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THE ELECTRICAL DOUBLE LAYER.

GENERAL DISCUSSION.[*]

Dr. M. H. Gorin (*New York*) (with regard to the paper of Tiselius and Svensson, page 16) : In comparing the procedures of obtaining the net charge of proteins by membrane potentials and titration curves two points arise. Titration curves primarily give information about acid and base binding and cannot without further assumptions be used to furnish information about specific interaction of the protein with other ions in the system. On the other hand, in the ideal sense, membrane potentials should give this information and, therefore, should yield an unequivocal value of the net charge. However, in the presence of considerable electrolyte and protein some uncertainties are present in the interpretation and corrections involved in the calculation of the net charge from membrane potentials. Titration data, on the other hand, obtained in regions not far removed from neutrality yield definite information about changes in acid and base binding, for the titration correction in the change in hydrogen ion of the solvent is usually negligibly small under these conditions.

The method introduced by Abramson[1] for determining the net charge from titration curves in the neighbourhood of the isoelectric point involves the assumption that in this region the binding of ions other than hydroxyl and hydrogen is approximately independent of *p*H. This assumption appears to be ordinarily justifiable since the non-specific interaction of ions with protein should be expected to depend on the total charge of the protein rather than upon its net charge. In addition, this assumption also has justification because of its success in correlating experiment with theory.

The two methods (titration curve and membrane potential) cannot be directly compared in the case of the very valuable data of Tiselius and Svensson for the measurements are so far removed from the isoelectric point that the assumption involved in applying the titration curve analysis would be open to question. In comparing, however, the conclusions of Tiselius and Svensson based on the present data and the conclusions of Moyer and Abels[2] on some of Tiselius' older data in the neighbourhood of the isoelectric point, there remains a discrepancy of 20 %. It was shown[3] that in order to get agreement with the equation

$$v = \frac{Qf(\kappa r)}{6\pi\eta r(1 + \kappa r)}$$

that a value of the radius of 32·6 A. had to be assumed. On the other hand, Tiselius and Svensson were able to get agreement using membrane potential data by assuming a value of 27·5 A. for the radius. This amounts to about a 20 % difference in the predicted mobility from the same data.

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[*] On papers published in this volume at pages 1 *et seqq*.

[1] H. A. Abramson, *J. Gen. Physiol.*, 1932, **15**, 575 ; *Electrokinetic Phenomena*, New York, 1934, Chapter V.

[2] Moyer and Abels, *J. Biol. Chem.*, 1937, **121**, 331.

[3] H. A. Abramson, M. H. Gorin, and L. S. Moyer, *Chem. Reviews*, 1939, **24**, 345.

The comparison above, of course, is made at ionic strength of 0·02. The discrepancy between the two methods would undoubtedly disappear at infinite.

It would be of interest to apply the more complete equation [3]

$$v = \frac{Qf(\kappa r)(1 + \kappa r_i)}{6\pi\eta r[1 + \kappa(r + r_i)]},$$

where r_i is the "average" radius of electrolyte ions in the solution, to the data of Tiselius and Svensson. The term $(1 + \kappa r_i)$ would be of considerable importance at the higher ionic strengths (for $r_i = 3{\cdot}0$ A., $1 + \kappa r_i = 1{\cdot}437$ at $\mu = 0{\cdot}20$).

Prof. G. S. Adair (*Cambridge*) : Dr. Gorin has expressed doubt as to the values of the valence of egg albumin quoted by Tiselius and Svenson [4] on the grounds that the conditions are unfavourable for the application of Abramson's method of calculation. It would appear that he has overlooked the fact that these values for the valence of egg albumin are supported by an extensive series of measurements of membrane potentials with different concentrations of protein, different ionic strengths of buffers and varying proportions of bivalent and univalent phosphates. Moreover, confirmatory evidence has been obtained from determinations of osmotic pressures and the distribution of ions across the membranes.[5]

No colloidal electrolyte is known to me for which the evidence for the value of the valence (z_p) is better established.

Prof. H. A. Abramson (*New York*) (on the same paper) : It is always a pleasure to hear from Professor Tiselius. There are several points in his paper which are of interest to me at this time. Prof. Tiselius mentions that Moyer and I have studied the relation between the migration velocity of protein-coated particles and the titration curves of the respective proteins. I would like to add that we have not only studied the migration velocity of protein-coated particles but we also have compared the electric mobility of *dissolved* protein with the titration curves of the protein. Examples of this type of comparison on the electric mobility of dissolved protein and the titration curves of dissolved protein were given at the symposium and have also been published elsewhere. The data for the dissolved proteins were those taken from Tiselius' own work. In addition, the effects of gelatin and deaminized gelatin coated quartz particles in aqueous media and in alcoholic media have been definitely correlated with the titration curves. Indeed, the titration curve of deaminised gelatin has been predicted from electric mobilities. All of these data, both for dissolved proteins and adsorbed proteins, fit in with the notion that the titration curves are certainly very useful in handling problems dealing with the net charge of proteins and that the titration curves within the limits of experimental error and within boundaries of reasonable assumptions still may function to aid in the explanation of electrokinetic data.[6]

Investigators who publish data on the microscopic method of electrophoresis should give a value for some standard particle obtained by their technique. In this way a better basis for discussing the theory of electrophoresis will be obtained.

Many measurements appearing in the literature are not quantitative, although quantitative conclusions are frequently drawn. May I therefore suggest that the human red cell be adopted as a standard when suspended in M/15 phosphate buffer at *p*H 7·4 ? This solution has a specific resistance

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[4] Tiselius and Svenson, *Trans. Farad. Soc.*, 1940, **36**, 16.

[5] Adair and Adair, *ibid.*, 23.

[6] See, for example : H. A. Abramson, *J. Gen. Physiol.*, 1932, **15**, 575 ; J. Daniel, *ibid.*, 1933, **16**, 457 ; L. S. Moyer and J. C. Abels, *J. Biol. Chem.*, 1937, **121**, 331 ; L. S. Moyer and H. A. Abramson, *ibid.*, 1938, **123**, 391 ; M. H. Gorin, L. S. Moyer, and H. A. Abramson, *Chem. Rev.*, 1939, **24**, 2.

of approximately 126 ohms. The value for the electrical mobility of the red cell which I obtained about ten years ago has been confirmed by Moyer and also by other investigators at the General Electric Company.

Dr. J. J. Bikerman (*Glasgow*) : on the papers of Abramson and of Powney and Wood (pp. 15, 59) : The charge-concentration curves of Abramson (p. 15) are calculated neglecting the effect of the surface conductance on mobility. In order to show the magnitude of this effect Fig. i opposite has been drawn. It is based on Fig. 1 in the paper of Powney and Wood (p. 59), and refers to their curve for NaCl. The normality of NaCl is plotted on the abscisse. Curve 2 shows the ζ potential calculated from equation (8) on page 157, and has to be compared with curve 1 which represents the uncorrected values of ζ and is identical with the NaCl curve of Powney and Wood. It is seen that ζ in water (whose conductivity was $2 \cdot 10^{-6}$ ohm^{-1} cm.$^{-1}$) was about 0·093 volt ; according to Smoluchowski this value would correspond to the mobility of 7·4 μ/sec. per volt./cm. Consequently the introduction of the surface conductance lets disappear the maxima of ζ for $NaHCO_3$ and Na_2CO_3 ; only NaOH considerably increases the potential of paraffin oil droplets. The little precision of the calculation does not warrant a decision on the maxima of the curves for Na_2SiO_3 and $Na_4P_2O_7$.

Curve 3 represents the surface charge densities σ ((in arbitrary units) based on curve 1 and starting, like Abramson's curves, from nothing at concentration = 0. When the corrected values of ζ are used and the ions present in water are taken into account, curve 4 results. It is seen that the increase of charge on an addition of electrolytes is less pronounced than Fig. 10 on page 15 would let one believe.

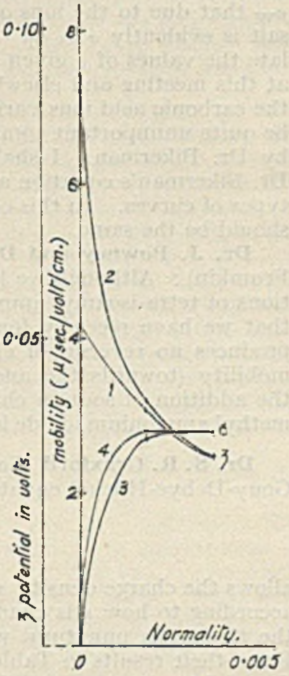

FIG. i.

Prof. A. Frumkin (*Moscow*) (on the paper of Powney and Wood) : It is of interest to mention the paper of A. Gilman and N. Bach,[7] who observed that a gas bubble acquires a negative electrokinetic charge in a solution of sodium palmitate and a positive one in a solution of tetra-isoamyl-ammonium chloride.

Prof. H. A. Abramson (*New York*) (in reply to Dr. Bikerman) : The charge concentration curves calculated by Dr. J. J. Bikerman are of great interest, and I am very pleased to see that the general shape of Bikerman's σ-c curve agrees with that already published. Unquestionably, Dr. Bikerman's correction in the lower concentration range is of immediate importance. Also, pertinent to our discussion is the fact that the shape of Dr. Bikerman's curve approaches our curves at higher concentrations of salt where the correction for surface conductance becomes very small. There is one point which I believe should be clarified. Dr. Bikerman has stated that my curves start from zero where the concentration is equal to zero. As a matter of fact, all of the σ-c curves which I have published here and elsewhere have been corrected as far as possible for the ions present in the water itself. This is done in the following way : It is assumed that at room temperature there are about 1 × 10^{-5} moles per litre of carbonic acid dissolved. Since k'_a of carbonic acid is of the order of

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[7] *Acta Physicochimica, U.R.S.S.*, 1938, 9, 27.

3×10^{-7}, a solution in equilibrium with the carbon dioxide of the air has approximately 2×10^{-6} moles of H^+ and HCO_3^-. In order to calculate the change of the net charge due to added salts, the value of the net charge in this equilibrium water should be first estimated. Therefore, if σ_T is the charge due to the ions of dissolved carbonic acid and the added salt, and σ_W that due to the ions of the carbonic acid alone, the charge due to the salt is evidently $\sigma = \sigma_T - \sigma_W$. This relationship has been used to calculate the values of σ given in all of my curves, both in the paper presented at this meeting and elsewhere. Of course, it is possible that the effect of the carbonic acid ions varies with the ionic strength but that effect should be quite unimportant compared with other corrections which are proposed by Dr. Bikerman. I shall look forward to seeing calculations made by Dr. Bikerman's equation and the simpler form with comparison of the two types of curves. In this case the correction for the ionic strength of water should be the same.

Dr. J. Powney and Dr. L. J. Wood (*London*) (in reply to Professor Frumkin): Although we have no data for cataphoretic mobilities in solutions of tetra-isoamyl ammonium chloride, it is perhaps worth mentioning that we have recently found that 0·2 % tetra-methyl ammonium iodide produces no reversal of charge on Nujol droplets, the small decrease in mobility (towards the anode) being comparable with that produced by the addition of sodium chloride. The interfacial activity of 0·2 % tetra-methyl ammonium iodide is only slight (γ xylene = 34 dynes/cm. at 20° C.).

Dr. S. R. Craxford (*London*) (on Ham and Dean's paper, p. 52): The Gouy-Debye-Hückel equation for the diffuse part of the double layer

$$\zeta = \frac{\alpha 4\pi r}{D(1 + \kappa r)}$$

allows the charge density α either to increase or to decrease as ζ decreases, according to how κ is changing, but Drs. Ham and Dean appear to reject the theory as unnatural when it allows α to increase while ζ decreases. From their results in Table I therefore, they consider the theory to break down above a concentration of about 0·00001, but yet according to the results in Table II it holds good up to 0·005 m. Actually for these exceedingly small potentials there is no reason for the Debye-Hückel-Gouy equation to break down seriously below about 0·001 m. They also say that as the amount of $LaCl_3$ added increases and α increases while ζ becomes very small, then if the $LaCl_3$ had been a little more active ζ would have become zero and hence α would have had suddenly to decrease from a high value to zero, which would be improbable. Here it seems that it is the supposition which is itself improbable, because ζ is only approaching zero asymptotically and will never reach it. Hence α may go on steadily increasing (up to the limit of applicability of the theory). Finally, Ham and Dean rightly accept the Stern theory of the double layer in spite of the fact that it contains this Gouy equation for the diffuse part of the layer, and degenerates to it for very dilute solutions and very small potential differences.

Dr. J. J. Bikerman (*Glasgow*) (on the same paper): Paraffin oil emulsions coagulate when their ζ potential falls below about 0·03 volt. Is any explanation forthcoming of why the octadecane sols were stable at ζ = 0·001 volt? It is true that the measurements were carried out some degrees below the freezing point of octadecane, but this fact alone cannot account for the extraordinary difference of stabilities.

Dr. A. J. Ham (*Liverpool*) in reply: The experience of this laboratory is that the critical ζ potential of 0·03 volt claimed by Powis[8] has little significance for much work on hydrocarbon-water emulsions. Other hydrocarbons have given results closely analogous to those which we quoted for octadecane, and it appears that the time factor is all important.

[8] *Z. physik. Chem.*, 89, 186.

All such emulsions will coagulate eventually, and Powis' data refer to appreciable changes in turbidity over a matter of days as "rapid coagulation."

