	78.15				
13.86	10.06	76.08	47.67	1.74	50.59	
9.41	18.36	72.23	51.08	1.81	47.11	
9.22	22.64	68.14	49.08	2.96	47.96	
8.58	25.05	66.37	53.04	2.45	44.51	$NiSO_4 \cdot 6H_2O$
5.06	30.10	64.84	54.74	1.92	43.34	
2.62	42.88	54.50	49.25	7.27	43.48	
4.68	50.72	44.60	51.36	6.28	42.36	
5.42	52.88	42.30	51.10	15.83	33.07	$NiSO_4 \cdot 6H_2O$ and $NiSO_4 \cdot H_2O$
4.15	58.12	37.73	39.63	33.30	27.07	$NiSO_4 \cdot H_2O$
3.71	60.11	36.18				
0.24	75.19	24.57				
			Trace	82.12	17.88	$H_2SO_4 \cdot H_2O$ and $NiSO_4 \cdot H_2O$
0.18	79.83	19.99	26.24	59.44	14.32	
0.11	86.67	13.22	Trace	84.96	15.04	
0.09	90.82	9.09	32.33	57.96	9.71	$NiSO_4 \cdot H_2O$
0.07	94.25	5.68	41.85	49.95	8.19	
0.06	97.19	2.75	24.58	69.13	5.29	

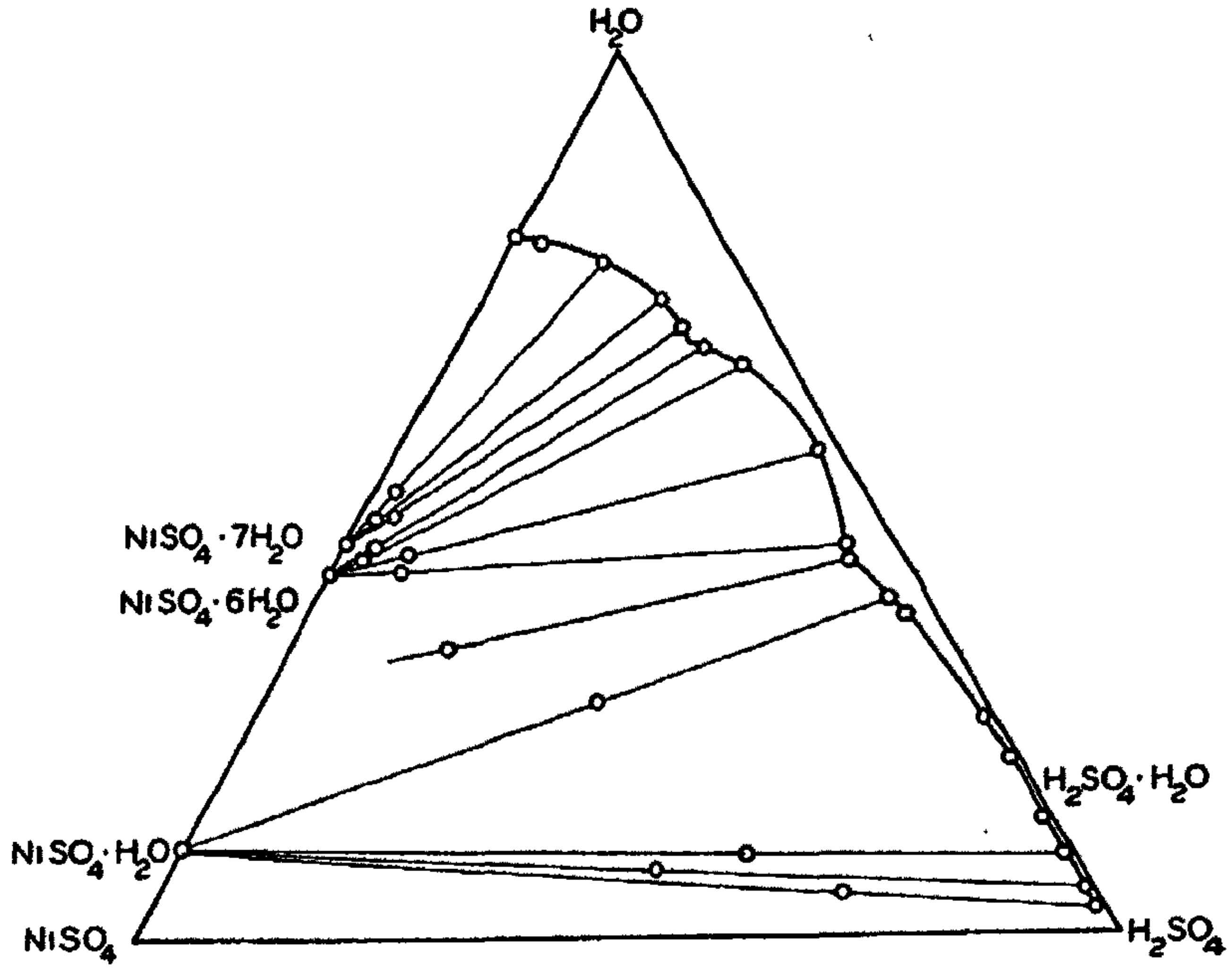

Fig. 2. Plot of the data for the 0°C. isotherm

At 25°C. the solubility of the various hydrates decreases with increasing sulfuric acid concentration. The solubility decreases rapidly at about 60 per cent sulfuric acid. The stable solid phases at 25°C. are the heptahydrate, the hexahydrate, the monohydrate, and anhydrous nickel sulfate. Evidence of a metastable tetrahydrate of nickel sulfate was found between approximately 45 per cent and 50 per cent sulfuric acid. These solid phases agree with those reported by Rohmer (2).

The solubility curves at 0°C. exhibit the same general shape as those at 25°C. The stable solid phases at 0°C. are the heptahydrate, the hexahydrate, and the monohydrate of nickel sulfate. The monohydrate of sulfuric acid also exists as a stable solid phase at this temperature. Anhydrous nickel sulfate, which was found at 25°C. and reported by Montemartini and Losana (1) to be present at 12.5°C., was not found at 0°C. The dihydrate of nickel sulfate was not present at 0°C., although Montemartini and Losana (1) found this hydrate to be stable at 12.5°C.

SUMMARY

The 25°C. and 0°C. isotherms for the system nickel sulfate–sulfuric acid–water have been determined.

The stable solid phases at 25°C. are $NiSO_4 \cdot 7H_2O$, $NiSO_4 \cdot 6H_2O$, $NiSO_4 \cdot H_2O$, and $NiSO_4$. $NiSO_4 \cdot 4H_2O$ exists as a metastable phase.

The stable solid phases at 0°C. are $NiSO_4 \cdot 7H_2O$, $NiSO_4 \cdot 6H_2O$, $NiSO_4 \cdot H_2O$, and $H_2SO_4 \cdot H_2O$.

The author is grateful to Dr. H. D. Crockford for suggestions concerning this work.

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LUMINESCENCE AND COLOR EXCITED BY RADIUM IN ZINC BORATE GLASSES WHICH CONTAIN MANGANESE

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INTRODUCTION

It is well known that radiations from radium color certain soda-silicate glasses a deep violet color. Rutherford (9) attributes to M. and Mme. Curie the first observations of this effect. Clarke (1) found that glasses colored purple by exposure to radium contained manganese, whereas the purple color was not produced in the absence of manganese. As early as 1901 Wiedemann (10) showed that certain solids when exposed to radium exhibited the property of thermoluminescence. Because exposure to radium produces both coloration and thermoluminescence and because heat discharges both the luminescence and the color, these effects have been associated by many of the workers in this field. However, on the basis that the thermoluminescence could be liberated without markedly changing the visible color, Lind (6) indicated that the connection between color and luminescence was not always so close as had commonly been supposed. An investigation of the effects of exposure to radium of synthetic zinc borate glasses, each of which contained a known concentration of manganese, offered promise of more exact information than has hitherto been available. This paper is the report of such an investigation.

THERMOLUMINESCENCE

A series of zinc borate glasses in the form of 6-mm. squares, each 2.7 mm. thick, which contained known amounts of manganese ranging between 0 and 5 per cent were prepared as indicated by Cohn and Harkins (3). These samples were exposed to 140 mg. of radium at a distance of 1.7 cm. for the equivalent of approximately seven gram-days.[1] Under the conditions of exposure the radiation responsible for the energizing of the

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[1] Exposure to 1 g. of radium for one day is referred to as a gram-day; if a glass were exposed to 0.1 g. for ten days, this also would be indicated as one gram-day.

glass specimens was mainly gamma rays, although beta radiation may have contributed a small fraction of the energy. The thermoluminescence was determined by a modification of the total light area method of Nyswander and Lind (8). Intensity-time areas of glass samples heated at a constant temperature of 100°C. were taken as a measure of the energy emitted in the process of luminescence. The values of the areas were then each multiplied by the same factor, so that the maximum luminescence would have the value 100. The results are presented in figure 1, curve A. The values of manganese concentration are plotted on a non-uniform scale in order to spread the values for the lower concentrations, as the greatest changes were in this region. Semilogarithmic cross-section paper was used for this purpose. From this graph it can be seen that a change in the amount of manganese in a glass specimen has an effect which is quite similar to the effect of activators when other sources of energy are used to excite the luminescence. It will be observed that the optimum concentration of manganese is approximately 0.05 per cent. To determine the effect of the time of exposure to radium upon the optimum concentration the luminescence was measured in a set of samples whose exposure to radium was equivalent to approximately 120 gram-days at a distance of 1.7 cm. This time the maximum intensity method of Nyswander and Cohn (7) was employed. It was found that the optimum concentration remained at 0.05 per cent manganese. The optimum concentration is therefore independent of time of exposure. This is of considerable interest, as is evident from the comparison of curves A and B in figure 1. Curve B presents the values for the thermoluminescence excited by ultraviolet light (mercury arc in quartz) and was obtained by Cohn and Harkins (3). It can be seen that the optimum concentration for the thermoluminescence

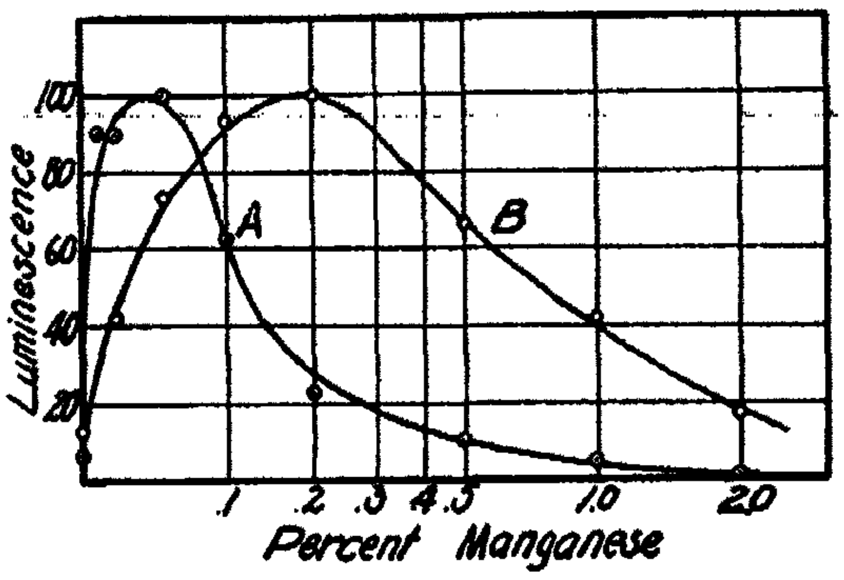

FIG. 1. Thermoluminescence in zinc borate glasses which contain manganese. Curve A, thermoluminescence excited by exposure to radium; curve B, thermoluminescence excited by exposure to quartz mercury arc.

is approximately 0.2 per cent in the latter case. A possible reason for the shift of the optimum will be indicated later in this paper.

The emission spectrum of the luminescence induced in these zinc borate glasses is a band in the red, yellow, and green with its maximum intensity in the red at about 6000 Å. The spectrum was examined visually with the aid of a transmission grating, using the edge of a glowing specimen as its own slit. The emission spectrum appears the same whether radium or ultraviolet light is used to excite the thermoluminescence. Indeed, the spectrum emitted appears to be independent of the means of excitation or of the type of luminescence (fluorescence or thermoluminescence). Similar emission in the type of glasses used was found by Cohn (2) for ultraviolet fluorescence, and by Kabakjian (5) in the case of cathode-ray fluorescence. Both workers used zinc borate glasses which contained manganese.

COLOR PRODUCED BY EXPOSURE TO RADIUM

A series of zinc borate glasses as indicated in the preceding section were exposed to radium. Before irradiation the glass squares appear colorless when they contain less than 1 per cent of manganese. They have a very slight yellowish tint beginning at 1 per cent of manganese and increasing in intensity for samples up to 3 per cent of manganese. Samples which contained 4 and 5 per cent of manganese are a light amber color. Upon exposure to radium the samples which contain manganese acquire a violet-purple tint of much smaller intensity than is the case in soda lime glasses. The sample which contained the highest concentration of manganese acquired the violet-purple tint first, and so on in the order of manganese content. After exposure at a distance of 1.7 cm. for the equivalent of approximately seven gram-days the specimen which contained 0 per cent of manganese appeared slightly yellow; the 0.01 per cent manganese glass was of neutral gray tint; the 0.02 per cent sample exhibited a trace of blue-violet, which tint appeared to increase in intensity with increase of manganese concentration to samples which contained 0.2 per cent manganese. The samples which contained more than 0.2 per cent manganese exhibited about the same intensity of coloration. However, the color tint in specimens which contained more than 1 per cent of manganese was of pink-violet hue as opposed to the blue-violet color of the others. It was found that the color change appeared to approach a maximum value for a given concentration of manganese. For example, the change in the visible absorption determined in samples exposed approximately 120 equivalent gram-days at a distance of 1.7 cm. was almost the same as for glasses exposed 7 gram-days at the same distance. The small difference in the absorption in these glasses after a strong exposure agrees with a similar finding by Kabakjian (4), who found that the coloring due to exposure to radium approached a constant value provided the intensity of the source remained constant.

LIGHT ABSORPTION IN THE ULTRAVIOLET REGION

Spectra were photographed of the transmission of the lines from a quartz mercury arc through the original samples as compared with samples which had been exposed to radium. This was done by placing the glass squares one above the other in front of the slit of a Gaertner quartz prism spectrograph, and photographing the resulting spectrum. Figure 2 shows a set of the comparison spectra for a zinc borate glass which contained 0.1 per cent of manganese. The upper spectrogram presents (upper half) the spectrum of a quartz mercury arc when the light was caused to pass through 2.7 mm. of zinc borate glass which had been exposed to radium. The lower half of the upper spectrogram shows the mercury spectrum as received upon the slit of the spectrograph. The lower spectrogram presents a direct comparison between a zinc borate glass which had been exposed to radium (upper half) as compared with a zinc borate glass of the same thickness which had not previously been exposed to radium (lower half). The concentration of manganese in both glasses was 0.1 per cent. From the lower spectrogram it is evident that exposure of the glass to radium produced a striking change in its transmission for shorter wave lengths of light.

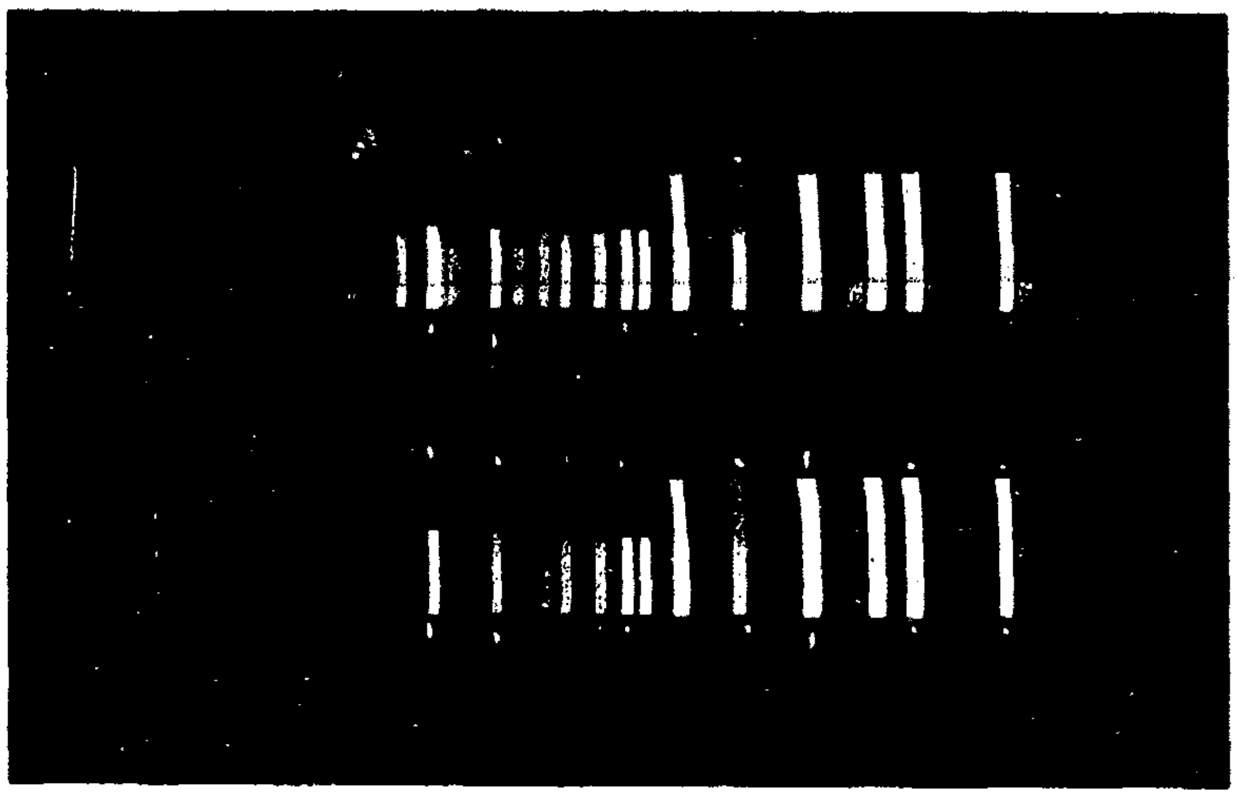

FIG. 2. Comparison spectra through zinc borate glass which contains 0.1 per cent of manganese. Upper spectrogram: top, through 2.7 mm. of glass exposed to radium; bottom, mercury arc lines. Lower spectrogram: top, through 2.7 mm. of glass exposed to radium; bottom, through 2.7 mm. of same glass not exposed to radium.

Quantitative measurements of the change in transmission in the ultraviolet region were made. The measurement of the density of the photographic deposit caused by ultraviolet light passing through (*a*) glasses which had not previously been exposed to radium and (*b*) glasses of the same manganese content which had previously been exposed to radium were made with the aid of a densitometer arranged for the purpose. The photographic plates were Eastman D.C. Orthochromatic and were developed by Rodinal (1 part) and water (15 parts) for 4 minutes at 20°C. using rocked-tray technique. They were placed for 45 minutes in a fixing bath at 20°C., and then were thoroughly washed and dried in a dust-free atmosphere. The densitometer consisted of a light source, a microscope, a photronic cell equipped with a slit, and a galvanometer. The image of the spectrum line on the photographic plate was thrown upon the slit of the photronic cell, and the light intensity was recorded by means of the galvanometer. The intensity of the light source was held constant by means of a voltage regulator. The densities of the deposits on the photographic plate were computed, and the curves for the changes in density due to the exposure of the glasses to radium were determined. The photographic density (D) for each spectrum line was computed by the formula

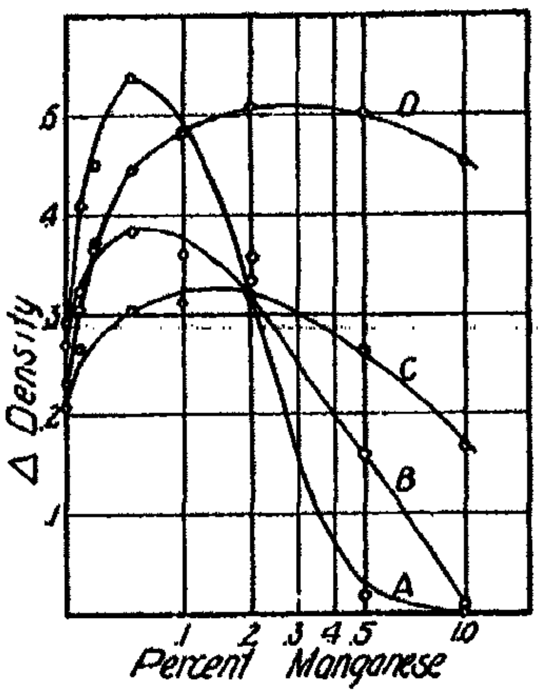

FIG. 3

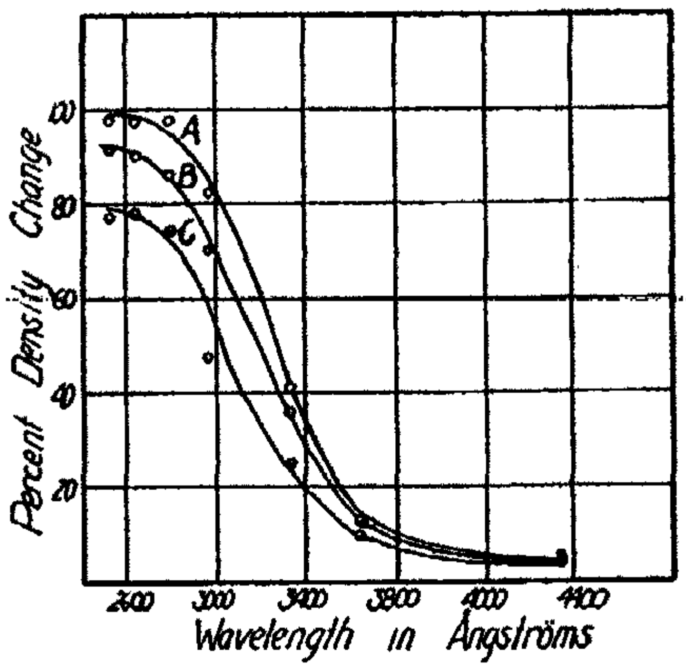

FIG. 4

FIG. 3. Change in absorption caused by exposure to radium. The absorption is indicated as density changes at given wave lengths as a function of the concentration of manganese. Curve A, 2537 Å.; curve B, 2654 Å.; curve C, 2804 Å.; curve D, 2967 Å.

FIG. 4. Per cent absorption change caused by exposure to radium. The absorption is indicated as per cent density change graphed as a function of wave length. Curve A, 0.2 per cent manganese; curve B, 0.05 per cent manganese; curve C, 0.01 per cent manganese.

$$D = \log_{10} G_0/G$$

where G_0 was the value of the galvanometer deflection given by the projection of light through the clear plate in the vicinity of the spectrum line, and G was the galvanometer deflection when the image of the spectrum line covered the slit aperture of the photronic cell. The change in density was expressed as the difference $D_N - D_R$, where D_N was the density of the spectrum line obtained by passage of the light through the original glass and D_R was its density after passage through a glass which had been exposed to radium.[2]

In figure 3 are presented curves which show the change in density $(D_N - D_R)$ due to exposure to radium plotted as a function of the concentration of manganese. Curve A represents the change in absorption at

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[2] The approximate relationship between the values of the change in density (ΔD) computed from the measurements on a photographic plate with the value of the change in extinction coefficient (ΔE) which could be obtained from direct measurement is indicated in the following. By definition the extinction coefficient (E) is given by

$$E = 1/d \log_{10} I_0/I$$

where I_0 is the light transmitted initially, I is the intensity transmitted through the specimen, and d is the thickness of the specimen. If measurements were made with two specimens, one exposed to radium giving a transmitted intensity I_R, the second of the same original material but not exposed to radium, giving a transmitted intensity I_N, and with the same light intensity from a monochromator, I_0, one would obtain

$$\Delta E = E_R - E_N = \left(\frac{1}{d} \log_{10} I_0/I_R\right) - \left(\frac{1}{d} \log_{10} I_0/I_N\right)$$

or

$$\Delta E = \frac{1}{d} (\log_{10} I_N/I_R)$$

Assuming (*1*) the Abney-Schwarzschild law of the photographic plate,

$$D = \gamma \log_{10} I\, t^p - i$$

(*2*) a fixed time of exposure, and (*3*) a constant developmental procedure, one obtains for (ΔD) from this equation

$$\Delta D = D_N - D_R = \gamma \log_{10} I_N/I_R$$

From the definition for D above in terms of galvanometer deflections and the assumption of the direct proportionality of galvanometer deflection to light at the slit of the photronic cell, one obtains

$$\Delta D = \log_{10} G_R/G_N = \gamma \log_{10} I_N/I_R$$

From these two values one obtains for ΔE the result

$$\Delta E = \frac{1}{d\gamma} \log_{10} G_R/G_N = \frac{1}{d\gamma} \Delta D$$

The change in extinction coefficient is therefore approximately equal to the change in density divided by the product of the thickness of the sample and the photographic constant gamma.

2537 Å., curve B at 2654 Å., curve C at 2804 Å., and curve D at 2967 Å. A progressive shift of the maximum absorption toward higher manganese concentration with increasing wave length is quite apparent. It will be noted that the exposure to radium has caused the appearance of an absorption band in the ultraviolet region of the spectrum; that for the region in the vicinity of 2500 Å. the absorption band has its maximum concentration at approximately 0.05 per cent manganese, but that at longer wave lengths this absorption band is displaced toward a higher concentration of manganese. At 2967 Å. the maximum of the absorption band corresponds approximately to 0.3 per cent manganese. From this it would seem that the optimum concentration for the thermoluminescence is very closely related to this absorption in the ultraviolet region, as a similar shift in the optimum thermoluminescence was observed in figure 1. It is readily understood that the optimum condition for luminescence will be at that concentration where conditions are most favorable for the production of that luminescence. If the luminescence due to radium is an optimum at 0.05 per cent manganese, it means that the conditions are most favorable when the ratio of zinc to manganese atoms in the zinc borate glass has a given value. Since the optimum for thermoluminescence induced by exposure to radium closely approximates a change of absorption in the region of 2500 Å., it is probable that the particular reaction between material and light which produces luminescence is directly related to the absorption in the ultraviolet region.

It is of some interest to obtain the approximate form of the absorption curve as a function of the wave length. To do this the values of the changes in density similar to those presented in figure 3 were divided by the corresponding initial density for each concentration and spectrum line. These values were graphed as a function of wave length. Curve A of figure 4 gives the values of the per cent density change due to exposure to radium for zinc borate glasses which contain 0.2 per cent of manganese. Curve B presents the same relation for samples which contain 0.05 per cent of manganese, whereas curve C presents the values for samples which contain 0.01 per cent of manganese. This curve can be taken only as an approximate indication of the absorption, owing to the fact that a variation of the value of the photographic constant gamma with change of wave length is to be expected.

An even more striking fact is brought out when the difference in densities is again determined after the samples have been heated to discharge the luminescence. This was done by heating the samples for one hour at 135°C. Most of the luminescence is discharged by this process, although a small portion of energy available as luminescence may still remain. These values of change in density are subtracted from the original change in density to give a measure of the difference in the absorption which was caused by the process discharging the luminescence. The process of obtaining these data is illustrated by figure 5. The change in density for wave length 2537 Å. before heating is presented in curve A. The difference of density after heating is indicated in curve B. The difference between the densities in curve A and curve B represents the change in absorption which occurred during the interval the luminescence was emitted, and is represented by curve C. The similarity in the shapes of each of these curves is apparent and appears to indicate the diminution in intensity of an absorption band. In figure 6 are graphed the changes in density during the emission of luminescence for wave lengths 2537 Å. (curve A), 2654 Å. (curve B), 2804 Å. (curve C), and 2967 Å. (curve D). The maximum density for each wave length is given a value of 100 for the purpose of comparison, and therefore the ordinates are indicated as per cent density change. This has been done to eliminate the intrinsic difference of the intensity of the mercury spectrum lines from the comparison. The change of absorption maximum with the wave length is quite evident.

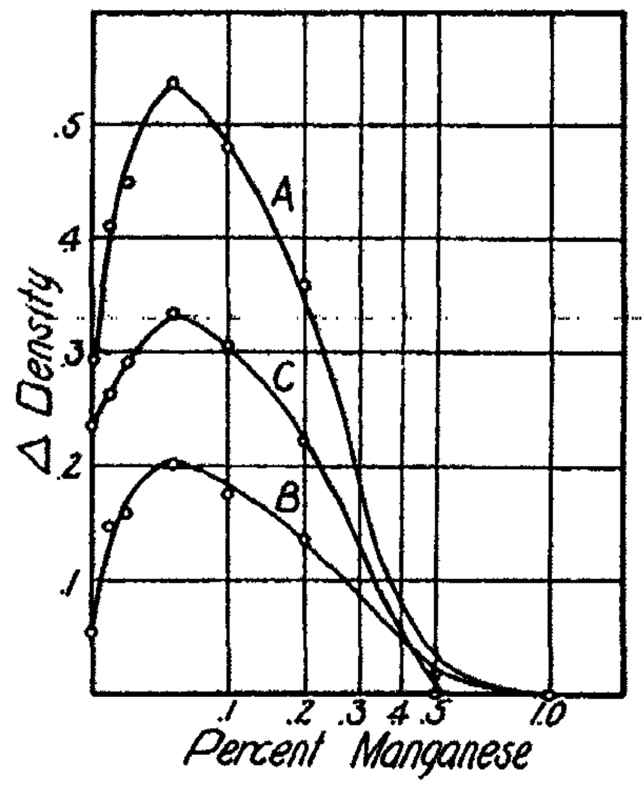

FIG. 5

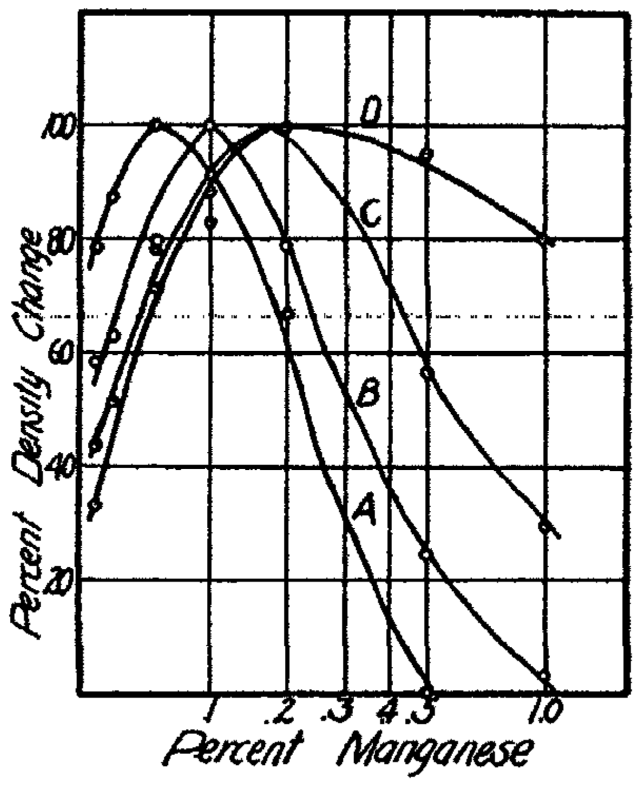

FIG. 6

FIG. 5. Absorption change during luminescence emission. The curves are all given for absorption changes at 2537 Å. Curve A, absorption caused by exposure to radium; curve B, absorption which remains after the emission of thermoluminescence; curve C, change in the absorption during the interval thermoluminescence was emitted.

FIG. 6. Change in absorption during the emission of luminescence. Curve A, 2537 Å.; curve B, 2654 Å.; curve C, 2804 Å.; curve D, 2967 Å.

In figure 7 curve A represents the change in absorption density at the wave length 2537 Å. during the time luminescence was emitted, whereas curve B represents the luminescence which had its origin in the excitation due to exposure to radium. The densities and the luminescence have both been computed in such a way that an arbitrary value of 100 represents the maximum value of either curve. A similarity between the two curves is apparent. In figure 8 curve A represents the change in absorption at 2804 Å., while curve B represents the luminescence emitted when the luminescence is excited by ultraviolet light (see figure 1). The correspondence is again quite evident. From these results it appears that changes in the optimum concentration can be caused by the variation of the absorption of the exciting energy with wave length. It can be predicted that a change in the wave length of an ultraviolet source used for the purpose of excitation of thermoluminescence would shift the optimum concentration for an activator.

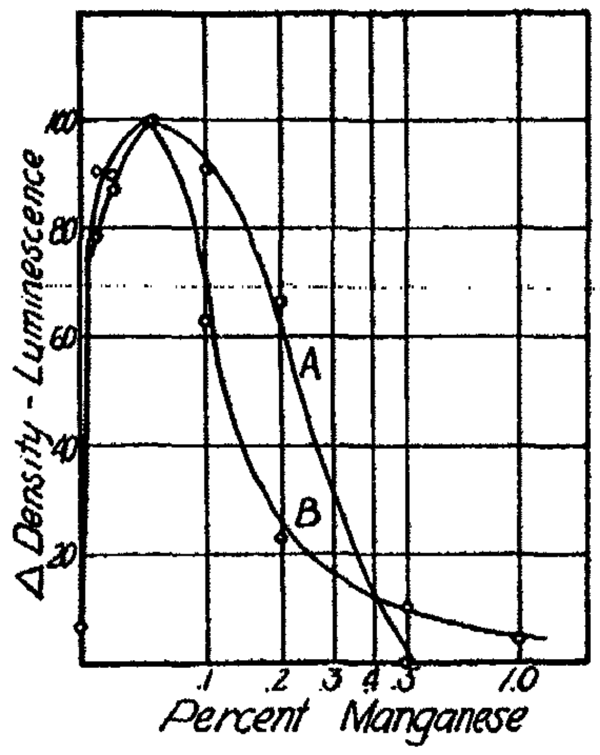

FIG. 7

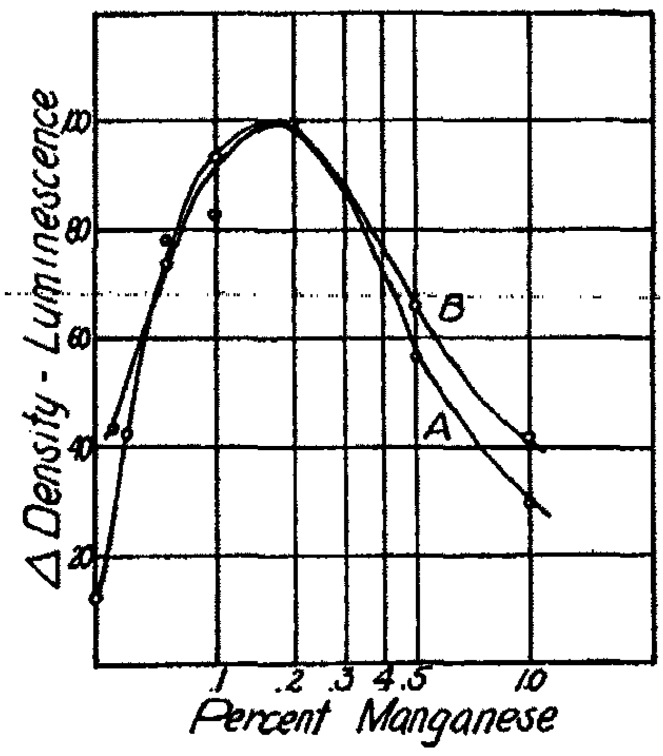

FIG. 8

FIG. 7. Comparison curves of absorption change and luminescence. Curve A, absorption change at 2537 Å. (figure 6, curve A); curve B, luminescence emitted due to radium (figure 1, curve A).