In our experiments emulsions were prepared and left for 24 hours when particles of approximately uniform size remained, coarser particles leaving the emulsion. Various salts were then added to such emulsions —in some cases rendering ζ as low as 0·001 volt—and a mobility determination made; the salts did not affect the stability of the emulsions in the time during which temperature equilibrium was being reached and determinations of mobility carried out, which in no case exceeded one hour.

Dr. J. J. Bikerman (*Glasgow*) (on the paper of Prof. Gortner, p. 66): I agree with Professor Gortner that the high streaming potentials observed in his laboratory "can only be accounted for by assuming a transfer of ions from one electrode to the other." I would only suppress the word "high" as it is difficult to envisage a constant current produced by displacement of dipoles only. If we admit that streaming potentials (and the ζ potentials derived from them) are due to ions, then the ions present in the organic liquids (as distinct from the liquids themselves) will be responsible for the observed effects. Some ions may have contaminated the liquid before it has been placed in the streaming cell, some others may enter the liquid from the cellulose or alumina membranes; in a few cases the electrolytic dissociation of the liquid may also produce ions. The relative importance of these various sources of ions can be estimated when the specific conductivity of the liquid both outside and in the diaphragm is known.

Table I is obviously misprinted as the ratio $\zeta : \delta e$ is not always the same for cellulose and Al_2O_3.

Prof. R. A. Gortner (*Minnesota*), in reply to Dr. J. J. Bikerman: The origin of the potentials is unquestionably due to "the transference of ions from one electrode to the other," but the real problem is why there are sign reversals in a given solid-liquid homologous series. With such reversals the sign of the potential can hardly be due to ions derived from the solid phase. Since such reversals are shown where both cellulose and Al_2O_3 are the solid phase and since certain systems give rise to a different sign against a cellulose surface than is the case for an Al_2O_3 surface, it would appear from our studies that the solid surface has a specific influence upon the "dissociation" of the liquid. It was this possibility which led me to suggest "that a specific surface forces a dissociation of these organic molecules."

I doubt very seriously whether the ionic behaviour can be estimated by comparing only the specific conductivity of the liquid outside and in the diaphragm. Certainly such studies would not reveal the sign of the potential nor apparently the magnitude of the potential. "Surface conductance"[9] is relatively important in cellulose-organic liquid systems, *i.e.*, the conductance in the diaphragm is much larger than conductance of the liquid in bulk. On the other hand surface conductance in Al_2O_3-organic liquid systems is not an important factor.

I am indeed grateful to Dr. Bikerman for calling attention to certain gross errors in the calculation of some of the data in the table on page 66. The values for δe of all of the alcohols in contact with cellulose, with the exception of heptyl alcohol, are in error by a misplacement of the decimal point and should be ten times as great as printed. I have recalculated the original data with the results shown in Table I.

TABLE I.

Organic Liquid.	Cellulose-liquid Interface δe (e.s.u. × 10^6).
Methyl alcohol	464·1
Ethyl alcohol	136·3
n-propyl alcohol	101·3
iso-propyl alcohol	112·8
n-butyl alcohol	265·2
iso-butyl alcohol	66·4
n-hexyl alcohol	118·4
n-heptyl alcohol	18·8

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[9] *Colloid Symposium Monograph*, VI, 41-52, 1928.

In recalculating the original table two other errors were found. $\delta\varepsilon$ for *n*-propionic acid : Al_2O_3 should be 16·0 × 10^{-6} instead of 16·7 × 10^{-6} as printed, and the ζ-potential for ethyl *n*-propionate : Al_2O_3 should be − 19·1 mv. instead of − 10·8 mv. as printed.

With the above corrections the ratios of ζ to $\delta\varepsilon$ are all within satisfactory agreement. Minor differences in the ratios are accounted for by normal experimental errors.

Dr. J. J. Bikerman (*Glasgow*), to the paper of Rutgers, pp. 71, 76: Equation (8) on p. 71 assumes that the walls of the capillary are perfectly smooth. In reality every glass surface, and especially that cleaned by strong acids, etc., is rough, and the ratio $\Omega : S$ of the circumference of the capillary to its cross-section is larger than $2/r$, r being the radius of the capillary. Fortunately a reasonable increase of the factor $2/r$ alters the value of ζ (see equation (15)) by a few per cents. only, but it strongly reduces the value of the surface conductance σ_w (see equation (14)). If the real surface area of the capillaries was 4 times as large as their geometrical area then the values of σ_w for very dilute KCl solutions would agree with the theoretical values. But there is certainly no agreement between the theory and the high values of σ_w in more concentrated KCl solutions. Maybe the more detailed account of the experiments by Mr. Verlende will help to clear up this discrepancy. It is, of course, obvious that the error made when calculating σ_w from equation (14) is the higher the nearer are the values of ζ_2 and ζ_1.

Prof. A. J. Rutgers (*Ghent*), in reply: I do not think that Eqn. (8) assumes that the walls of the capillary are perfectly smooth. From Eqn. (8) it follows that σ_w is the surface conductance per cm. of circumference of the capillary, *this circumference being measured with the ordinary macroscopic means.* The only supposition made is, that this σ_w will be the same for walls of capillaries of different diameters, which seems a very plausible assumption. As a consequence of this I think that Eqn. (14) and Eqn. (15) need no correction.

The point raised by Dr. Bikerman becomes important as soon as we try to compare experimental and theoretical values of σ_w. Nevertheless I think that the big ratio of calculated and theoretical values of σ_w can only partially be explained by the lack of smoothness of the wall ; this ratio, *e.g.*, depends strongly on the concentration of electrolyte, and it is difficult to understand why the correction factor, provided by the lack of smoothness—which is of a geometrical nature—should depend so strongly on concentration.

Dr. J. J. Bikerman (*Glasgow*), to the papers of Craxford, Frumkin, and Barclay and Butler, pp. 89, 125, and 129 : The capacity of the double layer calculated from the theory of Gouy is 250 μF/sq. cm. according to Craxford (p. 89), 240 μF/sq. cm. according to Barclay and Butler (p. 129), and 2·36 μF/sq. cm. according to Frumkin (p. 125). I find in agreement with Frumkin 2·3 μF/sq. cm. for the minimum of the capacity curve in a 10^{-4} N solution at 20°. At the potential 0·233 volt (the potential at the minimum is assumed to be zero) Gouy's capacity is 24 μF/sq. cm. whilst the lowest curve of Fig. 4 (p. 124) gives 15 and 27 μF/sq. cm. In view of the fact that Gouy's theory is perfectly general and contains no adjustable constants the agreement is rather convincing. It would be futile to expect a closer agreement here or an agreement at still higher potentials or higher concentrations as Gouy's derivation neglects the inter-ionic forces ; already at 0·233 volt in 10^{-4} N solutions the concentration of " counter-ions " at the mercury-solution boundary is about 1 N, that is so large that individual properties of ions (their apparent radius, etc.), can no longer be neglected. An extension of Gouy's theory so as to include the inter-ionic forces would be more satisfactory than the cutting of the potential field in two independent parts like those assumed by the theory of Stern.

May I also correct a statement repeated in several papers? Helmholtz's double layer does not consist of two condenser plates; that is the picture suggested by Lamb. There is no contrast between Helmholtz's and Gouy's theories, but Gouy determined the relation between potential and distance which was indefinite in Helmholtz's equations.

Prof. A. Frumkin (*Moscow*), on the paper by Craxford, p. 93: Dr. Craxford quotes my paper in *Z. physikal. Chem.*, 1923, as supporting the concentration polarisation theory of electrocapillarity which he rejects. I think this indication is incorrect. I never expressed the opinion that the surface conditions of mercury in the capillary electrometer are determined in a kinetic sense by the volume concentration of mercurous ions regardless of the value of this latter. The kinetic mechanism is not discussed in the paper quoted, but considering in another paper the mechanism of the dropping electrode,[10] I make just the same distinction between the behaviour of mercury in solutions containing high and low concentrations of mercurous ions as Dr. Craxford.

The use of thermodynamic symbols relating to mercurous ions in the solution in the derivation of Lippmann's equation appears to me legitimate as far as an idealised equilibrium system is concerned; the results obtained must be certainly correct independently of the physical meaning of the concentrations involved. Besides, the difficulty encountered in deriving Lippmann's equation from the equation of Gibbs if there is any can be avoided if the mercurous ion is considered as a component of the metallic phase. The equilibrium conditions are certainly not strictly realised in the capillary electrometer, and it is impossible to say *a priori* without further experiments whether the result of the thermodynamic theory can be applied to the experimental electrocapillary curve, but the same can be said if Lippmann's equation is derived from the conception of a completely polarisable electrode.

Dr. S. R. Craxford (*London*), in reply: It is very gratifying to receive Professor Frumkin's unambiguous statement that he also rejects the concentration polarisation theory as the kinetic basis of the behaviour of a polarised mercury solution interphase. But in spite of this he is still prepared to use this admittedly false assumption as the basis of the thermodynamical theory of the interphase, "as far as an idealised equilibrium system is concerned". Since thermodynamics is merely another way of writing the results of the kinetic theory, it cannot be sound to apply thermodynamic equations to systems of such low concentration that the usual kinetic theory equations become meaningless. His use of the thermodynamic theory of concentration polarisation for such cases made it not unreasonable to suppose that he also believed the assumptions underlying those equations to be true.

TABLE 2.

Charge/cm.² microcoulombs.	Capacity/cm.² microfarads.
0·0	74
0·176	77
3·31	85
12·8	131
26·0	202
41·3	272
131·0	590

Dr. S. R. Craxford (*London*), in reply to Dr. Bikerman: I had not stressed the point about the high capacities obtained from Gouy's theory of the diffuse layer, since that theory is only important nowadays as a special case of Stern's theory. But since Dr. Bikerman has questioned the figure I quoted, I will supplement it by Table 2 recalculated from Gouy[11] for $N/10$ solutions. For similar surface charges these capacities are all very much bigger than the experimental value of 19·5 microfarads. It is not surprising that Dr. Bikerman's results in 0·0004 N solutions agree with Gouy's theory because for such dilute solutions Stern's equation approximates to Gouy's. But however Gouy's theory is elaborated by taking inter-ionic forces into account, it will still be impossible to make

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[10] *Erg. ex. Naturwiss.*, 1928, 7, 243.

[11] *Ann. Physique*, 1917, 7, 163.

it into a general theory of the double layer, as it can give no information about the one integration limit required for its completion, *i.e.*, the number of ions in contact with the interface. Stern's assumption as to this may not be perfect but it is the only one produced so far.

Dr. J. J. Bikerman (*Glasgow*), in reply to Dr. Craxford : According to Gouy's equations the concentration of "counter-ions" near the surface, when the surface in a N/10 solution is charged to 131 microcoulombs/cm.^{2}, is some 500 N. It is evident that the equations are not applicable in such cases, whatever the experimental value for the capacity might be.

It seems natural to attempt an adaptation of the theory of Gouy to higher concentrations and higher potentials without sacrificing (as Stern's theory does) the sound basis of Gouy's reasoning.

In addition to inter-ionic forces there must be considered the competition between ions and the molecules of solvent for the space near the interface. If the field intensity in the distance x from the interface is X (towards the boundary), the force on the charge e is Xe. If the molecule of the solvent has the moment μ the force pushing the molecule to the boundary is $-\mu dX/dx$. Both "counter-ions" and dipoles tend to crowd into the surface layer. As the compressibility of liquids is very small, an ion can move nearer to the interface only by displacing (approximately) one molecule from its position. The resulting electric force on the ion is, therefore, $Xe - (-\mu dX/dx)$ instead of Xe as before. When the double layer is very diffuse dX/dx is small, and the original equations of Gouy are valid ; at high densities of charge and high concentrations dX/dx is large and reduces the attraction of "counter-ions" to the interface quite considerably. Thus, the term $\mu dX/dx$ makes the diffuse double layer more diffuse ; its "thickness" increases and, consequently, its capacity diminishes.

If Xe were equal to $-\mu dX/dx$ the resulting electric force on the ion were $= 0$. As μ/e is about $4 \cdot 10^{-9}$ cm., this would occur if the chief drop of the potential took place in a layer $4 \cdot 10^{-9}$ cm. deep. The "equivalent thickness of the double layer" corresponding to the capacity of 590 μF/sq. cm. is about $12 \cdot 10^{-9}$ cm. The term $\mu dX/dx$ in this case is of the same order of magnitude as Xe.

A detailed discussion of the above theory will be published later. Then Stern's assumption will cease to be "the only one produced so far."

Dr. Craxford maintains that Gouy's theory gives no information regarding the number of ions in contact with the interface. If the concentration of ions far from the interface is C, and the potential difference between the water side of the interface and the solution far from it is ζ, then the average concentration of ions in contact with the interface is $Ce^{\nu F\zeta/RT}$.

Dr. S. R. Craxford (*London*), on the paper of Kruyt and Overbeek, p. 110 : Professor Kruyt's system of silver iodide particles in a solution of sodium iodide which also contains a Ag/AgI electrode to measure the iodide ion activity, may be represented as in Table 3.

TABLE 3.

I.		II.		III.
Solution of NaI	Na + Na + Na + Na + Na +	I − I − I − I − I −	Solid AgI	Solid Ag

When considered in this way it is difficult to see anything in the argument on pp. 113 and 114 more profound than the bald assumption that the change in ${}^{\rm I}\Delta^{\rm III}\phi$ on adding excess of a foreign electrolyte is equal to the potential difference across the diffuse part of the double layer. Before adding the foreign salt

$${}^{\rm I}\Delta^{\rm III}\phi = \text{const.} + \frac{RT}{F}\ln a_{\rm I^-}.$$

After the addition the double layer changes as in Table 4, and

$$ {}^{\mathrm{I}}\Delta^{\mathrm{III}}\,\phi' = \text{const.} + \frac{RT}{F}\ln a'_{\mathrm{I}^-}. $$

The following factors control a_{I^-} :—

(i) It is decreased by adding foreign electrolyte, quite apart from any interchange of I^- with the double layer.

(ii*a*) It is increased by the suppression of the diffuse layer, the iodide ions forming this layer moving out into the bulk of the solution.

(ii*b*) It may be increased or decreased by subsequent adjustment of the adsorbed layer.

(iii) It is decreased by specific adsorption of the foreign electrolyte, more I^- having to enter the layer from the bulk of the solution to maintain the potential.

TABLE 4.

I.		II.		III.
Solution of NaI and foreign salt	Na + Na +	I — I —	Solid AgI	Solid Ag

Professor Kruyt neglects (i) and (iii), and then, in order to explain the experimental fact that a'_{I^-} is less than a_{I^-} he assumes that (ii*b*) out-weighs (ii*a*). This is equivalent to saying that the electrostatic capacity of the diffuse layer is less than that of the adsorbed layer, which is incorrect. (See my reply to Dr. J. J. Bikerman in this discussion.)

Dr. J. J. Bikerman (*Glasgow*), on same paper: I am unable to understand the method of De Bruyn, and hope his own publication will contain a more detailed justification of equation (4). In the meantime I would like to have a clear picture of the experimental side. The e.m.f. of a cell AgI(solid)/suspension of AgI + some NaI/liquid junction/reference electrode is measured; then to the suspension a large excess of a nitrate is added, and the e.m.f. determined again. The difference between both values of the e.m.f. is supposed to be equal to the ζ potential of the AgI suspension before addition of the nitrate. Is this a fair account of De Bruyn's method ?

Prof. A. Frumkin (*Moscow*), on paper by Barclay and Butler, p. 132 : The significance of the two flat stages on the curve expressing the relation between the potential and the charge of the electrode in presence of amyl alcohol can be readily explained. As it is known from electrocapillary data, amyl alcohol is not adsorbed with sufficiently high positive charges of the mercury surface. If the positive potential is decreased the adsorption sets in at a fairly definite value of the potential and a unimolecular layer of amyl alcohol is formed. With further negative polarisation we can reach another limit of the existence of this layer, the transition being in this case less sharply pronounced as on the positive branch. A molecular theory of this transition has been given elsewhere.[12] As the transitions from a surface covered only by an ionic double layer to one covered by a layer of amyl alcohol molecules and vice versa necessitate a large change of the surface charge and a corresponding consumption of the polarising current, two flat stages on the oscillogram must appear. In the first stage a large part of the initial positive charge of the mercury is removed and in the second a part of the negative charge is communicated. If instead of measuring the charge of the electrode we measure the capacity as a function of the potential two maxima must appear on the resulting curves, corresponding to the two flat stages on the oscillogram given on p. 132. Such measurements have been carried out with octyl alcohol solutions by Proskurnin and Frumkin [13] and with

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[12] Frumkin, *Z. Physik*, 1926, 35, 792.

[13] *Trans. Faraday Soc.*, 1935, 31, 115.

buytl alcohol solutions by Ksenofontov, Proskurnin and Gorodetzkaja.[14] Fig. 1, taken from the latter paper, shows that this maxima occur indeed at potentials which correspond to the limits of the adsorption region of the organic molecules marked on the electrocapillary curves by well pronounced breaks.

Dr. J. J. Bikerman (*Glasgow*), on paper of Audubert, p. 146: The equations used by Professor Audubert are rather empirical than theoretical since the theory underlying them does not apply to colloids. As I have already pointed out [15] the impossibility of transferring Debye's equations to sols I will restrict these remarks to a comparison between the observed mobilities and those given by equation (3).

From Fig. 6 and 7 it is seen that $1/aA$ is about $50 . 10^{-3}$; hence $aA\sqrt{\mu} > 1$ when $\sqrt{\mu} > 50 . 10^{-3}$. At the concentrations involved $aA\sqrt{\mu}$ obviously is less than 1. Equation (3) requires then an almost linear increase of mobility with the radius a of the particle. This is in contradiction with experiments. If a is large and aA is over 1000 (see Table IV) equation (3) shows that the mobility is almost independent of the concentration above, say, $\sqrt{\mu} = 0{\cdot}01$; this is not confirmed by experiments.

The values recorded in Table I are not convincing. The particles of the As_2S_3 sol used by Freundlich and Zeh were invisible in ultramicroscope and therefore very probably less than $1{\cdot}43 . 10^{-6}$ cm. On the other hand mastic sols usually have larger particles of the order of magnitude of 10^{-4} cm. (see Table 4).

Prof. R. Audubert (*Paris*), in reply: (1) In agreement with the remark of Bikerman, the data recorded in Table I are not intended to represent real radii of the particles of the systems investigated. Indeed, the calculation gives only average radii since the listed sols and suspensions are heterodisperse.

(2) Equation (3) questioned by Bikerman is confirmed only in the case when the hypotheses on which it is based are valid ($E = 4\pi a^2\sigma$). That is the reason why it was preferred to take for the variable, instead of the mobility u, the relative change u/u_0 of the mobilities, see equation (4). This relation is not experimental; it is an expansion of the theories of Debye to disperse systems. Experience shows that it is indeed confirmed in the range of small concentrations; the agreement is the better the smaller is the valency of the ions. Equation (4) assumes that the charge E is constant. The observed disagreement between the relative mobilities calculated from (4) and those measured can be interpreted as due to a variation of E. When applied to mastic granules this hypothesis is confirmed by experiments (equation (13), Table IV).

We believe, therefore, that the theory of Debye and Hueckel in its simple form is applicable to disperse systems at very large dilutions only; at smaller dilutions it is necessary to assume a variation of E with the ionic strength of the intermicellar liquid. In the range of high concentrations the classical theory of Debye cannot be used, as it is not allowed, then, when developing the exponential function, to neglect the terms of an order higher than unity.

Prof. L. S. Moyer (*Minnesota*), on paper of Bikerman p. 157: In regard to the statement of Bikerman that the values previously obtained by Moyer and Bull [16] for the charge density at cellulose surfaces will be altered by consideration of the surface conductance, it may be well to mention that our calculations were based on streaming potential data of Bull and Gortner.[17] In their data, corrections for the influence of surface

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[14] *Acta Physicochimica, U.R.S.S.*, 1938, **9**, 41.
[15] J. J. Bikerman, *Z. Electrochem.*, 1933, **39**, 526.
[16] L. S. Moyer and H. B. Bull, *J. Gen. Physiol.*, 1935, **19**, 239.
[17] H. B. Bull and R. A. Gortner, *J. Physic. Chem.*, 1931, **35**, 309, 456, 700.

conductance had been introduced by measurement of the specific conductance within the pores of the diaphragm. The procedure used was that of Briggs.[18]

Dr. S. R. Craxford (*London*), on Guggenheim's paper, p. 139: For a double layer of unspecified ionic distribution the equation for electro-osmosis, for example, is obtained by combining the Poisson equation with the Stokes-Navier law, and is

$$u = \frac{D}{4\pi\eta}(\phi_1 - \phi_2) = \frac{D}{4\pi\eta} . \zeta . \qquad . \quad . \quad . \quad (1)$$

This involves a number of assumptions, one of which is that D, the dielectric constant, is constant throughout that part of the double layer that is responsible for electrokinesis. If D were not constant there is no reason to suppose that the electro-osmotic equation would take the above form. Dr. Guggenheim considers the equivalent condenser, with capacity

$$K = \frac{\text{charge}}{\zeta} = \frac{D'}{4\pi\delta} \qquad . \quad . \quad . \quad . \quad (2)$$

and assumes in his turn firstly that the electro-osmotic equation has the form of (1) in spite of the variable D, and secondly that D in (1) is the same as D_1 in (2). He is thus enabled to eliminate D and ζ and replace them by the moment of a condenser equivalent to that part of the double layer responsible for electrokinesis. His equation, therefore, seems to be no freer from assumptions than (1), and it would be difficult to maintain that the moment of the equivalent condenser gives a clearer picture of electrokinetic phenomena than the potential difference across the diffuse and slipping double layer.

The argument that the moment comes in directly and naturally if the electrokinetic equations are derived from the concept of a parallel plate condenser at the interphase, as was done first by H. Lamb, is not[19] valid, because the fact that the correct equation can be derived from a false assumption does not make the derivation correct. It is therefore without importance that in this erroneous derivation Dr. Guggenheim's equation occurs first and equation (1) can subsequently be obtained from it.

Dr. E. A. Guggenheim (*London*): It seems to me that Craxford has put the cart before the horse. The main point of my paper is that my formula (3·1) does not involve Poisson's equation, whereas Craxford's formula (1) does.

The derivation of my formula (3·1) is actually extremely simple. Denoting velocity parallel to the field by u, and considering a thin strip of liquid, we have as a condition of steady motion

$$\eta \mathrm{d}u = X \mathrm{d}\tau. \qquad . \quad . \quad . \quad . \quad . \quad (A)$$

Integrating from the wall to the interior, we obtain for the velocity u in the interior of the liquid

$$u = X\tau/\eta. \qquad . \quad . \quad . \quad . \quad . \quad (B)$$

In a tube of circular cross-section the flow f expressed as volume per unit time is given by

$$f = \pi r^2 u, \qquad . \quad . \quad . \quad . \quad . \quad (C)$$

where r is intermediate between the radius r_e of the tube and the radius r_i of the cylinder of liquid whose velocity differs inappreciably from u. In practice the distinction between r_e, r_i and r is trivial. Substituting (B) into (C), we recover my formula (3·1)

$$f = \pi r^2 X\tau/\eta. \qquad . \quad . \quad . \quad . \quad . \quad (3·1)$$

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[18] D. R. Briggs, *J. Physic. Chem.*, 1928, 32, 641.

[19] *Phil. Mag.*, 1888, 25, 52.

To transform formula (B) into Craxford's formula (1) we have to use my formula (3·3)

$$\zeta = 4\pi\tau/D, \qquad . \quad . \quad . \quad . \quad . \qquad (3·3)$$

which is the integral of Poisson's equation. I think that Craxford agrees with me that this substitution is meaningless unless D is constant across the layer.

Dr. J. W. Wrzeszinski (*London*), on Verwey's paper, p. 192 : I have been investigating the role of emulsifiers for some time. I differ from Verwey's conclusions on a few points.

He states that emulsifying agents can be classified into two main groups—

(*a*) colloidal electrolytes and lyophilic colloids ; *

(*b*) finely divided solids ;

and furthermore, that both have the effect of giving the drops properties comparable with those of solid particles, and of shifting the double layer potential drop towards the outer phase.

While it is certainly correct to say that finely divided solids acting as emulsifying agents have the effect of imparting to the dispersed globules properties comparable to those of solids, it is in my view less clear whether the same can be said regarding the stabilising action of colloidal electrolytes, *e.g.*, soaps, and of lyophilic colloids, such as saponin and agar agar (for O/W emulsions).

From results obtained in this laboratory it would appear that the action of a given electrolyte on an emulsion depends very much on whether the emulsion has been prepared with the aid of a finely divided solid or a substance which gives a colloidal solution in the dispersion medium. Using fairly concentrated O/W emulsions, the actual concentrations were kept between 80 and 90 per cent. of oil,—I observed that emulsions stabilised by substances like sodium oleate and saponin remained unaffected by the addition of the sulphates of the alkali metals, but were broken by the corresponding thiocyanates and iodides, while exactly the reverse was true of emulsions stabilised by finely divided solids, *e.g.*, alumina, bentonite. The effect of these salts on the solutions or dispersions of the emulsifying agents was next studied, and was found to correspond exactly to the action of the salts on the emulsions prepared with the aid of the emulsifying agents under investigation. These observations show that the stability of stabilised emulsions is very closely related to the state of the solution (or dispersion) of the emulsifying agent used, and, moreover, that the resistance to inorganic salts is different with emulsions prepared with colloidal solutions on the one hand, and those stabilised by (solid) suspensions on the other.

The second function of emulsifying agents is said to be to shift the double layer potential drop towards the outer phase. I find it somewhat difficult to attribute a change in the stability of a stabilised emulsion to a change in the potential drop however determinative this be for the stability of an oil-hydrosol. I investigated the influence of electrolytes on the cataphoretic mobility of the dispersed particles in stabilised O/W emulsions. Using various emulsifying agents, I obtained results which closely resembled those published by Dr. Limburg.[20] Like Limburg I found that, although the influence of electrolytes on the electrokinetic properties of a stabilised emulsion may be frequently very similar to their influence on the cataphoretic velocity of oil-hydrosols, there was no similarity in the change of stability on the addition of electrolytes. No minimum of stability was observed at the isoelectric point.

I have been led to the conclusion that with a sufficiently high concentration of emulsifying agent—0·6 to 0·7 per cent. (calculated on the internal

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* See Corrigenda, p. 732.

[20] Limburg, *Rec. trav. chim.*, 1926, 45, 772, 854.

phase) in a great many cases—the electrical behaviour of an emulsion will bear a relatively insignificant relation to its stability. This is also exemplified by the high resistance such emulsions are able to offer to the addition of electrolytes. It is understood that there is no chemical reaction between the emulsifying agent and the electrolyte added. If this happens the emulsion is immediately rendered unstable, irrespective of the concentration of emulsifying agent. This question has been considered before in greater detail.[21] Excluding chemical interaction, emulsions will be stable if the agent used is present in sufficient concentration. If the concentration of emulsifying agent is lowered the mechanical rigidity of the protective film is materially decreased, and the smaller the concentration becomes, the more will the properties of the emulsion resemble those of a lyophobic colloid whose stability is mainly determined by the charge on the particles.