FIG. 8. Comparison curves of absorption change and luminescence. Curve A, absorption change at 2804 Å. (figure 6, curve C); curve B, luminescence emitted, excited by mercury arc (figure 1, curve B).

LIGHT ABSORPTION IN THE VISIBLE REGION

It has been indicated that there appears to be a definite correspondence between the absorption changes in the ultraviolet region and the luminescence which is emitted from zinc borate glasses which contain manganese as an activator. It was desirable also to investigate quantitatively the changes in the visible transmission of these samples. Unfortunately, the change in the visible transmission was so small that photographic measurements could not give the necessary accuracy for the determination of the difference in density. For this reason a direct measurement of the transmission of light confined to given spectrum regions was obtained by means of filters. The densitometer used consisted of a light source, filter, lens, aperture, photronic cell, and galvanometer. The light source was a 40-watt tungsten-filament lamp which was supplied with current from the secondary of a regulating transformer. During the measurements the voltage across the lamp remained at 112.4 volts ±0.1 volt. The density (D) for each sample was computed from the photometric measurement by

$$D = \log_{10} I_0/I$$

where I_0 is the galvanometer reading corresponding to the initial intensity and I is the galvanometer reading after the light has traversed the sample. The values for the changes in density are given by $D_R - D_N$, where D_R is the value of the density after light has traversed the sample which has been exposed to radium and D_N is the density obtained when the light has traversed the original sample.[3]

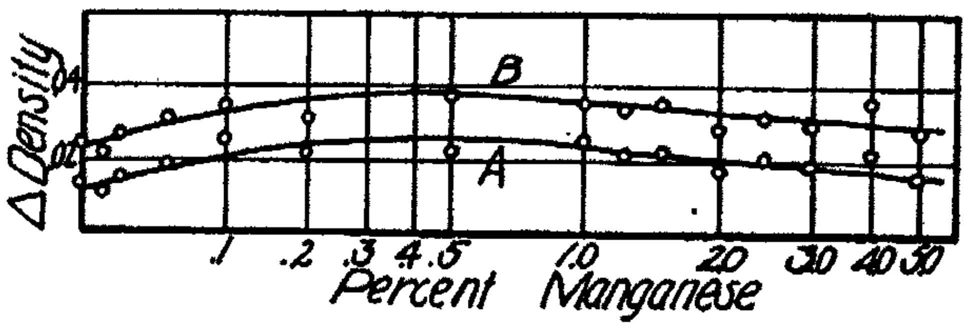

FIG. 9. Absorption change in visible region due to exposure to radium. Curve A, density change in violet portion of spectrum; curve B, density change in red region of spectrum.

The results obtained in this way are presented in figure 9. The values of the manganese concentration are again plotted on a non-uniform scale to spread the values for the lower concentrations. Curve A shows the change in density before and after exposure to radium for the violet portion of the spectrum. To isolate this region Corning Glass Code 554 and Glass Code 306 filters were used in combination. Curve B gives the change in density when the light transmitted was red of wave lengths greater than 6100 Å. The red region was isolated with the aid of a Corning Glass Code 224 filter. It is observed that the change in density in the red region is greater than that in the violet portion of the spectrum. It would appear from these curves that the blue-violet tint which results from the exposure to radium of zinc borate glasses which contain man-

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[3] The value of the visible absorption is given in terms of the density, because the ultraviolet absorption was expressed in somewhat similar terms. The two are related in that if the density differences are taken as indicated the values of the changes in density on the photographic plate when divided by gamma are comparable with the density obtained by the direct method (see note 2).

ganese is to be attributed to a greater relative change of the absorption in the red region of the spectrum. More important, these curves show that the maximum absorption in the visible region is in the vicinity of 0.5 per cent manganese. As the thermoluminescence optimum is at 0.05 per cent manganese concentration, it appears that there is no direct relationship between the visible color and the thermoluminescence emission.

Curves similar in form to those of figure 9 were obtained when the glasses had been subjected to heat treatment. The results show that the visible color is greatly reduced by prolonged heat treatment, but that any residual color which remains has a maximum in the region of 0.5 per cent manganese and therefore the change in color intensity bears no direct relation to the emission of thermoluminescence. It was also found that both the ultraviolet transparency and the visible transparency of the glasses were restored to approximately their initial values by prolonged heat treatment at 300°C.

SUMMARY

1. The luminescence produced by the exposure to radium of zinc borate glasses which contain manganese indicates that the ordinary rules which govern activators are applicable when radium is the source of the excitation.

2. The optimum concentration of manganese in zinc borate glasses when the luminescence is excited by exposure to radium is 0.05 per cent of manganese.

3. Exposure to radium of zinc borate glasses which contain manganese produces a change in visible color which reaches a maximum at approximately 0.5 per cent of manganese.

4. The violet tint developed by exposure to radium of zinc borate glasses which contain manganese is caused by a greater relative absorption in the long wave-length region of the visible portion of the spectrum.

5. Exposure to radium of zinc borate glasses which contain manganese results in a general increase of absorption in the ultraviolet portion of the spectrum.

6. For each wave length in the ultraviolet region there is a curve which represents the change of absorption as a function of the manganese concentration, and each of these curves has a maximum.

7. The maxima of absorption in the ultraviolet region occur at the same concentrations as luminescence optima.

8. From the results it is inferred that the absorption in the ultraviolet region is closely related to the luminescence which is emitted when the specimens are heated.

9. The initial visible and ultraviolet transparencies are almost completely restored by heating for prolonged periods at temperatures at or above 300°C.

One of the authors (B. E. C.) gratefully acknowledges the financial aid given by the van't Hoff Foundation to complete this work. The authors wish to express their thanks to Drs. Robert Livingston and R. E. Hull for technical assistance and constructive criticism.

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NEW BOOKS

Practical Methods in Biochemistry. By **Frederick C. Koch.** Second edition. 23 x 15 cm.: 302 pp. Baltimore: William Wood and Company, 1937. Price: $2.25.

A manual designed primarily for use by medical students, this book contains an abundance of information and experiments which will be found valuable in biochemistry laboratory courses in general. Sufficient fundamental information is given with each experiment to orient the student properly as to the purpose and meaning of the experiment. References given facilitate the student's interpretation of results obtained.

Two hundred and thirty-two experiments are described. Duplication of methods has been reduced to a minimum in this second edition, those being retained which have been proven to give best results. The preparation of all materials used in these experiments is fully described in an appendix.

There are three parts to the manual. Part I deals with the chemistry of the cell constituents, i.e., carbohydrates, lipids, proteins, and nucleic acids, and with the determination of hydrogen-ion concentration. Part II studies the chemistry of salivary, gastric, and intestinal digestion, and of the bile. Part III contains experiments on blood and hemoglobin, and the quantitative analysis of blood and of urine, with a chapter on the chemical examination of urine for pathological conditions.

David R. Briggs.

Principles of Powder Metallurgy. By W. D. Jones. 189 pp. New York: Longmans, Green and Co., London: Edward Arnold and Co., 1937. Price: $5.00.

This book appears to be the first one written on the subject of powder metallurgy. The author has accomplished his task remarkably well. A large number of references are included and due credit has been given the many research workers in powdered metals. The contents appears to be quite complete and well arranged into six main chapters. About thirty good illustrations are given.

The author begins his treatise by elaborating on the meaning of welding and sintering and shows the influence of many factors, such as particle size and shape, temperature, gases and vapors, and pressure, and methods of application of pressure on sinters.

Shrinkage of sinters, as affected by hot and cold pressing methods, and the physical properties of the resulting sinters are discussed from the standpoint of physics at boundary interface, recrystallization, grain growth, and electrical conductivity. The author also covers compacts of one, two, and three constituents and shows industrial applications and technic in considerable detail in the case of powders of iron, nickel, nickel-iron, chromium, bronzes, tungsten, hard metal carbides such as tungsten carbide, tantalum carbide, diamond-impregnated grinding wheels, etc.

About twenty pages are given to the properties and manufacture of metal powders of carbonyl, electrolytic, pulverized, ground and stamped, and miscellaneous types.

This treatise is exceptionally good and is highly recommended to those interested in powder metallurgy. Throughout the book the author discusses the many factors in an unbiased manner. It is likely that his work will materially aid others in expanding one of the most important fields of metallurgy to many new applications.

Ralph L. Dowdell.

Polymerization and its Application in the Fields of Rubber, Synthetic Resins and Petroleum. By Robert E. Burk (Professor of Chemistry, Western Reserve University), Howard E. Thompson (Research Chemist, The Harshaw Company), A. J. Werth (Associate Director of Research of the Bakelite Corporation), and Ira Williams (Research Chemist, E. I. du Pont de Nemours and Company). Monograph Series No. 75. 15.5 x 23.5 cm.; 312 pp.; 6 fig. New York City: Reinhold Publishing Corporation, 1937. Price: $7.50.

The object of the authors, as stated in Chapter I, is "to collect facts and theories relative to the subject of polymerization, and to arrange them in a way which will be interesting and helpful to workers in the field." In the first part of the book the theoretical aspect of the subject is presented in five chapters. The latter part of the book is concerned with the industrial applications.

The second chapter, by H. E. Thompson, deals with the relation between molecular structure and the rate of polymerization. The influence of unsaturation, conjugation, substitution of alkyls and halogens, and cyclic structures are reviewed. A quite complete alphabetical list of polymerization catalysts, together with the literature or patent reference, substances polymerized, conditions and products, is found in Chapter III (written by R. E. Burk).

The open-chain mechanism of polymerization as proposed by Carothers, Staudinger, and Solomon is taken up in Chapter IV (by R. E. Burk). A detailed discussion of the mechanism of the polymerization of specific unsaturated and cyclic hydrocarbons and some of their derivatives is included. In the chapter on "The Liquid State and the Structure of Polymers," equations by Staudinger, Raman, Ornstein Andrade, Einstein, and others, giving the relationship between the viscosity of a liquid and some of its physical constants, are discussed.

"Polymerization in the Rubber Industry"—including the field of the synthetic rubbers—is the subject of Chapter VI, written by I. Williams. The seventh chapter, "Polymerization and Synthetic Resins," written by A. J. Werth, includes discussions of the thermoplastic styrene, vinyl, cumar, indene, and petroleum hydrocarbon resins and the thermosetting glyptal, phenol-aldehyde, urea-formaldehyde resins or condensation products, and the relation of their chemical structure to their physical properties.

The final chapter, "Polymerization in the Petroleum Industry," takes up the influence of acids, clay, and other catalysts in the refining processes. This discussion is followed by one on the deterioration of petroleum products, owing to the oxidation and polymerization of the unsaturates, and the rise of inhibitors to prevent oxidation and polymerization. The usefulness and importance of polymerization in the synthesis of asphalt, motor fuels, and lubricating oils are also pointed out.

The numerous references to the literature make the book particularly valuable. The industrial concerns are to be congratulated on permitting publication of the information accumulated by their staffs, and the authors for the very interesting and readable presentation of the subject.

G. B. Heisig.

THE INFLUENCE OF NEUTRAL SALTS UPON THE INVERSION OF SUCROSE

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The influence of neutral salts upon reaction velocities in general and upon the rate of inversion of sucrose by acids in particular has been the object of a number of researches. Many theories have been advanced to explain the salt effect, and several ideas have been put forth to explain the mechanism of the inversion process.

According to the newer theories (2, 5) the salt effect is due to the influence of these interionic forces upon the activities of the reactants and particularly upon that of the oxonium ion. While these theoretical relations apply beautifully to very dilute solutions, they do not always apply so well with solutions of higher salt concentration. According to Hückel the neutral salt effect must always be positive if the substrate has a weaker dipole nature than the solvent. Water has a very strong dipole character.

Over against this theory of interionic force effect and its influence upon reaction velocity is the theory of dehydration dating from Lowenthal and Lenssen (15). According to this theory, the apparent increase in the oxonium-ion activity is due to a removal of water by the hydration of the ions of the added salt. Although a strong advocate of the theory of interionic attraction, Bjerrum (3) states that it is not possible to prove with certainty, for a given ion concentration, what the activity of the ions would be if no forces existed between them. This difficulty is especially noticeable in concentrated solutions. He states also that we must consider the water content of the ions in the solution, for, if the ions form hydrates, the mole fractions, and hence the activities of the ions and of the reactants, will be greater than they would without this hydration. Bjerrum considers only the equilibrium between the oxonium ion and the water, thus

$$H_3O^+ + mH_2O \leftrightarrows (H_3O \cdot mH_2O)^+$$

where m is the hydration number. The activity of the water is diminished by the neutral salt effect. According to Bjerrum, the pure neutral salt effect is given by the expression, $(p_0/p)^m$, where p_0 is the vapor pressure of pure water and p is that of the solution. The hydration number, m, has been calculated by various authors and has been found to vary between 8 and 11.

Schmid and Olsen (18) appear to favor the view that dehydration is the principal effect exerted by the neutral salts. Employing the concept of the oxonium ion, the effect is best illustrated by the equilibrium,

$$(H_3O \cdot mH_2O)^+ + S \leftrightarrows [H_3O^+ \cdot (m - x)H_2O] + S \cdot xH_2O$$

Here S refers to the neutral salt, including the ions. Thus the addition of a neutral salt increases the measurable concentration of the oxonium ion.

Somewhat earlier Harned (11) found that the effect of the different salts on reaction velocity constants is proportional to their ionic hydration values. He assumes that the increase in the hydrogen-ion activity of hydrochloric acid solutions by neutral salts is due (*1*) to the high hydration of the hydrogen ion and (*2*) to the hydration of the ions of the added salt. Scatchard (17) states that the addition of neutral salts will affect the activity of each component. The activity of the hydrogen ion will be increased because of the decrease in the number of water molecules. With decrease in the activity of the water there should be also an increase in the activity of the sucrose. Experiments by Corran and Lewis (4) with cells containing both sucrose and hydrochloric acid showed that both the hydrogen-ion activity and the geometric mean activity are increased by the presence of the sucrose. This should be expected from the relatively high degree of hydration of the sucrose molecule.

MECHANISM OF THE INVERSION PROCESS

The fact that the inversion reaction has not appeared to obey rigidly the law either of a monomolecular or of a bimolecular reaction has led to much discussion. Jones and Lewis (12) believe that the reaction proceeds in two steps. The first consists of a rapid union between a molecule of sucrose and a hydrogen ion, both unhydrated. This complex sucrose-hydrogen ion then reacts with one molecule of water with measurable velocity. Thus they consider the inversion reaction to be typically bimolecular. Fales and Morrell (7) find that the reaction is bimolecular, when the hydrogen-ion concentration lies between 0.01 and 0.03 molar. For higher concentrations, however, the reaction becomes monomolecular, but only after the reaction has proceeded for some time. Euler and Olander (6) agree that the reaction should be regarded as bimolecular, with water acting as one of the reactants. Pennycuick (16) has found that, although the first-order velocity constants apparently increase with time, the deviation from constancy involved when the reaction is considered as monomolecular is not larger than the experimental error. Hence he considers that the velocity constants calculated on the monomolecular basis are acceptable.

It is now quite generally believed that the inversion reaction involves the formation of an unstable intermediate complex and its subsequent decomposition. The first step is assumed to be the hydration of the sucrose molecule:

$$C_{12}H_{22}O_{11} + nH_2O \rightarrow C_{12}H_{22}O_{11}\cdot nH_2O$$

The number of molecules of water of hydration, n, is not definitely known. Fraser and Myrick (8) have found that the degree of hydration of sucrose varies with its concentration. They also found that for a 1 molar solution the osmotic pressure, calculated on the assumption of six molecules of hydrate water, is practically identical with the experimental value of the osmotic pressure at room temperature.

In attempting to determine the number of molecules of water of hydration, Scatchard (17) has resorted to considerations of the probable kinetics and equilibria involved. He found that the monomolecular constant, K, at 20°C. is constant if the sucrose molecule is considered as attached to six molecules of water. The value of K decreases with rising concentration of sucrose when n is less than 6, and increases when n exceeds 6. Although the degree of hydration decreases with rising temperature, the best constancy for K at 40°C. was obtained by assuming n to be 6. Scatchard, therefore, concludes that the hydration of the sucrose molecule must be the first step.

According to Hantzsch and Weissberger (10), the proton attaches itself to the hydrated sucrose molecule to form an intermediate complex, possibly in the form of an oxonium compound. This complex is unstable and decomposes to give the final products of the reaction, glucose and fructose, thus:

$$C_{12}H_{22}O_{11}\cdot xH_2O + H^+ \rightarrow C_{12}H_{22}O_{11}\cdot xH_2O\cdot H^+$$

which is followed immediately by the reaction,

$$C_{12}H_{22}O_{11}\cdot xH_2O\cdot H^+ \rightarrow 2C_6H_{12}O_6 + (x - 1)H_2O + H^+$$

He considers that the electrical charge on the intermediate complex is the sum of the charges on the reacting molecular species; the charge on the sucrose complex would therefore be positive. The effect of the neutral salts added is determined by the charge on the complex. He states that when the ions in the solution bear the same charge as the complex the effect upon the rate of formation of the complex is positive. Ions having an opposite charge retard the rate of formation of the complex.

Schmid and Olsen (18) find that for those cases in which neutral salts accelerate the reaction velocity, the influence of the salt concentration upon the velocity coefficients may be represented by

$$K = K_0\cdot 10^{rM}$$

where M is the molarity of the salt, r is a constant for the specific salt used, and K and K_0 are the velocity coefficients in the presence of the salt and in the salt-free acid solution, respectively. It has been found that this equation applies for salt concentrations above 0.05 M; at lower concentrations the salt effect is linear. Kapanna and Shirkhande (13) have found that the salt effect is given by $K = K_0e^{aC}$, where a is a constant characteristic of the salt and C is the molar concentration.

In so far as we have been able to find, practically every study of the rate of inversion of sucrose by acids, whether in the presence or absence of added salts, has involved the use of solutions in which all of the components present are expressed in moles per liter of solution. It is quite evident that an increase in the molar concentration of one constituent must decrease the concentration and hence the activity of the remaining constituents. Since the reaction appears to be monomolecular, it appears logical that the influence of added salts on the inversion velocity can be determined best only when the concentration of the salt is the only variable.

In this paper we present the results obtained from a study of the rate of inversion of sucrose in which all of the components are present in molal proportions. Each solution used contained exactly 0.1 mole of sucrose, 1.0 mole of hydrochloric acid, and m moles of salt in 1000 g. of water. The concentration of the salt is the only variable. In this way we hoped to gain further insight into the nature of the neutral salt effect.

MATERIALS AND APPARATUS

The purification of the salts and the preparation of the solutions were performed according to the most approved methods. Conductivity water was used throughout.

The rate of inversion was measured by means of a Schmidt and Haensch triple-field polariscope with a scale readable by two verniers to 0.01°. The 400-mm. inversion tube was surrounded by a nickel jacket which was further insulated by a thick roll of asbestos. Water was forced through the jacket through insulated glass tubes by means of a high-speed Ford water pump connected with a large constant-temperature water bath. The temperature of the bath, as well as that of the inversion tube, was electrically maintained and electrically controlled to within +0.01°C. of the desired temperature. The temperatures of the bath and of the reaction tube were read from two standard thermometers. The intense light from an "Akatos" sodium arc lamp served as the source of illumination.

EXPERIMENTAL PROCEDURE

The required weight of constant-boiling hydrochloric acid solution was placed in a tared glass-stoppered flask. The sucrose and salt were placed in a second similar flask and dissolved in that weight of water which, added to the water of the acid solution, would equal 100 g. The two solutions

TABLE 1

Velocity coefficients for the inversion of sucrose in 1 molal hydrochloric acid solutions with added neutral salts at 25°C.

m	k_1	k_2	k (MEAN)
	Potassium chloride		
0.0000	0.01149	0.01148	0.01149
0.0500	0.01165	0.01165	0.01165
0.1000	0.01189	0.01187	0.01188
0.2000	0.01218	0.01220	0.01219
0.3000	0.01273	0.01262	0.01267
0.5000	0.01338	0.01335	0.01336
1.0000	0.01526	0.01527	0.01527
	Sodium chloride		
0.0000	0.01149	0.01148	0.01149
0.0500	0.01174	0.01178	0.01176
0.1000	0.01197	0.01200	0.01199
0.2000	0.01233	0.01235	0.01234
0.3000	0.01287	0.01289	0.01288
0.5000	0.01375	0.01374	0.01375
1.0000	0.01601	0.01599	0.01600
	Barium chloride		
0.0000	0.01149	0.01148	0.01149
0.0671	0.01202	0.01205	0.01203
0.1114	0.01228	0.01230	0.01229
0.2003	0.01291	0.01295	0.01293
0.3289	0.01398	0.01397	0.01398
0.4985	0.01501		
0.5046		0.01524	
m	k	m	k
	Lithium chloride		
0.2234	0.01239	0.6669	0.01480
0.2236	0.01244	0.6605	0.01490
0.3352	0.01292	0.8013	0.01585
0.3352	0.01295	0.8024	0.01584
0.4481	0.01364	1.0779	0.01781
0.4462	0.01353	1.1128	0.01795
	Aluminum nitrate		
0.1003	0.01242	0.3230	0.01532
0.1113	0.01254	0.3244	0.01533
0.1713	0.01343	0.4062	0.01661
0.1754	0.01335	0.4065	0.01658
0.2040	0.01366	0.5225	0.01832
0.2300	0.01405	0.5226	0.01836

were allowed to stand for one hour in the constant-temperature bath at the working temperature. The solutions were then quickly mixed and vigorously shaken. The instant of mixing was taken as the zero time. The resulting solution was then placed in the inversion tube and polarimetric readings were taken until the inversion reaction approached completion.

TABLE 2

Velocity coefficients for the inversion of sucrose in 1 molal hydrochloric acid solutions with added neutral salts at 35°C.

m	k_1	k_2	k (MEAN)
		Potassium chloride	
0.0000	0.04461	0.04462	0.04462
0.1000	0.04518	0.04526	0.04522
0.2000	0.04622	0.04625	0.04624
0.4000	0.04896	0.04884	0.04890
0.6000	0.05262	0.05265	0.05264
0.8000	0.05551	0.05530	0.05540
1.0000	0.05891	0.05898	0.05895
		Sodium chloride	
0.0000	0.04461	0.04462	0.04462
0.1000	0.04605	0.04614	0.04610
0.2000	0.04772	0.04769	0.04770
0.4000	0.05108	0.05063	0.05085
0.6000	0.05383	0.05407	0.05395
0.8000	0.05798	0.05774	0.05786
1.0000	0.06125	0.06127	0.06126
m	k	m	k
		Barium chloride	
0.1087	0.04654	0.4362	0.05651
0.1073	0.04699	0.6537	0.06110
0.2236	0.05014	0.6687	0.06081
0.2168	0.04997	0.8186	0.06546
0.4366	0.05607	0.8552	0.06756
		Aluminum nitrate	
0.1125	0.04950	0.4521	0.06458
0.1127	0.05023	0.6783	0.07514
0.2269	0.05357	0.6789	0.07425
0.2253	0.05389	0.8911	0.08918
0.4482	0.06475	0.8784	0.08893

In the work at 25°C. the rotation angles were read at 15-minute intervals for 3.5 to 4 hours. At 35°C. the time intervals were 5 minutes. Because of the accelerating influence of both the temperature and the neutral salt, the reactions at this temperature were practically complete in one hour.

The velocity coefficients were calculated by the method of Guggenheim (9). A group of six to eight rotation readings, $a_1, a_2, \ldots a_n$, were taken at times $t_1, t_2, \ldots t_n$ minutes after mixing. After a constant interval following the initial reading a second series of rotations, $a_1', a_2', \ldots a_n'$, were taken at times $t_1', t_2', \ldots t_n'$. This constant interval was taken as 2 hours for readings at 25°C. and half an hour for 35°C. At each temperature the time interval is more than twice the half-time of the reaction. The mathematical considerations of Guggenheim lead finally to the following equation for calculating the velocity coefficients,

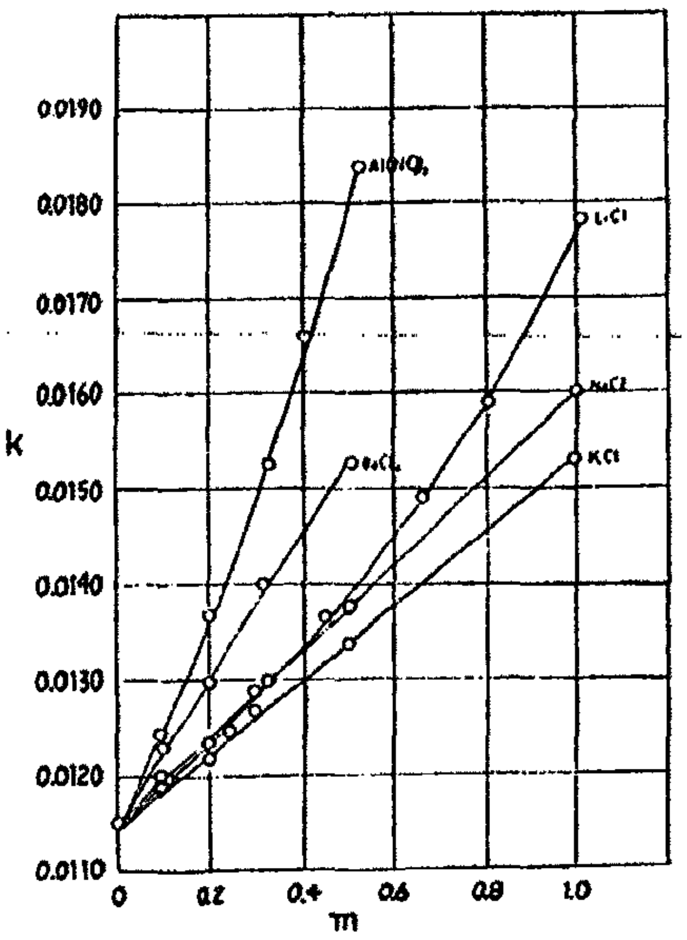


Fig. 1

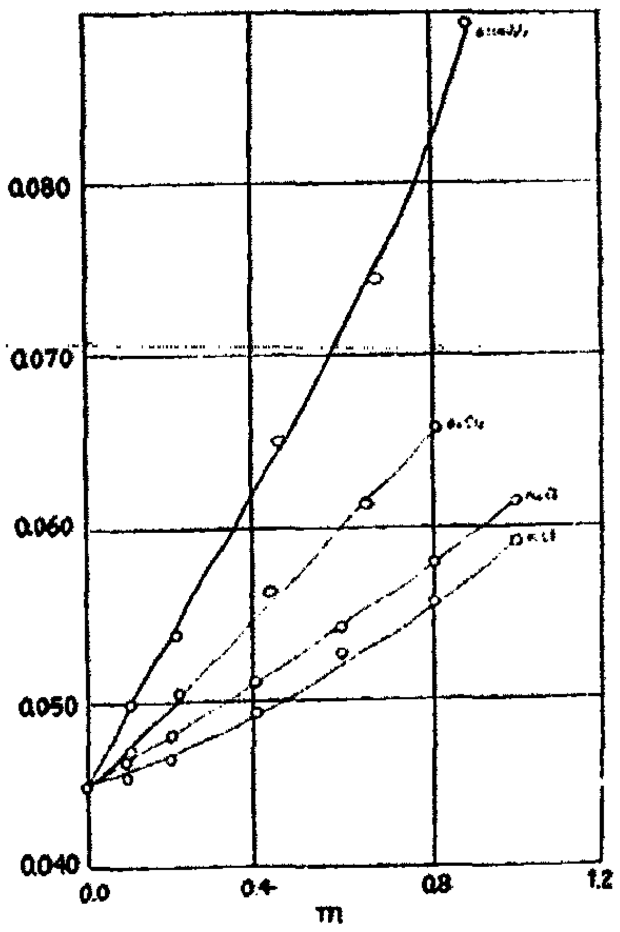


Fig. 2

Fig. 1. Variation of the velocity coefficient with the concentration of the added salt at 25°C.

Fig. 2. Variation of the velocity coefficient with the concentration of the added salt at 35°C.

$$2.303 \log \frac{(a_1' - a_1)}{a_2' - a_2} = k(t_2 - t_1)$$

Thus, to obtain the inversion coefficient, k, it is necessary to know only two pairs of readings whose members are $(t_2 - t_1)$ minutes apart. This method has the advantage over others in that it eliminates the use of the uncertain initial and final readings, namely, a_0 and a_x.

The final velocity coefficients are recorded in tables 1 and 2. Each value given is the mean of the individual coefficients calculated from at least two independent series. Here m is molality of the added salt, and k_1 and k_2 are the monomolecular velocity coefficients for two series of the same concentrations. For any given salt concentration the values of k in duplicate series rarely differed by as much as 0.1 per cent at 25°C. and 1.0 per cent at 35°C. It is very evident that the inversion of sucrose by acids in the presence of added salts is a monomolecular reaction. The variation of the velocity coefficients with the concentration of the added salt at 25°C. is shown in figure 1; that at 35°C. in figure 2.

TABLE 3

Temperature coefficients and heats of activation

m	$k_{35°}$	$k_{25°}$	$k_{35°}/k_{25°}$	Q
		Potassium chloride solutions		
				calories
0.0000	0.04462	0.01149	3.883	24778
0.1000	0.04522	0.01188	3.806	24429
0.2000	0.04624	0.01219	3.793	24349
0.4000	0.04890	0.01301	3.758	24182
0.6000	0.05264	0.01374	3.831	24530
0.8000	0.05540	0.01451	3.818	24468
1.0000	0.05895	0.01527	3.861	24670
		Sodium chloride solutions		
0.0000	0.04462	0.01149	3.883	24778
0.1000	0.04610	0.01199	3.845	24598
0.2000	0.04770	0.01234	3.865	24693
0.4000	0.05085	0.01332	3.818	24468
0.6000	0.05320	0.01420	3.746	24122
0.8000	0.05786	0.01510	3.832	24534
1.0000	0.06126	0.01600	3.829	24519
		Barium chloride solutions		
0.0000	0.04462	0.01149	3.883	24778
0.1000	0.04710	0.01230	3.829	24522
0.2000	0.04960	0.01300	3.815	24455
0.4000	0.05460	0.01450	3.760	24215
0.5000	0.05730	0.01540	3.721	23997
		Aluminum nitrate solutions		
0.0000	0.04462	0.01149	3.883	24778
0.1000	0.04885	0.01257	3.886	24791
0.2000	0.05310	0.01366	3.886	24791
0.4000	0.06175	0.01627	3.810	24427
0.5000	0.06642	0.01792	3.709	23937

Recalling that the masses of sucrose, acid, and water have been maintained constant and that only the concentration of the salt has been varied, we see at once the relative influence of the individual salts. In general, the salt effect increases with increase in the valence of the cation. At 25°C. the inversion rate increases practically rectilinearly with increase in the concentration of the sodium and potassium chlorides. For solutions containing lithium chloride, barium chloride, and aluminum nitrate at 25°C., and for all of the salts at 35°C., the velocity coefficients increase at a continuously increasing rate with increase in the salt concentration. The order of influence of the univalent cations at both temperatures is $Li^+ > Na^+ > K^+$.

The heats of activation, Q, were calculated from the temperature coefficients thus obtained by means of the relation,

$$\log \frac{k_{35^\circ}}{k_{25^\circ}} = \frac{Q}{4.5787}\left(\frac{T_2 - T_1}{T_2 \cdot T_1}\right)$$

The heats of activation in the salt solutions are slightly lower than in the salt-free acid solutions. The temperature coefficients and the heats of activation are collected in table 3. Both appear to be practically constant and independent of the nature of the salt or its concentration.

DISCUSSION

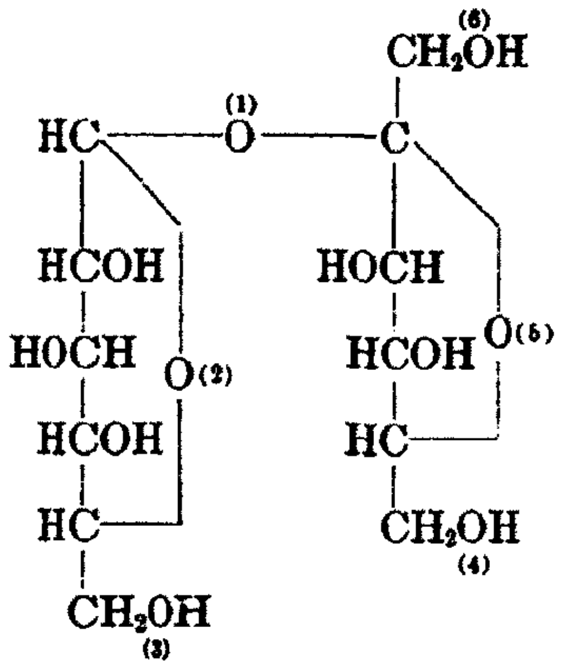
Followers of Debye and Hückel and of Brönsted would ascribe the influence of the salts upon the inversion velocity chiefly to the increase in the activity of the oxonium ion owing to interionic forces. While the activity of the oxonium ion, and hence the velocity of inversion, may unquestionably be increased in part by the influence of these interionic forces, the relative salt effects of the individual salts are in exact accord with the effects which may be predicted on the basis of ionic hydration. That these cations are hydrated appears to have been definitely established by Webb (19). Working in conjunction with Debye, he calculated the free energy of hydration of the ions as a function of the ionic radii. He found that the free energy of hydration of the ions is not only large, but that it increases rapidly with decrease in the value of the ionic radius, and also with the valence of the ion. With the actual removal of solvent by the hydration of the ions of the added salt the concentration, and, therefore, the activity of the remaining constituents—the sucrose and oxonium ion—must increase; the activity of the water must decrease.

As has been stated, two theories have been advanced as to the rôle played by the solvent in the inversion of the sucrose. According to one, the proton combines with a sucrose molecule and this complex then reacts with a water molecule, giving rise to a bimolecular reaction in which water is one of the reactants. The second assumes the first step to be a hydration of the sucrose molecule, which then combines with a proton to form a $C_{12}H_{22}O_{11} \cdot H_2O \cdot H^+$ complex which decomposes as a first-order reaction. Since our results show definitely the existence of a monomolecular reaction, the first theory must be excluded. The cryoscopic study of sucrose solutions by Fraser and Myrick (8), as well as the theoretical calculations of Scatchard (17), show definitely that the sucrose molecule becomes hydrated as soon as it is placed in water. For this reason we can hardly say that the first step is one of hydration of the sucrose molecule. It is this hydrated form that is initially present as one of the reactants.

In order to explain the influence of salts upon, and the mechanism of, the inversion process, the structure of sucrose has been studied from the standpoint of modern physics. By means of quantum mechanics Bernal and Fowler (1) have shown that, in addition to its two binding energy centers, the oxygen atom also possesses two non-binding centers. Hence the atom is tetrahedral in form. They postulate for water a structure in which a hydrogen atom of one water molecule is connected to the oxygen atom of an adjacent water molecule through the subsidiary non-binding forces of the oxygen atom. They have shown that the liquid structure of water may be similar to that of quartz, or of cristobalite, or of tridymite, and they further postulate that all three forms are in equilibrium.

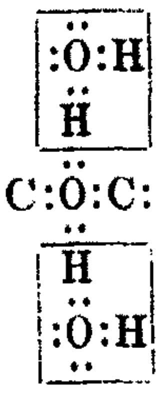
The high solubilities of hydroxide compounds in general, and of sucrose in particular, suggest that the oxygen atoms in sucrose may be connected with water molecules in the same manner. Thus we may be able to think of the sucrose structure as being more or less continuous with that of the water. If this view may be accepted, the maximum number of water molecules which could be attached to one sucrose molecule is eleven, that is, one molecule of water for each oxygen atom in the sucrose molecule. However, since the work of Fraser and Myrick (8) and of Scatchard (17) has shown that the average hydration of the sucrose molecule is six, it is evident that five of these oxygen atoms do not form attachments with water molecules. This may be due to steric hindrance.

While the plane projection of the sucrose molecule, as ordinarily written, is



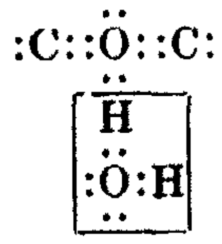
such a projection does not accurately depict the nature of the molecule. It may be seen that five hydroxyl groups are attached to carbon atoms in the two lactone rings. Because of the stable saturated nature of these rings, the probability of adding water molecules to the oxygen atoms in these hydroxyl groups may be considered as small. Perhaps these, then, are the five oxygen atoms which do not form such attachments. Three oxygen atoms in the sucrose molecule are present in the primary alcohol groups. The well-known hydrating ability of the alcohols suggests that here, at least, continuity of structure with the surrounding water may be said to exist. The remaining three oxygen atoms in the sucrose are present as oxide oxygen. Addition products of oxide oxygen have long been recognized, and therefore it is to be expected that water molecules may also be added at these points. Hence the points at which water molecules are most likely to be added are those at the oxygen atoms, 1 to 6, in the plane projection formula.

Such a connection would be:



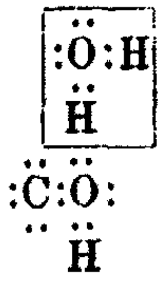
(a)

or



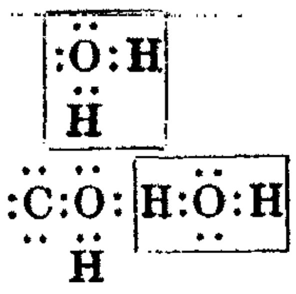
(a)

and



(b)

or



(b)

where formulas a and b represent the addition of water to the oxide oxygen and to the primary alcohol oxygen, respectively, depending upon whether or not the oxygen is capable of adding one or two molecules of water. If all the oxygen atoms (1 to 6) take on two molecules of water each, the total water of hydration would be twelve molecules. This, however, appears improbable in the light of former work (8, 17). In either case the sucrose is surrounded by a sheath of loosely bound water molecules. Further, it has been shown by Bjerrum and others that the oxonium ion is also physically hydrated to the extent of eight or nine molecules of water.

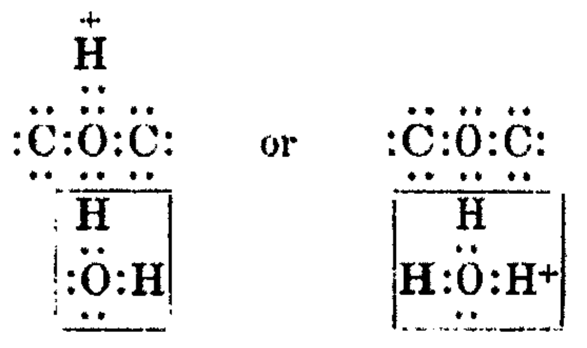
THE INFLUENCE OF THE ADDED SALT

The vulnerable point in the inversion process is at the position of the oxygen atom joining the two branches of the sucrose molecule. It is at this point that the sucrose molecule and the oxonium ion must make intimate contact. Since both are hydrated, the rate of inversion will depend upon the occurrence of favorable collisions between the two, that is, collisions in which the oxonium ion may approach sufficiently close for a hydrogen atom of the oxonium ion to attach itself to the oxygen atom through coördinate valence linkages. For a given sucrose and acid concentration the probability of such a favorable collision is definite and fixed for a given temperature. Because of decrease of hydration with rise in temperature the probability of favorable collisions, and hence the velocity of inversion, should increase. This is in harmony with experimental data.

The addition of either sucrose or acid alone to water lowers the activity of the water. For this reason the degree of hydration of both should be somewhat diminished and the hydration should be still further reduced by the addition of highly hydrated ions of a dissolved salt. The influence of the salt on the hydration of the uncharged sucrose molecule may be expected to be considerably greater than that on the hydration of the positively charged oxonium ion.

MECHANISM OF THE INVERSION

Is it the proton which combines with a hydrated sucrose molecule, or is it the oxonium ion which combines with the unhydrated sucrose molecule? Thus:



(a) (b)

According to Webb (19), for the free energy of hydration of one mole of protons, ΔF is $-$ 249,000 cals. Unless the protophilic nature of the anhydrous sucrose is comparable with that of water it would appear that it must be the oxonium ion which adds directly to the sucrose oxygen as in formula b. This gives us a hydrated molecular complex containing all of the necessary constituents in the exact proportions for the inversion, and the reaction should be monomolecular. If, on the other hand, the proton adds directly to the oxygen as in formula a, the presence of the positive charge should displace the electronic system of the oxygen in its direction, and thus diminish, if not entirely remove, the possibility of the addition of water. In this case the reaction should be bimolecular, with water as one of the reactants. The rate of reaction would then be dependent upon the probability of favorable collisions between the sucrose-proton ions and the water molecules. For similar reasons the repulsion of water molecules by the addition of an oxonium ion is also probable, but perhaps to a less extent.

In the light of these considerations we believe that the oxonium ion is added to the unhydrated oxygen of the sucrose molecule, as in formula b, and that the monomolecular reaction which we measure is the decomposition of the resulting complex.

SUMMARY

1. The rate of inversion of sucrose by hydrochloric acid in the presence of neutral salts has been studied at 25°C. and 35°C.

2. It is found that all of the salts used increase the reaction velocity. The order of decreasing effectiveness in so doing is aluminum nitrate, barium chloride, lithium chloride, sodium chloride, potassium chloride.

3. Heats of activation and temperature coefficients were found to be practically constant and independent of the nature of the salt.

4. The effect of salts is explained by the theory of hydration.

5. The hydration of sucrose is attributed to addition of water to tetrahedral oxygen atoms. Hence the structure is believed to be continuous with the liquid water structure proposed by Bernal and Fowler.

6. The accelerating effect of the salts is attributed to decreasing the thickness of the envelope of solvent molecules surrounding the reactants.

7. The mechanism of the reaction is explained to be the addition of the oxonium ion to the sucrose molecule to form a complex, whose rate of decomposition determines the rate of inversion of the sucrose.

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THE INTERFACIAL TENSIONS OF SOME MERCURY-HYDROCARBON OIL SYSTEMS. II

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In a recent paper from this laboratory (2) a report was made of a study of the interfacial tensions at mercury-hydrocarbon oil interfaces. Measurements were made in that work by means of the drop-weight method of surface tension determination. In the course of the work it was found impossible to extend the period of drop formation beyond a three-minute interval, else the oil would creep into the tip from which the mercury was dropped, thus vitiating the result. In view of the fact that with certain oils a decrease in the interfacial tension was observed to take place as the period of contact of mercury with oil was increased in length, it was recognized that the approximately three-minute limitation on the period of drop formation rendered it unlikely that the measurements so obtained represented true equilibrium values. It was therefore decided that an effort should be made to determine the extent to which this factor was operative in that work. The capillary-tube method of Bartell and Miller (1) seemed most likely to yield satisfactory results for this system, and hence was chosen for the work. Three objectives were set up: first, to test an apparatus of the type used by Bartell and Miller for interfacial tension measurements involving mercury as one phase; second, to determine whether the measurements previously made by the drop-weight method deviated appreciably from equilibrium values; and third, to observe the effect of some solutes in the oil on the mercury-oil interfacial tension.

APPARATUS AND MATERIALS

The apparatus used in the work was similar to that described and illustrated by Bartell and Miller (1). Owing to the great difference between the densities of the two liquids the cup for the oil was made longer than that for the mercury, since in many cases the height of the oil above the interfacial meniscus was ten times as great as the height of the mercury. Capillary heights were measured on the mercury column by means of a measuring microscope and on the oil column with a cathetometer. The readings in each case had a precision of ± 0.2 of 1 per cent of the total reading.

The mercury was washed with dilute nitric acid and with water, then dried in air and distilled twice.

Three of the oils which had been used in the previous work (2) were used in order to make a comparison of the methods. A fourth oil was prepared from a water-white paraffin oil (Central Scientific Co.). The preparation consisted in washing, in turn, with several portions of furfural, water, sulfuric acid, water, sodium hydroxide, and finally again with water. The treatment with sulfuric acid portions was continued until no discoloration of the acid was noted even after several hours of agitation with the oil by means of a motor-driven stirrer. After the final washing with water, the oil was dried with calcium chloride, filtered, dried over sodium, refiltered, and then stored over sodium until used. The final product had a molecular weight of 486, as determined by the freezing-point method in benzene, showed no saponifiable matter, and absorbed only a trace of iodine.

RESULTS AND DISCUSSION

The mercury-oil interfacial tension values obtained for the three oils previously used are given in tables 1, 2, and 3 for the temperature range 25°C. to 90°C. For purposes of comparison the values obtained in the previous work (2) are included. Values obtained for the paraffin oil prepared for this investigation are given in table 4, the oil being designated as oil No. 4. In table 4 also are given the interfacial tension values for four systems involving solutions of ethyl bromide and bromobenzene in oil No. 4. The relations indicated in table 4 are graphically shown in figure 1.

As may be observed in tables 1, 2, and 3, the measurements made by means of the capillary-tube apparatus at 25°C. were found to agree very well with the measurements previously made using the drop-weight method, the values being within a 1 per cent range. This was considered a satisfactory check for a mercury-oil system, but it is noteworthy that in all three cases the capillary-tube method yields values slightly lower than the drop-weight method. Since, as was previously indicated, the measurements by the drop-weight method must be made within a limited time of oil-to-mercury contact and no such limitation was necessary with the capillary-tube method, the writers are of the opinion that there is a slight, though real, difference between the measurements made by the two methods, and that the values obtained by the drop-weight method were in no case equilibrium values, although at 25°C. the error involved is very slight. At higher temperatures and in those cases in which in the previous work it had been observed that the interfacial tension decreased with increase in the time of oil-to-mercury contact, the measurements fell considerably below the drop-weight measurements. Since no reading could be obtained in the capillary-tube measurements in less than about fifteen minutes after mercury and oil had made contact (time for the

TABLE 1

Interfacial tensions of the system mercury-oil No. 1

TEMPERATURE	INTERFACIAL TENSIONS	
	Capillary-tube method (this investigation)	Drop-weight method (reference 2)
°C.	*dynes per cm.*	*dynes per cm.*
25	362	364
50	359	3[illegible]2
75	355	3[illegible]0
90	351	[illegible]59*

* Values at 90°C. for the drop-weight method in this table and tables 2 and 3 are interpolated from a graphic representation of the data in the reference quoted.

TABLE 2

Interfacial tensions of the system mercury-oil No. 2

TEMPERATURE	INTERFACIAL TENSIONS	
	Capillary-tube method (this investigation)	Drop-weight method (reference 2)
°C.	*dynes per cm.*	*dynes per cm.*
25	345	348
50	341	343
75	333	max. 339 min. 335
90	325	max. 333 min. 328

TABLE 3

Interfacial tensions of the system mercury-oil No. 3

TEMPERATURE	INTERFACIAL TENSIONS	
	Capillary-tube method (this investigation)	Drop-weight method (reference 2)
°C.	*dynes per cm.*	*dynes per cm.*
25	337	339
50	329	332
75	312	325
90	293	max. 323 min. 317

system to attain constant temperature) and no changes were observed even when a series of observations was made on a single system through a twenty-four-hour interval, it is believed that these represent stable

TABLE 4

Interfacial tensions of the system mercury-oil No. 4

TEMPERATURE	INTERFACIAL TENSIONS				
	Mercury-oil	Mercury-1 per cent ethyl bromide in oil	Mercury-5 per cent ethyl bromide in oil	Mercury-2 per cent bromobenzene in oil	Mercury-5 per cent bromobenzene in oil
°C.	*dynes per cm.*	*dynes per cm.*	*dynes per cm.*	*dynes per cm.*	*dynes per cm.*
25	348	333	313	317	309
50	267	263	253	256	249
75	243				
90	237	229	222	225	219

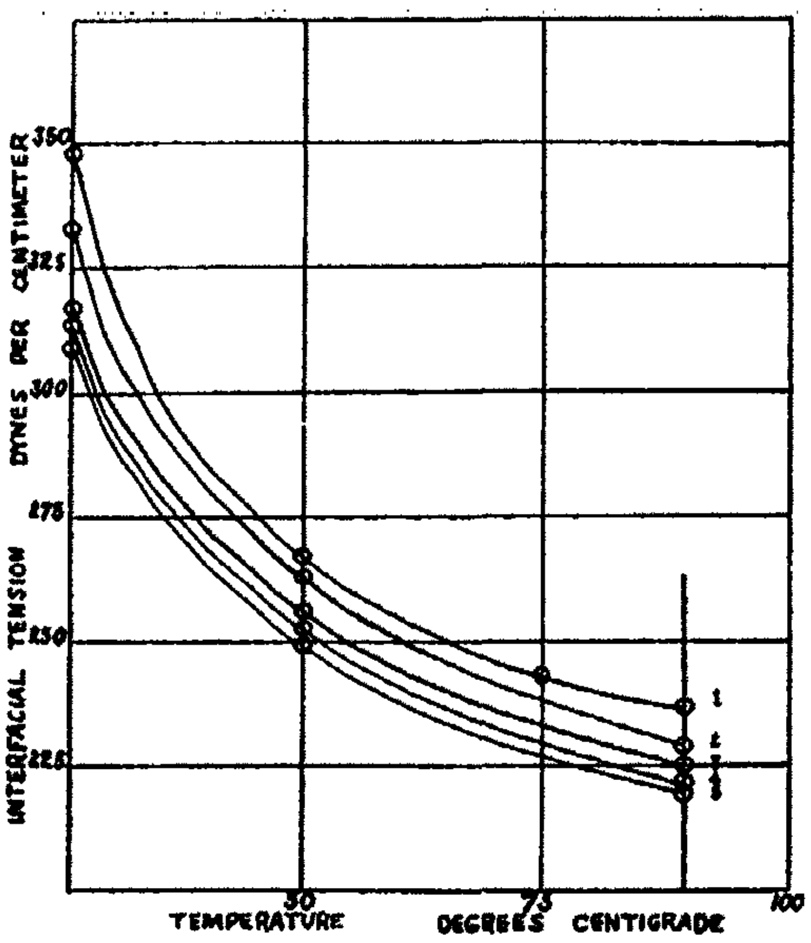

FIG. 1. Interfacial tension values for four systems involving solutions of ethyl bromide and bromobenzene in oil No. 4. Curve 1, mercury-oil No. 4; curve 2, mercury-1 per cent ethyl bromide in oil No. 4; curve 3, mercury-2 per cent bromobenzene in oil No. 4; curve 4, mercury-5 per cent ethyl bromide in oil No. 4; curve 5, mercury-5 per cent bromobenzene in oil No. 4.

values. It would furthermore appear that the results of this investigation are consistent with the idea expressed in the previous paper (2), i.e., that in the case of lubricating oils the evidence indicates progressive adsorption at the oil-mercury interface. This may now be qualified to the extent that the capillary-tube measurements indicate that the adsorption is substantially complete within a fifteen-minute interval.

The specially prepared oil No. 4 yields an interesting contrast to the others in that the mercury-oil interfacial tension versus temperature curve is decidedly convex toward the axes, while those for Nos. 1, 2, and 3 are slightly concave. The writers are not prepared to offer any adequate theory to account for this difference, though it is no doubt due to differences in surface-active components. The fact that with ethyl bromide and bromobenzene dissolved in the oil (see table 4) the oil-mercury interfacial tension is lowered but the shapes of the curves remain approximately the same suggests that in oils 1, 2, and 3 the surface-active components are structurally quite different from the simple brominated compounds.

SUMMARY

The method of Bartell and Miller has been found suitable for interfacial tension measurements at a mercury-oil interface.

Simple brominated hydrocarbons are found to lower the mercury-oil interfacial tension when the bromine compounds are dissolved in the oil.

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ADSORPTION ON CURVED SURFACES AND EMULSIFICATION

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The increase of the vapor pressure (potential) of a one-component liquid, owing to an increase of the curvature of its surface, can be described, from the thermodynamical point of view, as a consequence of the capillary pressure exerted upon the internal phase on account of the surface tension. From the molecular point of view, on the other hand, this effect is to be understood as the reduction of the attractive field, owing to the removal of the fluid masses contained in the interspace between the tangential plane and the spherical body of the liquid. Although the same considerations, undoubtedly, hold in the case of adsorbed molecules bound by a spherical adsorbent, the change of the potential of the adsorbed substance as a function of the curvature of the adsorbing surface, apparently, has not been treated thermodynamically.

The following deductions concerning this problem are based entirely upon the Gibbsian theory of capillarity.

THERMODYNAMIC THEORY

We consider a spherical mass of radius, r, consisting of a solvent (1) and a capillary-active substance (2) dissolved in it being in equilibrium with the vapor (external) phase containing the same two components. By μ_1, μ_2 we shall designate the potentials; by c_{1in}, c_{2in} and c_{1ex}, c_{2ex} the concentrations (masses per unit volume) of the components in the internal and external phases, respectively. We also have to take into consideration, of course, the interface between the homogeneous phases with the superficial densities Γ_1 and Γ_2. Let p_{ex} and $p_{in} = p_{ex} + \sigma C$ be the total pressures in the external and internal phases, where σ denotes the interfacial tension and $C = 2/r$ the curvature, supposing that the radius is sufficiently defined by the size of the internal mass.

The problem we have to deal with concerns the potential, μ_2, of a film of a given density, Γ_2, as a function of the curvature, C; i.e., we wish to know the value of the differential coefficient, $\left(\frac{\partial \mu}{\partial c}\right)_{\Gamma_2}$, as a function of the interfacial tension, the curvature, and the mass distribution given by the c_{1in}, c_{2in} and c_{1ex}, c_{2ex}.

Generally, μ_2 is a function of Γ_2, μ_1, and C, so that

$$d\mu_2 = \frac{\partial\mu_2}{\partial\Gamma_2}d\Gamma_2 + \frac{\partial\mu_2}{\partial\mu_1}d\mu_1 + \frac{\partial\mu_2}{\partial C}dC \tag{1}$$

On the other side, for a given curvature, Γ_2 is a function of μ_1 and μ_2:

$$d\Gamma_2 = \frac{\partial\Gamma_2}{\partial\mu_1}d\mu_1 + \frac{\partial\Gamma_2}{\partial\mu_2}d\mu_2 \tag{2}$$

For $d\Gamma_2 = 0$ we therefore obtain:

$$\left(\frac{d\mu_2}{dC}\right)_{\Gamma_2} = \frac{\partial\mu_2}{\partial\mu_1}\frac{d\mu_1}{dC} + \left(\frac{\partial\mu_2}{\partial C}\right)_{\mu_1} \tag{1a}$$

and

$$\frac{\partial\mu_2}{\partial\mu_1} = -\frac{\partial\Gamma_2}{\partial\mu_1}\bigg/\frac{\partial\Gamma_2}{\partial\mu_2} \tag{2a}$$

The establishment of equilibrium, furthermore, requires the following equations (of state) to be fulfilled simultaneously:

$$dp_{in} = C_{1in}\,d\mu_1 + C_{2in}\,d\mu_2 \tag{3a}$$

$$dp_{ex} = C_{1ex}\,d\mu_1 + C_{2ex}\,d\mu_2 \tag{3b}$$

$$-d\sigma = \Gamma_1\,d\mu_1 + \Gamma_2\,d\mu_2 \tag{3c}$$

Hence we may derive the relation:

$$\frac{\partial\Gamma_1}{\partial\mu_2} = \frac{\partial\Gamma_2}{\partial\mu_1} \tag{4}$$

as an expression of the "displacement effect" (4).

Consequently equation 1a, because of equation 2a, can be written in the form:

$$\left(\frac{d\mu_2}{dC}\right)_{\Gamma_2} = -\frac{d\mu_1}{dC}\cdot\frac{\partial\Gamma_1}{\partial\mu_2}\bigg/\frac{\partial\Gamma_2}{\partial\mu_2} + \left(\frac{\partial\mu_2}{\partial C}\right)_{\mu_1} \tag{5}$$

Now, for the case of plane surfaces, Gibbs (12) has shown that we can consider the dividing surface as being located so that the total quantity of the first component in the vicinity of the surface of discontinuity is the same as if the density of this component were uniform on each side quite up to the dividing surface. Such a location might be objectionable only with regard to a component which has very nearly the same density in the adjacent phases.

Extending this procedure to the case of curved surfaces we could say that the radius of the dividing surface had to be determined so as to make the quantity Γ_1 vanish. However, an even less restrictive demand is implied in the assumption that the value of Γ_1 shall be constant for a given value of the curvature. On this basis it is justified to consider $\partial\Gamma_1/\partial\mu_2$ as very small in comparison to $\partial\Gamma_2/\partial\mu_2$ and to use

$$\left(\frac{d\mu_2}{dC}\right)_{\Gamma_2} = \left(\frac{\partial\mu_2}{\partial C}\right)_{\mu_1} \tag{6}$$

as a reasonable approximation.

If, finally, we take into account the condition of mechanical equilibrium:

$$dp_{in} - dp_{ex} = \sigma dC + C d\sigma \tag{7}$$

we obtain the result:

$$\left(\frac{d\mu_2}{dC}\right)_{\Gamma_1} = \frac{\sigma}{c_{2in} + C\Gamma_2 - c_{2ex}} \tag{8}$$

In perfect analogy to the behavior of a one-component droplet (Gibbs-Thomson formula), the potential of a film of given thickness (density), Γ_2, is larger upon the smaller droplets than upon the larger ones if

$$C_{2in} + C\Gamma > C_{2ex} \tag{9}$$

whereas the opposite will be true if

$$C_{2ex} > C_{2in} + C\Gamma_2 \tag{10}$$

In other words, for a given potential, μ_2, under the first condition (inequality 9) the films of greater curvature must be thinner; under the second condition (inequality 10), however, they must be thicker than those of smaller curvature. This might be formulated quantitatively:

$$RT\,\frac{\partial \log \Gamma_2}{\partial C} = \frac{-\sigma}{c_{2in} + C\Gamma_2 - c_{2ex}} \tag{11}$$

In regard to the analogy with droplets in bulk the inequality 10 will be considered as the "stability criterion" for films of given curvatuve and interfacial density.

Some consequences drawn from this definition will be briefly discussed.

The decision as to whether or not condition 10 can be satisfied depends entirely on the individual shape of the adsorption isotherm represented in a Γ_2-c_{2ex} diagram (see figure 1). Here it is assumed as a first approximation that the course of the isotherms does not vary with the curvature. The adsorption isotherms A and A' correspond to those of the normal type, the latter representing an increase of the adsorption as possibly due to a lowering of the temperature. On the other hand, the stability condition is represented in the Γ_2-c_{2ex} diagram by the course of the discriminant line:

$$\Gamma_2 = r/2\,(c_{2ex} - c_{2in}) \tag{12}$$

only those parts of the isotherms located below the discriminant corresponding to "stable states" of films with given curvature. Since the discriminants are approximately straight lines starting in the origin of the diagram, there may occur one or two intersections with the isotherms or none at all.

If we had to deal with monolayers only, the isotherms would reach saturation and only one intersection of the discriminants could occur, but we know, principally from the work of Perrin (16), that, for instance on the surface of soap solutions, a multiplicity of layers can exist. This means that the isotherms surpass saturation, as could also be shown in the case of other organic molecules adsorbed from the vapor phase on mercury (7, 8). Then, of course, a second intersection may take place.

In general, a minimum concentration, c_{2ex}, has to be reached before stability is possible, and, in case of the second intersection, a definite maximum concentration cannot be surpassed without annihilating the stability Moreover, for any given isotherm, a minimum radius must be guaranteed in order to obtain stability (see the tangent discriminants in figure 1).

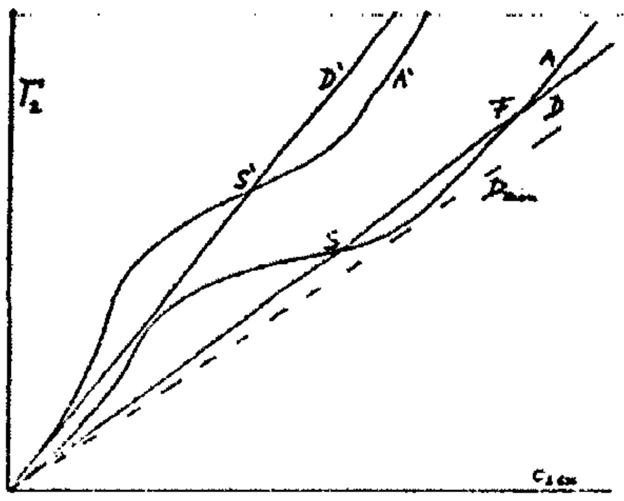

FIG. 1

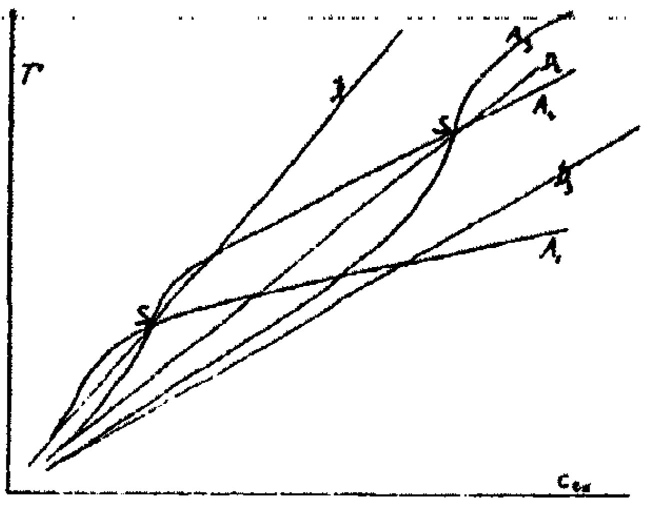

FIG. 2

If the course of the isotherm is shifted in the direction of smaller concentrations (as indicated by the isotherm A'), the range of stability on a given discriminant, i.e., for a given curvature, shrinks more and more until the isotherm fails to be cut. Stability, then, is possible only for discriminants of a steeper slope, i.e., for films of larger radii.

It might, finally, be emphasized that the present deductions are not restricted by the special assumptions concerning the adsorption isotherms as drawn in figure 1.

On the basis of equation 11 the influence of the curvature upon the course of the isotherms may be easily derived. In figure 2 the essential features of this effect are shown for a series of adsorption isotherms, A_1, A_2, A_3 on surfaces with presumably increasing curvatures $r_1 > r_2 > r_3$. The intersections S_1, S_2, S_3 with the discriminants D_1, D_2, D_3 are now spread over a wider range instead of defining a sharp limit.

COMPARISON WITH EXPERIMENTAL FACTS

No direct experiments seem to be available which would allow of a verification of this theory. An indirect test, however, is possible in the field of emulsions (5, 6).

By the word "emulsion" we will understand a dispersion of finely divided droplets or gas bubbles suspended in a liquid medium. Tolman (18) has shown that such systems are thermodynamically stable only if the interfacial tension is zero. Otherwise they collapse as time goes on and change to the stable state of two coexisting masses in bulk. However, a "pseudo-stabilization" may be obtained, at least to a certain degree, by the addition of a third component, the emulsifying agent, which is soluble in the external phase and produces a film around the particles, thus preventing their coalescence (9). This implies the assumption that the growth of solvent droplets through condensation is negligible.

One has to be aware, however, that the collision of particles does not necessarily result in their coalescence, i.e., in the formation of larger homogeneous units. In many cases, usually regarded as examples of reversible coagulation (the terms "agglutination" and "flocculation" are applied in different fields), the particle boundaries are preserved, being separated and sticking together by means of the interfacial layers of emulsifying agent.

According to the present aspect the coagulation is simply understood as due to the capillary condensation of the emulsifier in between adjacent particles, which naturally must occur if the stability condition, defined above, is not fulfilled. Generally coagulation has to be considered as the pre-stage of final coalescence.

In comparing the present theory with experimental facts we introduce the somewhat hypothetical assumption that the criterion, $\partial\mu_2/\partial C < 0$, represents a necessary condition for the pseudo-stability of emulsions, but one has to keep in mind that it can *not* be *a sufficient stability condition*. For this condition might well be satisfied also when the films are not thick enough to exert the protective action. Moreover, the compensation of gravity is necessary, which may be partially ascribed to the Brownian movement, and partially to the electric forces of adsorbed ions.

Since the potential of the external solvent present in the case of emulsions is almost independent of the variations in concentration of the other components which always form sufficiently dilute solutions, the formulas derived above are applicable without alterations. (To destroy any doubts one might consider the same assumption to be the basis of the generally acknowledged pH scale!)

THE INVERSION OF EMULSIONS

As a matter of fact, two types of emulsions may be formed with the same solvents (15). The decision as to which phase is to be the dispersing agent depends greatly on the nature of the emulsifying substance. Alkali soaps, which are readily soluble in water and far less soluble in oil, give oil-in-water emulsions, while soaps of other bases, whose solubility is greater in oil, yield the water-in-oil type (2). Generally the rule of Bancroft holds, that the better solvent for the emulsifier is the external phase. This statement is in full conformity with the stability condition for the films as defined above.

A few exceptions stand in the way of acknowledging the generality of Bancroft's rule (2). For instance, oleic acid is soluble in benzene but not markedly soluble in water. Contrary to expectation, however, benzene is actually emulsified in water. Other examples are those of ethyl ether and some organic solvents emulsified in water, supposedly by the action of iodine as emulsifier.

From the standpoint of the present theory, it seems probable that in these cases a fourth component not taken into consideration has actually operated in producing the protective film. In this regard, the oxygen of the air is open to suspicion because, in the presence of air, unsaturated acids as well as ether easily undergo changes. Undoubtedly, the possibility of emulsification offers a very sensitive analytical test for certain compounds, the type of emulsion obtained, furthermore, allowing a statement concerning their relative solubility.

In the case of supposedly insoluble emulsifiers, as, for instance, soot or alumina, we remain in agreement with the theory by regarding the particles of these substances as the molecules dissolved in the adjacent phases, the solubilities being regulated by the interfacial energies of these "molecules" (14). This view of the mechanism of emulsification is practically identical with that first suggested by Ramsden (17).

THE STABILITY RANGE OF EMULSIONS

The theory provides that an excess as well as the removal of the emulsifier causes the collapse of emulsions. This explains the fact that for the practice of preparing emulsions it is advisable to apply the emulsifier in small portions instead of as a whole.

An obvious confirmation of the theory is the observation of Bartsch (3) and others that optimum concentrations of stabilizing agents exist for the durability of dispersed systems.

Experiment, furthermore, proves the theoretical expectation that the size of the emulsified particles is limited by a minimum radius. For example, Kistler (13), applying a colloid mill for the emulsification of water in toluene with aluminum stearate as the emulsifier, could not detect droplets smaller than 0.2μ in diameter, estimated microscopically.

The theory also explains the otherwise astonishing fact that (9) the stability of emulsions can be noticeably improved by "homogenization", i.e., by reducing the radii of the droplets and decreasing the concentration of the emulsifying agent through the development of new surfaces.

Finally, the theory accounts for the "salting out of emulsions" without recurring to the simple idea of neutralizing the electric surface charges. The effect of electrolytes upon the emulsifying agents, if it is not a chemical reaction, consists in changing their activity coefficients (10). Accordingly, in case of increased activity (2, 11), the adsorption isotherm must be shifted into the direction of lower concentrations. The effect upon the stability of an emulsion, under such conditions, corresponds to the effect of temperature changes, as described in connection with figure 1.

But reliable data are lacking for decision as to whether or not the breaking of emulsions by heat treatment is in agreement with the theoretical deductions. Probably the thermal effects can be understood only if the conditions sufficient for emulsification are also taken into account.

CONCLUSION

The theory, on the whole, is in satisfactory agreement with the facts known about emulsions. However, experiments are missing which would permit a quantitative test in detail.

On the other hand, it seems to be allowable to extend the theory here developed to the inhibiting action of "protective colloids" and "peptizing agents" in general.

SUMMARY

The thermodynamic theory of adsorption on curved surfaces leads to a relation analogous to the Gibbs–Thomson formula for the vapor pressure of droplets as a function of the curvature. In regard to the lack of direct experiments the theoretical expectations are checked by experience with emulsions. The basic idea is that emulsions can be stable only if the interfacial density of the emulsifying films is greater for surfaces of larger than for those of smaller curvature. There are no data available which would allow a quantitative comparison, but no facts seem to be known which are in contradiction with the theory.

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AN INVESTIGATION OF THE LANTHANUM AMALGAM ELECTRODE FOR PRECISE ELECTROMOTIVE FORCE MEASUREMENTS[1]

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INTRODUCTION

The purpose of this investigation was to determine whether a suitable galvanic cell involving a lanthanum amalgam electrode could be constructed for precise E.M.F. measurements. A need for such measurements arises from the fact that, with the exception of the work of Hakomori (7) on indium chloride, there has been very little data obtained on electrochemical cells involving salts of trivalent metals.

The more common trivalent metal salts, such as those of iron, chromium, aluminum, and indium, are highly hydrolyzed in aqueous solution and do not lend themselves to precise E.M.F. measurements. The addition of an acid to prevent hydrolysis introduces a difficult correction factor when the data are treated theoretically. Attention is turned to lanthanum which, according to Ley (18), is not hydrolyzed to any appreciable degree. If this metal can be developed into a reproducible electrode, it will give free energy measurements that may be employed to test further the interionic attraction theory of Debye and Hückel as extended by LaMer, Gronwall, and Greiff (14) for electrolytes of the unsymmetrical valence type. Furthermore, if the temperature coefficients of the cell are obtained, certain thermodynamic quantities of the cell process can be calculated by means of the Gibbs-Helmholtz equation. The free energy change for the cell process, the entropy, and the heat capacity may also be investigated.