Dr. E. J. W. Verwey (*Eindhoven*), in reply : The object of my paper was to point out first of all that in order to understand completely the action of emulsifying agents, we must understand the fact that emulsions without emulsifiers are never stable. In this respect the emulsions differ fundamentally from other lyophobic colloids. It seems to me that this fundamental problem is for the main part solved by the considerations in my paper on the stability of emulsions.

I do not claim that the few remarks at the end of the paper are more than provisional suggestions about the phenomena underlying the action of emulsifiers. I understand that Dr. W. distinguishes between O/W emulsions and oil-hydrosols, the latter being the more diluted systems. It may be that in some types of highly concentrated emulsions, especially when stabilised by a sufficiently high amount of emulsifiers, the stability conditions are rather complicated. It may be that, apart from the double layer, also another stability factor plays a part, such as solvatation, like in the case of lyophilic colloids. Writing about emulsions, however, I had in mind the work of Ellis, Powis, Limburg, and others, about which has been reported again in the paper by Eilers and Korff. Here we are dealing with systems where the stability of the oil droplets with respect to coagulation and the electrophoretic mobility are clearly correlated. Even if no special emulsifiers had been added deliberately to these systems, the very fact of the high zeta-potentials of their particles proves, according to the arguments given in my paper, that their particles were stabilised by some emulsifying agent. These substances had undoubtedly the effect that the double layer assumed properties as at solid particles, and the double layer potential drop was shifted towards the outer phase.

Prof. L. S. Moyer (*Minnesota*), on paper by McFarlane, pp. 258 and 261 : I was much interested in the observations of McFarlane on the remarkable behaviour of this unusual virus. However I am unwilling to agree with McFarlane that " the work of Abrahamson (should be Abramson) and Moyer suggests that the mobility of the proteins is accounted for solely by the ionisation potential, and consequently that the adsorption of salt ions must be negligible in amount ". As a matter of fact in our papers we have been careful to state, referring to this citation, that " this will probably be found to be not true, in general, for some process tantamount to adsorption of ions of the salt may occur, the shape of the $v_m - c$ curve remaining essentially the same but shifted because of the effect of salts on the isoelectric point ".[22, 23] To assume that " in normal working conditions the molecules of soluble proteins in general may not associate with the wall of the Tiselius U-tube " is not supported by what we know of their behaviour. Abramson and I, among many others, have pointed

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[21] King and Wrzeszinski, *Trans. Faraday Soc.*, 1939, 35, 741.

[22] H. A. Abramson, *J. Gen. Physiol.*, 1933, 16, 593.

[23] L. S. Moyer and J. C. Abels, *J. Biol. Chem.*, 1937, 121, 331.

out repeatedly [24, 25] that, with the possible exception of red cells [24] or particles already coated with certain proteins,[26] surfaces (including glass or quartz) readily adsorb all sorts of soluble proteins: egg albumin, the serum proteins, casein, insulin, gelatin, gliadin, etc., upon immersion of the surface in their solutions, and thereupon become endowed with their electrokinetic properties. I believe that another explanation must be looked for to explain the anomalous boundaries observed with vaccinia virus.

Dr. A. S. McFarlane (*London*), communicated: By contrast with Moyer's above quotation relating to the effect of adsorbed salt ions on the mobility of proteins there is the recent statement by Abramson, Gorin and Moyer [27]: " For if, at constant ionic strength in simple systems, the average charge of the molecule is known to be almost completely determined by the average number of equivalents of hydrogen or hydroxide ions bound, it follows that changes in the isoelectric point incidental to surface film formation must be directly correlated with changes in the relative strengths of the amino and carboxyl groups ". I am therefore grateful to Prof. Moyer for now making it quite clear that he and his collaborators accept the view that adsorbed salt ions contribute to the mobility of proteins. Their claim, however, that the contribution of these ions is a constant over the *p*H range in which protein mobilities are usually determined, affecting neither the slope nor the shape of the *p*H-mobility curve is difficult to accept. It is based on the following procedure [27]: " In a plot with the number of equivalents of acid (base) bound per gram of protein as ordinate and the *p*H as abscissa, the zero point on the ordinate is found by shifting in co-ordinates vertically until the curve goes through zero at the isoelectric point as determined by electrophoresis. The mobility data are then compared with the titration data by taking any single point on the smoothed mobility curve and multiplying the mobility by a factor that will make the two curves correspond. If when all the experimental points are multiplied by this same factor, they fall on the titration curve within the limits of error, this proportionality is to be considered as demonstrated." The mobility curve is thus rotated about the isoelectric point until its mean slope is arbitrarily made to coincide with the mean slope of the titration curve, and the presence of any factors (other than acid or base ionisation) which affect the mobility of a protein in a linear manner with changing *p*H could not be detected by examination of these superimposed curves. At present there seems to be as much evidence for the view that the absorption of salt ions on proteins varies progressively with *p*H as for the view that there is a fixed degree of salt adsorption over a wide *p*H range. The presence of non-linear changes of salt adsorption with *p*H would presumably be demonstrated by deviations of the mobility curve from the superimposed titration curve but the significance of such deviations can only be assessed in relation to the experimental errors involved in the determinations of mobility and acid (base) binding capacity and these are not discussed by the authors.

I note with interest Moyer is not in favour of the suggestion that in normal working conditions soluble proteins may not associate with the wall of the Tiselius U-tube. It would be interesting to know what alternative explanation can be offered for the complete absence of any signs of endosmotic flow at the walls of the U-tube containing protein materials, including the very large plant virus molecules, other than vaccinia.

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[24] H. A. Abramson, *Electrokinetic Phenomena*, New York, 1934.

[25] L. S. Moyer, *Cold Spring Harbor Symposia on Quantitative Biology*, 1938, 6, 228.

[26] L. S. Moyer and E. Z. Moyer, *J. Biol. Chem.*, 1940, 132, 357, 373.

[27] H. A. Abramson, M. H. Gorin, and L. S. Moyer, *Chem. Rev.*, 1939, 24, 345.

Dr. S. Levine on the papers of Hamaker, p. 188, Derjaguin, pp. 208-10, Levine, and G. P. Dube, pp. 215-19 **(Coagulation of Hydrophobic Sols and minimum in Electrical Energy).** Objections of an apparently serious nature to our expression for the interaction of two colloidal particles have been raised by Hamaker and Derjaguin. These relate to our minimum which I believe is of paramount importance in hydrophilic sols, so that it becomes necessary to answer their criticisms. The question arises as to whether the minimum influences the coagulation process of hydrophobic sols. I shall try to show that at least for small particles, the minimum cannot be the position where the particles coalesce, although it does affect the rate of coagulation. Firstly, in order to explain slow coagulation, it seems essential that there exists an energy barrier over which the colliding particles must pass before forming secondary particles. Secondly, the position of the minimum s_{min} (in units of the radius) is in many cases too far out. As examples, if we consider the critical coagulation points illustrated in Figs. 1 and 4 (pp. 218 and 223) for the three electrolyte types 1-1, 2-1 and 3-1, the radius being $a = 15$ mμ, then $\tau = \kappa a = 10{\cdot}0$, $2{\cdot}74$ and $1{\cdot}22$ and $s_{\mathrm{min}} = 2{\cdot}13$, $2{\cdot}6$ and $3{\cdot}5$ respectively. These values are readily obtained from the formulæ and numerical results given in our earlier papers. For larger particles of radius 50 mμ, at the same critical precipitation values for the three electrolytes, the corresponding values of τ are 32·9, 9·00 and 4·03, and those of s_{min}, 2·04, 2·14, and 2·36 respectively. In truly hydrophobic sols, such as gold and platinum, very little water is carried down by the precipitate, and it is unlikely that the particles are separated by distances of the order 2·5 times the radius. For the smaller particles, therefore, the minimum cannot be the position of flocculation, although for the larger particles the situation is not so clear.

However, this last problem is partially solved by examining the depth of the minimum F_{min} in the electrical energy, which may not be large enough to yield a stable position permitting coagulation. Thus, returning to the two sets of examples referred to above, and assuming the same critical potentials as in Fig. 1, p. 218 (45 m.v. for the 1-1 type and 25 m.v. for the 2-1 and 3-1 types), F_{min}/kT_0 is equal to 4·5, 0·93 and 0·44 when $a = 15$ mμ and to ~ 20, 4·6 and 4·0 when $a = 50$ mμ for the three electrolytes 1-1, 2-1, and 3-1 respectively. The only value of F_{min} that seems to cause trouble is that for the 1-1 type with $a = 50$ mμ. One may compare the effect of a minimum even of depth $5kT_0$ in dilute sols to that of the van der Waals attractive energy between molecules in a gas. It should be noted that two atoms forming a stable molecule have an energy of binding of the order of 1 electron volt $\approx 40kT_0$.

When we come to large particles there arises a difficulty which is pointed out by Hamaker and which was already known to us. For large τ, it can be shown that $s_{\mathrm{min}} \approx 2 + 1{\cdot}16/\tau$ and $F_{\mathrm{min}} \approx -\,0{\cdot}085\zeta^2 Da$ (asymptotically) which is directly proportional to the radius, as illustrated by Hamaker in Fig. 2, p. 188. At $D = 80$, $a = 50$ mμ and $\zeta = 100$ mv., for example, $F_{\mathrm{min}} = -\,94kT_0$. This implies that all large spherical particles should coagulate rapidly in the position of the minimum and indeed cannot form stable sols (suspensions or emulsions), at variance with experiment, as remarked by Hamaker. Further, this appears to contradict our conclusion on p. 220 concerning the absence of an upper limit to the particle radius in stable sols, which was based on the properties of the energy at contact and of the energy maximum. Thus it becomes necessary to remove this discrepancy between our theory and experiment.

It might be thought at first that the approximation used here, which is reliable for small values of τ, leads to a considerable error for large τ, but the following illustration suggests that this does not solve the difficulty. Consider two spherical particles, from which we have cut away spherical caps of depth $1/\kappa$, so placed that the two circular plane sections (discs) are parallel to one another at a distance $1/\kappa$ apart (Fig. ii). Neglecting the influence of the rest of the spheres, we will assume this model to approximate to two large particles almost in contact (the radius $a \gg 1/\kappa$). In one of the earlier papers [28] we applied our method to calculate the electrical energy per unit area associated with two infinite parallel plates and found it to be always negative, assuming that the surface charge density on the plates remains constant. Noting that the angle θ in Fig. ii is given by $a \cos \theta + 1/\kappa = a$, *i.e.*, by $\cos \theta = (\tau - 1)/\tau$, the area of each disc is $\pi a^2 \sin^2 \theta \approx 2\pi a^2/\tau$ for $\tau \gg 1$. Substituting this expression for the area and also $1/\kappa$ for the distances between the two plates into formulæ (40) and (38) in the above mentioned paper, the electrical interaction energy of our model becomes $-0{\cdot}036\ \zeta^2 Da$ yielding the same order of magnitude as our asymptotic form for the minimum energy for two particles.

Using the original Debye-Hückel equation, Corkill and Rosenhead [29] recently computed the electrical forces between two parallel plates, and found that there was an attraction when either the charge or potential on the plates is kept constant. Only when the difference of potential between the surface of the plates and the median plane is kept constant do the electrical forces become repulsive. This suggests one source of error in our results, namely, that the charge on the particles should not be constant, independent of the separation. However, whereas in the case of two parallel plates, it is not difficult to suggest other conditions, this is not so simple in the case of two spherical particles. A discussion of this problem has already been given by us [1] and its solution appears difficult.

Models for large particles.

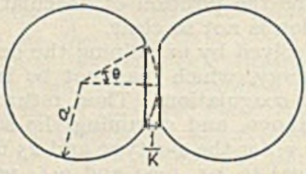

Fig. ii.

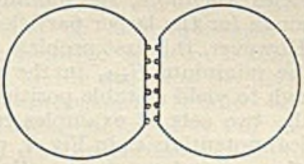

Fig. iii.

Effect of Surface Irregularities.

I wish to suggest another solution to this dilemma. It is well known that the surface of a crystal has irregularities which are at least of the order of 1 mμ in depth (and length). Particularly, crystal growth proceeds in a random fashion when there are impurities, which is usually the case during the formation of colloidal particles. If the uneven character of the particle surface is taken into account, colliding particles will usually touch at the projecting points. This receives confirmation from the surprisingly small values of the van der Waals constant A that we obtained in our paper. Further the charge will tend to concentrate at these protuberances on the surface,[30] which indeed are the active spots proposed by Kruyt and Verwey.[31]

To illustrate the influence of these active spots on the form of the electrical energy for large particles we return to the model in Fig. ii for two particles of say 100 mμ in radius, and cover each disc with a layer of smaller particles of radius 1 mμ, such that neighbouring particles are about 10 mμ apart, yielding about 60 particles on each disc (Fig. iii). (The following argument does not hold if the density of small particles is so high that they are, say, 4 mμ apart, but this would imply an

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[28] Levine and Dube, *Trans. Faraday Soc.*, 1939, **35**, 1125.

[29] Corkill and Rosenhead, *Proc. Roy. Soc. London*, (*A*), 1939, **172**, 410.

[30] According to Jeans, *Electricity and Magnetism*, p. 194, this is the case for a hemispherical boss on a plane conducting surface.