Müller (21) carried out an investigation of certain electrochemical cells with lanthanum. He was interested primarily in the effect of varying the lanthanum content of the amalgam rather than the concentration of the salt. Furthermore, his cells contained a salt bridge, which introduces factors that are difficult to treat theoretically. His data were not reproducible enough to give significant results when subjected to a rigorous mathematical treatment.

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[1] This article is based upon a thesis submitted by Richard W. Kingerley to the Faculty of Rhode Island State College in partial fulfillment of the requirements for the degree of Master of Science in Chemistry, June, 1937.

PREPARATION OF MATERIALS

Lanthanum salts

Several salts of lanthanum were investigated in order to obtain a very pure sample of lanthanum oxide. The most likely impurities in a sample of any lanthanum compound would be the rare earths, principally cerium and praseodymium. Cerium was tested for by the hypochlorite method of Baxter, Tani, and Chapin (4) and found to be absent in all samples. In testing for the presence of the rare earths, absorption spectra of several aqueous salt solutions were taken. Lanthanum is the only one of its group that does not give an absorption in the visible range (25). Any visible absorption was checked against the iron arc for wave length and then identified. A C.P. sample of lanthanum chloride showed absorption bands at 4445 Å., 4654–4667 Å., and 4775–4789 Å. in a 1 *N* solution through 13.5 cm. of solution on an Eastman 40 plate at 2 minutes exposure. This absorption corresponds definitely to that of praseodymium as described by Yntema (25), and indicates approximately 0.5 per cent. A sample of lanthanum ammonium nitrate obtained from the Maywood Chemical Co. showed no absorption and therefore was selected as the starting material.

Lanthanum oxide

Approximately 200 g. of lanthanum ammonium nitrate was dissolved in half a liter of water, and the solution filtered free from any insoluble matter. To this solution was added slowly with stirring a saturated solution of oxalic acid until precipitation was complete. It was then stirred for an hour and filtered on a Büchner funnel with abundant washing to remove soluble salts. This precipitated lanthanum oxalate was then ignited in a platinum dish for 4 hours at a temperature of 600°C. According to Kolthoff and Elmquist (13), the oxalate is completely decomposed at this temperature. The lanthanum oxide was preserved in a glass-stoppered bottle and was used for the preparation of all lanthanum salts.

Lanthanum chloride

Forty grams of the prepared lanthanum oxide was suspended in water and treated with slightly less than the required amount of hydrochloric acid. The lanthanum chloride was then recovered from the filtered solution. Since the salt is exceedingly soluble in water and extremely deliquescent, the ordinary methods of recrystallization were not applicable. It was necessary to pump off the water in a vacuum desiccator and then to remove the water of crystallization by continued pumping for 5 days at 90°C. (22). Analysis showed this salt to have one molecule of water of crystallization instead of seven, as when it crystallizes from water.

Repeated attempts to remove this last molecule of water resulted in decomposition of the salt into a basic chloride (8). This decomposition took place either on prolonged heating at 90°C. or upon shorter heating at any temperature above 100°C. Therefore the $LaCl_3 \cdot H_2O$ was used. It was preserved in a glass-stoppered bottle sealed with paraffin.

Mercury

Redistilled mercury was stirred with dilute nitric acid overnight and then twice distilled by the Hulett (9) method in a slow current of air.

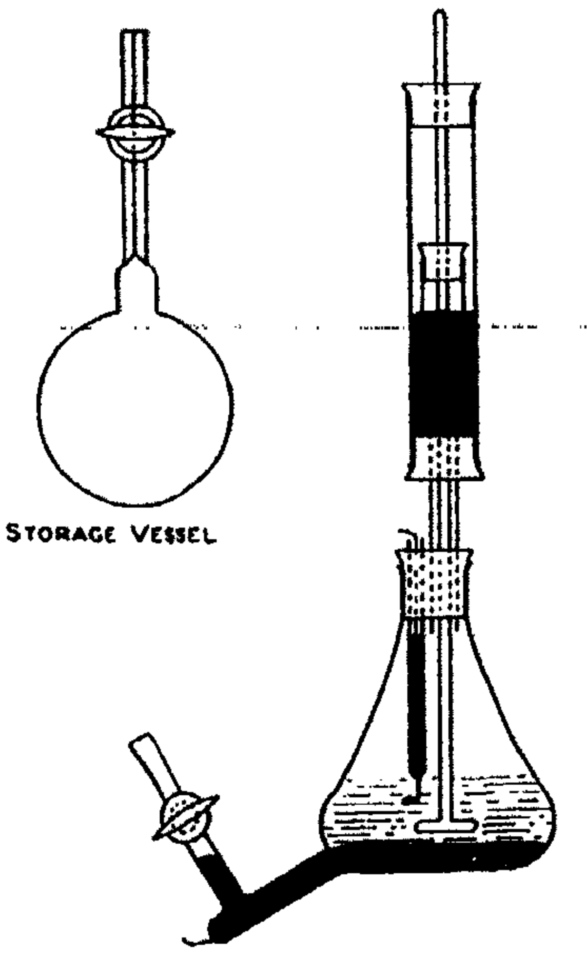

FIG. 1. Apparatus for preparation of amalgams

Lanthanum amalgam

The lanthanum amalgam was prepared by electrolysis of $LaCl_3 \cdot H_2O$ in absolute ethyl alcohol using a mercury cathode (2, 11). The solution was made by dissolving 40 g. of the salt in 100 cc. of alcohol. Any slightly cloudy appearance in the solution was removed by centrifuging it for a short time. The electrolytic cell construction is shown in figure 1. It was made by sealing a right-angled bend with a glass stopcock, as shown, into the bottom of a 250-cc. Erlenmeyer flask. A platinum wire was sealed into the glass bend for electrical connection to the pool of mercury. In this cell was placed the alcoholic solution, together with 600 g. of mercury. The flask was stoppered with a rubber stopper that admitted a platinum anode and an air-tight mercury-sealed stirrer for agitation of the mercury. The whole system was cooled continuously by running water. A potential of 50 volts was applied, which allowed a current of 0.3 ampere per square centimeter of mercury surface to flow. The water successfully kept the solution cool over a considerable period of time. The current was passed through the solution for 20 hours. Then the cell was tipped and the amalgam drawn through the stopcock into a bulb also shown in figure 1. The bulb was alternately evacuated and filled with nitrogen to remove last traces of oxygen, and then the amalgam set aside until used.

Nitrogen

Tank nitrogen was purified by passing it through potassium pyrogallate, sodium hydroxide, and sulfuric acid. The gas was then passed over heated copper gauze in a quartz tube to remove last traces of oxygen. Finally, before entering the cell vessel it was passed over soda lime and calcium chloride, and then through a saturating column containing a solution of the same concentration as that in the cell.

EXPERIMENTAL METHODS

Cell and electrodes

An attempt was made to construct a cell that would successfully measure the electrode process between lanthanum and one of its salts. Lanthanum chloride appears to be the most suitable salt, as it can be prepared readily. The silver-silver chloride reference electrode is standard and very reproducible (5). Therefore it appeared logical to try first to measure the cell

$$\text{La-Hg (2-phase)-LaCl}_3(m)\text{-AgCl-Ag} \qquad \text{(I)}$$

in which the cell reaction is represented by

$$\text{La} + 3\text{AgCl} \rightleftharpoons \text{LaCl}_3 + 3\text{Ag} \qquad \text{(II)}$$

Lanthanum metal is very reactive and readily combines with oxygen to form the oxide or with water to form the hydroxide. The amalgam is even more active. It is therefore necessary to use some type of cell that will allow the lanthanum amalgam to remain in contact with the solution for only a brief period of time. The dropping electrode used by Lewis and Kraus (16), MacInnes and Parker (19), and Richards and Conant (24) was adapted with some modifications. If the apparatus is successful it will allow measurements to be made before any appreciable reaction takes place between the amalgam and the solution. This dropping electrode is shown by A in figure 2. It consists of a tube of 30-cc. capacity to which are sealed four stopcocks; three of them are sealed in short arms on the top of the electrode and one is sealed in the bottom. The lower stopcock is part of a long capillary tube which is bent in the form of a hook at the bottom. Into this capillary tube and just below the lower stopcock is sealed a platinum wire with a connecting tube for electrical contact. When this electrode is in use, the bulb can be filled with amalgam and placed in the cell vessel. By turning stopcock 1 a drop of amalgam can be balanced upon the upturned end of the capillary tube, and, as electrical connection is provided for through the amalgam column, the potential developed between this drop and the standard electrode can be measured. The electrode vessel, shown by B in figure 2 and also by C (top view), is composed of a central compartment from which extend three side arms.

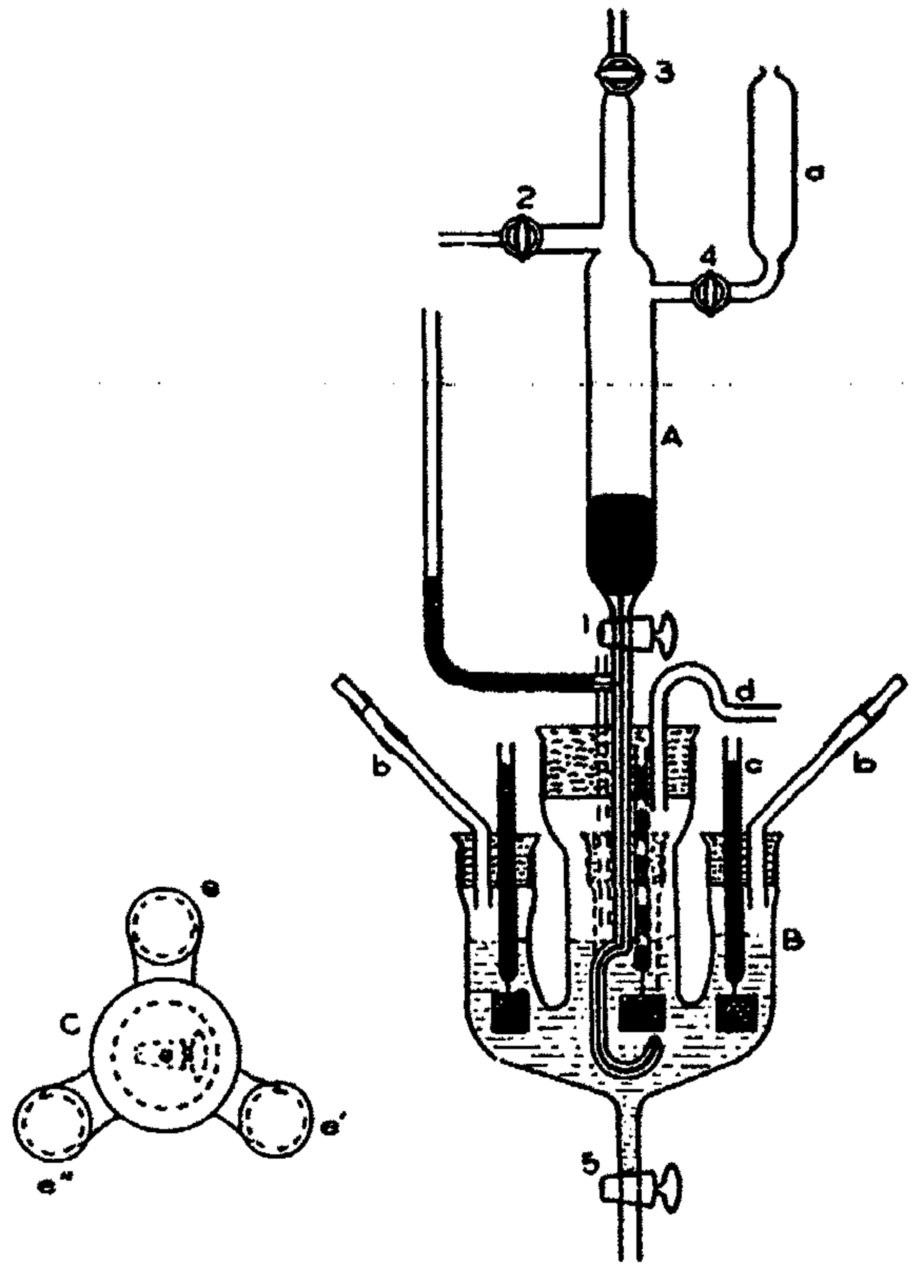

FIG. 2. Electrode vessel

Each of these arms, e, e′, e″, contains a reference electrode and a small glass tube, b, bent at 60° for introducing nitrogen into the cell. The tube, d, in the top of the cell is the exit for nitrogen gas. Having three reference electrodes serves as a convenient means of checking the constancy of each half-cell. The stopcock 5 at the bottom of the vessel is for removing the amalgam after measurements have been made. This prevents any reaction between the amalgam and the solution due to continued contact.

The technique for filling the cell was as follows: A 0.03 molal stock solution of the lanthanum chloride was made up and diluted by volume to the required concentration for each measurement. After carefully cleaning and drying the electrode vessel, 100 cc. of this lanthanum chloride solution was introduced, and the three silver–silver chloride electrodes and nitrogen tubes put in place. A large stopper was placed in the top of the central compartment, and the cell placed in the constant-temperature oil bath while the dropping electrode was assembled. After being carefully cleaned and dried, the electrode was alternately filled with nitrogen and evacuated to remove oxygen. The amalgam was introduced into the tube by placing the amalgam reservoir in boiling water until it became one phase and then connecting it to the vertical arm of the electrode. Any oxide which formed on the surface of the amalgam was removed by filling the electrode through the fine capillary on the end of the reservoir. A slight pressure of nitrogen was introduced above the amalgam to facilitate its flow through the capillary. The dropping electrode was then put into place in the cell vessel and the whole unit clamped firmly in the oil bath. Nitrogen was now bubbled slowly through each leg of the vessel for 20 minutes. At the end of this time the tubes were sealed by means of a short piece of rubber and a glass plug. The cell was allowed to remain in the bath for 2 hours before any measurements were attempted.

In making measurements stopcock 1 was opened and the amalgam allowed to run down the capillary and form a single drop on the end. The potential was measured as soon as possible and repeated every minute for a period of about twenty minutes. At the end of this time another drop was formed and its potential measured against one of the other reference electrodes. This process was continued for a period of 3 hours and then the cell was discarded. Measurements were taken at eight concentrations and three temperatures. In many cases duplicate determinations were made to check the results.

Preparation and analysis of lanthanum chloride solutions

For all concentrations of lanthanum chloride less than 0.03 molal the solutions were made from the stock solution by dilution. The stock solution was analyzed by the method suggested by Jukkola, Audrieth, and Hopkins (11). The lanthanum was precipitated in a neutral solution as the oxalate and ignited to the oxide. It was possible to obtain triplicate determinations to check within 0.1 per cent. Several cases gave results to agree within 0.03 per cent. Other methods of analysis were tried, including the precipitation of the chloride as silver chloride and the titration of the precipitated lanthanum oxalate with potassium permanganate. These methods were abandoned, as they were not as reproducible as the oxide procedure.

Analysis of the amalgam

In the preparation of the lanthanum amalgam the electrolysis was continued for a sufficient time to produce two phases. The time was calculated from the solubility of lanthanum in mercury as determined by Parks and Campanella (22). As long as a two-phase amalgam existed it was not necessary to know the exact concentration of lanthanum. However, each new supply of amalgam prepared was analyzed. This was accomplished by allowing a sample of amalgam to remain in contact with the air for a period of 10 days. The lanthanum separated from the mercury as a white solid consisting of lanthanum hydroxide and carbonate. According to several investigators (2, 20) this separation is complete. To the precipitate 0.1 *N* hydrochloric acid was added and the liquid was brought to a boil. The solution was back titrated with standard sodium hydroxide and the per cent of lanthanum was calculated.

The apparatus

For maintaining the cell at constant temperature a large oil thermostat with automatic heating and cooling coils was used. The desired temperature was maintained to ± 0.05°C. The Beckmann thermometer was checked against a laboratory standard certified by the Bureau of Standards. The potentiometer was a Leeds and Northrup type K with a high-resistance galvanometer, external critical damping resistance 2300 ohms, and a period of 3.0 seconds. The potentiometer was calibrated and checked against a certified Weston standard cell.

EXPERIMENTAL DATA

Constant potentiometer readings were not obtained when the drop was formed on the electrode. A constant shift in the E.M.F. was observed, which increased with increasing temperature. After considerable investigation it was found that the maximum E.M.F. developed could be reproduced within 1 millivolt. In table 1 is given an example of the measurements taken.

A maximum E.M.F. was reached after approximately seven minutes at this temperature. However, in some cases the maxima were not reproducible and some showed several inflection points. All readings except the best were discarded. The cause of the drifting E.M.F. is undoubtedly due to the reaction of the amalgam with the solution. In order to determine whether this maximum was of any value it was measured at eight different concentrations of lanthanum chloride at 0°, 25°, and 50°C. Then, using the equation

$$E_0' = E_0 + \frac{Nu}{n}\frac{RT}{F}\ln m \qquad \text{(III)}$$

TABLE 1

Variation of the E.M.F. *of the cell* La–Hg(*2-phase*)–$LaCl_3$(*m*)–AgCl–Ag *with time*
Temperature, 25°C.; 0.0010 *M* $LaCl_3$

TIME IN MINUTES	DROP NO. 2	DROP NO. 4
1	1.5139	1.5133
2	1.5311	1.5188
3	1.5341	1.5199
4	1.5368	1.5251
5	1.5454	1.5390
6	1.5572*	1.5548
7	1.5560	1.5556
8	1.5535	1.5559*
9	1.5540	1.5529
10	1.5500	1.5489
11	1.5524	1.5452
12	1.5516	1.5439
13	1.5483	1.5422
14	1.5462	1.5410
15	1.5439	1.5400

* Maximum.

TABLE 2

Maximum electromotive force of the cell La–Hg(*2-phase*)–$LaCl_3$(*m*)–AgCl–Ag

t............... Lanthanum amalgam.....	0°C. 0.055 per cent		25°C. 0.018 per cent		50°C. 0.025 per cent	
MOLALITY	$E_{obs.}$	E'_0	$E_{obs.}$	E'_0	$E_{obs.}$	E'_0
0.02162	1.154	1.034	1.191	1.060		
0.01082	1.201	1.059	1.335	1.180		
0.006187	1.220	1.060	1.407	1.233		
0.004922	1.235	1.068	1.433	1.251		
0.003610	1.271	1.094	1.461	1.268		
0.001970	1.313	1.118	1.521	1.308		
0.001032	1.367	1.151	1.558	1.324		
0.005280	1.454	1.217	1.586	1.327		
0.02247					1.290	1.149
0.01125					1.383	1.216
0.006428					1.461	1.374
0.005115					1.502	1.306
0.003753					1.536	1.329
0.002048					1.628	1.397
0.001075					1.678	1.423
0.0005495					1.716	1.437

values for E'_0 were calculated and plotted against the square root of the concentration. The results are shown in table 2 and figure 3. The curves shown in figure 3 should be parallel, since the difference at any given concentration should be governed entirely by the temperature coefficient of the E.M.F. However, the curves are not only not parallel, but at 0°C. the curve approaches the potential axis at a very high value, if not infinity. It follows from this that the cell process (II) must be complicated by a side reaction. After careful investigation it was found that in addition to the true cell potential, the hydrogen overvoltage was being measured. This conclusion was reached from the fact that a drop of amalgam on standing a short time in contact with some of the lanthanum chloride solution would change the pH of the solution, especially in the immediate area of the amalgam, from 5.7 to 8.0 or slightly above. This was followed over a longer period of time by a slight evolution of hydrogen. Neither one of these processes could be brought about without hydrolysis, and in the cell would definitely cause interference with the cell process. It was necessary to abandon the use of aqueous solutions and endeavor to find a suitable non-aqueous solvent for lanthanum chloride.

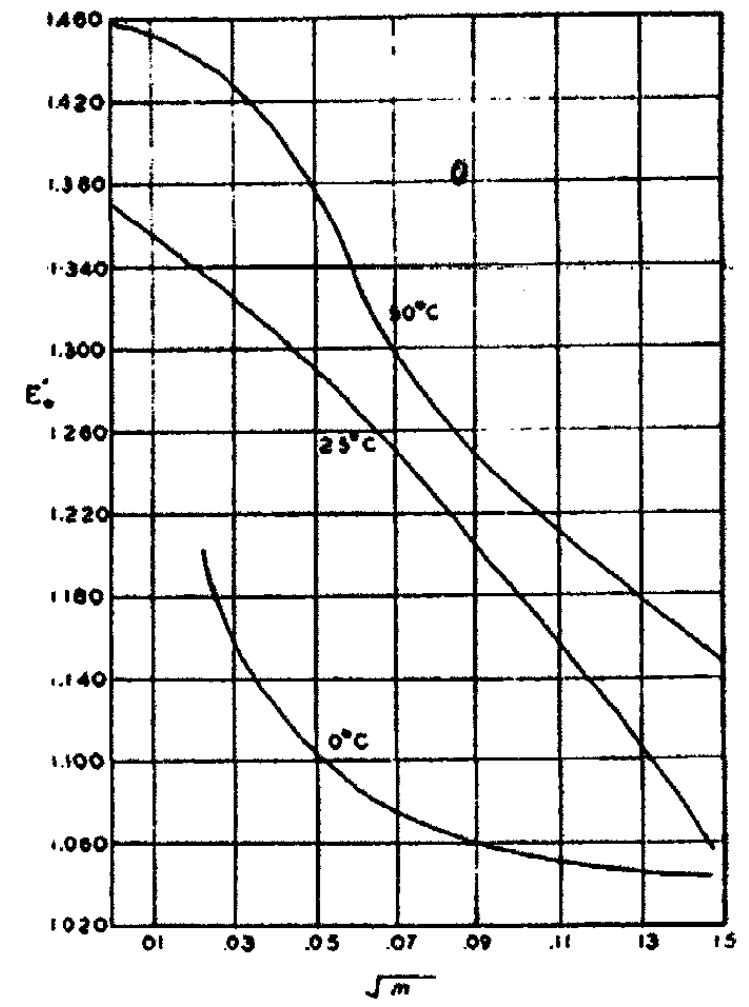

FIG. 3

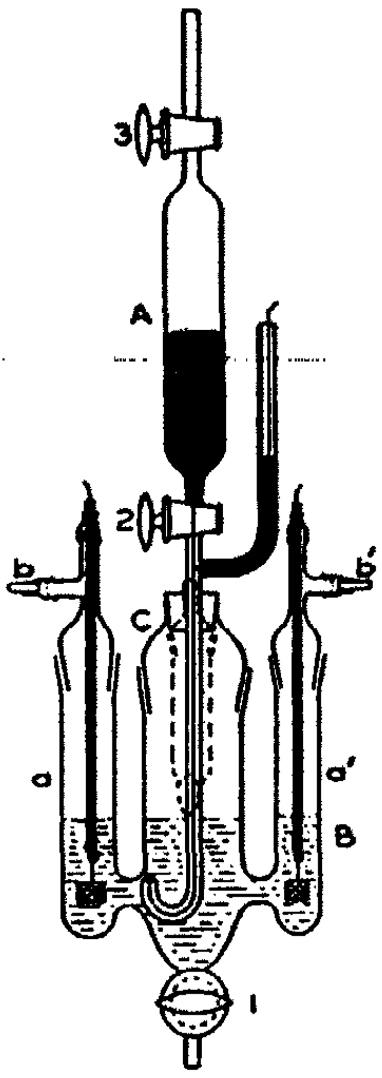

FIG. 4

FIG. 3. Plot of values for E_0' against the square root of the concentration
FIG. 4. Electrode vessel

ORGANIC SOLVENTS

The solubility of lanthanum chloride was determined in various organic solvents. To 25 cc. of the solvent 3 g. of lanthanum chloride was added and the solution refluxed for 15 minutes. The solution was then filtered and the filtrate evaporated in a Pyrex dish. The residue, if any, was weighed. The results obtained are tabulated in table 3. Upon examination of these data it is seen that the solvents for lanthanum chloride fall into two definite groups: first, the aliphatic alcohols, and second, the aromatic tertiary amines. Acetone appears to be an exception to this rule. However, the solvent action of acetone is attributed to the difficulty of removing the last traces of water. Different samples of acetone gave varying results.

TABLE 3

Solubility of lanthanum chloride in various organic solvents

SOLVENT	SOLUBILITY
	grams per liter
1,4-Dioxane	Insoluble
Tributylamine	Insoluble
Nitrobenzene	Insoluble
Acetone	Slightly soluble
Benzene	Insoluble
Dibenzylamine	Insoluble
Aniline	Insoluble
Chloroform	Insoluble
Carbon tetrachloride	Insoluble
Quinoline	Slightly soluble
Piperidine	Insoluble
Pyridine	Very soluble
Chlorobenzene	Insoluble
Pyrrolidine	Soluble
Furfuran	Too low boiling point
Ether	Insoluble
Ethyl alcohol	Very soluble
n-Propyl alcohol*	$300^{20°}$ $425^{40°}$
Ethylene glycol*	$166^{20°}$ $450^{40°}$
Glycerol*	$50^{30°}$ $150^{40°}$

* Private communication from Professor B. S. Hopkins.

Apparatus

In the work with organic solvents the apparatus was reconstructed as shown in figure 4. Since purification of large volumes of organic solvents is cumbersome and sometimes difficult, the new cell had a capacity of only 30 cc. The cell vessel, B, had only two side arms, a and a′, fitted with interchangeable ground-glass joints which were drawn down to small diameter to form a close fit with the reference electrodes. The top of each side arm contained a tube, b and b′, which was used for passing nitrogen into the apparatus. The dropping electrode had a total capacity of 15 cc. It was held in place by a small stopper that fitted into an interchangeable glass joint. The glass joints made the assembling of the cell much easier and more rapid; this decreased evaporation and also the accumulation of impurities. The operating technique of the cell was similar to that of the original.

Alcohol cell

As one of the classes of solvents for lanthanum chloride was aliphatic alcohols, this type was first investigated by using ethyl alcohol. Since water interferes with the cell reaction, anhydrous conditions were necessary throughout. Both anhydrous lanthanum chloride and absolute alcohol were prepared. The preparation of anhydrous lanthanum chloride by the dehydration of $LaCl_3 \cdot 7H_2O$ was impossible, owing to the formation of the insoluble basic chloride (18). Therefore, it was necessary to seek some other method. Several were tried; the most satisfactory is that proposed by Reed, Hopkins, and Audrieth (23). Ten grams of lanthanum oxide was heated with 15 g. of ammonium chloride in a glass bulb to 250°C. This temperature was maintained and the excess ammonium salt removed by pumping in an all-glass apparatus. However, the anhydrous chloride prepared in this way, contrary to the statement of Reed, Hopkins, and Audrieth (23), does not give a clear solution in water. The salt was dissolved in absolute alcohol, and the insoluble material removed by centrifuging. This solution was diluted to the correct concentration and introduced into the cell.

The absolute alcohol was prepared by treating C.P. absolute alcohol with sodium metal and distilling slowly from an efficient column 120 cm. long. The first and last 150-cc. portions of the alcohol were discarded.

E.M.F. measurements were made on the cell,

$$\text{La-Hg (2-phase)-}LaCl_3(C_2H_5OH)\text{-}AgCl\text{-}Ag$$

The same shift in the E.M.F. was encountered here as in the aqueous cell. However, the maximum was reached in much less time, usually only 15 to 20 seconds being required. This made reading the cell very difficult and the results not very reproducible. Upon investigation it was found that hydrolysis was taking place, even though extreme care had been taken to obtain anhydrous conditions. The pH of the solution would change slowly over a period of three to four hours when in contact with lanthanum amalgam. Probably the following reactions took place:

$$6C_2H_5OH + 2La \rightleftharpoons 2(C_2H_5O)_3La + 3H_2$$

$$(C_2H_5O)_3La + 3H_2O \rightleftharpoons La(OH)_3 + 3C_2H_5OH$$

This type of cell with the aliphatic alcohols as solvent was discarded on this evidence. If ultimately absolute conditions were obtained, the cell would still offer side reactions in that the lanthanum would replace hydrogen from the alcohol.

Aromatic tertiary amine cell

The second class of solvents for lanthanum chloride was that of aromatic tertiary amines. The one most easily purified and most readily obtained was pyridine. It also dissolves the lanthanum chloride to the greatest degree, thereby being useful over a wider concentration range. Double salts of the rare-earth salts and tertiary amines are reported (3, 12). However, double-salt formation is not particularly undesirable. The formation of complexes of the Werner type is not likely to occur, since lanthanum salts do not form complex compounds with ammonium hydroxide.

The pyridine was purified by distillation and then treated with 100 g. of activated aluminum oxide for every 500 cc. of pyridine. After standing for 24 hours the mixture was distilled twice, and the fraction boiling at 115.3°-115.5°C. was collected (1).

When the cell was set up it was found that pyridine dissolved the silver chloride from the reference electrode. It was necessary either to find a silver halide that would not dissolve in pyridine or to saturate the pyridine with the silver halide and find the correction to be applied. If we draw an analogy between the solubility of the halides of silver in ammonium hydroxide and what we should expect to find in pyridine, we should look for a lower solubility of the iodide, the solubility increasing to the chloride. The only reference in the literature was that of Laszczynski (15), who reports the solubility of silver iodide as 0.1 g. per 100 grams of pyridine at 10°C. and 8.01 g. at 121°C. The solubility of silver chloride was found to be 1.9 g. per 100 grams of pyridine at 25°C., a value that appeared to be greater than the solubility of the iodide at the same temperature. The silver-silver bromide electrode was prepared by the method of Lewis and Storch (17), and the iodide electrode by a procedure outlined by Jones and Hartman (10). The iodide cell could not be investigated, because it was found impossible to prepare anhydrous lanthanum iodide.

Since the chloride cell offered the smallest correction factor we attempted to saturate some pyridine with silver chloride and then dissolve lanthanum chloride in this solution to the desired concentration. Unfortunately, the mercury of the amalgam replaced the silver chloride dissolved in the pyridine and precipitated metallic silver. From this evidence it was necessary to discard any combination where pyridine and the halide reference electrodes were used together. The same objection held in the case of pyrrolidine and quinoline.

The possibility of a lead-lead sulfate or mercury-mercurous sulfate reference electrode led to the preparation of lanthanum sulfate and an investigation of its solubility in organic solvents. The lanthanum sulfate was prepared by dissolving lanthanum oxide in an excess of sulfuric acid, from which it crystallizes in the form of $La_2(SO_4)_3 \cdot 9H_2O$ when the solution is cooled. It may be dehydrated by heating to 150°C. for 4 hours. There was no organic solvent found that would dissolve this anhydrous lanthanum sulfate.

The results of this investigation definitely prove that an E.M.F. method involving a lanthanum amalgam electrode is not applicable to the study of lanthanum salts without considerable difficulty. Some other method such as vapor-pressure or freezing-point measurements should be used even though they are not very satisfactory in dilute solutions.

SUMMARY

1. A dropping electrode apparatus was constructed for use with the very active lanthanum amalgam in electrochemical cells.

2. The electromotive force of the cell La(satd. amalgam)-$LaCl_3$ (H_2O)-AgCl-Ag was investigated at 0°, 25°, and 50°C. for concentrations of lanthanum chloride of 0.0005, 0.001, 0.002, 0.003, 0.005, 0.011 and 0.022 molal.

3. The solubility of lanthanum chloride was investigated in various organic solvents.

4. The following electrochemical cells were also investigated:

La(satd. amalgam)-$LaCl_3$ (ethyl alcohol)-AgCl-Ag
La(satd. amalgam)-$LaCl_3$ (pyridine)-AgCl-Ag
La(satd. amalgam)-$La_2(SO_4)_3$ (H_2O)-Hg_2SO_4-Hg

5. In all cells where water served as the solvent the E.M.F. was disturbed by the hydrogen overvoltage on lanthanum. A similar reaction occurred when aliphatic alcohols were employed. In cells involving tertiary aromatic amines there was a large solvent action on the reference electrode which could not be corrected for in the customary manner.

6. From this investigation it is definitely concluded that lanthanum amalgams are unsatisfactory for precise E.M.F. measurements.

We wish to express our thanks to the National Research Council for a Grant-in-aid which in part made possible the construction of the apparatus used in this investigation.

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THE DISTRIBUTION OF SOLUTES IN SILICA GEL[1]

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It has been shown that within a hydrogel of silicic acid a solute is associated with a greater quantity of water than outside the hydrogel. If the concentrations are expressed as molalities, then it is found that the concentration inside the gel is less than the concentration outside. This conclusion was reached on the basis of the experimental studies of the diffusion of electrolytes in hydrogels by Allan (1) and the analytical studies of Love (7). These papers gave results for sodium sulfate and hydrochloric acid.

Allan and Love were also led to believe that the activity coefficient of the solute in the gel was different from the activity coefficient outside, since the activities at equilibrium must be equal. However, this conclusion is based on the assumption that all of the water in the gel is acting in the rôle of solvent. This is probably not true, because there is considerable evidence for the existence of what is called bound water. The hydration of molecules or ions in solution is one example. Substances such as gelatin, gum arabic, silica gel, and alumina have the property of adsorbing water. This water does not exhibit its normal vapor pressure or other colligative properties. Neuhausen and Patrick (11) have shown that a silica gel can be heated to 300°C. in a vacuum produced by a Gaede pump for a period of 6 hours without reducing the water content below 4.8 per cent. In recent years the extensive series of measurements of bound water initiated by the studies of Newton and Gortner (12) on bound water in plant saps leave little doubt that such a thing as bound water exists.

A satisfactory, absolute definition of bound water has never been made. Briggs (2) says that "there are nearly as many definitions of bound water as there are methods for determining it. The methods are consistent in that they remove or otherwise change the state of a fraction of the water leaving a portion unaccounted for, this being designated as bound. The

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[1] This article is based upon the dissertation submitted by Sutton Redfern to the Faculty of Philosophy of the Johns Hopkins University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1936.

[2] Present address: The Fleischmann Laboratories, 810 Grand Concourse, New York, New York.

usual idea of bound water carries with it a picture of a portion of the water in the system as being associated with the colloid phase with such strength that it is no longer free to exhibit those properties which are characteristic of water, i.e. it is no longer available to act as a solvent, or it cannot be separated from the colloid by freezing it or by subjecting the system to pressure, as in an ultrafilter."

Very probably there is a definite bound water $\rightleftharpoons$ free water equilibrium which is measured at a different point in each different method. This makes it difficult to get check results, although Sayre (15) has obtained check results by three different methods on a gum arabic sol.

The purpose of this study is to test accurately the whole question from an experimental standpoint, and furthermore to formulate if possible a rational explanation of the phenomena involved.

BRIEF STATEMENT OF METHOD

The method of studying the distribution of the various solutes between the gel and its surrounding equilibrium solution is in brief as follows: A cylinder of silica gel, of previously determined water content, was placed in a flask with the desired solute solution; the flask was placed in the thermostat and allowed to stand, with occasional shaking, for two weeks or longer. Then duplicate samples of the external solution were removed to tared weighing bottles, and the molal concentration of the solute determined by the appropriate method. The gel was removed from the solution and carefully wiped with filter paper to remove any excess solution. Four samples of the gel were then cut off and the silicon dioxide content of two of them and the solute content of the other two were determined. The above analyses gave sufficient data from which the concentration of solute in the gel and the concentration of solute in the external solution could be calculated.

PREPARATION OF GELS

Gels prepared from sulfurous acid (1) have a greater mechanical strength than gels prepared from sulfuric or hydrochloric acids and so were used. The sodium silicate used to prepare the gels was a commercial product containing Na_2O and SiO_2 in the ratio 1:3.51. It was diluted until it contained 6 per cent Na_2O. The gels were prepared by adding the diluted sodium silicate solution to a saturated aqueous solution of sulfur dioxide and pouring the resulting sol into paraffined glass molds 3.4 x 10 cm. After the sol set to a gel, it was removed and washed overnight in tap water in order to remove most of the soluble salts. The gel cylinders were then washed alternately in 6 N and 12 N hydrochloric acid until no more iron was extracted, and finally washed in distilled water until free of chloride. Gels washed in this manner with hydrochloric acid did not contain more than 0.1 per cent residue based on the weight of silica after the silica was removed with hydrofluoric acid and sulfuric acid.

After being washed, the gels were dried superficially in the open air. They were now approximately 85 per cent water and could be used directly as representing this water content. For lower water contents, the gel cylinders were dried slowly under raised bell jars. The drying process was followed by weighing the cylinders. Since these dried gels would crack when placed in water, they were resaturated with water vapor by Allan's method (1).

EQUILIBRATION AND SAMPLING OF GELS

The solutes used in this investigation were potassium chloride, potassium bromide, sodium chloride, sodium bromide, lithium chloride, magnesium chloride, barium chloride, calcium chloride, strontium chloride, and dextrose. These solutes were all of C.P. grade and were used without further purification.

A gel cylinder was placed in a 250-ml. wide-mouth Erlenmeyer flask and covered with a solution of the solute. The flask was tightly stoppered with a rubber stopper, placed in a thermostat maintained at 25.00°C. ±0.05°, and left for two weeks or longer. The dextrose solutions were covered with a layer of toluene to prevent the formation of mold. It is a safe assumption that the toluene did not interfere. Jones and Gortner (5) also used toluene "because of its inactivity towards aqueous colloidal systems." When the gel had come to equilibrium, duplicate samples of the external solution were removed, weighed, and the amount of dissolved solute determined. The gel cylinder was then removed and immediately wiped off carefully with filter paper. Two samples of gel were then broken off with a knife and placed in weighing bottles. The silica was determined in these samples. The rest of the gel was split into two pieces, and the solute removed and analyzed by an appropriate method.

METHODS OF EXTRACTION AND ANALYSIS

The gel samples were extracted in a Soxhlet extraction apparatus. When dextrose was extracted with boiling water, a slight decomposition took place. Therefore the extraction apparatus was modified so that it could be run under a constant reduced pressure of 80 mm. of mercury. The lowered boiling point prevented decomposition. Difficulty was experienced with bumping under the reduced pressure, so a slow stream of nitrogen was introduced through a tube sealed through the side of the flask. A water pump supplied the necessary vacuum.

The Mohr method was used for the analysis of all the electrolytes except barium chloride; in this case the Volhard method was used. The dextrose was analyzed by the Quisumbing and Thomas (14) modification of Fehling's method. Silica was determined by the Willard and Cake (20) perchloric acid method. It was not necessary to go through this procedure for the samples containing dextrose. In this case the gel was weighed directly into a platinum crucible and ignited.

The initial water content of each gel cylinder was determined before it was placed in the solution. Duplicate samples of the resaturated gel were removed from each end of the cylinder, placed in platinum crucibles, and ignited.

CALCULATIONS

The analysis of the equilibrium solution and the gel gave the following ratios:

$$A = \frac{\text{Solute}}{\text{H}_2\text{O in solution}} \qquad B = \frac{\text{Solute}}{\text{Gel}} \qquad C = \frac{\text{SiO}_2}{\text{Gel}}$$

These ratios, of course, are expressed as grams per gram. By calculation the following ratios were obtained:

$$D = \frac{\text{H}_2\text{O}}{\text{Gel}} = 1 - (B + C) \qquad E = \frac{\text{Solute}}{\text{H}_2\text{O in gel}} = \frac{B}{D} \qquad \Delta = A - E$$

The Δ is the difference between the concentration outside and inside and is found to be always positive.

If the free water of the system is defined as the fraction of the total water which is acting as a solvent and gives a solution inside the gel of the same concentration as the surrounding equilibrium solution, then the bound water is defined as the difference between the total water and the free water. In general, all methods for determining bound water depend on the determination of the total and free water, and define the bound water by difference.

In order to apply the above definition, let X = the number of grams of bound water in 1 g. of gel. Then must

$$\frac{B}{D - X} = A$$

or

$$\frac{X}{D} = \frac{A - E}{A} = \frac{\Delta}{A}$$

but X/D is the fraction of the total water which is bound. However, a better expression of the amount of bound water is to give the number of grams of bound water per gram of silica. This ratio, called W, is given by

$$W = \frac{D \cdot \Delta}{C \cdot A} = \frac{\text{grams H}_2\text{O}}{\text{grams SiO}_2}$$

In order to see whether there was any correlation between the activity of the water in the equilibrium solution and the amount of bound water, the activity of the water in the different solutions was calculated from the activity coefficients of the solute by the following formula:

$$-\log a_{(m_1)} = \frac{m_1 \nu}{127.84} + \frac{\nu}{55.51} \int_0^{m_1} m \, d \log \gamma$$

where $a_{(m_1)}$ = activity of water when the molality of the solute is m_1,
m_1 = molality of solute,
ν = total number of ions formed from solute, and
γ = activity coefficient of solute.

TABLE I

85 per cent gel series

SOLUTE	WATER CONTENT OF GEL	MOLALITIES OF EQUILIBRIUM SOLUTION	Δ	BOUND WATER IN GRAMS PER GRAM OF SiO_2	ACTIVITY OF WATER	RATIO A/E
$MgCl_2$	86.79	0.4231	0.00215	0.302	0.981	1.056
$CaCl_2$	86.72	0.3990	0.00187	0.273	0.981	1.044
$SrCl_2$	86.66	0.4043	0.00314	0.320	0.981	1.052
$BaCl_2$	86.33	0.4190	0.00438	0.318	0.981	1.053
NaCl	86.89	0.8322	0.00168	0.231	0.973	1.036
NaBr	87.00	0.8264	0.00309	0.239	0.972	1.038
LiCl	88.29	0.8260	0.00107	0.228	0.971	1.032
KBr	88.22	0.8324	0.00253	0.187	0.973	1.026
KCl	84.06	0.8273	0.00181	0.160	0.974	1.030
KCl	84.06	0.4033	0.00095	0.175	0.987	1.033
Dextrose	82.68	0.8656	0.00660	0.201*	0.985	1.044
Dextrose	85.16	0.4227	0.00357	0.272	0.992	1.049

* These results deviate from the general rule that the amount of bound water decreases as the silica content of the gel increases.

By plotting m against $\log \gamma$, the last integral can be graphically integrated. The necessary values of the activity coefficients were taken from the Landolt-Börnstein (6) tables. The coefficients for magnesium chloride were at the freezing point of the solution, but it was assumed that these were not greatly different from the values at 25°C. The curves were carefully plotted and integrated with a polar planimeter. In the case of the dextrose solutions the activity of the water was calculated from the measurements of Morse (9) on the osmotic pressures of dextrose solutions.

DATA

All of the data on the gels can be conveniently divided into three groups, depending on the approximate initial water content of the gel. The three groups are designated as the 85 per cent gel series, the 70 per cent gel series, and the 50 per cent gel series. Tables 1, 2, and 3 give the results for the respective series. Calculations were also made assuming that the dextrose molecule is monohydrated in solution. It was found that the formation of a monohydrate increases the difference in concentrations

TABLE 2

70 per cent gel series

SOLUTE	WATER CONTENT OF GEL	MOLALITIES OF EQUILIBRIUM SOLUTION	Δ	BOUND WATER IN GRAMS PER GRAM OF SiO_2	ACTIVITY OF WATER	RATIO *A/E*
$MgCl_2$	73.02	0.5149	0.00444	0.263	0.973	1.100
$CaCl_2$	72.16	0.4557	0.00469	0.257	0.976	1.102
$SrCl_2$	71.35	0.4625	0.00818	0.300	0.978	1.126
$BaCl_2$	63.76	0.4864	0.01420	0.272	0.977	1.163
NaCl	72.40	0.9616	0.00441	0.218	0.968	1.085
NaBr	72.24	0.9422	0.00867	0.246*	0.968	1.098
LiCl	65.73	0.9642	0.00395	0.204*	0.966	1.107
KBr	67.15	0.9671	0.00980	0.178	0.969	1.093
KCl	65.93	0.9582	0.00477	0.141	0.970	1.072
KCl	70.94	0.4718	0.00267	0.197*	0.985	1.082
Dextrose	69.01	1.007	0.01660	0.210	0.982	1.101
Dextrose	72.84	0.4723	0.00712	0.233	0.992	1.091

* These results deviate from the general rule that the amount of bound water decreases as the silica content of the gel increases.

TABLE 3

50 per cent gel series

SOLUTE	WATER CONTENT OF GEL	MOLALITIES OF EQUILIBRIUM SOLUTION	Δ	BOUND WATER IN GRAMS PER GRAM OF SiO_2	ACTIVITY OF WATER	RATIO *A/E*
$MgCl_2$	50.69	0.5052	0.01062	0.240	0.974	1.283
$CaCl_2$	55.21	0.4741	0.00833	0.204	0.975	1.188
$SrCl_2$	54.04	0.4877	0.01575	0.256	0.977	1.256
$BaCl_2$	54.10	0.4888	0.02010	0.244	0.977	1.246
NaCl	54.62	0.9996	0.00933	0.202	0.967	1.190
NaBr	54.19	0.9912	0.01620	0.198	0.966	1.189
LiCl	55.88	0.9800	0.00653	0.208	0.965	1.186
KBr	54.61	0.9990	0.01440	0.150	0.968	1.138
KCl	55.46	0.9962	0.00776	0.135	0.968	1.117
KCl	55.31	0.4899	0.00420	0.155	0.984	1.130
Dextrose	53.78	1.056	0.03450	0.205	0.981	1.222
Dextrose	52.94	0.5033	0.01670	0.212	0.991	1.226

outside and inside. These calculations are not tabulated, because the only evidence for the hydration of dextrose is the fact that dextrose forms a crystalline monohydrate. Sucrose in dilute solutions forms a hexahydrate (16), and Newton and Gortner (12) always corrected their freezing-point measurements by assuming the formation of the sucrose hexahydrate.

The accuracy of the determinations is as follows: In the determination of the water content of the gels, the maximum deviation from the mean was ± 0.5 per cent. The deviation from the mean of ratio *A* was ± 0.2 per cent; of ratio *B*, ± 1.0 per cent; and of ratio *C*, ± 0.75 per cent. It is therefore believed that the results are accurate to at least ± 2.0 per cent.

DISCUSSION

According to a tentative theory of one of the authors, it was originally expected that the dextrose would be equally distributed. This expectation was pointed out to Dr. I. Langmuir in the spring of 1935; he immediately suggested that the electrolytes showed a difference because the dielectric constant inside the gel was different from that in the outside solution. This would mean a difference in the electrical energy of the ions and a Boltzmann distribution would result. However, the experimental results showed that this suggestion was not the explanation. Furthermore, the idea that the dielectric constant of the largest fraction of the water in the gel is different from the water outside is probably not true. Marinesco (8) measured the dielectric constant of aqueous solutions of hydrophilic colloids, and by application of the dipole theory of Debye determined the quantity of water fixed by these colloids. In effect free water has a dielectric constant of 80, while in the water which is bound by colloids the molecular dipoles are blocked and can no longer lead to polarization, so that the dielectric constant is now no more than of the order of 2 to 3. Other evidence for a lower dielectric constant of the bound water is to be found in the literature (10, 17, 18, 19).

The calculations made on the assumption of bound water show definite qualitative trends, although no quantitative results can be deduced from the present set of measurements. The data show that in all cases except four, which are starred, the amount of bound water decreases as the silica content of the gel increases. This decrease is easily explained qualitatively. The gel cylinders when dried shrink considerably in volume and this shrinkage is irreversible. Therefore the gels of lower water content have a smaller internal volume, which means less surface for the layer or layers of bound water; consequently there is less bound water per gram of silica.

The same results were found for gelatin gels and sols by Jones and Gortner (5) using the dilatometric method and by Newton and Martin (13) using the cryoscopic method. In the gelatin-water system, however, the water binding appears to be an adsorption reaction, because a logarithmic relationship was found to exist between the concentration of the gelatin gel and the grams of water which were bound per gram of dry gelatin. An attempt was made to plot the present results on log-log coördinate paper, but the measurements did not give a straight line.

Briggs (2) found that the amount of bound water associated with the colloid varied with the activity of the water. The higher the activity of the water, the greater the quantity of bound water. Measurements of the gum arabic–water systems with the cryoscopic technique showed that different solutes gave a smooth curve of water content against water activity.

The results on silica gel do not show any such simple relations. For example, an examination of the results for magnesium chloride, calcium chloride, strontium chloride, and barium chloride in the 85 per cent gel series shows different values for the amount of bound water, although the activity of the water is the same for each salt. The water contents of the different gels are sufficiently close to remove this variable. However, in the case where the same solute was used, potassium chloride or dextrose, the bound water is greater the greater the activity of the water. Apparently Briggs' statement—"At any given activity of the water in a system in which colloids and crystalloids are in equilibrium, provided the various non-water components have not reacted with each other upon mixing, the amount of water associated with or bound by a given weight of any of the non-water components will always be the same, and it will be the same as that which the given weight of the component will be associated at the same water activity when it is the only non-water component in equilibrium with water."—is not true for the silica systems.

It was thought that perhaps a Donnan equilibrium was responsible for the unequal distribution. The Donnan equilibria are characterized by the presence in a system of electrolytes of a species of ion which is restrained in *any* way from diffusing to all parts of the system, and this gives rise to unequal distribution of every species of diffusible ion present. These equilibria are immediately thrown out because of the experimentally determined unequal distribution of dextrose, and also because the same distribution would be expected for all the uni-univalent chlorides and the same for all the bi-univalent chlorides; the latter is found not to be true. Furthermore, it is hard to find the restraint necessary for the distribution.

Adsorption also will not explain the results. Grettie and Williams (4) found that even activated silica, i.e., silica which had been heated to 120° C. for several hours, only adsorbed dextrose to the extent of 0.7 per cent. The silica gel used in the present experiments was certainly not activated and would be expected to show no adsorption. However, adsorption is in the opposite direction to that which was actually found. If the gel does adsorb chloride ions, as was found by Ganguly and Krishnamurti (3) for a silica sol prepared from silicon tetrachloride, then this would also produce the opposite effect, namely, a greater concentration inside the gel than outside.

It is frankly admitted that at present the authors cannot suggest a reasonably satisfactory explanation of the results described herein.

SUMMARY

1. A study has been made of the distribution of potassium chloride, potassium bromide, sodium chloride, sodium bromide, lithium chloride, magnesium chloride, calcium chloride, strontium chloride, barium chloride, and dextrose between a hydrogel of silicic acid and the surrounding equilibrium solution.
2. In all cases the molal concentration of solute inside the gel was found to be less than the molal concentration outside.
3. Calculations made on the assumption that part of the water was not acting as a solvent but was bound water showed that the amount of bound water decreased as the silica content of the gel increased.
4. No correlation was found between the activity of the water and the quantity of bound water.
5. The results could not be explained satisfactorily on the basis of bound water, adsorption, or Donnan equilibria.

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SUGAR ALCOHOLS. X

THE EFFECT OF CERTAIN SUGAR ALCOHOLS AND THEIR ANHYDRIDES ON THE DISSOCIATION OF BORIC ACID

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INTRODUCTION

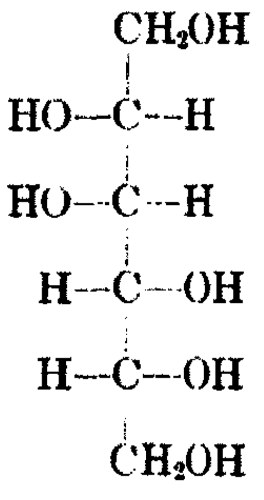
In previous communications the authors (7, 8) have studied the influence of various sugar alcohols and their anhydrides on the dissociation of boric acid. Later the physicochemical properties of the erythritan-boric acid complex were studied (9). For the metabolism work carried out in this laboratory several more sugar alcohols, anhydrides, and other related compounds have been prepared for study. The availability of these substances prompted a further extension of the work on the dissociation of boric acid.

MATERIALS AND METHOD

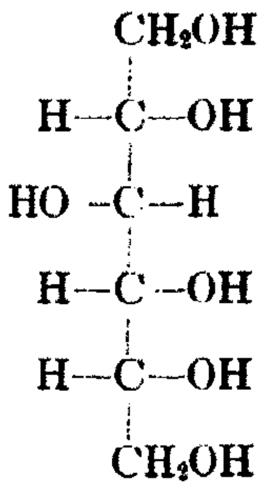
The boric acid was of buffer quality. The mannitan was prepared from mannitol by a slight modification of the method of Vignon (13), in which the dehydration is accomplished by means of sulfuric acid. Analysis gave the following values: carbon, 44.08 per cent; hydrogen, 7.04 per cent. The calculated values are: carbon, 43.90 per cent; hydrogen, 7.32 per cent. The α-mannitan was prepared by the method of Bouchardat (5), in which mannitol is dehydrated by boiling with hydrochloric acid. The compound melted between 139° and 140°C. (uncorrected); the value found for its specific rotation, $[\alpha]_D^{20°}$ was $-22.0°$. The polygalitol was extracted from *Polygala amara* (4). The compound melted between 142° and 143°C. (uncorrected); $[\alpha]_D^{16°} = +47.8°$. The styracitol was prepared by the reduction and hydrolysis of tetraacetyloxyglucal by the method of Zervas (15). The compound melted at 157°C. (uncorrected). The β-*d*-mannoheptitol was extracted from *Primula officinalis* by the method of Bougault and Allard (3). The compound melted at 153°C. (uncorrected). The pinitol was extracted by the method of Sherrard and Kurth (10), from *Pinus libertiana* which was kindly supplied by C. L. Hill of the U. S. Department of Agriculture. The purified compound melted between 183° and 185°C. The hydroxypyruvic aldehyde was prepared by a modification of Evans' method (5). The nitrogen content of its dioxime was 23.40 per cent. The calculated value is 23.73 per cent. The *l*-arabitol was Pfanstiehl's C.P. product. The sorbitol and mannitol were kindly supplied through the courtesy of the Atlas Powder Co. of Wilmington, Delaware.

Solutions of the various compounds studied contained 4 g. of the compound in 100 cc. of 0.1 molar boric acid. Stronger concentrations were employed for conductivity measurements. To 10-cc. portions of this solution was added 0.1 normal sodium hydroxide in quantities varying from 1 cc. to 12 cc. Immediately after the addition of the alkali the pH of the solution was determined electrometrically at 25°C. ± 0.5°, using the Wilson type hydrogen electrode (14).

The following formulas indicate the structural relationship existing among the compounds.



d-Mannitol



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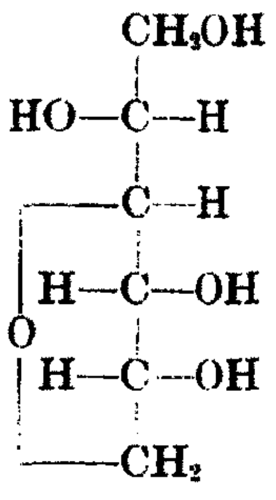
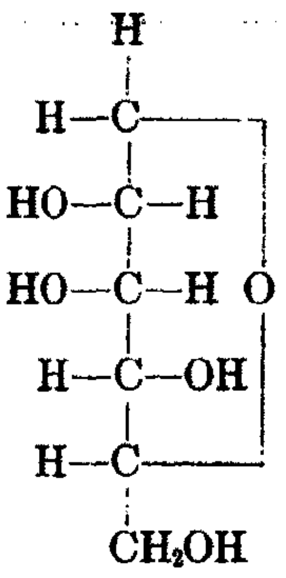


α-Mannitan



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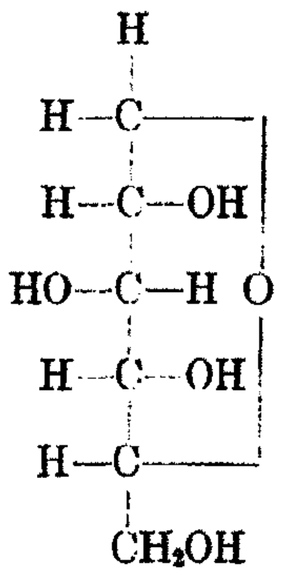

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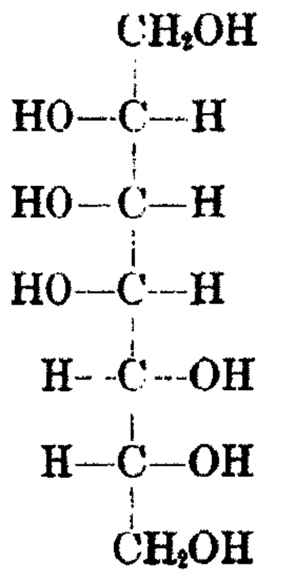
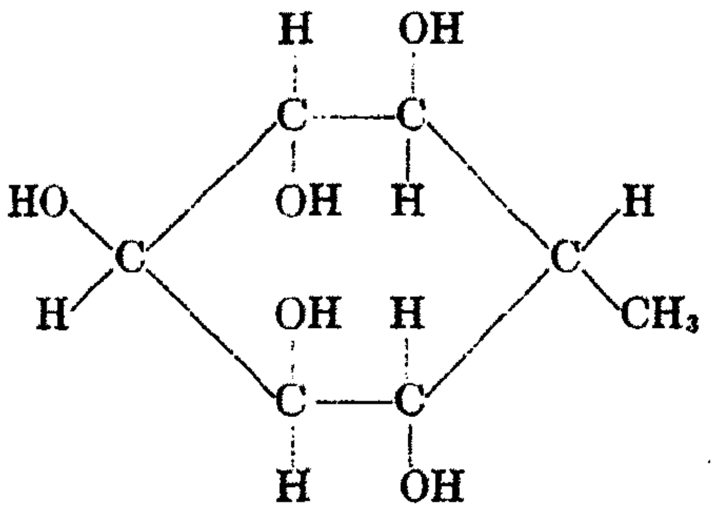
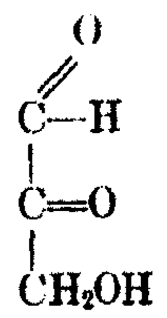


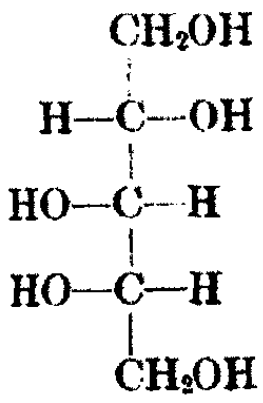
β-*d*-Mannoheptitol



Pinitol



Hydroxypyruvic aldehyde



l-Arabitol

Recent work by Freudenberg and Rogers (6) indicates that the structure of styracitol is that which was assigned formerly to polygalitol and *vice versa*.

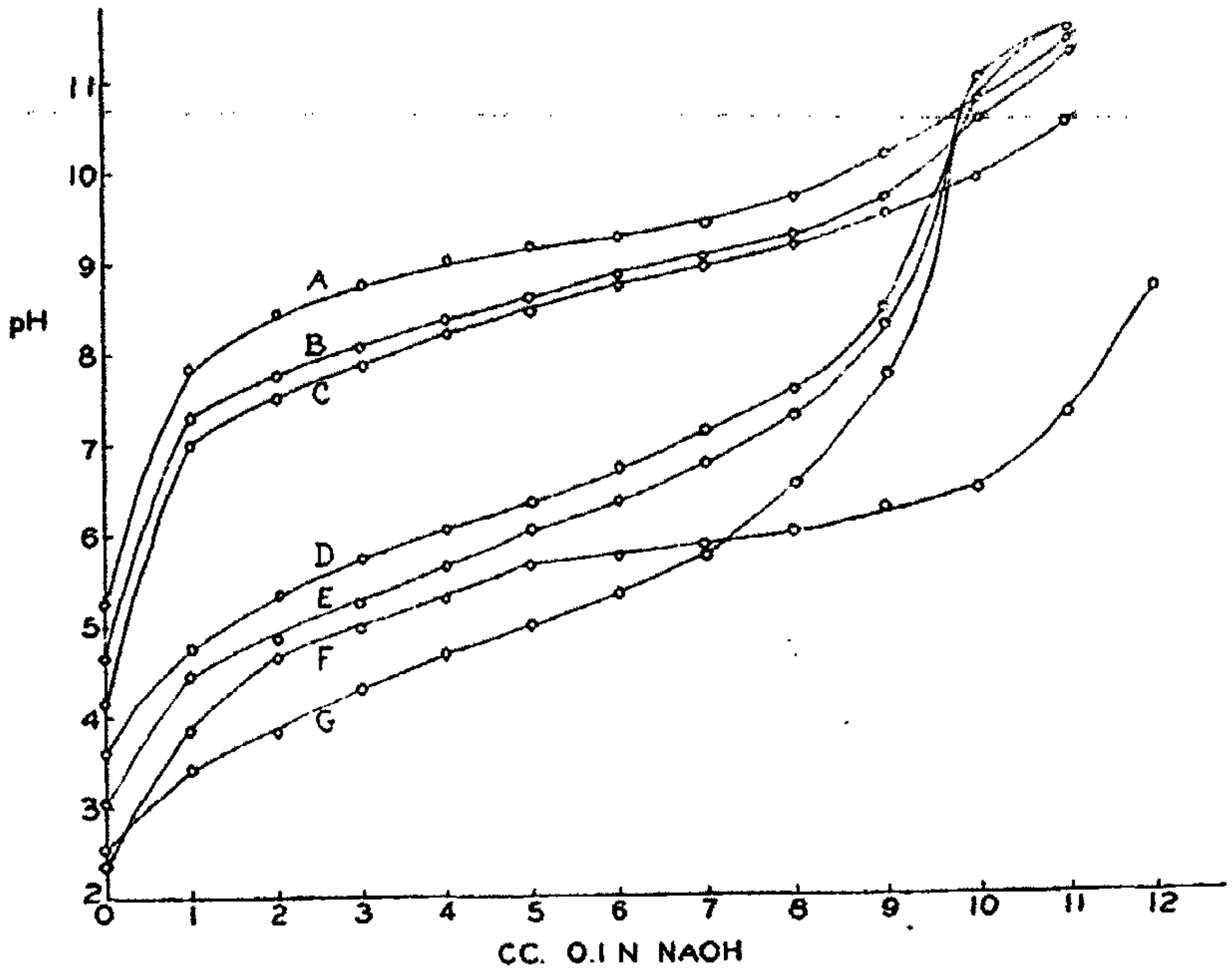


FIG. 1. The effect of sugar alcohols on the dissociation of boric acid. Curve A, *M*/10 boric acid; curve B, styracitol, polygalitol, and pinitol; curve C, syrupy mannitan; curve D, *l*-arabitol; curve E, β-*d*-mannoheptitol and sorbitol; curve F, hydroxypyruvic aldehyde; curve G, α-mannitan.

The results of pH measurements are set forth in figure 1.

DISCUSSION

There are many features of interest that may be gleaned from a study of figure 1. First, the heptahydric alcohol β-*d*-mannoheptitol is no more effective in its downward displacement of the titration curve of boric acid than its hexahydric homologues, mannitol and sorbitol; the curves of these three boric acid complexes practically coincide. Second, the slight potentiation of the dissociation constant of boric acid by styracitol, 1,5-anhydrosorbitol, is identical with that produced by its epimer polygalitol, 1,5-anhydromannitol. Third, pinitol, monomethylinositol, is quite as ineffective in potentiating the dissociation of boric acid as is its homologue, *i*-inositol, studied previously by the authors.

Further, the extraordinary titration curve of the hydroxypyruvic aldehyde–boric acid complex requires special comment. This extremely labile substance forms a complex with boric acid, as evinced by the greater degree of hydrogen-ion concentration conferred upon the boric acid solution by the addition of hydroxypyruvic aldehyde. However, one equimolecular weight of alkali was not sufficient to neutralize the complex, and at the boric acid–alkali equimolar point the pH of the solution was 6.45. We attribute this to the enolization of hydroxypyruvic aldehyde with the resulting increased alkali-consuming power. After the solution became alkaline (pH = 8.64) upon the addition of sodium hydroxide (12 cc. of *N*/10), drifting potentials were obtained with the hydrogen electrode.

The action of *l*-arabitol on the acidity of boric acid is especially interesting. One would expect, according to the Böeseken (12) hypothesis, that this substance, having two hydroxyl groups on the same side of adjacent carbon atoms, would cause a very strong downward displacement of the titration curve of boric acid. Its effect was, however, less marked than that of mannitol or sorbitol and far less pronounced than that of α-mannitan. The extraordinary effects of syrupy mannitan and of α-mannitan require special comment. In concentrations in which syrupy mannitan exhibited a pH of 4.20 (7) the α-mannitan–boric acid complex gave a pH of 2.56. The syrupy mannitan employed by the authors therefore showed a value quite different from Böeseken's value. Böeseken, in conference with one of the authors (J. C. K., Jr.) in The Hague, suggested that our values showed a lesser degree of potentiation of the dissociation of boric acid because of the contamination of syrupy mannitan with isomannide. Isomannide is known to be ineffective. In testing this hypothesis, it was found that isomannide as such had no interfering effect on the potentiation of the dissociation constant of boric acid by mannitan. Furthermore, with α-mannitan known to be isomannide-free, the removal of as much as 20 per cent of the α-mannitan and its replacement with isomannide changed the original pH of 2.56 to only 2.70. The combustion analysis data preclude the probability of the presence of more isomannide. Therefore this hypothesis does not account for this difference in response.

To investigate this problem further conductivities of various sugar alcohol–boric acid complexes were measured. These results are shown in table 1. The effect of dilution on the α-mannitan-boric acid complex is shown in figure 2.

TABLE 1

Specific conductivities

Aqueous solutions at 25°C.; cell constant = 0.1444

SOLUTION	SPECIFIC CONDUCTIVITY
	mhos
0.5 *M* H_3BO_3	32.9×10^{-6}
0.5 *M* H_3BO_3 + 0.2 *M* mannitol	357×10^{-6}
0.5 *M* H_3BO_3 + 0.2 *M* mannitan	959×10^{-6}
0.5 *M* H_3BO_3 + 0.2 *M* α-mannitan	939×10^{-6}
0.2 *M* α-mannitan	26×10^{-6}
0.2 *M* mannitan (second batch)	1099×10^{-6}
0.5 *M* H_3BO_3 + 0.2 *M* polygalitol	42.9×10^{-6}
0.5 *M* H_3BO_3 + 0.2 *M* styracitol	46.0×10^{-6}

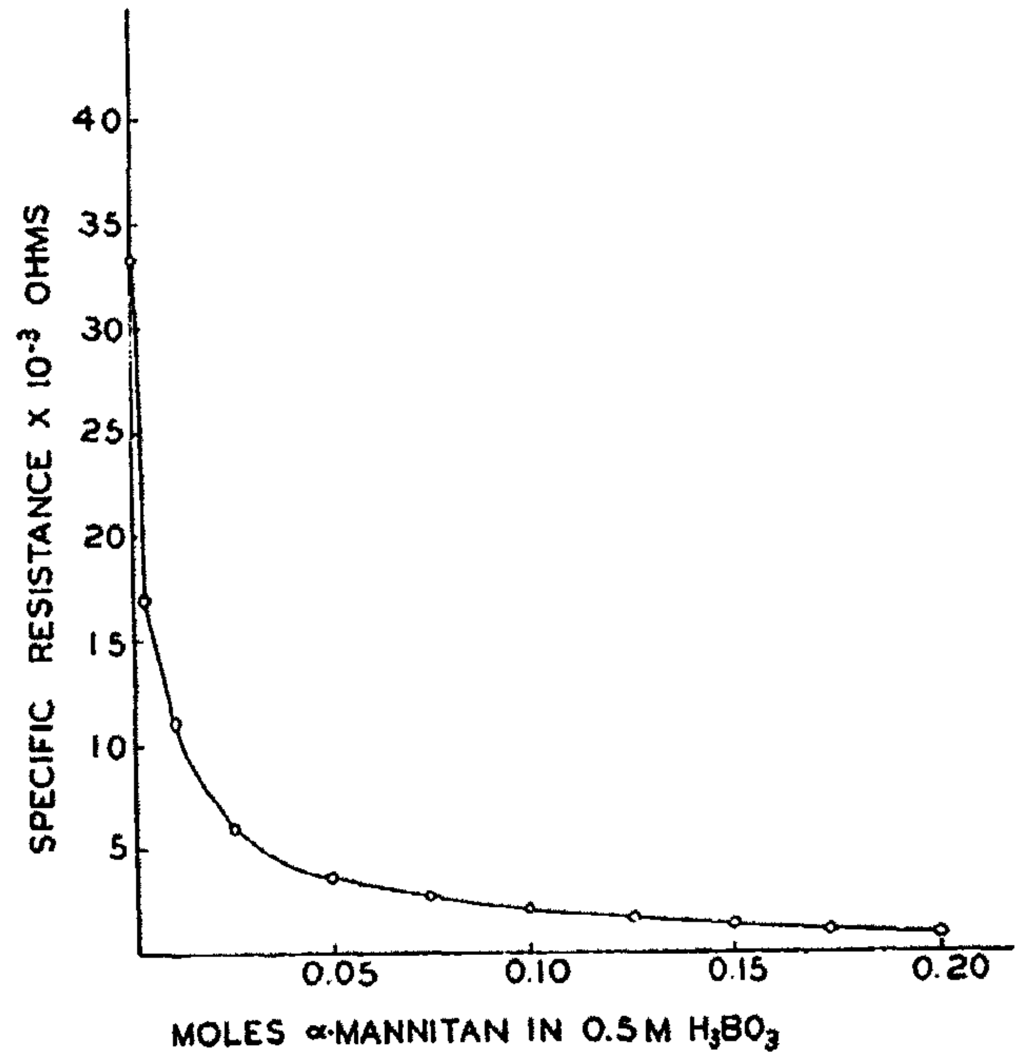


FIG. 2

Hydrogen-ion concentration measurements were made on the solutions on which conductivities were determined. The values were as follows: mannitol complex, pH 2.82; syrupy mannitan complex, pH 3.62; the α-mannitan complex, pH 2.45. Thus there is apparently the anomalous situation of the mannitan–boric acid complex exhibiting a high conductivity and a relatively low hydrogen-ion concentration. A further examination of table 1 reveals, however, that the syrupy mannitan alone showed a conductivity comparable to that of its boric acid complex. This results from electrolytes present in the mannitan because they were incompletely removed during its purification. Although the authors have succeeded in preparing syrupy mannitan barium-free and sulfate-free, the compound invariably is contaminated with traces of the ammonium salt of the sulfonic acids of mannitol. Distillation *in vacuo* removes the sulfonate, but during the process most of the mannitan is converted into isomannide. Knowing that at best the syrupy mannitan is contaminated with sulfonated products, the authors are inclined to believe that the striking agreement in the conductivity of the mannitan–boric acid complexes was fortuitous. Further studies with different batches of mannitan supported this hypothesis.

van Romburgh and van der Berg (12) in their conductivity measurements of the mannitol– and mannitan–boric acid complexes obtained values practically identical with those herein reported. They did not state whether the mannitan was syrupy or crystalline α-mannitan. The conductivity values for their mannitan exceeded the values reported here for α-mannitan. The structure assigned to mannitan by these investigators is that reported in this communication. Their conclusion was based on the fact that α-vinyldihydrofurane could be obtained from mannitan tetraformate by reduction with hydrogen. Further evidence to support this proposed structure was presented by Valentin (11), who showed that 3,6-anhydromannose reduced with sodium–mercury amalgam in weakly alkaline solution yielded 3,6-anhydromannitol, the constants of which are identical with those of the crystalline α-mannitan of Bouchardat. α-Mannitan is levorotatory, $[\alpha]_D^{20^\circ} = -22.0^\circ$, and syrupy mannitan is dextrorotatory, $[\alpha]_D^{20^\circ} = +33.7^\circ$: this, in addition to the different effects on the dissociation constant of boric acid, suggests different structures for these two compounds.