[31] Verwey, *Chem. Rev.*, 1935, **16**, 363.

extremely rough surface.) Assuming an electrolyte concentration of 1 mMol./l., so that $\tau = 10$ and 0·1 for the large and small particles respectively, and taking $\zeta = 100$ mv., we readily calculate that the minimum electrical energy of pairs of large and small particles are $-150\ kT_0$ and $-0{\cdot}023\ kT_0$ respectively, whereas the corresponding values of the energy at contact are $210\ kT_0$ and $10\ kT_0$. If the charge is all concentrated on the adhering small particles in our model, this implies that the equivalent of 6500 pairs of small particles (say 81 on each disc) must simultaneously be in their position of minimum electrical energy in order to attain a total minimum energy of $-150\ kT_0$, which is not possible. On the other hand, only 21 pairs of small particles in contact give the contact energy for the spherical large particles. Since this model is an extremely crude one we can only reach a very qualitative conclusion, namely that the presence of an uneven surface may reduce the minimum electrical energy by as much as a factor of 5 or 10, whereas the change in the electrical energy at contact is rather uncertain.

The implication of this discussion is rather far reaching, namely, that no large particles which are truly spherical can form stable sols, suspensions or emulsions. It is well known that emulsions which contain large particles (and often coarse suspensions also) are stable only when protected by a layer of smaller particles, which may be either colloids, certain organic ions such as alkali soaps or very finely divided particles. This is the type of model for large colloidal particles that we have postulated above. In the case of a soap emulsifier the surface would hardly be uneven if a closely packed monolayer of the soap molecules had formed on the particles. However, there is no real evidence to disprove the assumption that before this takes place an appreciable part of a second layer has already been deposited, producing an irregular surface.[32] Verwey claims that an unprotected emulsion is unstable because a sufficiently high ζ potential can never be reached. Lack of space prevents me from comparing in greater detail his explanation with the alternative one put forward here.

The general effect of surface indentations would be to diminish the rapidity with which the van der Waals energy and (to a lesser extent) the electrical energy fall off with particle separation, compared to the case of two hypothetical truly spherical particles, whose radius is equal to the average radius of the real particles. This would tend to move both the maximum and minimum farther out from particle contact, and would account, for example, for the difficulty mentioned in our paper in footnote 14 on p. 225. We shall discuss this phenomena in more detail in another paper.

On first sight the preceding analysis appears to invalidate the explanation in our paper for the dependence of the stability properties of sols on the particle radius. However, it appears that for large particles the change in the electrical interaction energy at the maximum as a result of surface imperfections is much less than that in the minimum, and we have based our conclusions on the properties of the former. Furthermore the fact that we are getting qualitative agreement with experiment suggests that we cannot be far wrong. It must be remembered that a mathematical treatment of particles of irregular shape would be quite difficult and the best that we can do is to work with idealised cases, at least in the initial stages of the investigation.

Mutual Free Energy of Particles.

There is another source of error in our calculations which is the object of attack by Derjaguin, namely that the free energy and not the ordinary internal electrical energy associated with the double layers should be

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[32] I am indebted to Dr. A. S. C. Lawrence for this suggestion, and also for lengthy discussions on the properties of gels.

calculated. Derjaguin asserts that the free energy of an electrolyte should be obtained by charging all the ions proportionally when Debye's method is used. However, Onsager[33] and Halpern[34] have shown that one can charge the ions in any manner, provided the solution is kept electrically neutral and certain conditions of self-consistency are satisfied, which is the case with the approximate Debye-Hückel solution. When the original Debye-Hückel is used, this is no longer true, but Muller[35] showed that two simple methods of charging the ions, namely those of Debye-Hückel and of Guntelberg, lead to ionic activity coefficients which were only slightly different. The method of charging the ions and colloidal particles described on p. 179, in the second of our papers,[36] to which Derjaguin is referring was chosen as an illustration to show that κ may be kept constant during the charging process. However, we may also use Debye's method of charging and still obtain a term expressing the work of charging the ionic atmospheres of the colloidal particles, which Derjaguin wishes to omit.

The problem is to find the mutual free energy of the colloidal particles which are all assumed to have fixed positions. The particles may then be considered as *external fields* acting on the ions over whose positions we must average. Then the free energy of such a system is obtained by charging both the particles and ions. The fact that the macroscopic state of this system is independent of the positions of the ions does not imply that we must not charge the ions; otherwise we could not charge the ions in an ordinary electrolyte to obtain its free energy. Since the external field exerted by the particles changes with the relative position of the particles, the work of charging the ions will vary with these positions, so that we must have a contribution to the interaction energy of the particles which comes from charging the ions. This is still true when the Debye method of charging is employed. To avoid the difficulty of dealing with a sol which is not electrically neutral, in his thermodynamic argument Derjaguin is compelled to introduce a hypothetical large conductor which would change the thermodynamic system under consideration. No such conductor exists in actual sols. Finally I have not been able to verify Derjaguin's equation (19), the Gibbs-Helmholtz relation.

Our derivation of the work function expressing the interaction of the particles is based on keeping κ constant which cannot be valid for concentrated sols (*e.g.* gels). It turns out that this assumption leads to the ordinary average electrical energy when the approximate Debye-Hückel equation is used. On using their original equation, however, there is an appreciable difference between the internal energy and our work function, as shown in an earlier paper.[37] It should be instructive to reconsider the work of Corkhill and Rosenhead from this point of view. Also, it would be desirable to investigate the error involved in assuming κ constant. The relation of our theory to that of Langmuir[38] has already been discussed.[22]

Role of Minimum in Hydrophilic Sols; Gelation.

No conclusive evidence could be found to prove that the minimum need exist at all in order to explain the stability properties of hydrophobic sols. Consequently it becomes imperative to seek for properties of hydrophilic sols which suggest the existence of the minimum. I believe that the phenomena of gelation and in particular of thixotropy can be attributed, at least partially, to the minimum in the electrical energy. Now gels

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[33] Onsager, *Chem. Rev.*, 1933, **13**, 73.
[34] Halpern, *J. Chem. Physics*, 1934, **2**, 85.
[35] Muller, *Physik. Z.*, 1927, **28**, 324.
[36] Levine, *Proc. Roy. Soc. A*, 1939, **170**, 165
[37] Levine, *J. Chem. Physics*, 1939, **7**, 831.
[33] Langmuir, *ibid.*, 1938, **6**, 873.

usually consist of non-spherical particles and are quite concentrated, so that the computation of the mutual energy of two spherical particles can hardly lead to a detailed theory of gel structure. Hence only a brief and qualitative discussion can be presented here.

At present, there are three theories of gelation, the first based on the existence of layers of bound water, the second on a network of particles in actual contact, and the third on long range forces between the particles. The first theory, that of solvation, is not supported by both experimental[39] and theoretical[40] work on the change of dielectric constant of water with field strength (a measure of the saturation or solvation effect) which is shown to be quite weak, because of the strong coupling between the water molecules, preventing orientation in an external electric field. This does not refer to the water absorbed by short range forces inside the particles or in the cracks on the surface of the particles, but to the layers of water surrounding the particle. The absence of bound water receives further confirmation from recent work on viscosity, which shows that the anomalous viscosity of dilute hydrophilic sols is mainly due to the asymmetric shape of the particles.[41]

It is proposed that for hydrophobic sols, whose particles have " hard " surfaces, the van der Waals energy of interaction brings about coalescence at coagulation, whereas in hydrophilic sols, whose particles are permeated with water, the van der Waals energy is quite small, and the only " coalescence " which can occur is at the minimum (process of gelation), unless the water is removed from the interior of the particles by the addition of sufficient electrolyte (salting out). I therefore assume with Hamaker[42] that the fundamental difference between hydrophobic and hydrophilic sols can be represented by the mutual energy curves for two particles, as shown in Fig. iv, the intensity of the van der Waals attraction being the determining factor. This permits of a gradual transition from truly hydrophobic to truly hydrophilic sols, depending on the amount of water imbibed by the particles.

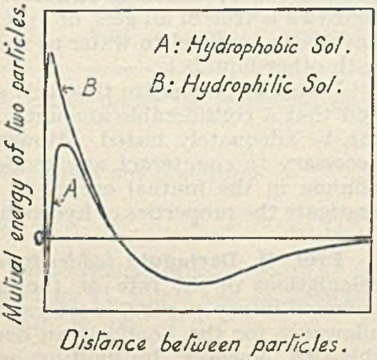

FIG. iv.

One of the chief difficulties of the second theory of gelation, the link or scaffolding theory,[43] is to reconcile the failure of the (hydrophilic) particles to coalesce in dilute sols with their apparent ability to make contact in the more concentrated state (gelation), the electrolyte concentration being the same in the cases. The scaffolding theory was proposed chiefly to explain why rod-like particles in relatively dilute concentrations can form gels more readily than particles of other shapes, whereas spherical particles seldom form gels. However, the theory of long range forces (based on our minimum) can also explain this property in the following manner. Since hydrophilic particles are usually quite small, and the energy minimum is roughly proportional to the minimum, it is not easy to form a stable lattice of small spherical particles. However, a rod-shaped particle may be compared to a rigid row of small spherical particles, and when two of these are parallel to one another, assuming as a first approximation that the electrical energy is additive, we shall have a much

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[39] Malsch, *Physik. Z.*, 1929, **30**, 836.

[40] Debye, *ibid.*, 1935, **36**, 193; Piekara, *Proc. Roy. Soc. A*, 1939, **172**, 360.

[41] *Cf.* Robinson, *Proc. Roy. Soc. A*, 1939, **170**, 519.

[42] Hamaker, *Rec. Trav. Chim. Pays-Bas*, 1936, **55**, 1015; 1937, **56**, 1, 727.

[43] *Cf.* Goodeve, *Trans. Faraday Soc.*, 1939, **35**, 342.

deeper minimum, which is roughly proportional to the length of the rods. This suggests that a gel should consist of minute clusters of parallel particles, which form a stable configuration, and which overlap in some way.[44] This receives confirmation from the existence of tactoids and from the work of Bernal and Fankuchen[45] on virus proteins and from that of Hauser[46] on bentonite. Further, the gel still remains optically empty, although when the gel is sufficiently concentrated it may become birefringent, when the possibility of larger tactoids exists. The fact that orientating the particles does not ordinarily produce gelation can be attributed to the sensitivity of the position of the minimum to electrolyte concentration and also to particle size. It would be accidental if the concentrations of sol and electrolyte were just right so as to bring all the particles into their equilibrium position on alignment. Brownian motion must bring the particles close enough together and then orientate them so as to form clusters, the orientation process apparently being facilitated by rolling or tapping (rheopexy). The difference between thixotropic and non-thixotropic gels is perhaps only one of the energy of binding at the minimum, which is greater for the smaller particles. It seems quite natural to assume that the same electrical forces which act in thixotropic gels should continue to do so in ordinary gels. Of course, it is likely that there are many gels which have a scaffolding structure, but it should not be assumed *a priori* that this is true of all gels, or even of the majority of them. (My remarks have been confined to water as the dispersion medium, and need not hold with other liquids.)

I wish to emphasize that this proposed theory of gelation is tentative, and that a considerable amount of theoretical work is necessary before it can be adequately tested. However, I thought the preceding discussion necessary to counteract any tendency to lightly dismiss the existence of minima in the mutual energy of colloidal particles. It is hoped to investigate the properties of hydrophilic sols in greater detail in a later paper.

Prof. B. Derjaguin (*addendum to paper by author, pp.* 203-11): The calculations of the rate of the slow coagulation of lyophobe colloids, included in my paper,[47] were carried out without making the necessary allowance for the London–van der Waals forces. We may easily fill in this gap, however, by limiting ourselves to the case of particles with a large radius r.

For this purpose, making use of Hamaker's formula for the energy of the van der Waals attraction, $U_A(H)$ of two spheres,[48] we supplement the expression for the total energy of interaction, $U(H)$, of two spherical particles :

$$U(H) = U_\psi(H) + U_A(H) = \kappa T n\left\{\ln(1 + e^{-z}) - \frac{m}{z}\right\}, \qquad . \quad \text{(I)}$$

where,

$$n = \frac{Dr\psi_0^2}{2\kappa T}, \quad z = \kappa H, \quad m = \frac{1}{6}\frac{A\kappa}{D\psi_0^2}, \qquad . \quad . \quad . \quad \text{(I')}$$

and A is the constant of van der Waals energy.[2]

The expression for $U(H)$ will disclose one minimum, and left of it, a maximum, if the value for m is less than a certain value m_0, roughly taken to be equal to 0·5 (see Table I). At $m > m_0$, $U(H)$ decreases monotonically with a decrease in H, consequently, in this case the colloid system is unstable without any doubt.

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[44] The idea that gels consist of minute tactoids was suggested to me by Prof. J. D. Bernal.

[45] Bernal and Fankuchen, *Nature*, 1937, 139, 923 ; Bernal, *ibid.*, 1939, 143, 663. *Cf.* Langmuir, *loc. cit.*

[46] Hauser and Reed, *J. Physic. Chem.*, 1937, 41, 911.

[47] B. Derjaguin, *Trans. Faraday Soc.*, 1940, 36, 203.

[48] Hamaker, *Physica*, 1937, IV, 10, 1058.