SUMMARY

1. The downward displacement of the titration curve of boric acid effected by styracitol, polygalitol, *l*-arabitol, *β-d*-mannoheptitol, pinite, and hydroxypyruvic aldehyde has been determined.

2. The heptahydric alcohol, *β-d*-mannoheptitol, shows no greater potentiation of the dissociation constant of boric acid than its hexahydric homologues, mannitol and sorbitol.

3. Extra-stoichiometric alkali-consuming power of the hydroxypyruvic aldehyde–boric acid complex was observed.

4. The quantitatively different displacements of the titration curve of boric acid by syrupy mannitan and α-mannitan are recorded and discussed.

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THE SOLUBILITY OF SILVER IN MERCURY. III

15B-42

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Systematic investigations of the solubility of silver in mercury have been reported by Joyner (3), Sunier and Hess (5), and DeRight (1). Since below 30°C. the results of DeRight were not in agreement with those of Joyner, and since DeRight encountered serious experimental difficulties in this region, the present work was undertaken in an attempt to extend below room temperature, by the use of a technique different from that of DeRight, the precise knowledge of the solubility of silver in mercury. The work has been interrupted and there is little possibility that it will be continued, but the data which have been collected are considered of sufficient value to warrant publication.

MATERIALS

The silver used was in the form of 1000 fine foil obtained from the U. S. Mint in Philadelphia. One portion of the mercury used was purified by dropping it five times through a five-foot Meyer tube containing 6 *N* nitric acid, washing three times with distilled water in the same fashion, and triple distilling under reduced pressure according to the method of Hulett and Minchin (2). The other portion of mercury used was obtained from the Taylor Instrument Company and was stated to have been triple distilled. The conditions of distillation were not specified. When evaporated according to the method of analysis the mercury left no weighable residue. Under the same conditions there was no detectable loss in weight of the silver. In some cases a mixture of silver foil and solid phase from previous runs was used in preparing the amalgam.

APPARATUS

Except in runs F and G, where a smaller thermostat was used, the thermostat was that used by DeRight (1). The temperature was automatically controlled by a mercury thermoregulator and electrical heating units. As read on a Beckmann thermometer, the thermostat temperature was constant to better than ± 0.02°C. Temperatures were read from a Hiergesell Bros. thermometer of the double diamond grade to 0.02°C. This thermometer was calibrated against a thermometer certified by the Bureau of Standards.

EXPERIMENTAL

The apparatus for preparing the amalgams is shown in figure 1.

The amalgams were prepared by placing an excess of silver in contact with mercury in flask A suspended in the thermostat. The mixture was agitated by a stirrer, and after a given length of time the liquid phase was drawn off by lowering the sintered glass filter C, making connection, by means of the rubber stopper D, to a flask which could be evacuated. The thermostat temperature was always below room temperature. The filter was model 154 G-1, made by Schott and Jena, with a pore size of from 100 to 120 microns, according to the makers. With such a filter, 200 cc. of amalgam could be drawn off in a few minutes. The liquid phase was separated into samples which were analyzed according to the method described by DeRight (1). It should be noted that the procedure here used differed from that of DeRight (1) and Sunier and Hess (5) in that each sample which they analyzed represented a separate solubility determination. The weights used were calibrated and compared with a weight certified by the Bureau of Standards.

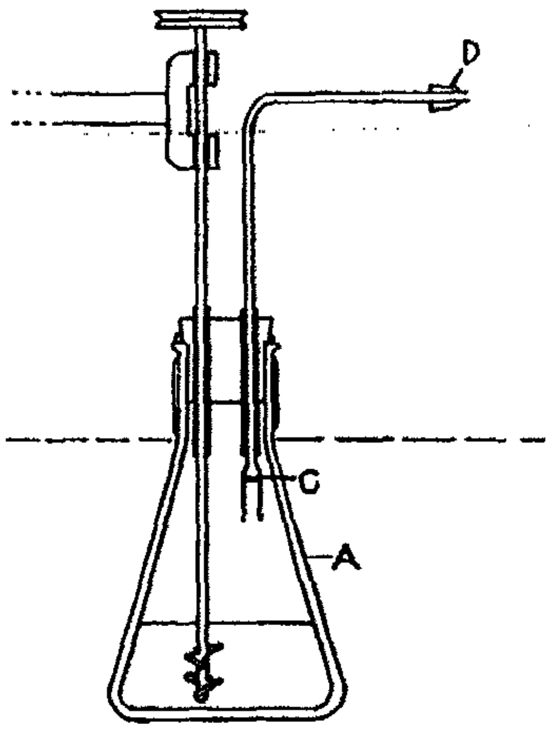

FIG. 1. The apparatus for preparing the amalgams

Table 1 shows the results of a check run upon an unsaturated amalgam. Some difficulty was experienced in run A in bringing the silver residues to constant weight, using several short periods of heating (5 hours) at 500°C. in a stream of hydrogen. In all succeeding runs, after evaporation of the mercury the residues were heated continuously for 50 hours or more at 500°C. in a stream of hydrogen. The residues then showed no change in weight on further heating. The rather large deviation (5.8 parts per thousand) between the known and measured atomic per cent of silver in run A may be due to the above-mentioned difficulty in obtaining constant weights of the residues. It is not believed that a constant error of this magnitude was present in the other runs.

TABLE 1

Results of a run upon an unsaturated amalgam

Run A (test run): temperature, 28 ± 2°C.; length of run, 3 hours; weight of silver taken, 0.9894 g.; weight of mercury taken, 2700 g.; atomic per cent of silver taken, 6.81×10^{-2}

SAMPLE NUMBER	WEIGHT OF SILVER	WEIGHT OF AMALGAM	ATOMIC PER CENT OF SILVER × 100	DEVIATION FROM MEAN
	grams	*grams*		*p.p.t.*
A-1	0.0838	226.9	6.87	2.9
A-2	0.0725	195.5	6.90	7.3
A-3	0.0750	203.1	6.87	2.9
A-4	0.0703	191.3	6.83	2.9
A-5	0.0614	167.5	6.82	4.4
A-6	0.0627	170.4	6.84	1.5
A-7	0.0672	182.5	6.85	0.0

Average atomic per cent of silver .... 6.85×10^{-2}
Average deviation from mean .... 3.1 parts per thousand
Deviation from atomic per cent taken .... 5.8 parts per thousand

TABLE 2

The results of a typical experiment

Run G: temperature, 5.72°C.; length of run, 30 hours; equilibrium approached from high side

SAMPLE NUMBER	WEIGHT OF SILVER	WEIGHT OF MERCURY	ATOMIC PER CENT OF SILVER × 100	DEVIATION FROM MEAN
	grams	*grams*		*p.p.t.*
G-1	0.0620	274.4	4.03	0.0
G-2	0.0611	270.6	4.03	0.0
G-3	0.0613	271.2	4.03	0.0
G-4	0.0652	289.0	4.03	0.0
G-5	0.0652	288.2	4.04	2.5
G-6	0.0658	290.1	4.21	45.0 Exclude
G-7	0.0644	285.8	4.01	5.0

Average atomic per cent of silver .... 4.03×10^{-2}
Average deviation from mean .... 1.3 parts per thousand

Table 2 gives the results of a typical experiment. Table 3 summarizes the data. In it are presented the temperatures at which the solubility determinations were made, the solubility in atomic per cent as measured and as calculated from DeRight's equation, the number of samples taken for analysis, the average deviation from the mean of the samples, and the time allowed for equilibrium to be reached. In runs D and E equilibrium was approached from the unsaturated side; in all other runs equilibrium was approached from the supersaturated side. One sample in run D and

TABLE 3

Summary of the data

RUN	TEMPERATURE	SOLUBILITY ATOMIC PER CENT × 100		DEVIATION FROM MEAN	NUMBER OF SAMPLES	TIME
		Measured	From equation			
	°C.			*p.p.t.*		*hours*
B	19.24	6.52	6.42	7.7	8	8
C	16.12	5.86	5.85	4.1	9	8
D	18.98	6.25	6.37	1.4	8	8
E	12.39	5.19	5.21	1.5	8	11
F	9.71	4.74	4.79	1.3	7	20
G	5.72	4.03	4.21	1.3	6	30

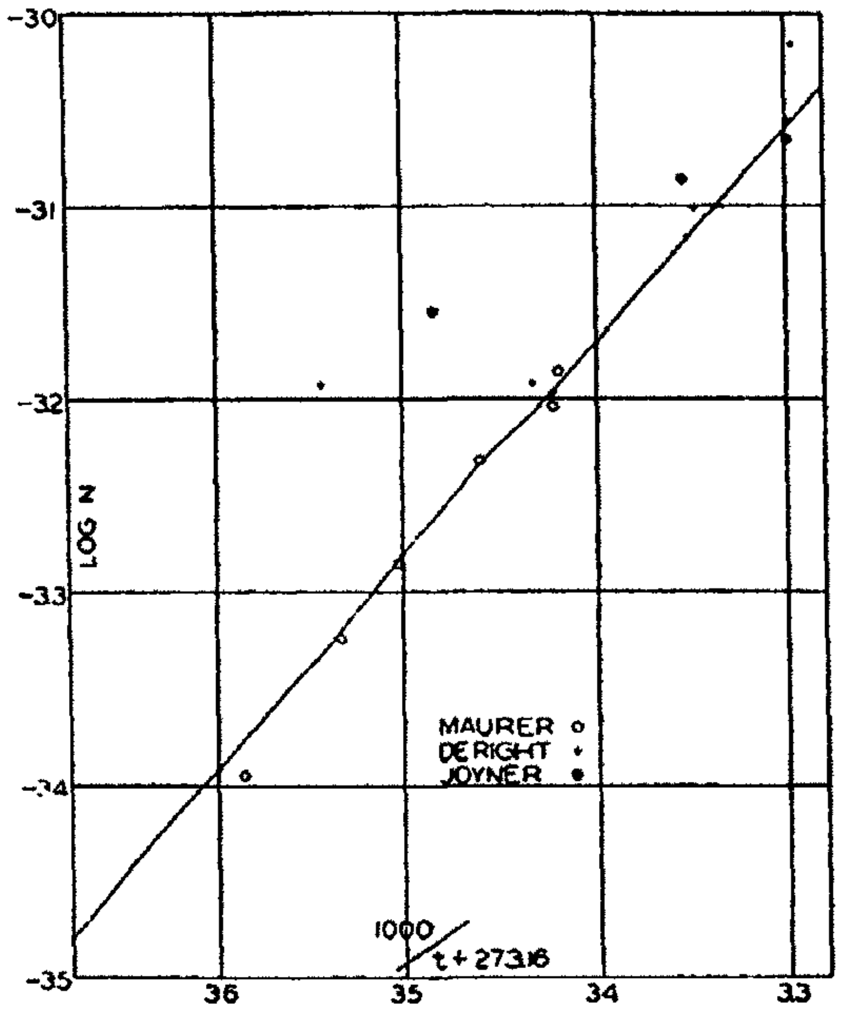

FIG. 2. Plot of the data obtained and also of the data of DeRight and Joyner

one sample in run G were excluded because they deviated from the mean by more than four times the average deviation.

DISCUSSION

The results of the present investigation are shown in figure 2 for comparison with the data of DeRight and of Joyner below 30°C. The straight line given by the equation

$$\log N = -\frac{1105.8}{T} + 0.5894$$

is that proposed by DeRight as the best fit for his data from 80° to 10°C. If a large-scale plot of the data of Sunier and Hess, DeRight, and the present data, covering the range 5° to 200°C., is made, a slight deviation from a straight line, as suggested by the present data, is definitely noticeable.

It is felt that the use of a sintered glass filter is an improvement over the use of glass wool and a capillary for filtration as used by DeRight and by Parks and Campanella (working with lanthanum amalgams) (4), in that the conditions of filtration are more reproducible. The use of sintered filters of various pore sizes might shed light upon the question of the influence of the conditions of filtration upon apparent solubility. No support can be found in the present work for the hypothesis of DeRight that below 40°C. silver aggregates of various sizes are present. At least the use of a sintered filter gives sufficiently reproducible conditions to eliminate erratic results.

SUMMARY

1. The solubility of silver in mercury has been determined at six temperatures between 5° and 20°C., confirming the extension of DeRight's equation into this region.

2. A sintered glass filter proved highly satisfactory as a means of separating solid and liquid phases.

The writer wishes to thank Doctor Arthur A. Sunier, who suggested this work and maintained a constant interest in it.

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THE POTENTIALS OF PLATINUM ELECTRODES IN PHOTOGRAPHIC DEVELOPERS[1]

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In a recent communication from these Laboratories, R. M. Evans and W. T. Hanson (2) have described the measurement of potentials of blank platinum electrodes immersed in solutions of photographic organic developers and discussed the photographic significance of the potentials so measured. They regarded these potentials as belonging to a possible oxidation-reduction system present, and postulated the existence of a small and essentially constant amount of the oxidized form of the system in equilibrium with sodium sulfite and with the reduced form of the monosulfonate of the developing chemical. Their measurements were made in a vessel exposed to the air, and an investigation of the part which oxygen might play in the production of the potentials was undertaken by the writer in an effort to clarify the precise origin of the observed potentials.

EXPERIMENTAL

Measurements were made in a 250-ml. water-jacketed beaker which was fitted with a glass cap carrying the necessary electrodes, salt bridge, stirrer, etc. Any desired atmosphere could be maintained in this reaction vessel by passing gas in through a porous alundum bubble head. Rapid stirring with a motor-driven glass paddle which entered the reaction vessel through a water seal aided in securing equilibrium conditions.

Readings of the electrode potentials were made with a Leeds and Northrup student type potentiometer with a current galvanometer of medium sensitivity. Readings were, in general, made with a series resistance of 10,000 ohms to avoid or minimize polarization of the electrodes. No criterion of correctness of readings was available, so that agreement of two electrodes within 2 to 3 millivolts was considered satisfactory. Electrodes of virgin platinum foil 1 cm. square were used and were stored in a solution of chromic acid in sulfuric acid between readings. With these electrodes it was found that the potentials were stable and reproducible under stable and reproducible conditions.

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[1] Communication No. 654 from the Kodak Research Laboratories.

The values of the pH of the solutions were determined with a glass electrode, using a ballistic galvanometer and one microfarad condenser as an indicator of the potentiometric balance. The electrode was frequently calibrated against the hydrogen electrode in solutions of the same sodium-ion and buffer-ion composition as those in which the potential measurements were made. To make these calibrations the sodium sulfite in the developer solutions was replaced with sodium sulfate. The sodium-ion content of all solutions was maintained at 1.5 *N* by adding anhydrous sodium sulfate, and the buffering ion was 0.2 *N*. The values of pH as recorded are correct to within 0.05 pH unit.

The 3.5 *N* calomel half-cell with the bridge employed is assigned a value of 0.2502 volt against the normal hydrogen electrode at 20°C., and this value has been used throughout in the calculations of E_H. All measurements were made at 20°C. ± 0.01°.

TABLE 1

Behavior of the potential as a function of pH for two partial pressures of oxygen

8 g. of elon and 64 g. of sodium sulfite per liter

pH	E_H 21 PER CENT OXYGEN	E_H 100 PER CENT OXYGEN
3.60	0.309	0.323
4.45	0.247	0.269
5.43	0.188	0.211
5.85	0.174	0.205
6.45	0.129	0.159
7.13	0.097	0.124
9.05	0.016	0.036
9.10	0.020	0.039
9.30	0.029	0.049
10.10	−0.030	−0.008
10.90	−0.038	−0.012
11.25	−0.028	−0.001
11.43	−0.053	−0.035

The photographic developing agents used were Eastman tested photographic chemicals, and all other chemicals used were of reagent quality. Mixtures of oxygen and nitrogen were prepared from cylinders of the compressed gases and were stored over water. These mixtures were analyzed for oxygen each time the mixture was used, by adsorption in alkaline pyrogallol solution according to the standard gas analysis procedure.

A preliminary investigation with *p*-methylaminophenol (elon) solution in the presence of sodium sulfite at pH = 9 showed that the potentials were dependent upon the partial pressure of oxygen and that the plot of potential against $\log_{10}$ of the percentage of oxygen in the saturating mixture was linear from 1 per cent to 100 per cent. The behavior of the potential as a function of pH was determined for two partial pressures of oxygen, and the data in table 1 are shown graphically in figure 1.

Constancy of behavior with respect to dependence upon the partial pressure of oxygen is indicated in any given range of pH by parallelism of the straight lines for 100 per cent oxygen and 21 per cent oxygen, while a change in this dependence is indicated by a change in the relative spacing of the two lines on the potential axis. It will be noted that a change in the effect of oxygen occurs at pH = 8.5. Similar data for hydroquinone are given in table 2.

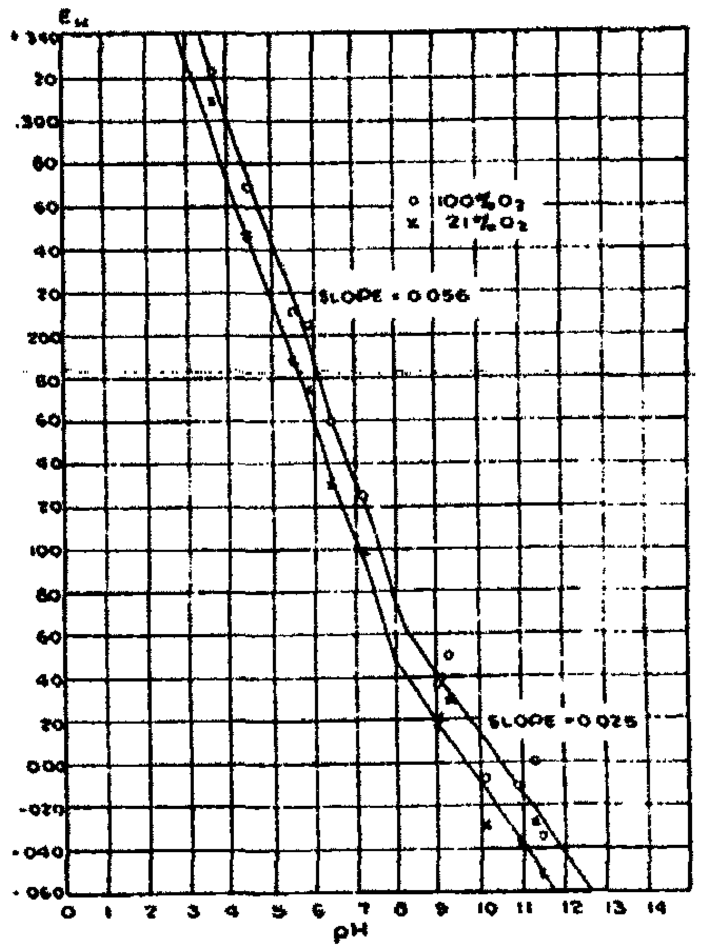

FIG. 1

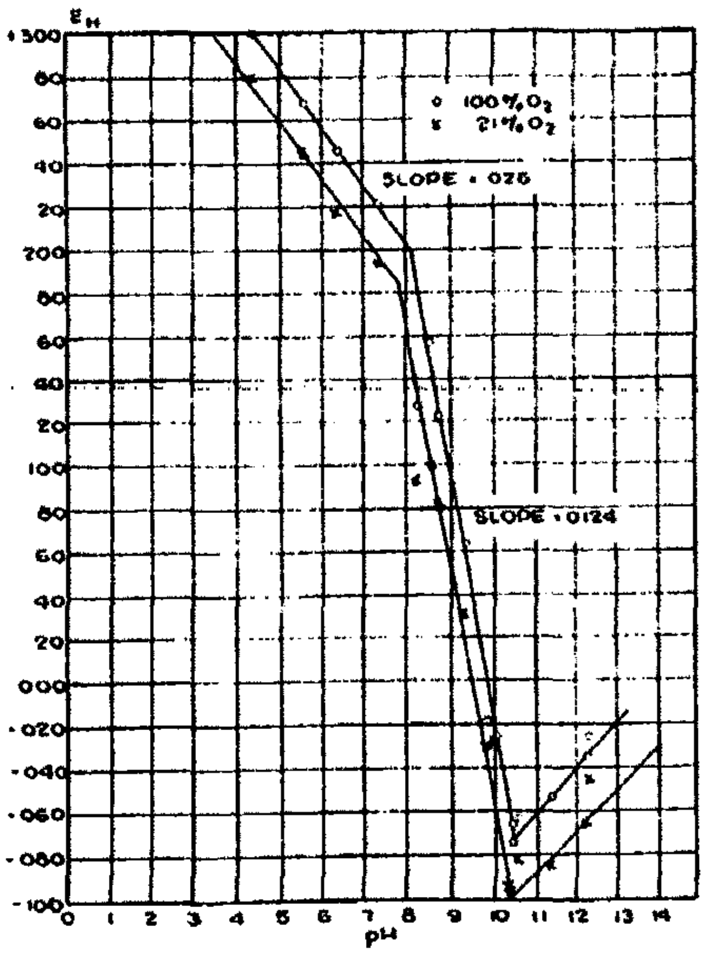

FIG. 2

FIG. 1. Potentials of electrodes in a solution of 8 g. of sodium sulfite per liter, as a function of pH at two different oxygen concentrations.

FIG. 2. The potentials of platinum electrodes in a solution of 5.12 g. of hydroquinone and 64 g. of sodium sulfite per liter, as a function of pH.

It will be noted from the plot of these data in figure 2 that there are three different reaction regions. The readings taken with hydroquinone and with elon at the higher values of pH are not so reliable, however, because of the very rapid reaction of the compounds with oxygen, which makes maintainance of saturation of the solution with oxygen very difficult.

The dependence of the potentials upon the partial pressure of oxygen and upon the concentration of the reducing agent was determined in the

TABLE 2

5.12 g. of hydroquinone and 64 g. of sodium sulfite per liter

pH	E_H 21 PER CENT OXYGEN	E_H 100 PER CENT OXYGEN
4.40	0.280	0.301
5.60	0.246	0.268
6.40	0.218	0.246
7.40	0.195	0.222
8.30	0.093	0.127
8.68	0.100	0.157
8.80	0.083	0.123
9.35	0.031	0.063
9.85	−0.030	−0.019
10.05	−0.045	−0.025
10.40	−0.097	−0.075
10.40	−0.094	−0.066
10.55	−0.081	−0.063
11.35	−0.084	−0.053
12.25	−0.065	−0.035
12.30	−0.044	−0.026

TABLE 3

Dependence of the potentials upon the partial pressure of oxygen and the concentration of the reducing agent

64 g. of sodium sulfite per liter

pH	PER CENT OXYGEN	GRAMS OF ELON PER LITER	E_H
5.85	2.7	0.8	0.180
5.85	21.0	0.8	0.219
5.85	100.0	0.8	0.250
5.85	1.4	8.0	0.128
5.85	21.0	8.0	0.174
5.85	100.0	8.0	0.205
5.85	1.4	16.0	0.108
5.85	21.0	16.0	0.159
5.85	100.0	16.0	0.188
9.30	1.2	0.8	0.033
9.30	21.0	0.8	0.071
9.30	100.0	0.8	0.095
9.30	1.2	4.0	0.005
9.30	21.0	4.0	0.043
9.30	100.0	4.0	0.065
9.30	1.3	8.0	−0.005
9.30	21.0	8.0	0.029
9.30	100.0	8.0	0.049

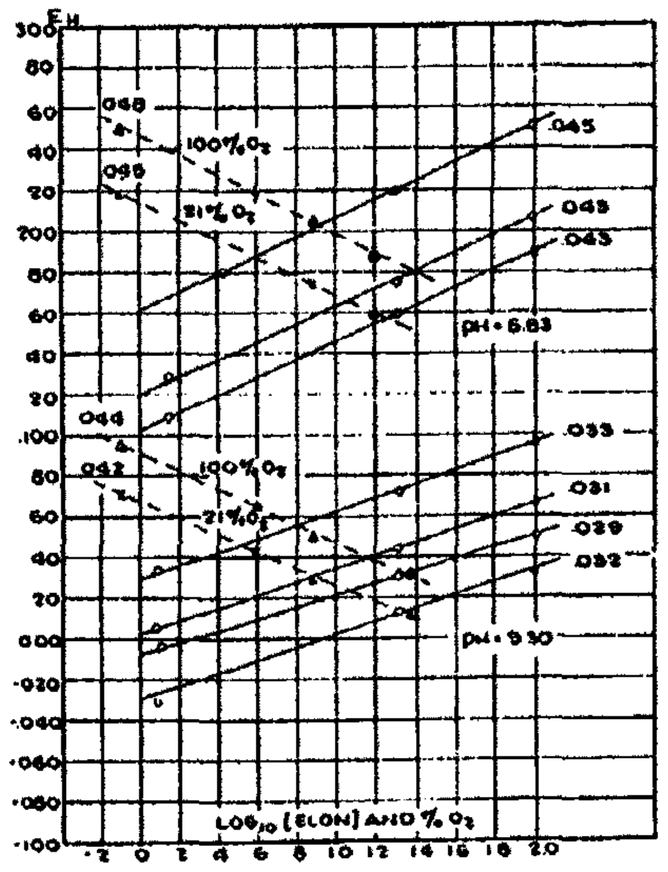

Fig. 3

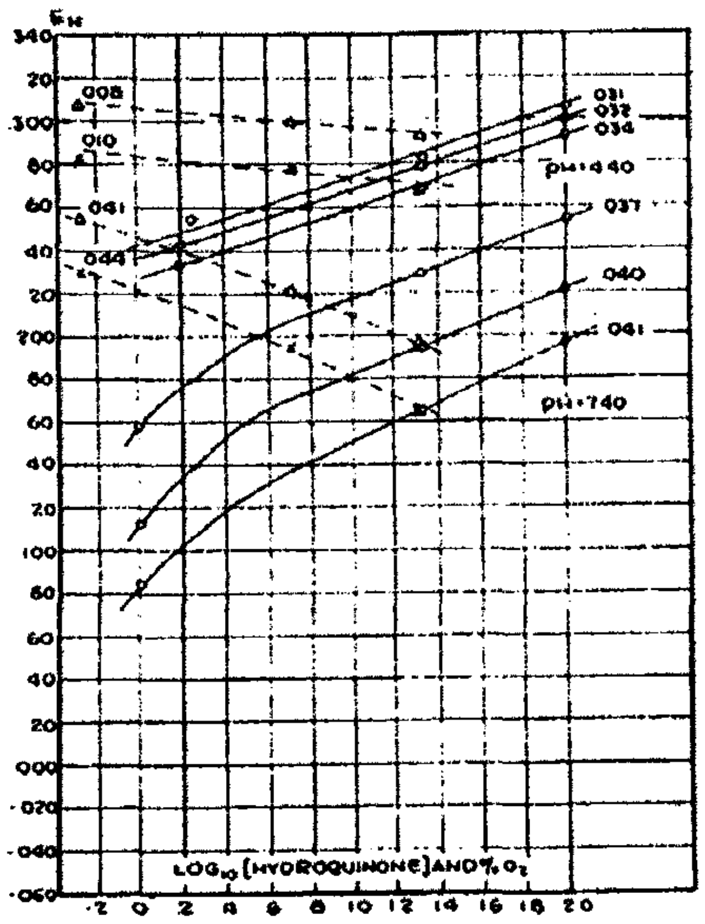

Fig. 4

Fig. 3. Electrode potentials as a function of the concentration of elon and percentage of oxygen at constant pH, with 64 g. of sodium sulfite per liter.

Fig. 4. Electrode potentials as a function of the concentration of hydroquinone and percentage of oxygen at constant pH with 64 g. of sodium sulfite per liter.

TABLE 4

Dependence of the potentials upon the partial pressure of oxygen and the concentration of the reducing agent

64 g. of sodium sulfite per liter

pH	PER CENT OXYGEN	GRAMS OF HYDROQUINONE PER LITER	E_H
4.40	1.7	0.51	0.255
4.40	21.0	0.51	0.283
4.40	100.0	0.51	0.307
4.40	1.6	5.12	0.243
4.40	21.0	5.12	0.280
4.40	100.0	5.12	0.301
4.40	1.6	20.50	0.234
4.40	21.0	20.50	0.269
4.40	100.0	20.50	0.294
7.40	1.0	0.51	0.159
7.40	21.0	0.51	0.230
7.40	100.0	0.51	0.255
7.40	1.0	5.12	0.113
7.40	21.0	5.12	0.195
7.40	100.0	5.12	0.222
7.40	1.0	20.60	0.084
7.40	21.0	20.60	0.165
7.40	100.0	20.60	0.197

TABLE 5

Dependence of the potentials upon the concentration of sodium sulfite

MOLES OF SODIUM SULFITE PER MOLE OF ELON	E_H 21 PER CENT OXYGEN	E_H 100 PER CENT OXYGEN
8 g. of elon per liter; pH = 9.05		
0.35	0.038	0.056
0.35	0.033	0.051
0.70	0.043	0.059
2.10	0.033	0.050
3.52	0.033	0.050
4.57	0.039	0.058
4.57	0.027	0.046
5.63	0.015	0.034
5.63	0.020	0.040
5.63	0.022	0.042
11.25	0.009	0.035
11.25	0.015	0.034
11.25	0.017	0.037
8 g. of hydroquinone per liter; pH = 9.40		
0.87	−0.005	0.016
1.75	−0.017	0.003
1.75	−0.009	0.010
3.49	−0.013	0.011
3.49		0.007
7.00	−0.020	0.003
7.00		0.000

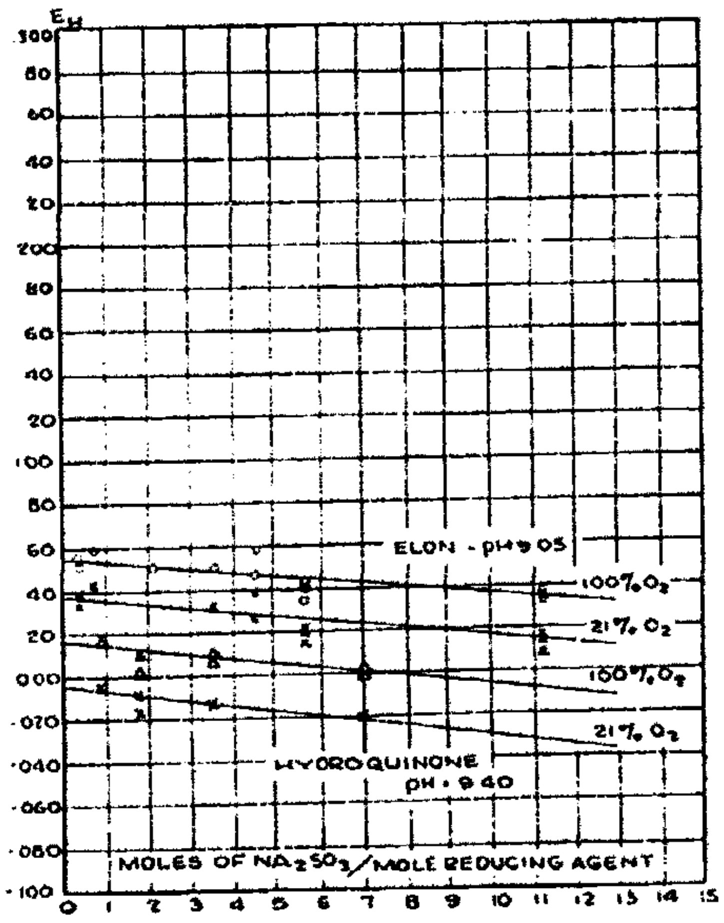

Fig. 5. Electrode potentials of solutions containing 8 g. of elon or 8 g. of hydroquinone per liter, as a function of concentration of sodium sulfite at constant pH.

ranges of pH in which the potential-pH relationship indicated constancy of behavior. The data are given in table 3 and are shown graphically in figures 3 and 4. Because of the extremely rapid reaction with oxygen at high pH values, the range above pH = 10 was not investigated in this manner.

The dependence of the potentials upon the concentration of sodium sulfite was investigated for both compounds. The results are tabulated in table 5 and plotted in figure 5.

DISCUSSION

The dependence of the potentials upon the partial pressure of oxygen eliminates the possibility that the observed potentials are due to a thermodynamically reversible oxidation-reduction system, the oxidized form of which is present in small and essentially constant concentration. Furthermore, the potential-pH relationships for the two compounds investigated show no parallelism in behavior to the oxidation-reduction potentials of the systems. Fieser (3) has determined the oxidation-reduction potential of *p*-methylaminophenol from pH = 0 to pH = 8 by a discontinuous titration method, and the writer has extended these measurements to pH = 13.5. The oxidation-reduction potential of this compound as a function of pH shows the following behavior:

pH range	*Slope*
0 - 4.0	0.058
4.0 - 5.75	0.087
5.75-10.40	0.058
10.40-13.50	0.029

The slopes as given are those which are theoretical for 20°C., and the experimental points fell very precisely upon them. The slopes found for the electrode potentials for elon in the presence of sodium sulfite, referring to figure 1, are as follows:

pH range	*Slope*
3.5- 8.3	0.056
8.3-11.5	0.025

The numerical slopes are in rough agreement with those of an oxidation-reduction system, but the 0.087 slope, which should appear between pH = 4 and pH = 5.75, is absent. Furthermore, there is a discrepancy of two pH units in the two cases between the change from the 0.058 slope to what approximates an 0.029 slope in the case of the potentials in the presence of sodium sulfite.