Employing formula (21) of our communication, in a slightly altered form, instead of (22″) we obtain :

$$\frac{L - L_0}{L_0} = \frac{1}{2r}\int_0^\infty\left\{\left[(1 - e^{-z})e^{-m/z}\right]^n - 1\right\}dz. \qquad . \qquad . \quad \text{(II)}$$

For colloid systems with $r > 10^{-5}$ and $\psi_0 > 15m\text{V.}$, $n > 25$. In particular, similar large values of n are present for most stable emulsions. As a result of this, the value of the integral in II will be large at such sufficiently small values of the parameter m, at which the maximum of the function

$$K(z) = (1 + e^{-z})e^{-m/z},$$

corresponding to a certain value of z, will exceed unity, at least if only slightly. From the values of the maximum (and the minimum) of the function $K(z)$ corresponding to different values of m, given in Table 5, it is seen that a sharp decrease in the stability of the system should take place at a value of m which lies approximately between 0·15 and 0·3.

TABLE 5.

m . .	0	0·1	0·15	0·2	0·3	0·4	0·5
$K(z)_{\max}$.	(2)	1·32	1·21	1·13	1·02	0·94	absent
$K(z)_{\min}$.	(1)	0·98	0·97	0·96	0·94	0·92	absent

Thus, the emulsion will be sufficiently stable under the condition that

$$m < 0{\cdot}15,$$

or, in accordance with (I′), approximately, under the condition :

$$\frac{D\psi_0^2}{\kappa} > A. \qquad . \qquad . \qquad . \qquad . \quad \text{(III)}$$

The criterion of the stability which we developed theoretically is in agreement with the empirical rule obtained by H. Eilers and I. Korff [49] :

$$\frac{\zeta_0^2}{\kappa} = const = C, \qquad . \qquad . \qquad . \qquad . \qquad . \quad \text{(IV)}$$

where ζ_0 is the critical value of the zeta-potential. In particular, the above authors found that relation (IV) describes very well Povis's experiments with emulsions of cylinder oil in water (H. Eilers and I. Korff, Table IV) as well as with the hydrosol As_2S_3 (ebenda, Table VI), if a value of the order of 10^{-3} is assumed for C when ζ_0 is expressed in millivolts, and a value of the order of 10^{-14}, when ζ_0 is expressed in c.g.s.E.

Upon equating ψ_0 with ζ_0 in (IV), and making use of these values of C, from (III) and (IV) we obtain the following value for A :

$$A \sim 10^{-12} \qquad . \qquad . \qquad . \qquad . \qquad . \quad \text{(V)}$$

which agrees with the " mean " value of this constant.[48]

It should be noted that these computations, being based on the simplified Debye-Hückel equation, hold, strictly speaking, only while the values of the quantity

$$\frac{z_i\psi_0}{\kappa T}, \qquad . \qquad . \qquad . \qquad . \qquad . \quad \text{(VI)}$$

where z_i is the valence of the ith ion, are not large—of the order of unity. By the way, the critical values of this quantity were of the order of 1·5-2·0 in Povis's experiments. Thus the results obtained, particularly relation IV, cannot lay claim to a great degree of accuracy.

A more exact calculation, based on the complete Debye-Hückel equation, will form the subject of the following paper.

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[49] Eilers and Korff, *Trans. Faraday Soc.*, 1940, 36, 229.

Corrigenda.

Page 200, line 2, *for* Lyophobic *read* Lyophilic.

Page 204.—Formula (2′) should read :

$$\kappa = \sqrt{\frac{8\pi F^2 10^3}{DRT} \sum \frac{z_i^2 \gamma_i}{2}} \quad . \quad . \quad . \quad . \quad . \quad (2')$$

Page 212.—Formula (25) should read as follows :

$$P = \frac{8D\left(\frac{\kappa T}{e}\right)^2}{\pi d^2} e^{-\frac{2h}{d}} \quad . \quad . \quad . \quad . \quad . \quad (25)$$

Page 213.—In Table I the values of $P_{\text{calc.}}$ should be multiplied by 80, after which Table I will read as follows :

TABLE I.

$h = 115$ mμ.			$h = 75$ mμ.		
γ	$P_{\text{exp.}}$	$P_{\text{calc.}}$	γ	$P_{\text{exp.}}$	$P_{\text{calc.}}$
10^{-4}N	1500 dyn./cm.	160 dyn./cm.	—	—	—
10^{-3}N	400 dyn./cm.	2×10^{-4} dyn./cm.	10^{-3}N	1000 dyn./cm.	0·5 dyn./cm.

Page 219.—The statement made in the legend in Fig. 2 (and also in the text) that " ζ is independent of the radius and there is no adsorption of charge on addition of electrolyte " is inconsistent. In constructing Fig. 2, it is first assumed that ζ is independent of the radius. Then the form of ζ as a function of a (true for all κ by hypothesis) is obtained by the charge to be $50e$ and independent of κ (electrolyte concentration) for one radius only, namely $a = 10^{-6}$ cm., so that the form (9), page 218, is obtained for ζ.

AUTHOR INDEX.*

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* The references in heavy type indicate papers submitted for Discussion.

A THERMODYNAMIC STUDY OF BIVALENT METAL HALIDES IN AQUEOUS SOLUTION.

PART I. THE ACTIVITY COEFFICIENTS OF MAGNESIUM HALIDES AT 25°.

By R. A. Robinson and R. H. Stokes.

Received 16*th February*, 1940.

Prior to a study of the halides of zinc and cadmium we are investigating the halides of the alkaline earths, and especially those whose activity coefficients at 25° are not readily accessible by methods other than isopiestic measurements. We are now able to report on three magnesium halides at this temperature.

Table I relates to pairs of solutions which were found to be isopiestic, the second of each pair of figures referring to the molality of potassium chloride and the first to the molality of the isopiestic magnesium halide solution.

TABLE I.

Magnesium Chloride.

0·1120, 0·1579 ;	0·1587, 0·2271 ;	0·1917, 0·2782 ;	0·1944, 0·2808 ;
0·2656, 0·3936 ;	0·2795, 0·4156 ;	0·2933, 0·4379 ;	0·3492, 0·5299 ;
0·3644, 0·5548 ;	0·3924, 0·6035 ;	0·4040, 0·6242 ;	0·4387, 0·6818 ;
0·4815, 0·7559 ;	0·4840, 0·7617 ;	0·5293, 0·8516 ;	0·5600, 0·9033 ;
0·6503, 1·075 ;	0·7212, 1·217 ;	0·9856, 1·798 ;	0·9906, 1·806 ;
1·059, 1·970 ;	1·266, 2·487 ;	1·367, 2·765 ;	1·381, 2·805 ;
1·713, 3·732 ;	1·784, 3·962 ;	2·016, 4·712.	

Magnesium Bromide.

0·1086, 0·1557 ;	0·1127, 0·1614 ;	0·1341, 0·1939 ;	0·1770, 0·2600 ;
0·3250, 0·5101 ;	0·3575, 0·5668 ;	0·4284, 0·6988 ;	0·4592, 0·7607 ;
0·5171, 0·8734 ;	0·6057, 1·060 ;	0·6845, 1·240 ;	0·7192, 1·303 ;
0·8688, 1·659 ;	1·086, 2·307 ;	1·304, 2·852 ;	1·556, 3·627 ;
1·576, 3·697 ;	1·667, 4·009 ;	1·697, 4·092 ;	1·761, 4·301 ;
1·802, 4·462 ;	1·894, 4·782.		

Magnesium Iodide.

0·1049, 0·1518 ;	0·1217, 0·1789 ;	0·1266, 0·1867 ;	0·1958, 0·2982 ;
0·2696, 0·4233 ;	0·3595, 0·5934 ;	0·4989, 0·8626 ;	0·6225, 1·152 ;
0·6263, 1·153 ;	0·6363, 1·178 ;	0·7496, 1·449 ;	0·7598, 1·484 ;
0·8704, 1·776 ;	0·9268, 1·933 ;	0·9707, 2·058 ;	1·162, 2·621 ;
1·218, 2·803 ;	1·219, 2·821 ;	1·440, 3·543 ;	1·515, 3·806 ;
1·621, 4·188 ;	1·688, 4·423 ;	1·743, 4·647 ;	1·787, 4·81.

The osmotic and activity coefficients have been evaluated with reference to the data for potassium chloride given in a previous communication,[1] as shown in Table II.

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[1] Robinson, *Trans. Faraday Soc.*, 1939, 35, 1217.

TABLE II.

m.	$MgCl_2$.		$MgBr_2$.		MgI_2.	
	ϕ.	γ.	ϕ.	γ.	ϕ.	γ.
0·1	0·863	0·565	0·874	0·582	0·888	0·599
·2	·875	·520	·898	·546	·920	·577
·3	·897	·507	·931	·547	·960	·585
·4	·921	·508	·968	·560	1·002	·607
·5	·948	·514	1·005	·579	1·045	·637
·6	·978	·527	1·043	·604	1·092	·676
·7	1·010	·542	1·083	·635	1·143	·723
·8	1·043	·563	1·124	·671	1·198	·782
·9	1·077	·587	1·169	·714	1·255	·851
1·0	1·114	·613	1·216	·764	1·313	·929
1·2	1·190	·680	1·315	·885	1·426	1·112
1·4	1·271	·764	1·415	1·032	1·546	1·135
1·6	1·356	·867	1·517	1·214	1·666	1·653
1·8	1·444	·986	1·621	1·440	—	—
2·0	1·536	1·143	—	—	—	—

The activity coefficients of magnesium chloride were evaluated with reference to $\gamma = 0{\cdot}565$ at 0·1 M and 25°. This value was calculated by Redlich and Rosenfeld [2] from freezing-point data, together with the thermal data of Lange and Streeck.[3] At 0·2, 0·5, 1·0 and 2·0 M Redlich and Rosenfeld give $\gamma = 0{\cdot}528$, 0·521, 0·616 and 1·054 respectively. Apparently the thermal data of Lange and Streeck were available only to 0·1 M, and for higher concentrations the earlier results of Thomsen were used to correct activity coefficients from 0° to 25°. The agreement with our results is probably as good as could be expected.

There are no suitable data on which to base a value for the bromide and iodide at 0·1 M; from the trend of the osmotic coefficient curves it is apparent that the activity coefficients increase in the order $Cl < Br < I$, and to obtain an approximate value at 0·1 M the following procedure was adopted. According to the method of Randall and White,[4] activity coefficients can be evaluated from osmotic coefficient data by means of the equation:

$$- \ln \gamma = h + \int_0^m h/\sqrt{m}\,.\,d\sqrt{m},$$

where $h = 1 - \phi$.

Curves of $h/\sqrt{m}$ against $\sqrt{m}$ were drawn from 1 M to 0·1 M for each of the halides, and extrapolated to a value of 1·340 at $m = 0$. The curvature was uncertain over the region of extrapolation, but three similar curves were obtained, and the integral evaluated graphically up to $m = 0{\cdot}1$. The correct value of the integral is known for magnesium chloride at 0·1 M, since both h and γ are known for this salt at 0·1 M. It was then assumed that the factor relating the correct integral to the approximate value obtained graphically was valid for the bromide and iodide. Although the method is admittedly approximate, the error cannot be large because of the analogous nature of the three curves. The values at 0·1 M so obtained were $\gamma = 0{\cdot}582$ and 0·599 for the bromide and iodide respectively.

[2] Landolt-Bornstein, " *Tabellen*," 3er. *Erg.*, p. 2151.
[3] *Z. physikal. Chem. A*, 1931, 157, 1.
[4] *J. Amer. Chem. Soc.*, 1926, 48, 2514.

PART II. THE ACTIVITY COEFFICIENTS OF CALCIUM, STRONTIUM AND BARIUM CHLORIDE AT 25°.

By R. A. Robinson.

Received 16th February, 1940.

In addition to a few isopiestic measurements on barium chloride, supplementing those reported previously,[1] some data on the chlorides of calcium and strontium have been obtained. Table I relates to solutions which were found to be isopiestic, the second of each pair of figures referring to the molality of the reference salt, potassium chloride. In Table II are given the activity coefficients of these three alkaline earth chlorides calculated from the above isopiestic data. Table III compares the activity coefficient of $CaCl_2$ derived from the three independent e.m.f. measurements of Lucasse,[2] Fosbinder,[3] and Scatchard and Tefft [4] (columns L, F and S) with the values derived from the above isopiestic results (R) and those derived from the freezing-point,[5] using the most recent thermal data for calcium chloride (column F. Pt).

TABLE I.

Calcium Chloride.			
0·0887, 0·1234 ;	0·1512, 0·2127 ;	0·1628, 0·2304 ;	0·1963, 0·2780 ;
0·3117, 0·4534 ;	0·3692, 0·5453 ;	0·5009, 0·7667 ;	0·5159, 0·7890 ;
0·5481, 0·8476 ;	0·8242, 1·361 ;	0·8512, 1·417 ;	0·9194, 1·554 ;
1·027, 1·781 ;	1·105, 1·958 ;	1·133, 2·010 ;	1·202, 2·167 ;
1·355, 2·523 ;	1·391, 2·616 ;	1·485, 2·843 ;	1·519, 2·934 ;
1·583, 3·098 ;	1·631, 3·224 ;	1·752, 3·532 ;	1·765 ; 3·580 ;
1·921, 4·014 ;	1·933, 4·021 ;	2·107, 4·534 ;	2·178, 4·747 ;
2·202, 4·81.			
Strontium Chloride.			
0·1195, 0·1627 ;	0·1574, 0·2194 ;	0·1935, 0·2749 ;	0·3942, 0·5757 ;
0·5501, 0·8290 ;	0·5601, 0·8434 ;	0·7120, 1·107 ;	0·8320, 1·328 ;
0·9452, 1·546 ;	1·028, 1·714 ;	1·094, 1·843 ;	1·259, 2·186 ;
1·317, 2·308 ;	1·472, 2·649 ;	1·682, 3·128 ;	1·837, 3·501 ;
2·043, 4·021 ;	2·068, 4·083 ;	2·157, 4·314 ;	2·258, 4·583.
Barium Chloride.			
0·08810, 0·1209 ;	0·1134, 0·1558 ;	0·1475, 0·2034 ;	0·1529, 0·2106 ;
0·1553, 0·2139 ;	0·3213, 0·4526 ;	0·4649, 0·6696 ;	0·5088, 0·7360 ;
0·5660, 0·8278 ;	0·7809, 1·175 ;	0·9302, 1·436 ;	1·227, 1·962 ;
1·322, 2·148 ;	1·405, 2·294 ;	1·454, 2·395 ;	1·492, 2·462 ;
1·497, 2·472 ;	1·649, 2·773 ;	1·782, 3·046.	

Minor adjustments have been made in order to reduce all five sets of data to a common basis of comparison with $\gamma = 0·531$ at 0·1 M. It is clear that the three sets of data derived from e.m.f. measurements, although

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[1] Robinson, *J. Amer. Chem. Soc.*, 1937, **59**, 84.

[2] *Ibid.*, 1925, **47**, 743.

[3] *Ibid.*, 1929, **51**, 1345.

[4] *Ibid.*, 1930, **52**, 2265, 2272.

[5] Landolt-Bornstein, " *Tabellen*," 3er *Erg.*, p. 2141.

in good agreement between themselves, are at variance with the values derived from freezing-point determinations. The isopiestic measurements substantiate the latter, and strongly suggest therefore that the calcium amalgam electrode is not reversible.

The results for strontium chloride are in reasonable agreement with the e.m.f. determinations of Lucasse,[2] there being an average difference of 0·003 in γ at the five concentrations at which comparison is possible. The maximum difference is 0·005, and the differences do not show any trend of the two curves away from one another.

The data for barium chloride may be compared with the e.m.f. data of Lucasse,[2] and of Tippetts and Newton,[6] as well as the computations of Scatchard and Tefft.[4] The present results are on an average 0·003 lower in γ than those of Lucasse, and 0·002 lower than those of Scatchard and Tefft. They are 0·0025 higher than those of Tippetts and Newton. Up to 1 M, however, they are only 0·001 higher than those of the lats authors, the average deviation being 0·005 above 1 M.

TABLE II.

m.	$CaCl_2$.	$SrCl_2$.	$BaCl_2$.
0·1	(0·531)	(0·514)	(0·492)
0·2	·482	·463	·438
0·3	·462	·440	·411
0·4	·456	·430	·398
0·5	·457	·425	·390
0·6	·462	·426	·386
0·7	·469	·430	·384
0·8	·479	·436	·385
0·9	·493	·444	·388
1·0	·509	·455	·392
1·1	·528	·467	·397
1·2	·550	·480	·402
1·3	·573	·494	·409
1·4	·599	·510	·416
1·5	·626	·527	·423
1·6	·657	·546	·431
1·7	·690	·566	·440
1·8	·726	·587	·450
1·9	·764	·611	—
2·0	·807	·636	—
2·1	·853	·664	—
2·2	·901	·694	—

Some measurements have been made of the isopiestic ratio between solutions of potassium chloride and solutions which contained both potassium and barium chloride in amounts corresponding to the salt, K_2BaCl_4. Later it is hoped to apply isopiestic measurements to investigate the possibility of complex ion formation in solutions of zinc and cadmium halides containing the corresponding potassium halide. These measurements with potassium barium chloride are control experiments on a pair of salts which are least likely to exhibit complex ion formation.

The first and second columns of Table IV give the molality of K_2BaCl_4 and KCl respectively, corresponding to equal vapour pressures; *m* designates the molality of the former solution, *i.e.* mols. of the double salt per 1000 g. of water. The data for pure potassium chloride solutions given earlier [7] have been calculated as relative molar vapour pressure

TABLE III.

m.	e.m.f. L.	e.m.f. F.	e.m.f. S.	R.	F.Pt.
0·1	0·531	0·531	0·531	0·531	0·531
0·2	·494	·494	·496	·482	·478
0·5	·513	·516	·535	·457	·447
0·7	·576	·575	—	·469	—
1·0	·730	·704	·737	·509	·505
1·5	—	1·181	1·080	·626	—
2·0	1·565	—	—	·807	—

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[6] *J. Amer. Chem. Soc.*, 1934, **56**, 1675.

[7] Robinson, *Trans. Faraday Soc.*, 1939, **35**, 1217.

lowerings, $R = (p_0 - p)/Mp_0$, a form very suitable for plotting against the molality. From this graph were read the relative vapour pressure lowerings at each of the potassium chloride concentrations in the second column. These gave the vapour pressure lowerings relative to the vapour pressure of pure water at 25° for each potassium chloride and therefore for each isopiestic potassium barium chloride solution. These values are given in the third column in mm. of mercury. They may be compared with four sets of figures calculated on different assumptions. In the first place, it may be assumed that in the mixed solution no complex ion formation occurs, and the barium chloride is completely dissociated. The further reasonable assumption is made that under these conditions the relative molal vapour pressure lowering of each salt is equal to that of the salt in a solution of the same total ionic strength ($\mu = 5m$) in the absence of the other salt. R for each salt can be plotted against the total ionic strength, the data for pure barium chloride being obtained from the isopiestic data reported earlier in this paper. From the plots the values of R for each single salt can be read at the appropriate ionic strength, and the vapour pressure lowering calculated; the latter are given in the fourth column of the table. Secondly, it may be assumed that formation of the complex salt $K_2(BaCl_4)$ is complete. The total ionic strength would be 3 m, and the R curve for this salt may be assumed to be of the same type as that of barium chloride. Consequently, the vapour pressure lowerings should approximate to those of barium chloride at the same concentration. These vapour pressure lowerings may therefore be obtained from the R curve for pure barium chloride. They need not be tabulated here, but are given as a plot in Fig. 1. Thirdly, it may be assumed that the potassium

TABLE IV.

m.	M – KCl.	Δp (mm. Hg). obs.	Δp (mm. Hg). calc.
0·06065	·2073	0·161	0·161
·1344	·4615	·353	·348
·2379	·8174	·620	·618
·3054	1·055	·799	·797
·3901	1·360	1·030	1·027
·5235	1·842	1·394	1·405
·6127	2·173	1·650	1·665
·6560	2·327	1·770	1·793
·8650	3·113	2·389	2·423
·9412	3·397	2·614	2·671
·9915	3·586	2·770	2·831
1·020	3·691	2·850	2·919
1·078	3·906	3·035	3·114
1·163	4·236	3·290	3·396
1·233	4·514	3·518	3·629

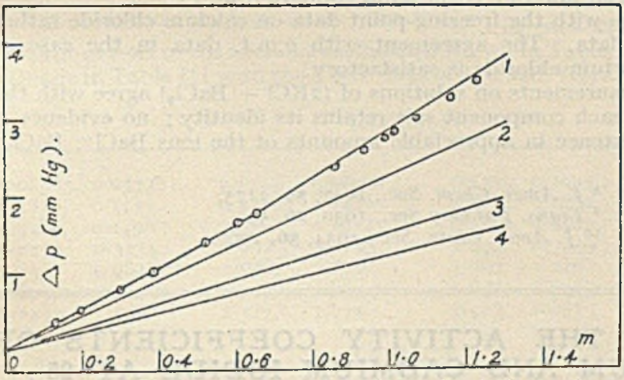

FIG. 1.—Vapour pressure lowerings of solutions of ($2KCl + BaCl_2$). ⊙ Experimental points.

Curve 1. Calculated for $2K^+ + Ba^{++} + 4Cl^-$
,, 2. ,, ,, $2K^+ + [BaCl]^+ + 3Cl^-$
,, 3. ,, ,, $2K^+ + [BaCl_3]^- + Cl^-$
,, 4. ,, ,, $2K^+ + [BaCl_4]^-$

barium chloride functions as $KCl + KBaCl_3$; to a first approximation the effect of the univalent $BaCl^-_3$ ion may be equated to that of a Cl^- ion and the solution is effectively one of potassium chloride at a molality 2 *m*. The vapour pressure lowerings have been calculated on this basis, and are shown in Fig. 1. Finally, there is a possibility that the potassium chloride represses the dissociation of the barium salt leading to a solution of

$$(2K^+ + BaCl^+ + 3Cl^-).$$

Again no great error would be introduced by assuming that the vapour pressure lowerings would correspond to a solution of potassium chloride at a molality 3 *m*, and the plot on this basis is also given in Fig. 1. This figure shows conclusively that no appreciable complex ion formation occurs and that there is no evidence for the existence of the $BaCl^-$ ion. No errors in the assumptions made above in equating the vapour pressure lowerings due to ions of the same valency would bring the calculated curve appreciably nearer the experimental points.

On the other hand, the agreement in the last two columns of the table between the observed vapour pressure lowerings and those calculated on the assumption that each salt retains its identity, is excellent. The agreement is not exact, but this would not be expected, because there must be a specific interionic effect. There is a maximum difference between the observed and calculated vapour pressure lowerings of 3 per cent. which is similar to that observed by Owen and Cooke [8] for mixtures of potassium and lithium chloride.

Righellato and Davies [9] concluded that conductivity data in dilute solutions indicated that barium chloride was a strong electrolyte. The implied absence of the $BaCl^+$ ion is consistent with these vapour pressure measurements. Shedlovsky and Brown [10] also found the conductivity of barium chloride to conform to the Onsager limiting law.

Summary.

Isopiestic measurements have been made on calcium, strontium and barium chloride and activity coefficients computed at 25°.

The data agree with the freezing-point data on calcium chloride rather than the e.m.f. data. The agreement with e.m.f. data in the case of strontium and barium chloride is satisfactory.

Isopiestic measurements on solutions of $(2KCl + BaCl_2)$ agree with the assumption that each component salt retains its identity; no evidence is found for the existence in appreciable amounts of the ions $BaCl^-$, $BaCl_3^-$ or $BaCl_4^{--}$.

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[8] *J. Amer. Chem. Soc.*, 1937, **59**, 2273.
[9] *Trans. Faraday Soc.*, 1930, **26**, 592.
[10] *J. Amer. Chem. Soc.*, 1934, **56**, 1066.

PART III. THE ACTIVITY COEFFICIENTS OF POTASSIUM AND CADMIUM IODIDE AT 25°.

By R. A. Robinson and (Miss) Jean M. Wilson.

Received 16*th February*, 1940.

The activity coefficients of the chlorides of the alkaline earth metals, reported in Parts I and II, exhibit a normal behaviour when compared with the coefficients of the alkali halides. The opposite extreme of anomalous activity coefficients is found in the case of cadmium iodide.

Before investigating this salt, some measurements were made on

TABLE I.

0·5358,	0·5471 ;	0·7015,	0·7192 ;	1·298,	1·348 ;	1·904,	1·990 ;
2·343,	2·461 ;	2·562 ;	2·692 ;	2·673,	2·809 ;	2·914,	3·067 ;
2·966,	3·120 ;	3·036,	3·194 ;	3·544,	3·724 ;	3·649,	3·831 ;
4·054,	4·251 ;	4·182,	4·388 ;	4·232,	4·434 ;	4·601,	4·81.

potassium iodide, for use in a further communication on solutions containing both potassium and cadmium iodide.

It has been shown [1] that the original isopiestic data [2] on the potassium chloride - potassium bromide salt pair gave slightly low activity coefficients of the bromide as a result of some corrosion of the first design of dishes by the bromide solution. This effect would be expected to be even more marked with iodide solutions, and we have therefore made a new determination of the isopiestic ratio between potassium chloride and potassium iodide, using "staybrite" steel dishes. The effect of the corrosive action of the iodide solution on silver becomes apparent only at concentrations greater than 2 M. Table I relates to solutions found to be isopiestic, the molality of potassium iodide being given first in each case. These determinations lead to the activity coefficients shown in Table II. A comparison is made in Table III with the e.m.f. data of Harned [3] (H) and of Gelbach [4] (G).

TABLE II.

m	0·1	0·2	0·3	0·5	0·7	1·0	1·5
γ	0·776	·731	·704	·675	·659	·646	·639
m	2·0	2·5	3·0	3·5	4·0	4·5	—
γ	·641	·649	·657	·667	·678	·692	—

TABLE III.

m.	V.P.	H.	G.
0·1	0·776	0·775	0·772
0·2	·731	·730	·721
0·5	·675	·678	·666
1	·646	·649	—
2	·641	·646	—

TABLE IV.

0·08585,	0·05736 ;	0·1227,	0·08092 ;	0·1559,	0·1021 ;	0·1774,	0·1129 ;
0·1817,	0·1155 ;	0·2338,	0·1446 ;	0·3111,	0·1862 ;	0·4163,	0·2463 ;
0·4188,	0·2498 ;	0·6258,	0·3811 ;	0·7164,	0·4412 ;	0·8135,	0·5113 ;
0·8279,	0·5234 ;	0·9578,	0·6125 ;	1·094,	0·7059 ;	1·147,	0·7485 ;
1·432,	0·9891 ;	1·578,	1·108 ;	1·597,	1·112 ;	1·607,	1·110 ;
1·675,	1·194 ;	1·725,	1·233 ;	1·842,	1·346 ;	1·955,	1·439 ;
2·143,	1·598 ;	2·317,	1·773 ;	2·423,	1·893 ;	2·432 ;	1·910.