In the case of the system hydroquinone-quinone, the oxidation-reduction potential has the slope of 0.058 from pH = 0 until the pK of the first acid ionization is reached. The ionization constant of the first acid ionization of hydroquinone at 18°C. is given by Von Euler and Brunius (1) as 1.33×10^{-10}, and the pK is 9.98. Sheppard (5) gives the first ionization constant as 1.75×10^{-10} at 25°C., and the corresponding pK is 9.75. Therefore, in the case of the hydroquinone–quinone system there should be a change from a slope of 0.058 to 0.029 at about pH = 9.90, and no change in slope before this. The potentials measured in the presence of sodium sulfite show none of this behavior. From pH = 4 to pH = 8 the slope is 0.026 instead of 0.058, and from pH = 8 to pH = 10.3 it is 0.124. Above a pH of 10.3 the slope seems to reverse its sign, although measurements in this region should not be too heavily relied upon because of the rapid reaction taking place between oxygen and hydroquinone.

TABLE 6

The slopes of the dependence of potential upon the partial pressure of oxygen and the concentration of the reducing agent

REDUCING AGENT	pH RANGE	SLOPE OF E_H-pH	SLOPE OF E_H-[Red]	SLOPE OF E_H-PER CENT OXYGEN
Elon	3.5- 8.3	0.056	0.048 0.045 Av. = 0.046	0.045 0.043 0.043 Av. = 0.043
	8.3-11.5	0.025	0.044 0.042 Av. = 0.043	0.033 0.031 0.029 0.032 Av. = 0.031
Hydroquinone	4.0- 8.0	0.026	0.008 0.010 Av. = 0.009	0.031 0.032 0.034 Av. = 0.032
	8.0-10.3	0.124	0.041 0.044 Av. = 0.042	0.037 0.040 0.041 Av. = 0.039

Potentials measured in an atmosphere of pure nitrogen are much lower than those recorded above and are unpoised, as would be expected in a solution containing only one component of an oxidation–reduction system. Readings agreeing roughly with those obtained in pure nitrogen can be secured from electrodes located at the bottom of a beaker of unstirred solution exposed to air. As the oxygen present in the solution is used up, the potentials fall and become less well poised.

The slopes of the dependence of potential upon the partial pressure of oxygen and the concentration of the reducing agent are summarized in table 6. It will be observed that in no case is the slope of the dependence of potential upon concentration of reduced form that which would be expected for a two-electron oxidation–reduction system. The general expression for such a system at constant pH is the following:

$$E_H = E_0 - 0.029 \log_{10} \frac{[\text{Red}]}{[\text{Ox}]}$$

from which it is apparent that a tenfold change in the concentration of the reduced form, the concentration of oxidized form being held constant, would cause a decrease in the observed potential of 0.029 volt.

The effect of sodium sulfite upon the potentials of these two systems is shown in figure 5. It will be noted that the effect of sulfite upon the potentials is a linear function of the sulfite concentration instead of being a linear function of the logarithm of this concentration. The sulfite removes the oxidized form as the monosulfonate, and destroys the oxidation–reduction system which would otherwise be present. Beyond this, no definite function can be ascribed to the sulfite as far as the determination of these potentials is concerned.

TABLE 7

Values of a and b

REDUCING AGENT	pH	a	b
Elon	3.5- 8.3	3	3
	8.3-11.5	3	2
Hydroquinone	4.0- 8.0	1	2
	8.0-10.3	3	3

If oxygen is regarded as the basic unit involved in the electrode reaction, involving an electron transfer of four for each molecule of oxygen, the following expression can be set up for the electrode potentials at constant pH and constant sulfite concentration:

$$E_H = E_0 - 0.015 \log_{10} \frac{[\text{Red}]^a}{[O_2]^b}$$

The values of the exponents *a* and *b* can be determined from the slopes of the potential-concentration relationships given in table 6. In the case of elon, the observed slopes seem to be definite multiples of 0.015, but in the case of hydroquinone this is not so well defined. The interpretation of these expressions in terms of an electrode reaction is not possible at the present time. It must be noted, however, that the reducing agent and molecular oxygen occur on *opposite* sides of the equilibrium, since an increase in concentration of the reducing agent shifts the potentials to lower values and an increase in concentration of molecular oxygen shifts it toward higher values.

A discussion of the significance of these potentials for photographic theory or practice lies beyond the intended scope of this paper. It may be indicated in passing, however, that measurements made in developer solutions which have been in contact with photographic emulsion may be in considerable error. Colloidal silver, an autoxidation catalyst, causes a shift of the potentials to lower values without changing the slope of the potential-oxygen concentration relationship. Silver ion causes the blank platinum electrode potentials to become independent of the oxygen concentration. The electrodes then behave like silver electrodes. This effect has been described by Kolthoff and Wang (4) for silver-ion concentrations above 0.01 *M*. Even very low concentrations of silver ion appear to cause this effect.

It appears to be possible to measure potentials which show similar behavior in any system, organic or inorganic, which does not give rise to a reversible oxidation-reduction system upon oxidation by molecular oxygen. Examples of these are benzoin in strongly alkaline solution and sodium sulfite.

SUMMARY

1. The potentials of blank platinum electrodes in photographic developer solutions are found to be functions of the oxygen concentration as well as of the concentration of the reducing agent.

2. The reducing agent and molecular oxygen take part in the electrode reaction upon opposite sides of the equilibrium.

3. The most apparent effect of sodium sulfite is to destroy any reversible oxidation-reduction system which might otherwise mask the "oxygen" electrode potential.

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THE POSTPRECIPITATION OF ZINC SULFIDE WITH BISMUTH SULFIDE[1]

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In previous investigations carried out in this laboratory it was shown that the induced precipitation of zinc sulfide from acid medium by copper sulfide (7) and mercuric sulfide (5) actually is a postprecipitation. The rate of precipitation of zinc sulfide from acid medium is small, but is greatly enhanced at the interphase of the copper or mercuric sulfides. Conclusive evidence was given that the promoting effect of these sulfides upon the postprecipitation of zinc sulfide is to be attributed to the presence of an adsorbed layer of hydrogen sulfide at the interphase, the acid being, partially at least, ionized in the adsorbed state. The results of Caldwell and Moyer (3) substantiate the views developed in previous papers (6). In the postprecipitation of zinc sulfide induced by copper sulfide the former precipitates as a separate phase and can be readily extracted from the mixed precipitate with 3 *N* hydrochloric acid. The zinc sulfide postprecipitated by mercuric sulfide forms to a limited extent mixed crystals with the latter; this explains why the zinc is not easily extracted from the mixed precipitate with 3 *N* hydrochloric acid. From our own work and from the extensive study by Böttger and Ahrens (1) it may be concluded that cadmium sulfide is also postprecipitated with mercuric sulfide, and that the mixed precipitates of the two consist of mixed crystals.

In the present study the effect of bismuth sulfide upon the precipitation of zinc sulfide was investigated. Bismuth sulfide was chosen not only because it has a different crystal structure from zinc sulfide (in this respect it is comparable with copper sulfide), but also because it is of a different formula type. Zinc sulfide crystallizes either in the cubic or in the hexagonal system, whereas bismuth sulfide crystals belong to the orthorhombic system.

EXPERIMENTAL

Materials used

All chemicals used were C. P. products. The stock solutions of bismuth chloride were 1 normal with respect to hydrochloric acid in order to pre-

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[1] This article is based on a thesis submitted by Frank S. Griffith to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1937.

vent the separation of bismuth oxychloride. After mixing with the zinc and other solutions the acid concentration was reduced and a white precipitate of bismuth oxychloride was formed, the latter being transformed to bismuth sulfide when the solution was saturated with hydrogen sulfide. It was also desirable to investigate the effect of bismuth sulfide separated from clear solutions. In such cases the stock solution of bismuth chloride was 0.4 *N* in hydrochloric acid and contained 50 g. of tartaric acid per liter. No precipitate separated from such a solution upon dilution.

Analytical

After the treatment with hydrogen sulfide the zinc was determined in the filtrate by titration with potassium ferrocyanide, using diphenylamine as indicator (8).

Reproducibility of experiments

In the early work great differences were found between results of apparently identical experiments; for example, 68 per cent and 46 per cent of the zinc were found precipitated in two experiments supposedly identical, but run on different days. After a systematic search it was found that, in general, the amount of postprecipitated zinc sulfide decreased with depletion of the Kipp generator in which the hydrogen sulfide was produced by the interaction of stick iron sulfide and commercial hydrochloric acid. The iron sulfide contains free iron which leads to a dilution of the hydrogen sulfide with hydrogen. The gas generated was tested for hydrogen by removing the hydrogen sulfide by absorption in sodium hydroxide. The amount of hydrogen present was found to vary between 2 and 18 per cent, depending upon the use and age of the generator. With fresh 3 *N* hydrochloric acid in the generator, 1.6 per cent hydrogen was found when the gas was withdrawn at a rapid rate; when the rate was decreased to 75 bubbles (about 20 ml.) per minute the percentage of hydrogen increased to 10 per cent. When the generator was allowed to stand unused for a few hours, the percentage of hydrogen in the gas at the start of the next discharge was found to be unusually high (18 to 20 per cent).

In order to keep the hydrogen sulfide pressure constant it would be preferable to use gas from a tank. As the latter was not available the error due to varying composition of the gas was mainly eliminated by running standard comparison experiments or identical experiments in series with the particular system investigated.

Experimental procedure

In general the same method of precipitation was used as described in the paper of Kolthoff and Moltzau (5). The precipitate was removed by filtration and washed eight to ten times with 0.1 *N* hydrochloric acid saturated with hydrogen sulfide. The solubility of the zinc sulfide in this wash solution was low. In some cases the precipitate was subjected to twenty-five more washings after the ten usual washings; it was found that only 1 per cent of the total zinc was removed by the twenty-five extra washings when the total amount of zinc in the system was about 1.25 millimoles.

TABLE 1

Effect of concentration of acid and time of shaking upon postprecipitation of zinc sulfide at 25°C.

CONCENTRATION OF HCl BEFORE PRECIPITATION OF ZINC	TIME OF SHAKING	ZINC PRECIPITATED*
N	*minutes*	*per cent*
0.15	5	30
0.15	15	75
0.15	60	90
0.15 (blank)†	60	2
0.20	5	0.5
0.20	15	31
0.20	60	82
0.20 (blank)†	0	0.5
0.25	5	0.0
0.25	15	0.5–3
0.25	60	32
0.30	60	2
0.30	180	7

* The average value of two to four experiments is given.

† The blanks contained 25 ml. of water instead of 25 ml. of the bismuth solution.

RESULTS

Effect of acidity upon postprecipitation

In the following experiments 25 ml. of 0.05 *M* bismuth chloride solution, which was normal with respect to hydrochloric acid, was mixed with 25 ml. of 0.05 *M* zinc chloride; a measured volume of 5.9 *N* sodium hydroxide was added to obtain the acid concentration (after precipitation of the bismuth as sulfide) indicated in table 1. The total volume was made up to 55 ml. The solutions were shaken continuously while hydrogen sulfide was passed through the flasks at a constant rate.

From the results, particularly in 0.25 *N* hydrochloric acid, it follows conclusively that we are dealing again with a postprecipitation of the zinc sulfide. From the analytical viewpoint it is of interest to notice that a quantitative separation of bismuth and zinc is obtained when the initial hydrochloric acid concentration is 0.3 N and the filtration is made a few minutes after the precipitation of the bismuth sulfide.

In the above experiments part of the bismuth was precipitated as oxychloride before hydrogen sulfide was passed through. In order to keep all of the bismuth in solution, experiments were carried out in the presence of tartaric acid. A mixture was prepared from 25 ml. of 0.05 M bismuth chloride which was 0.4 N in hydrochloric acid and 0.3 M in tartaric acid, 25 ml. of 0.05 M zinc chloride which was 0.1 N in hydrochloric acid, and 1 ml. of 5.15 N sodium hydroxide. The final hydrochloric acid concentration (after precipitation of the bismuth) was 0.2 N. The air was removed by passing a rapid stream of hydrogen sulfide through the flask for half a minute; this was continued for 2 minutes after the shaker was started, then decreased for 3 minutes to a stream which just broke into bubbles as it passed through the wash bottle, and finally decreased to a rate of about 150 bubbles per minute for the remainder of the precipitation period. In these experiments pure hydrogen sulfide prepared by heating a magnesium hydrosulfide solution and stored in a gas holder was used. Under identical conditions the experiments were well reproducible. The results are given in table 2.

TABLE 2

Postprecipitation of zinc sulfide from 0.2 N hydrochloric acid solutions containing tartaric acid at 25°C.

Time of shaking in minutes	18	33	48	63
Zinc precipitated in per cent	3	20	47	69

Again it is seen that the amount of zinc sulfide precipitated increases with the time of contact with bismuth sulfide when the solution is saturated with hydrogen sulfide. A comparison of the results with those in table 1 at the same acidity reveals that tartaric acid inhibits the postprecipitation. As the experiments in the two tables were carried out under different conditions of hydrogen sulfide treatment, a new set was made under identical conditions, using a shaking period of 30 minutes and a hydrochloric acid concentration of 0.2 N. In the absence of tartaric acid 45 per cent of the zinc was found precipitated; in the presence of tartaric acid 18 per cent. These experiments show conclusively the inhibiting effect of tartaric acid upon the postprecipitation of zinc sulfide on bismuth sulfide. In the absence of tartaric acid the greatest part of the bismuth sulfide is obtained by transformation of the precipitated bismuth oxychloride into sulfide, whereas in the presence of tartaric acid it is obtained from a clear solution. Apparently the structure of the sulfide formed in the absence of tartaric acid is such that it has a greater promoting effect upon the postprecipitation of zinc sulfide than when formed from tartaric acid-containing solutions. Addition of tartaric acid to 0.05 *M* zinc chloride which was 0.1 *N* with hydrochloric acid did not appreciably affect the rate of precipitation when no promoting sulfide was present. From this it is inferred that the inhibiting effect of the tartaric acid is, for the most part, not due to complex formation with zinc.

Incidentally, it may be mentioned that the rate of postprecipitation decreases with increasing sodium chloride content of the solution. The experiments reported in table 2 were repeated, but with the addition of 2.5 g. of sodium chloride to the mixture. After half an hour of shaking 1 per cent of the zinc was precipitated, whereas 18 per cent was found precipitated when no sodium chloride was added. A similar inhibiting effect of sodium chloride was found by Kolthoff and Pearson (7) in the postprecipitation of zinc sulfide by copper sulfide.

Comparison of the effectiveness of the sulfides of copper, bismuth, mercury, and zinc on the precipitation of zinc sulfide

The experiments were carried out with 1.25 millimoles of the promoting sulfide and 1.25 millimoles of zinc chloride, the hydrochloric acid concentration being 0.2 *N* after precipitation of the promoting sulfide and the total volume 55 ml. In all cases the hydrogen sulfide was passed through the mixture of the metal sulfide and zinc salt for 30 minutes. The zinc sulfide used as promoting agent was prepared by passing hydrogen sulfide through a slightly acid (0.002 *N*) solution of 0.05 *M* zinc chloride; the other promoting sulfides were precipitated in the presence of the zinc solution. The results are given in table 3.

TABLE 3

Comparison of promoting effect of sulfides of copper, bismuth, mercury, and zinc on precipitation of zinc sulfide

Promoting sulfide	Bi	Cu	Hg	Zn
Zinc precipitated in per cent	45	36	85	83
Sodium chloride present in grams	1.0	1.4	1.2	0.30

The results are not strictly comparable, as the sodium chloride contents of the various solutions were not identical. Still, it may be concluded that mercuric and zinc sulfides have about the same promoting effect on the precipitation of zinc sulfide, the effect of bismuth and copper being less. Such a result is probably explained by the fact that mercuric sulfide and zinc sulfide crystallize in the same system and form mixed crystals (5), whereas bismuth sulfide and copper sulfide crystallize in different systems. The induction period in the postprecipitation of zinc with mercuric sulfide may, therefore, be expected to be materially shorter than with the other sulfides. A quantitative comparison of the figures in table 3 is not permissible, as the promoting effect of a certain sulfide depends upon the conditions of precipitation. This is particularly true of the zinc sulfide. In the above case it was precipitated from very dilute acid solution and was very finely divided. If prepared from stronger acid medium it would be coarser and would have less inducing effect upon the precipitation of zinc from solution. This may explain the result of Glixelli (4), who found copper sulfide to be a more efficient promotor of the precipitation of zinc sulfide than the latter; he describes the zinc sulfide used as being fresh, but does not state the conditions under which it was precipitated.

Effect of aging of bismuth sulfide

In the following experiments a mixture of 25 ml. of 0.05 *M* bismuth chloride solution and enough 5.15 *N* sodium hydroxide to make the acid concentration 0.206 *N* after the precipitation of bismuth was treated with hydrogen sulfide and shaken, with a slow stream of hydrogen sulfide passing through it, until the sulfide had aged for a given period of time. Then 25 ml. of 0.05 *M* zinc chloride which was 0.1 *N* in hydrochloric acid was added, and the flask shaken while a slow stream of hydrogen sulfide passed through for 30 minutes. Acid had to be added to the zinc solution in order to prevent the precipitation of zinc sulfide, as the solution was pipetted into the flask full of hydrogen sulfide. In order to get results comparable with the effect of a fresh precipitate, a mixture of the bismuth-sodium hydroxide-zinc solution was treated with hydrogen sulfide for 30 minutes in exactly the same way. The reproducibility of the experiments was poor, but all of the twenty experiments showed the same trend.

The bismuth sulfide aged for 10 minutes caused the precipitation of 20 per cent less zinc than the fresh precipitate, the 15- to 20-minutes old precipitate 24 per cent less, the 60-minutes old precipitate 25 per cent less, but a 41-hours old precipitate 10 per cent *more*. A precipitate aged for a day had about the same promoting effect upon the precipitation of zinc sulfide as fresh bismuth sulfide. It was thought that the separation of bismuth oxychloride before the passage of hydrogen sulfide might account for the unexpected and badly reproducible results. For this reason a great number of experiments was run in which the precipitation of the oxychloride was prevented by addition of tartaric acid.

The final composition of the mixture was about the same as that used in the experiments of table 2, the period of precipitation of zinc being again 30 minutes. In all cases blanks were run with the entire mixture (fresh bismuth sulfide) in series with the experiments with aged bismuth sulfide.

In some instances the bismuth sulfide was aged at 85°-95°C.; the temperature dropped during the aging, as in general no further heat was supplied. After the period of aging the sample was cooled as quickly as possible, and resaturated with hydrogen sulfide, then the zinc chloride was added and the sample further shaken in a slow stream of hydrogen sulfide for 30 minutes. The results are given in table 4.

In the presence of tartaric acid the bismuth sulfide, even upon short periods of aging, becomes more effective in the promotion of the precipitation of zinc sulfide than a fresh product. The effectiveness increases with the age of the bismuth sulfide, until after a relatively long period a maximum is reached. Thus it is seen from table 4 that bismuth sulfide aged at room temperature for 42 hours caused the precipitation of 63 per cent more zinc than the fresh precipitate; after aging for 6 months it had about the same promoting effect as a fresh precipitate. Similar results are found when the bismuth sulfide is aged at 80°-90°C. The 10-minutes old product caused 69 per cent more of the zinc to precipitate than the fresh product; after aging for 4 days at 80°C. the sulfide became less effective than the fresh precipitate.

TABLE 4

Effect of aging of bismuth sulfide upon its promoting effect on precipitation of zinc sulfide

TEMPERATURE OF AGING	AGE OF BISMUTH SULFIDE	PER CENT ZINC PRECIPITATED* AFTER 30 MINUTES		DIFFERENCE BETWEEN (a) AND (b)
		Aged Bi_2S_3 (a)	Fresh Bi_2S_3 (b)	
°C.				
25	10 minutes	31	18	+13
25	1 hour	45	18	+27
25	42 hours	83	20	+63
25	6 months	15	16	−1
85-95	10 minutes	69	18	+51
80	4 days	10	16	−6

* Average values of three to six experiments.

No study has been made of the structural changes taking place during the short and long periods of aging of bismuth sulfide at various temperatures. From the data of table 4 it may be expected that such a study will yield interesting results.

It may be mentioned that it is immaterial whether the bismuth sulfide is shaken or allowed to stand quietly during the aging period. Entrance of air during the aging decreases the effectiveness of the bismuth sulfide somewhat; probably some sulfur formed by oxidation of hydrogen sulfide separates on the surface of the sulfide.

Postprecipitation at higher temperatures

Experiments were carried out with a mixture of bismuth and zinc chlorides of the same composition as that in the experiments reported in table

1. The hydrochloric acid concentration after the precipitation of bismuth was 0.2 *N*, and the time of shaking 60 minutes. One set of experiments was carried out at 50°C., another set at 25°C. In the former 32 per cent of the zinc was found precipitated, in the latter 80 per cent.

Extractibility of the zinc from the mixed sulfides

Precipitates obtained under the same conditions as those of table 2 after a shaking period of 60 minutes, and washing, were shaken for 1 hour with 75 ml. of 3 *N* hydrochloric acid at room temperature, the liquid decanted through a filter, and the residue shaken for 3 more hours with a fresh portion of the acid. The filtrates were evaporated to small volumes and diluted, and the bismuth which had dissolved was reprecipitated with hydrogen sulfide. The zinc was determined in the filtrates. The following results were obtained: per cent of zinc in the original filtrate, 30.0; in the first extraction, 68.1; in the second, 2.5; total, 100.6 per cent. It appears that the zinc is fairly easily extracted from the precipitate. It may be objected (Balarew (2)) that the easy extractibility is due to air oxidation of the zinc sulfide and to solution of some of the bismuth. In order to eliminate this objection experiments were carried out with a bismuth-zinc solution (final acidity 0.22 *N*, further composition as in table 1) treated for 30 minutes with hydrogen sulfide. The mixture was transferred to a volumetric flask of 100 ml. and made up to volume with 0.2 *N* hydrochloric acid saturated with hydrogen sulfide. After mixing and allowing to settle, 50 ml. of the clear solution was pipetted out and analyzed for zinc. The remainder was filtered, washed with 0.2 *N* hydrochloric acid saturated with hydrogen sulfide (called "remainder"), and then the precipitate with paper dropped into 50 ml. of 2 *N* hydrochloric acid saturated with hydrogen sulfide. The mixture was shaken for 40 minutes while hydrogen sulfide was passed through, was filtered (extraction 1), and the extraction was repeated (extraction 2). No bismuth dissolved during this extraction process. The following results were obtained: per cent of zinc in 50 ml. pipetted out, 12.1; in remainder, 20.4; in extraction 1, 69.0; in extraction 2, 0.2; total, 101.7 per cent.

Evidently, some of the zinc is already extracted by 0.2 *N* hydrochloric acid saturated with hydrogen sulfide, indicating that the zinc sulfide is very finely divided and hardly aged. Well-aged zinc sulfide is insoluble in 0.2 *N* hydrochloric acid saturated with hydrogen sulfide (Kolthoff and Moltzau (5)). Furthermore, it is seen that the zinc is easily extracted with 2 *N* hydrochloric acid under conditions which preclude oxidation of the zinc sulfide or solution of any of the bismuth. The ready extractibility contrasts markedly with the extractibility of zinc sulfide postprecipitated with mercuric sulfide (5). In the latter case the zinc sulfide forms a solid solution with the mercuric sulfide, whereas mixed-crystal formation does not occur between bismuth sulfide and zinc sulfide.

Kolthoff and Pearson (7) found that zinc sulfide postprecipitated with copper sulfide can be easily extracted from the mixed precipitate. Balarew (2) attributed this ready extractibility to air oxidation of the zinc sulfide. Some of Kolthoff and Pearson's experiments were repeated under the above extraction conditions precluding air oxidation. Again it was found that the zinc was easily extracted, contrary to Balarew's statements.

SUMMARY

1. Zinc sulfide is postprecipitated with bismuth sulfide.
2. Zinc can be separated quantitatively from bismuth when the hydrochloric acid concentration after precipitation of bismuth is at least 0.3 *N* and filtration is made within a few minutes after the bismuth has separated.
3. The rate of postprecipitation of zinc with bismuth sulfide is small during the early periods of shaking and becomes greater with longer periods of contact. In this respect the effect of bismuth sulfide is comparable to that of cupric sulfide, but in contrast to that of mercuric sulfide. In the latter case the rapid initial rate of postprecipitation is attributed to the similarity of the lattices of zinc sulfide and mercuric sulfide, which is responsible for the reduction of the induction period in the precipitation of zinc sulfide.
4. Mercuric and zinc sulfides are more effective in the postprecipitation of zinc sulfide than bismuth and copper sulfides.
5. Bismuth sulfide aged at room temperature or higher temperatures under specified conditions becomes markedly more effective in the postprecipitation of zinc. After long periods of aging it becomes less effective. Copper sulfide behaves in a similar way, but mercuric sulfide becomes less effective on aging.
6. The zinc can be readily extracted with 2 *N* hydrochloric acid from a mixed sulfide with bismuth or copper, but not from a mixed sulfide with mercury. In the latter case part of the zinc is incorporated in the precipitate as mixed crystals.
7. Addition of sodium chloride to the solution inhibits the rate of postprecipitation of zinc sulfide with bismuth (and copper) sulfide.

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A PRELIMINARY STUDY OF THE POSTPRECIPITATION OF NICKEL SULFIDE WITH COPPER, MERCURIC, AND ZINC SULFIDES[1]

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Baubigny (1) stated in 1882 that nickel sulfide is very slow to separate from slightly acid (0.01 *N* hydrochloric acid) solutions. The solid, however, rapidly changes in some manner to yield products which are much less soluble in 2 *N* hydrochloric acid than would be expected from its small rate of precipitation in dilute acid (3, 7, 6). The solubility of precipitated nickel sulfide decreases markedly on standing in contact with acid solution; in pure water the effect is less. Higher temperatures seem to hasten the transition. Thiel and Gessner (6) postulated the existence of different "modifications" of nickel sulfide, roughly designated as the α-, β-, and γ-forms, corresponding to more or less definite solubilities in hydrochloric acid of a given strength. They advanced the belief that the different preparations differed in the extent of polymerization, and that differences in solubility were to be attributed to this condition. Although this may be true to a certain extent, differences in crystal structure of the different "modifications" may have to be considered. Recently Levi and Boroni (4) found that nickel sulfide prepared from dilute sulfuric acid medium is identical with millerite, but that the product prepared from acetic acid solutions has a different crystal structure.

Since the solubility of nickel sulfide decreases considerably with increasing age, it was expected that other insoluble sulfides might induce the precipitation of nickel sulfide at acidities at which the latter is extremely slow to separate in the absence of promoting sulfides. For this reason a preliminary study was made of the postprecipitation of nickel sulfide with the sulfides of copper, mercury, and zinc, respectively.

EXPERIMENTAL

All of the chemicals used were of C. P. quality. The nickel left in the filtrate after the postprecipitation experiments was determined gravimetri-

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[1] This article is based on a thesis submitted by Frank S. Griffith to the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1937.

cally with dimethylglyoxime or, more rapidly, volumetrically by the cyanide method (5). In the latter method the nickel is transformed to the complex cyanide ion

$$Ni^{++} + 4CN^- \rightleftarrows Ni(CN)_4^{--}$$

and the end point is indicated by the disappearance of the turbidity of suspended silver iodide:

$$AgI + 2CN^- \rightarrow Ag(CN)_2^- + I^-$$

The location of the end point depends upon the concentrations of iodide and ammonia present. Accurate results were obtained by the following procedure: The nickel solution is diluted to 50–70 ml., 5 ml. of 6 *N* ammonia solution, 1 g. of ammonium sulfate, and 1 ml. of 25 per cent potassium iodide solution are added, and the mixture is titrated with standard potassium cyanide solution until the green-blue color fades. Three or four drops of standard silver nitrate are added and the titration with cyanide continued until the solution becomes clear. A correction is applied for the amount of silver added. The turbidity is best seen if the flask containing the solution is placed on a black underground with a black background behind the flask and a strong light coming from the side. Under the best lighting conditions the end point can be detected with an accuracy of 0.04 ml. of 0.02 *M* cyanide (= 0.01 mg. of nickel) in a total volume of 50 ml.

The ammonium sulfate is added to prevent the precipitation of nickel cyanide during the course of the titration. If such a precipitate forms, it is very slow to redissolve upon further addition of cyanide, thus spoiling the titration. Tartrate and citrate (2) are more effective than ammonium sulfate in preventing the precipitation of nickel cyanide. With the concentrations used in this work only in a few cases did any turbidity result from the separation of nickel cyanide.

The following standard solutions were used: (*1*) 0.1034 *M* silver nitrate (calculated from the weight of silver nitrate used, 0.1035 *M*; from titration against pure potassium thiocyanate, 0.1033 *M*). (*2*) 0.1370 *M* potassium cyanide. Twenty grams of potassium cyanide and 40 ml. of 6 *N* sodium hydroxide were diluted to a volume of 2 liters. The solution was standardized against silver nitrate by the Liebig-Dénigès method. (*3*) 0.05120 *M* nickel sulfate. By precipitation with dimethylglyoxime a molarity of 0.05122 was found; by the volumetric procedure described above a molarity of 0.05118.

If desirable, more dilute solutions were prepared from the standard solutions. In the titration of 25 ml. of the 0.05 *M* nickel solution by the recommended procedure the average deviation found was 0.0 per cent (six determinations; error deviated between + 0.05 and − 0.05 per cent; in the titration of 10 ml. of the nickel solution the average error was 0.13

per cent (varying between 0 and 0.3 per cent). Even very dilute nickel solutions (50 ml. of 0.000512 M solution = 1.5 mg. of nickel) could be titrated with an accuracy of 1 per cent. Small amounts of zinc (0.5 millimole) did not interfere with the titration.

TABLE 1

Postprecipitation of nickel sulfide with cupric, mercuric, and zinc sulfides, respectively (at 25°C.)

SET*	AMOUNT OF PROMOTING METAL SULFIDE	CONCENTRATION OF HCl	TIME OF SHAKING	NICKEL PRECIPITATED IN PER CENT IN THE PRESENCE OF			
				CuS	HgS	ZnS	Blank
	millimoles	N		*per cent*	*per cent*	*per cent*	*per cent*
1	0.2	0.004	3 hours	3.2	6.0	1.9	0.5
1	0.2	0.004	52 hours	31	56	77.0	23.5
1	0.2	0.004	96 hours	74	86		85.5
2	0.5	0.01	3 hours	0	0	0	0
2	0.5	0.01	12 hours	3.0	3.5	3.0	0
2	0.5	0.01	24 hours	6.5	36	33.0	0
2	0.5	0.01	36 hours	13.5	54	55	0
2	0.5	0.01	60 hours	37.0	82	88	0
3	0.5	0.02	23 hours	0.5	4.0	1.0	0
3	0.5	0.02	59 hours	2.0	46	4.5	0
3	0.5	0.02	81 hours	3.0	69	9.5	0
4	0.5	0.05	2 days	1.4	1.3	0	0
4	0.5	0.05	5 days	6.0	11	0	0
4	0.5	0.05	7 days	16	13	0	0

* Set 1: 100 ml. of 0.05 M nickel chloride + 4 ml. of 0.05 M cupric, or mercuric, or zinc chloride. Acid concentration after precipitation of promoting sulfide (0.2 millimole) was 0.004 N.

Set 2: 100 ml. of 0.05 M nickel chloride + 10 ml. of 0.05 M cupric, or mercuric, or zinc chloride. Acid concentration after precipitation of promoting sulfide (0.5 millimole) was 0.01 N.

Set 3: As set 2, but with 1 ml. of 1.21 N hydrochloric acid in addition.

Set 4: As set 2, but with 1.9 ml. of 2.42 N hydrochloric acid in addition.

Postprecipitation of nickel sulfide with other sulfides

Nickel sulfide is precipitated very slowly from acid medium. When a 0.04 M nickel chloride solution was kept in an atmosphere of hydrogen sulfide a first separation was noticed after 21 hours in 0.005 N hydrochloric acid, after 66 hours in 0.01 N acid, and none at all even after 20 days in 0.02 N acid. With 0.01 M nickel chloride solution a first separation of sulfide was noticed after 26 to 28 hours in 0.005 N acid, and after 5 days in 0.01 N acid.

The results of the postprecipitation experiments are combined in table 1.

Performance of experiments

The 250-ml. Erlenmeyer flasks containing the solutions were placed on a rotary shaker, and hydrogen sulfide was passed through continuously. From time to time the shaker was stopped, the precipitate allowed to settle, and 10 ml. of the liquid pipetted off for nickel analysis. The sample taken for analysis was filtered through a paper which had been previously washed with 0.02 *N* hydrochloric acid, the filter was washed with water, and the filtrate was analyzed for nickel by the cyanide method. Washing the filter with dilute acid appeared necessary, else a slight precipitation of nickel sulfide from the supersaturated solution would occur.

The acid concentration given in table 1 corresponds to that in the solution after precipitation of the more insoluble promoting sulfide. The experiments whose results are given in the column headed "blank" had no inducing sulfide present but were of the same volume and contained the same amounts of nickel and acid as the solutions with the promoting metals.

TABLE 2

Postprecipitation of nickel sulfide with copper sulfide at 80°C.

Total volume, 35 ml. Amount of copper sulfide, 0.5 millimole; amount of nickel chloride, 1.25 millimoles. Time of shaking, 19 hours

Hydrochloric acid concentration (*N*)	0.05	0.08	0.11
Nickel precipitated in per cent*	58	52	17

* Blanks run in the absence of copper showed no nickel precipitated.

From the first set of experiments (blank) it is seen that nickel sulfide in the absence of promoting sulfides is formed very slowly in 0.004 *N* hydrochloric acid. The induction period is relatively long. After the precipitation has started the nickel sulfide promotes its own precipitation, the precipitation curve being typical of an autocatalytic process. At hydrochloric acid concentrations of 0.01 *N* or greater the induction period in a pure nickel chloride solution is so long that no precipitate of nickel sulfide occurred in the time during which the experiments were run.

It is evident that nickel sulfide is postprecipitated with copper, mercuric, and zinc sulfides. Particularly from the experiments of set 2 it is seen that the induction period is relatively long in the presence of the promoting sulfides and that the postprecipitation curves are typical again of an autocatalytic process. Mercuric sulfide has a stronger effect on the postprecipitation than copper sulfide. The relative effect of zinc sulfide varies with the acid concentration. In set 1 the zinc sulfide is formed from neutral solution, the final acid concentration being 0.004 *N*. Under these conditions the zinc sulfide formed is extremely finely divided, and its effect is greater than that of mercuric sulfide. In set 2 the zinc sulfide is somewhat coarser (final acid concentration 0.01 N), and its effect equals that of mercuric sulfide. With increasing acidity of the solutions (sets 3 and 4) the zinc sulfide becomes coarser. In set 4 (0.05 N acid) the zinc sulfide formed is so coarse that it does not promote the precipitation of nickel sulfide at that acidity.

A few experiments were carried out on the postprecipitation of nickel sulfide with copper sulfide at 80°C. The results are given in table 2. The flasks containing the solutions were placed on the gravel in the hot room (temperature about 80°C.). A slow stream of hydrogen sulfide saturated with water vapor at this temperature was passed through the flasks for 19 hours. After this period the mixtures were filtered and the filtrates analyzed for nickel. The few results show that the rate of postprecipitation with copper sulfide is much greater at 80°C. than at room temperature.

SUMMARY

It has been shown that nickel sulfide postprecipitates with the sulfides of copper, mercury, and zinc, the effect of mercuric sulfide being greater than that of copper sulfide. The relative promoting effect of zinc sulfide greatly depends upon the acidity at which it is separated from solution. The rate of postprecipitation with copper sulfide at 80°C. is much greater than at room temperature. Nickel sulfide autocatalyzes its own precipitation.

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THE CHEMICAL EFFECT OF ELECTRICAL DISCHARGE IN GASEOUS HYDROCARBONS. IX

THE CONDENSATION OF ETHANE, PROPANE, BUTANE, AND PROPYLENE AS A FUNCTION OF TIME, AND COMPARISON OF RATES OF CONDENSATION OF LOWER MEMBERS OF THE PARAFFIN, OLEFIN, AND ACETYLENE SERIES[1]

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INTRODUCTION

In two previous papers (8, 9) of this series are reported the results obtained in the electrical condensation of gaseous hydrocarbons. These papers include work on the condensation of methane, ethylene, and acetylene and the changes which they undergo when exposed for different lengths of time to electrical discharge in an all-glass ozonizer system. Further investigation of electrical discharge in ethane, propane, butane, and propylene has been undertaken in order to extend the present knowledge concerning the nature of electrical condensation and to enable us to make a comparison of the rates of condensation for the lower hydrocarbons of the paraffin, olefin, and acetylene series. From this comparison certain conclusions are drawn as to the factors which govern the rate of electrical condensation of the hydrocarbons.

EXPERIMENTAL PROCEDURE

The apparatus and experimental procedure are described in detail in the previous papers (8, 9). For the sake of clarity we briefly repeat that the gases, after repeated distillation, were admitted to the discharge chamber, which was an all-glass Siemens tube.

In order to obtain comparable results, the same amount of gas was taken for each experiment and the same electrical conditions were applied, the current being kept constant at 6 amperes and 89 volts in the primary circuit and approximately 16,300 volts in the secondary circuit. After the runs the gases were completely analyzed by low-temperature fractiona-

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[1] This paper includes part of an investigation on "The Effect of Electrical Discharge upon Gaseous Hydrocarbons," which is Project 8 of American Petroleum Research. Financial assistance was received from the Research Fund of the American Petroleum Institute, which was donated by the Universal Oil Products Company.

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tion and the individual gases were identified, the unsaturates by means of liquid absorption in potassium permanganate or bromine water, and the saturates by combustion in a Hempel explosion pipet.

The interpretation of the individual analyses often is very difficult, although a great deal of experience has been acquired with regard to the analytical problems involved. The analysis of the reaction products was found to be increasingly troublesome for increasing molecular weight of the initial gas.[3] Hence these difficulties ought to be kept in mind when considering certain discrepancies in the analyses, since a few cubic centimeters of gas mixture to be analyzed have frequently proved to contain all individual representatives which conceivably could be present. It is for this reason that some experiments were repeated several times, in order to show the limits of error and to guarantee a reliable average.

During the course of investigation the ozonizer had to be replaced once. All experiments of this paper except those made with ethane were carried out in the new reaction chamber. The results thus obtained were correlated with the previous results by means of text experiments with ethylene, which showed that *ceteris paribus* a run of 24.5 minutes corresponds most closely to a run of 20 minutes in the old ozonizer, as judged by the pressure drop and by the analysis of final products. The experiments of 60 minutes' duration were accordingly extended to 73.5 minutes.

RESULTS

Ethane

The gas was taken from a tank and redistilled. Vapor pressure measurements checked the results of previous investigators within the limits of error. A total combustion proved its purity. The same care was taken in all the following experiments. The actual pressure changes during the run are omitted.[4] Table 1 shows the results of two runs of 20 minutes' duration and of three runs of 60 minutes' duration.

In spite of smaller discrepancies the following conclusions are arrived at with certainty:

(*1*) A small and definite increase in pressure takes place during the run. This is seen from the ratio of cubic centimeters of final gas to cubic centimeters of initial gas. This pressure increase is of course obvious at once from the actual pressure data, a typical set of which is here reproduced in

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[3] This is mostly due to mutual solubility of the liquefied gases, which makes the selection of proper temperatures for the cuts a rather arbitrary matter. Furthermore the liquid-gas mixture must be heated several times to much higher temperatures and cooled down again in order to assure a complete recovery of the gas which is to be distilled. Experiments not only with different gases but also for different lengths of time are required to warrant good results.

[4] These data are, however, available to anyone interested.

table 2. Attention is called to the fact that the apparent maximum which was previously reported for the similar reaction with methane (8) completely disappeared when the proper pressure reductions were applied.

(*2*) In agreement with this increase in pressure unsaturated compounds, —acetylene and ethylene,—are formed in the gas phase. There is, however, no evidence of the presence of propylene or higher unsaturates.

TABLE 1

Condensation of ethane under electrical discharge

Results and comparison for 20-minute runs and 60-minute runs

	20 MINUTES		60 MINUTES		
	Run a	Run b	Run a	Run b	Run c
Initial gas taken (cc. at N.T.P.)	268.6	269.8	258.7	257.7	267.9
Initial pressure (reduced)	495.6	489.9	474.5	475.5	490.3
Time of run (minutes)	20	20	60	60	60
Final pressure (reduced)	505.1	503.2	491.7	500.4	513.0
Final gas (cc. at N.T.P.)	274.0	274.0	263.9	272.0	275.5
Analysis of final gases (cc. at N.T.P.):					
CH_4	6.7	6.9	11.8	17.0	17.5
H_2	23.3	21.7	57.3	80.5	69.5
C_2H_2	2.0	0.5	3.0	4.8	3.7
C_2H_4	2.0	2.7	6.5	6.7	7.1
C_2H_6	228.0	221.0	164.9	137.4	151.3
C_3H_8	6.8	8.8	13.6	18.9	15.4
C_4H_{10}	1.9	2.5	6.6	2.6	6.1
C_5H_{12} and higher	0.6	1.5	Traces	1.2	1.6
Total	271.3	265.6	263.7	269.1	272.2
Ratio of $\frac{\text{cc. of final gas}}{\text{cc. of initial gas}}$	1.02	1.02	1.02	1.06	1.03
$H_2/(CH_4 + H_2)$	0.78	0.76	0.83	0.83	0.80
$-$Hydrocarbon/H_2	1.74	2.25	1.64	1.50	1.68
Formula of liquid calculated from atomic balance sheet	$C_nH_{2.2n}$	$C_nH_{2.4n}$	$C_nH_{2.2n}$	$C_nH_{2.1n}$	$C_nH_{2.2n}$
Liquid conversion (per cent)	6.2	7.2	16.3	23.2	20.4
Total hydrocarbon reacted (per cent)	15.1	18.1	36.2	46.7	43.5
Average	16.6		42.1		

(*3*) The percentage of hydrogen in the methane–hydrogen fraction does not change appreciably for different lengths of time. The absolute values lie somewhat lower than are found for ethylene, which is in agreement with the earlier investigations (7).

(*4*) The ratio of $-$H.C./H_2 drops off from 2.0 to 1.6 to 1.4 for 20 minutes, 1 hour, and 8 hours, respectively (6). The same drop holds in general for the condensation of saturates, although the validity of this statement may be somewhat hidden on account of the fluctuations apparent in the present case (cf. table 4). This change of the ratio is mostly due to the decrease in reaction velocity, while the slight increase in hydrogen production for longer runs acts in the same direction.

TABLE 2

Condensation of propane under electrical discharge

Results and comparison for 24.5-minute runs and 73.5-minute runs

	24.5 MINUTES		73.5 MINUTES	
	Run a	Run b	Run a	Run b
Initial gas taken (cc. at N.T.P.)	270.0	262.7	270.0	270.0
Initial pressure (reduced)	501.8	491.2	506.8	508.1
Time of run (minutes)	24.5	24.5	73.5	73.5
Final pressure (reduced)	528.8	516.4	563.7	569.4
Final gas (cc. at N.T.P.)	284	274.2	296.5	300.0
Analysis of final gases (cc. at N.T.P.):				
CH_4	6.1	7.8	27.8	30.2
H_2	16.0	15.4	51.6	60.8
C_2H_2			5.4	4.9
C_2H_4	Traces		6.1	7.4
C_2H_6	3.6	1.2	5.7	8.3
C_3H_4				
C_3H_6	13.2	16.8	15.5	19.1
C_3H_8	236.8	227.7	172.7	161.0
C_4H_{10}	4.1	3.5	6.8	6.2
C_5H_{12}	1.6	1.2	0.8	Traces
Total	281.4	273.6	292.4	297.9
Ratio of $\frac{\text{cc. of final gas}}{\text{cc. of initial gas}}$	1.05	1.05	1.10	1.11
$H_2/(CH_4 + H_2)$	0.72	0.66	0.65	0.67
$-$ Hydrocarbon/H_2	2.07	2.27	1.88	1.79
Formula of liquid calculated from atomic balance sheet	$C_nH_{2.2n}$	$C_nH_{2.6n}$	$C_nH_{2.1n}$	$C_nH_{2.1n}$
Liquid conversion (per cent)	2.7	3.1	18.1	20.6
Total hydrocarbon reacted (per cent)	12.3	13.3	36.0	40.4
Average	12.8		38.2	

(5) The formula calculated for the liquid shows no decisive change as the length of the runs increases. The liquid appears to be slightly richer in hydrogen than the liquid obtained from methane. It should, however, be remembered that the formula of the liquid bears all errors of the analysis, since it is obtained from an atomic balance by difference. This makes any definite statement about changes in this formula rather doubtful, in particular for runs shorter than 60 minutes.

(*6*) As may be seen from the "total hydrocarbon reacted" the condensation has begun to slow up before the expiration of the 60-minute interval: the amount of ethane reacting has just begun to drop below the proportionality relationship.

(*7*) Contrary to (*6*) the liquid production seems to be still proportional to the time. This means that the condensation to liquid must be first delayed or later speeded up, either assumption being identical with an induction period for the first stage of reaction. The induction period is not so pronounced, however, as was found for methane. The fact that the absolute amounts of hydrocarbons produced, e.g., methane, still increase between 20 and 60 minutes further supports this idea and proves incidentally that this induction is not complete in 20 minutes. This long duration of the induction period also tends to make the distinction between the main stage of reaction and the induction period somewhat indefinite.

(*8*) Relatively large amounts of propane are formed. This lends further support to the conclusion that for both electrical and alpha-ray condensation there is a closer relation between ethane and propane as well as between ethylene and propane than exists between ethylene and ethane. This is in agreement with earlier investigations (8, 9).

Propane

In the analyses difficulties were encountered for the first time in the determination of unsaturates in mixtures with higher hydrocarbons by means of bromine water. The latter was found to react distinctly with propane, thus invalidating the results of several runs before the reason for the discrepancies was located. An aqueous (3 per cent) solution of potassium permanganate finally gave satisfactory results (12). The results of the propane runs as compiled in table 2 may be summarized as follows: (*1*) The pressure increase appears to be real and is still more pronounced than for ethane. This is in line with earlier investigations (5). (*2*) The pressure increase would be explained by the presence of unsaturated hydrocarbons in the gas phase. These were actually found. (*3*) Here again the percentage of hydrocarbon in the fraction of methane-hydrogen produced appears to be constant for different lengths of time. (*4*) The hydrogen production, in relation to the total hydrocarbon reacted, and the liquid formula show the same general principles as pointed out for ethane when the length of runs is changed. The former drops slightly; the latter appears to be constant for increase in time. (*5*) A comparison of the liquid production and the total hydrocarbon reacted shows again that there is no direct relation between the two values. An induction period is evident from such a comparison. (*6*) Contrary to what would be expected is the fact that the action on propane is still proportional to the time for 73.5 minutes. In this connection it must be mentioned that propane is the only gas which does not fit into the general scheme, which is discussed more fully in connection with table 7. This is the more surprising as there is no evidence of other irregularities within the propane experiments or when propane is compared with other hydrocarbons.

n-Butane

The condensation of this gas furnishes such great difficulties in many respects that any too definite assertion would appear precarious. This was partially caused by the fact that, in spite of many distillations, the initial gas could not completely be freed from its isomer without application of a special distillation column which was not yet available. Isobutane remained to an extent of approximately one-fourth of the total. Moreover, isobutane seems to be formed under the influence of discharge. Its presence interferes greatly in separating the propane fraction from the

TABLE 3

Condensation of butane under electrical discharge

Preliminary results of one run of 24.5 minutes' duration

Initial gas taken (cc. at N.T.P.)	273.3
Initial pressure (reduced)	512.8
Final pressure (reduced)	550.3
Final gas (cc. at N.T.P.)	286.8
Analysis of final gas (cc. at N.T.P.):	
CH_4	10.5
H_2	15.6
C_2H_2	
C_2H_4	1.1
C_2H_6	5.0
C_3H_4	
C_3H_6	18.1
C_3H_8	48.4
C_4H_6	
C_4H_8	5.0
C_4H_{10}	179.5
C_5H_{12}	1.4
Total	284.6
Ratio of $\frac{\text{cc. of final gas}}{\text{cc. of initial gas}}$	1.05
$H_2/(CH_4 + H_2)$	0.60
$-$ Hydrocarbon/H_2	6.0
Formula of liquid	$C_nH_{2.2n}$
Liquid conversion (per cent)	11.3
Total hydrocarbon reacted (per cent)	34.3
Average of *all* experiments on butane up to now	32.9

butane fraction on account of its high vapor pressure. Chemical methods for separation which are reported in the literature, e.g., use of sulfuric acid of different strengths, have not yielded satisfactory results in our experiments. Therefore, from a good many data, only one run of 24.5 minutes' duration is reported in table 3. It gives an estimate of those data which are most urgently desired, and shows a general analogy to the other paraffin hydrocarbons investigated. One experiment was carried out using isobutane as initial gas. The isobutane was obtained from the attempted separation of this gas from butane (see above) and contained approximately 10 to 15 per cent of normal butane. The gas did not show any appreciable differences as compared with its isomer, which further supports the conclusion of Schoepfle and Fellows (11), based on the octanes, that straight-chain and branched-chain compounds behave essentially in the same manner when exposed to cathode rays. However, the variations in working with these gases are still so large that an improved method may well bring out minor differences which are not detected at the present time.

TABLE 4

Comparison of average values obtained from all experiments

(a) For 20 minutes

	CH_4	C_2H_6	C_3H_8	C_4H_{10}
(1) Pressure increase (per cent)	0	2	5	7
(2) $H_2/(CH_4 + H_2)$		0.78	0.69	0.61
(3) $-H.C./H_2$	1.47	2.01	2.17	5.85(?)
(4) Liquid formula	Approximately $C_nH_{2.1n}$			
(5) Liquid conversion (per cent)	1.1	6.7	2.9(?)	9.8
(6) Hydrocarbon reacted (per cent)	7.9	17.0	12.8(?)	32.9
(7) Number of runs	3	3	2	5

(b) For 60 minutes

(1) Pressure increase (per cent)	0	4	11	
(2) $H_2/(CH_4 + H_2)$		0.82	0.66	
(3) $-H.C./H_2$	1.35	1.61	1.83	
(4) Liquid formula	Approximately $C_nH_{2.1n}$			
(5) Liquid conversion (per cent)	7.5	20.0	19.4	
(6) Hydrocarbon reacted (per cent)	23.1	42.1	38.2	
(7) Number of runs	3	3	2	0

In table 4 the average values of all experiments without any exception are compiled for comparison. Values which are out of line are marked with a question mark. The high value of the ratio $-H.C./H_2$, which was found throughout the butane experiments, should not be taken too seriously, as it might be explained by the difficulties still inherent in these runs.

The low values for liquid production and reaction yield of the propane runs were mentioned above.

Furthermore, the differences and fluctuations in the formula of the liquid should be strongly questioned. Since it is based upon a difference method, the limits of error of each cut of the gas analyses will reappear in the atomic balance, which deprives the formula of a great deal of its significance. As the amount of gas reacted increases and hence the relative error of the analyses decreases with increasing lengths of runs, the liquid formula is more accurate for the 60(73.5)-minute runs than for the 20 (24.5)-minute runs. The only conclusion which appears to be justified is that the liquid shows the same or approximately the same composition regardless of the differences in time of exposure or in the nature of the paraffin used. Therefore the most probable value only is given.

For $H_2/(CH_4 + H_2)$ no value is given in the methane column, since methane is the initial gas of the experiment.

For butane, no runs of longer duration than 24.5 minutes are as yet available.

It is evident that there is no direct relation between liquid production and hydrocarbon reacted.

The pressure increase for different lengths of time as well as for increasing molecular weight of the initial gas is clearly evident from the comparison in this table.

Many conjectures may be made as to the correct interpretation of the second and third horizontal columns in tables 4a and 4b. Since the higher paraffins are acted upon more readily than the lower ones, the continuous increase of the ratio $- H.C./H_2$ is not surprising. The absolute hydrogen production per unit time appears to be approximately constant.

Propylene

The propylene runs are properly compared with the ethylene runs as previously (10) reported. From the analytical standpoint they involve considerably more difficulties than those made with ethylene.

We are greatly indebted to Dr. R. R. Palmer who made the 24.5-minute run in table 5 for us. As the experiment was undertaken with the main purpose of finding out the exact amount of hydrocarbon reacted for 24.5 minutes, a detailed analysis was avoided. For longer times the analysis of the final gases is somewhat easier.

The following conclusions may be drawn from table 5: (*1*) The condensation of propylene shows a distinct decrease of pressure, as was found for ethylene also. (*2*) While the formation of acetylenes plays a minor rôle in the case of saturated hydrocarbons, it is more pronounced for the olefins,—for ethylene as well as for propylene. The analysis of the 24.5-minute run, however, shows more acetylene than would be expected. (*3*) Both the "liquid conversion" in connection with the "total hydrocarbon reacted" and especially the slow start of pressure drop at the beginning of the experiments indicate the existence of an induction period. (*4*) The formula of liquid agrees well with the results for ethylene. (*5*) The value of $- \text{H.C.}/H_2 = 6.0$ and the ratio $H_2/(CH_4 + H_2) = 0.7$ are in agreement with the results of the ethylene runs.

TABLE 5

Condensation of propylene under electrical discharge

Results and comparison for 24.5 minutes and 73.5 minutes

	24.5 MINUTES	73.5 MINUTES	
	Run a	Run a	Run b
Initial gas taken (cc. at N.T.P.)	270.3	260.3	265.7
Initial pressure (reduced)	503	486.6	494.0
Time of run (minutes)	24.5	73.5	73.5
Final pressure (reduced)	432	222.6	216.0
Final gas (cc. at N.T.P.)	236.7	112.0	109.4
Analysis of final gases (cc. at N.T.P.):			
CH_4	4.8	15.0	17.2
H_2	14.0	41.4	41.3
C_2H_2	23.8(?)	6.2	4.4
C_2H_4	14.4	3.0	3.5
C_2H_6		4.4	6.4
C_3H_4		?	?
C_3H_6	140.0	15.0	13.3
C_3H_8	16.9	14.0	17.8
C_4H_6		0.4(?)	?
C_4H_8	18.1	1 (?)	?
C_4H_{10}			
C_6H_{12}	2.8	4.3	1.8
Total	234.8	112.2	110.5
Ratio of $\frac{\text{cc. of final gas}}{\text{cc. of initial gas}}$	0.87	0.43	0.41
$H_2/(CH_4 + H_2)$	0.75	0.73	0.71
$- \text{H.C.}/H_2$	9.3	5.9	6.1
Formula of liquid	$C_nH_{1.5n}$(?)	$C_nH_{1.7n}$	$C_nH_{1.7n}$
Liquid conversion (per cent)	20.4	74.6	77.3
Total hydrocarbon reacted (per cent)	48.2	94.2	95.1
Average		94.6	

In table 6 we have compiled for the sake of comparison the per cent hydrocarbon reacted for the runs reported in this communication together with the corresponding results for methane, ethylene, and acetylene from Paper No. VII in this series.

For the alpha-ray condensation of hydrocarbons, the rates of condensation, i.e., the chemical yields (M) per ion pair (N), are represented by simple M/N ratios: the value of this constant for all saturated hydrocarbons so far investigated is equal to about 2; for all unsaturates it exceeds the value of 2, having the value of 5 for ethylene and even of 20 for acetylene. Since the ionization produced by electrical discharge hinges upon so many different factors in the conditions applied, one cannot expect that the chemical yield should appear to remain so nearly constant for different gases as was found for the methane homologs under influence of alpha-radiation. Taking the amount of hydrocarbons reacted as a measure of the chemical change produced in the gas, one finds that in electrical discharge also the rates of condensation are higher for unsaturates than for saturated hydrocarbons.

TABLE 6

Reaction produced in different hydrocarbons during 20 (24.5) minutes

HYDROCARBON TAKEN	PER CENT REACTED	NO. OF RUNS
Methane	7.9	3
Ethane	17.0	3
Propane	12.9	2
Butane	32.8	5
Ethylene	39.6	3
Propylene	65.0	1
Acetylene	75.5	4

Insofar as the saturated hydrocarbons are concerned, one would expect an increase in condensation for the higher members of the series, since the "stopping power" toward electrons may be assumed to increase with increasing molecular weight. This is verified by the experiments.

One sees that the facts obtained from a study of the lower hydrocarbons fit into the general scheme and extend our knowledge about ionization accompanying electrical discharge.

But even a more quantitative aspect was established. From Lind's (4) study, we know the number of molecules reacting per ion pair if alpha-rays are the ionizing agent. The molecular ionization, i.e., the product of total specific ionization and stopping power $k \times s$ in terms of Bragg's equations (1), is also well known.

In 1928 Lind suggested (3) that the product of the M/N ratio and the molecular ionization may give an explanation, considering the results of Hutchinson and Hinshelwood (2) in the electrical decomposition of ammonia and nitrous oxide.

We have applied the same ideas to our experiments. Pressure drop and change in the nature of the gas complicate the ideal conditions, as was pointed out above. Furthermore, the values of $k \times s$ undergo a continuous change, the more the reaction products with their own values of $k \times s$ enter into the reaction. However, one finds that these ideas approximate most closely the results obtained. Therefore, not the yield of chemical action (M/N) alone is decisive for the electrical discharge, but the product $(M/N) \times ks$ is the integrating factor which seems to govern the electrical condensation of hydrocarbons.

In order to bring out this principle most clearly the experimental values of condensation, as given in table 1, may be compared with the values obtained from the alpha-ray investigations by reduction of the former by an arbitrary factor 3.95. For example, 7.9 divided by 3.95 = 2, 17.0 divided by 3.95 = 4.5, etc. It is evident that a different energy input or a different ozonizer than was employed in our experiments would have resulted in different values of the per cent hydrocarbon reacted, but a proportional change would have been observed in all of the gases. That is to say, any set of conditions which would have given the experimental value for methane would have given 4.5 instead of 17 for ethane, etc. This justifies the division of the "experimental values" by a factor of 3.95 as given in the fourth horizontal column of table 7.

TABLE 7

Comparison of the rates of condensation for different hydrocarbons

	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_2H_4	C_3H_6	C_2H_2
M/N from alpha-ray work	2	2	2	2	5.5	4.9	19.2
Bragg's $k \times s$	1.0	2.0	3.0	4.0	1.7	2.58	1.4
Experimental values from electrical discharge	7.9	17.0	12.9	32.8	39.6	48.0	75.5
Experimental values reduced to basis of $\left(\frac{M}{N}\right)_{CH_4} = 2$	2*	4.5	3.3	8.3	9.9	12.2	19.1
$\frac{M}{N} \times ks$	2	4	6	8	9.4	12.6	27.7

* This is arbitrarily set equal to 2 for methane, for the reasons set forth above.

To what extent our claim appears to be justified may be seen from the last two horizontal columns in table 2. Only the results of the acetylene condensation and of the propane condensation do not follow these considerations. However, for acetylene there exists an inhibiting factor, the nature of which we have thus far been unable to detect. If the reaction is slowed up in some way, this must result in lowering the rate of condensation of this gas and hence may account for the discrepancy between the acetylene runs and the general results obtained. For propane, the value of 3.3 as obtained by the experiments is in disagreement with the general increase of the rate for increasing molecular weight as well as with the value of 6 expected from the quantitative evaluation of the results. Since no explanation can be given for this, the propane runs certainly remain out of line.

SUMMARY

1. The condensation of ethane, propane, butane, and propylene under influence of electrical discharge has been studied with special consideration of its dependence upon the time.

2. A number of principles, which shed further light upon the extremely complex nature of electrical condensations, have been derived from detailed analyses of the reaction products.

3. The decisive differences between saturated and unsaturated hydrocarbons place paraffins and olefins in two different groups. More comprehensive data are offered to substantiate the group characteristics of these gases with special reference to different lengths of time.

4. A comparatively long induction period is found for each one of the gases investigated.

5. A comparison of different rates has been given for the electrical condensation of methane, ethane, propane, butane, ethylene, propylene, and acetylene. The product of molecular ionization and of the chemical yield under alpha-radiation checks most closely the results obtained and is considered to be the governing factor for the electrical condensation of gaseous hydrocarbons.

The authors wish to thank Mr. John L. Wilson who assisted in this work as American Petroleum Institute Research Assistant.

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NEW BOOKS

Numerical Data on Radioactivity. Nuclear Physics. Transmutations. Neutrons. Positrons. By I. JOLIOT-CURIE, B. GRINBERG, R. J. WALEN. Excerpt from Annual Tables of Constants. 57 pp. Paris: Gauthier-Villars, 1931-36.

This represents the data in the field of radioactivity and nuclear physics published during the period 1931 to 1936. Naturally most of the space is devoted to the new nuclear transmutations and to artificial radioactivity. Of the elements Nos. 1 to 30, only helium has not been transmuted, and only hydrogen, helium, beryllium, and chromium have not been shown to have artificial radioactive isotopes, though those for nickel and cobalt have not been positively identified. From No. 31 to No. 92 only nine elements of the non-radioactive elements have not been transmuted or made radioactive. In addition, new artificially radioactive isotopes have been produced from thorium and uranium.

S. C. LIND.

The Theory of the Properties of Metals and Alloys. By N. F. MOTT AND H. JONES. Oxford University Press, 1936.

The Theory of Metals. By A. H. WILSON. Cambridge University Press, 1936.

These two important books on the application of quantum mechanical theory to the theory of metals are both products of the school of younger English theoretical physicists. Both cover much the same territory,—namely, the theory of the *electronic* properties of metals and alloys,—and restrict themselves in the main to the mathematical theory. No attempt is made to survey the literature on the technical properties of the metallic state.

In spite of their similarity in scope, the two books differ considerably in emphasis and point of view. For the reader interested in obtaining a comprehensive treatment of the theory and its principal applications, with attention directed primarily to the successes of the theory rather than its limitations, the first volume, that of Mott and Jones, will probably be the more appealing. The first chapter gives a general discussion of the theory of the thermodynamic properties of the crystal lattice (specific heat and equation of state theory) and of the Bragg-Williams order-disorder theory of alloys, and is largely informative in nature. The second chapter gives a general treatment of the theory of electronic states in metallic lattices, with a good treatment of Brillouin zones. The bulk of the book is then devoted to various standard problems, magnetic properties, electrical resistance, etc. Attention may be called particularly to the discussions on cohesion, the resistance of liquid metals, and the various sections on alloys, all of which are largely absent from other books on the subject. The newer discussions of Slater on ferromagnetism and superconductivity are of course not treated. The discussion of the electrical resistance of bismuth, which has been contributed to the theory by Dr. Jones, will also be of special interest to some readers. This book can be recommended as one of the best and most informative works which has yet appeared in this field.

On turning to the volume by Dr. Wilson, we find the theory treated in a quite different spirit. Wilson adopts a much more critical attitude towards the theory, and writes not so much to inform the reader of its successful applications as to present a critical discussion of its foundations and method of approach to the problem in hand. The list of general topics studied is much the same as in the work of Mott and Jones, but the argumentation is much closer, which may make the book somewhat difficult reading for one without any particular previous acquaintance with the theory. It is not possible here to give any statement of the general criticisms which the author brings forth against the details of particular applications which have been made of the theory. On the whole these refer to well-known difficulties in the determination of the energy distribution of the electrons and the proper analysis of the lattice vibrations, particularly at low temperatures. The reviewer is quite in sympathy with the author, and believes that his discussion is a valuable contribution to the literature as well as a counterpoise to the prevailing tendency to overlook the deficiencies of the theory for the sake of its successes. It can only be hoped that it will soon be possible to remove at least some of its weaknesses and to put it on a firmer foundation.

E. L. HILL.

Reactivity of Solids (Reaktionsfähigkeit fester Stoffe). By J. A. HEDVALL. 243 pp.; 50 illus. Leipzig: Verlag Johann Ambrosius Barth, 1938. Price: 18 RM (paper); 19.20 RM (cloth).

The ancient dictum of Aristotle that "corpora non agunt nisi liquida," which means that only liquids can react, is quite wrong, since even in solids the atoms are in motion. Owing, however, to the slow diffusion velocity of atoms through the layer of reaction product, reactions of solids at low temperature are almost brought to a stop. For this reason such reactions have not been commonly recognized except by students of high-temperature phenomena.

Professor Hedvall, who has by his numerous researches made himself an authority in this field, points out that the weaker the forces holding the particles in their lattices the more easily will reactions occur, and every factor which weakens these forces will enhance the reactivity.

The book is divided into three parts. The first, which covers about one-fourth of the work, is concerned with the fundamental principles of crystal structure and with their relation to chemical composition. These developments have been of the greatest significance in the understanding of solid phase reactions. The various lattice types, ionic, molecular, metallic, layer, etc., are described and illustrated. The principles of polymorphism are discussed. A section is devoted to lattice energies and to lattice vibrations with their characteristic frequencies. An important discussion is given of surface properties of solids, in regard to recrystallization processes and to catalytic effects on mixed-oxide catalysts.

If the reader is already familiar with the general principles of crystal chemistry, he will undoubtedly find the second part of the book the most instructive. Part II covers more than one-half of the book. This second part treats of the historical developments in the subject of reactivity of solids, attention being given to experimental methods and to the deduction of the underlying principles. A systematic treatment is given of reactions involving ionic interchange (Platzwechselreaktionen) for bivalent oxides with sulfates, carbonates, phosphates, and silicates. The quantitative study of rates of gas-forming reactions by Braune, Jander, Fishbeck, and others is discussed. The pioneering work of Hüttig on the nature of intermediate phases is described in detail. The important studies of Hevesy, Phipps, Biltz, and others on electric conductivity and on diffusion in solids is presented and discussed to show the factors which determine ionic mobility in solids. The rôles of polymorphic change, radiation, etc., in loosening the lattice and permitting greater ease of atomic movement are described. The past history of an oxide, for example, whether formed from sulfate or carbonate, is shown to have great effect on its properties. Some discussion is given of fluorescence and phosphorescence.

The third part of the book should be of special value to ceramic and metallurgical workers. Reactions of glass melting, properties of certain refractories, and of certain calcined oxide colors are discussed. Some attention is given to the thermal properties of clays, chromite, dolomite, and other minerals. Sintering and grain growth in metal powders and catalysis of certain reactions by gas or liquid are also discussed.

In the writer's opinion this book marks a definite step forward in its field, for it brings together and treats systematically the observations and theories which hitherto have been scattered through many scientific journals. The book is well documented with literature references. Every worker who deals with the heat treatment of inorganic materials will find it full of stimulating ideas and concepts.

NELSON W. TAYLOR.

Experimental Food Study. By AGNES FAY MORGAN AND IRENE SANBORN HALL. 414 pp. New York: Farrar and Rinehart, Inc. Price: $3.00.

This laboratory text, while designed for beginning students, is based upon organic and physicochemical principles in large part. Since the students who will use it will not ordinarily have had extensive training in the physical and biological sciences it follows, perforce, that the treatment accorded these principles has been made very simple and elementary.

Thus in the early portion of the text appears a discussion of the properties of solutions, including vapor pressure, boiling point, and the relation of such properties to cooking problems. Experiments which demonstrate these principles are outlined. Particular reference is made to sugar solutions and the fundamentals of candy making. This is followed by a discussion of the freezing point of solutions which, in turn, is tied into the practical applications made in ice cream production.

Chemical constitution and the descriptive biochemistry of the carbohydrates is covered briefly, and this is followed by a chapter on acidity, pH, and buffers.

In part II appears a chapter on the colloidal state, and also a discussion of emulsions and foams; in addition there are chapters on proteins, fats, and the principal classes of food materials. An appendix includes various useful tables of data, including the proximate analysis and the mineral and vitamin content of the common foods.

The text and the series of laboratory experiments, which are presented in problem form, should prove stimulating to the students and encourage them in the effort to relate culinary practices to fundamental scientific principles.

C. H. BAILEY.

The Properties and Functions of Membranes, Natural and Artificial. A General Discussion held by The Faraday Society. April, 1937.

This General Discussion represents the Fifth Colloid Meeting organized by the Colloid Committee of the Faraday Society, which also comprises representatives of other societies, among them mainly societies interested in physiology and biology. Intentionally, therefore, the biological side of the matter was emphasized and the properties and functions of natural membranes were extensively discussed. Though very many facts are known, they appear most complicated, sometimes even conflicting; only a few, more general, conceptions can be extracted. This fairly negative result need not be considered disappointing; biological processes are probably centered in natural membranes, may they actually be two-dimensional organs (cf. A. Krogh's introductory paper) or merely membranes of a markedly specialized permeability. Hence we would have to know much more about life in general to be able to say more essential things about natural membranes and their functions.

Preliminary conceptions of the structure of the plasma membrane are frequently discussed. Perhaps Bungenberg de Jong's idea (mentioned on p. 990) of a membrane made of an amphoteric coacervate containing lecithin and the ions of macromolecules and other substances, presumably arranged in a special way towards the lecithin layer, would have deserved to be more thoroughly treated. Staudinger's interesting suggestion (Ann. **474**, 161 (1929)) that hormones and vitamins may act in such very small amounts because they change the permeability of a membrane, a conception fitting Bungenberg de Jong's membrane model well, also does not appear to be mentioned.

Among the lectures concerning artificial membranes Elford's contribution is outstanding. He describes the method for making uniform collodion membranes of graded porosities and their use as ultrafilters. His table on p. 1103, containing the diameters of small particles of biological importance, from bacilli (*Bacillus prodigiosus* 750 $m\mu$) to the molecule of egg albumin (4 $m\mu$), with the viri and phages between 250 and 10 $m\mu$, shows impressively that the latter are established as a new type of colloidal state.

H. Freundlich.