TABLE V.

m	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9	
γ	0·1074	·0685	·0523	·0433	·0377	·0337	·0307	·0284	·0266	
		1·0	1·2	1·4	1·6	1·8	2·0	2·2	2·4*	2·5*
		·0251	·0228	·0211	·0199	·0189	·0181	·0174	·0169	·0167

* Supersaturated.

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[1] Robinson, *Trans. Faraday Soc.*, 1939, **35**, 1217.

[2] Robinson, *J. Amer. Chem. Soc.*, 1935, **57**, 1161.

[3] *Ibid.*, 1929, **51**, 416.

[4] *Ibid.*, 1933, **55**, 4857.

Table IV relates to pairs of solutions of cadmium iodide and potassium iodide respectively found to be isopiestic. From these data the activity coefficient of cadmium iodide was calculated relative to a value of

$$\gamma = 0{\cdot}0685 \text{ at } 0{\cdot}2\ \text{M}$$

taken from the results of Bates and Vosburgh.[5] In this calculation the activity coefficients of potassium iodide obtained above were used. These gave the activity coefficients shown in Table V.

Getman[6] has derived the activity coefficient of this salt from measurements of cells with a silver-silver iodide and a lead-lead iodide electrode respectively, whilst Bates and Vosburgh[5] used a mercury-mercurous iodide electrode. Table VI compares the four sets of results.

TABLE VI.

m.	Electrode.			Vapour Pressure.
	Ag/AgI	Pb/PbI$_2$.	Hg/Hg$_2$I$_2$.	
0·1	0·10	0·11	0·108	0·1074
0·2	·065	·067	·0685	(·0685)
0·5	·037	·037	·0382	·0377
0·7	—	—	·0310	·0307
1	·025	·025	·0254	·0251
1·3	—	·022	·0222	·0220
2	—	—	·0183	·0181
2·366	—	—	·0171	·0171

Summary.

Measurements are reported of the activity coefficients of potassium iodide and of cadmium iodide, which are in good agreement with e.m.f. determinations.

Auckland University College,
New Zealand.

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[5] Robinson, *J. Amer. Chem. Soc.*, 1937, **59**, 1583.
[6] *J. physical Chem.*, 1928, **32**, 940.

PART IV. THE THERMODYNAMICS OF ZINC CHLORIDE SOLUTIONS.

By R. A. Robinson and R. H. Stokes.

Received 1st April, 1940.

E.m.f. measurements have been made of cells containing zinc iodide,[1] cadmium chloride[2] and cadmium bromide,[3] over an extended range of temperature. Measurements of similar cells containing zinc chloride have been made only at 25°. The e.m.f. of the cell:

$$\text{Zn-Hg (2-phase)} \mid ZnCl_2 \mid AgCl,\ Ag$$

has now been measured between 10° and 40°. From these determinations the standard potential of the cell and of the zinc electrode have

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[1] Bates, *J. Amer. Chem. Soc.*, 1938, **60**, 2983.
[2] Harned and Fitzgerald, *ibid.*, 1936, **58**, 2624.
[3] Bates, *ibid.*, 1939, **61**, 308.

been deduced and the activity coefficients, partial molal heat content and partial molal heat capacity have been calculated.

Experimental.

Silver-silver chloride electrodes of the Carmody [4] type and a two-phase zinc amalgam electrode were employed. In the preliminary experiments a cell containing two amalgam electrodes was used, but as the two electrodes always agreed within 0·01 mv. this cell was discarded and the main work done with a cell containing a single amalgam electrode and three silver-silver chloride electrodes. The agreement of the latter was usually about 0·03 mv. but occasionally one would give a very divergent result, in which case it was rejected. The stock solutions were prepared from Merck's $ZnCl_2$ and stored in an atmosphere of hydrogen. They were analysed for Cl^- gravimetrically and for Zn volumetrically, using the ferrocyanide titration with diphenylbenzidine indicator.[5] The original stock solution contained an excess of ZnO, and in the first series of experiments the solution was neutralised with sufficient HCl acid exactly to balance the zinc. Eight cells were made by dilution of this solution. The e.m.f.'s were not as steady as those registered with a solution of a different type described later, and were 1·7 ± 0·4 mv. lower at 25° over a concentration range 0·04 — 0·2 M than the e.m.f.'s observed by Scatchard and Tefft.[6] This suggests that the standard electrode potential of zinc should be defined, for practical purposes, in terms of the solution used. A similar acidity effect has been observed by Clayton and Vosburgh.[7]

The second solution, used in the main work, was made by adding sufficient acid to prevent precipitation on dilution but insufficient for complete neutralisation ; it contained Zn and Cl^- in the ratio 1·0055 : 2 ; in the following tables molalities of $ZnCl_2$ are calculated on the Cl^- content, and all e.m.f.'s observed have been increased by 0·07 mv. before being recorded in the tables in order to allow for this slight excess of Zn in the solution. This solution gave constant, reproducible e.m.f.'s in good agreement at 25° with those of Scatchard and Tefft.

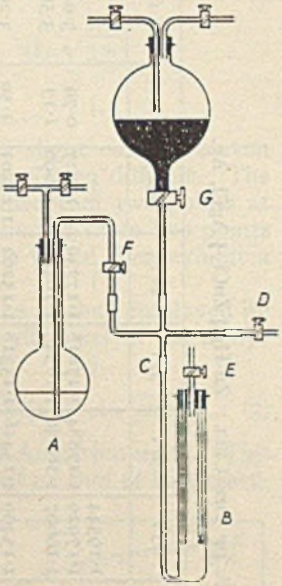

FIG. 1.—Cell and apparatus for filling.

The cell and apparatus for filling it are illustrated in Fig. 1. The flask, A, was used for weighing the stock solution, which, after dilution with air-free water, was boiled *in vacuo* and the flask then filled with hydrogen, allowance being made for the loss of water and the increased buoyancy of hydrogen. The cell, B, containing the Ag-AgCl electrodes which had been chloridised in HCl or $ZnCl_2$ solution immediately before use, was attacked at C. The cell was blackened to prevent exposure of the electrodes to light. The cell was evacuated at D and hydrogen admitted through E. Solution was then forced into the cell from A under hydrogen pressure after which amalgam was run into the cell from G. The amalgam in G was stored under hydrogen. A gas-tight electrical contact was then made with the amalgam through the side-arm of the cell.

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[4] Bates, *J. Amer. Chem. Soc.*, 1929, **51**, 2901.

[5] Cone and Cady, *ibid.*, 1927, **49**, 356.

[6] *Ibid.*, 1930, **52**, 2272.

[7] *Ibid.*, 1936, **58**, 2093.

Thus the whole operation of filling the cell with solution and amalgam was carried out either *in vacuo* or in an atmosphere of hydrogen. The cell was left in the thermostat overnight at 25° to attain equilibrium and measurements made next day on a Leeds and Northrup Type K2 potentiometer in the order 25° to 40°, 40° to 10°, 10° to 25° at 5° intervals. The e.m.f. at 25° was therefore measured three times and no divergence greater than 0·03 mv. was observed.

All weighings were vacuum corrected on standardized weights. The thermometer was calibrated against an N.P.L. certified thermometer.

Experimental Results.

Table I gives the observed e.m.f.'s at different temperatures, together with results for four cells at 25° only. The data at each concentration were examined critically by plotting first order temperature differences against temperature ;[8] on this basis there is good reason for believing that three e.m.f.'s (marked by asterisks in Table I) are erroneous to the

TABLE I.—E.M.F. OF THE CELL : Zn-Hg | $ZnCl_2$ | AgCl, Ag.

m.	10°.	15°.	20°.	25°.	30°.	35°.	40°.	E_{25}.	$-a \times 10^4$.	$-b \times 10^6$.
0·003151	—	—	—	1·19544	—	—	—	—	—	—
·005082	1·17980	1·17974	1·17956	1·17929	1·17884	1·17818	1·17739	1·17927	0·79	3·04
·007354	1·16788	1·16773	1·16739	1·16697	1·16636	1·16545	1·16444	1·16696	1·13	3·56
·01040	1·15650	1·15619	1·15569	1·15499	1·15416	1·15318	1·15202	1·15501	1·50	3·29
·01753	1·14014	1·13957	1·13879	1·13786	1·13678	1·13550	1·13396*	1·13788	2·03	3·58
·01854	1·13826	1·13764	1·13684	1·13584	1·13467	1·13333	1·13185	1·13584	2·14	3·49
·02201	—	—	—	1·13028	—	—	—	—	—	—
·02671	1·12677	1·12601	1·12504	1·12387	1·12257	1·12110	1·11954	1·12388	2·43	3·21
·04602	1·11001	1·10879	1·10763	1·10622	1·10473	1·10295	1·10110	1·10620	2·93	2·81
·06439	1·09970	1·09845	1·09702	1·09548	1·09379	1·09202	1·09012	1·09548	3·20	2·51
·1042	1·08496	1·08349	1·08193	1·08023	1·07836	1·07640	1·07438	1·08021	3·54	2·45
·1306	1·07770	1·07609	1·07440	1·07259	1·07067	1·06872	1·06674*	1·07258	3·69	1·81
·1856	1·06704	1·06532	1·06350	1·06161	1·05966	1·05763	1·05562*	1·06162	3·84	1·46
·3013	1·05028	1·04859	1·04678	1·04496	1·04321	1·04142	1·03960	1·04500	3·57	0·20
·3223	1·04893	1·04721	1·04544	1·04369	1·04193	1·04013	1·03835	1·04369	3·54	0·23
·4320	1·03891	1·03728	1·03571	1·03408	1·03247	1·03082	1·02923	1·03408	3·23	0·07
·7121	1·02290	1·02155	1·02028	1·01896	1·01765	1·01637	1·01510	1·01896	2·60	—0·16
1·031	1·01143	1·01030	1·00923	1·00813	1·00703	1·00596	1·00491	1·00812	2·18	—0·16
1·490	—	—	—	0·99732	—	—	—	—	—	—
2·830	—	—	—	0·97580	—	—	—	—	—	—

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[8] Harned and Nims, *J. Amer. Chem. Soc.*, 1932, 54, 423.

extent of 0·1 mv. This deviation occurred at 40° in each case. The remainder of the results were expressed by the equation:

$$E = E_{25} + a(t - 25) + b(t - 25)^2 ; \quad . \quad . \quad . \quad (1)$$

the three constants, E_{25}, a and b were obtained by the method of least squares; they are recorded in the last three columns of Table I. (Attention may be drawn to the considerable arithmetical simplicity obtained if measurements are made at an equal number of evenly spaced temperatures above and below 25°.) The mean deviation between the observed e.m.f.'s and those calculated by equation (1) was 0·015 mv.

The Standard Potential of the Cell.

An attempt was made to evaluate this at 25° by the Hitchcock extrapolation,[9] the function E'_{25} being plotted against the molality, where:

$$E'_{25} = E_{25} + k \log 4m^3 (1 + 0{\cdot}054m)^3 - 3k\mu\sqrt{3m}$$
$$k = 2{\cdot}303\ RT/2F$$
$$\mu = \text{limiting Debye slope} = 1{\cdot}012.$$

The result was, however, uncertain because of a slight curvature even in the most dilute region which made the extrapolation difficult. The curve suggested a value of $E°_{25} = 0{\cdot}9845$, provided that two points at the lowest concentration were neglected. Inclusion of these two points would lead to a value of 0·9830 v. but the curve would then exhibit a marked change in direction at 0·008 M.

A better extrapolation is obtained by using the method employed by Bates[1] in which allowance is made for the ionic diameter in the Debye term. A new E' function is defined by:

$$E'_{25} = E_{25} + k \log 4m^3/(1 + 0{\cdot}054m)^3 - 3k\mu\sqrt{3m}/(1 + A\sqrt{3m}) \quad . \quad (2)$$

where $A = 0{\cdot}329\ a$, a being the ionic diameter in Ångstrom units. This method of extrapolation, although an improvement on that of Hitchcock, may be misleading if an incorrect ionic diameter is assumed. Since this method of extrapolation implies the extended Debye-Hückel equation, $E'_{25} = E°_{25} - 3kBm$, where B is the constant of the linear term in the Debye-Hückel equation, E'_{25} should be a linear function of m, extrapolating to a limiting value $E°_{25}$. Fig. 2 illustrates a series of plots for an ideal case where $E°_{25} = 1{\cdot}00000$ v., $a = 5$ A and $3kB = 0{\cdot}006$. The plot for $a = 5$ A is linear in m. The figure also contains curves calculated from equation (2) for four other ionic diameters. It will be observed that if too low a value of this diameter is used, the curve bends upwards with increasing dilution, and *vice versa* for too high a value of the diameter. This series of

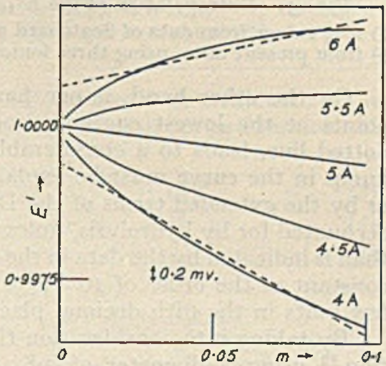

FIG. 2.—Illustrating the effect of ionic diameter on the extrapolation of a standard potential.

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[9] Harned and Nims, *J. Amer. Chem. Soc.*, 1928, **50**, 2076.

curves makes it clear that the absence of reliable data at low concentrations combined with the scattering of points due to unavoidable experimental errors may easily create an illusion of linearity for diameters other than the correct one. Extreme examples of this are illustrated by the dotted lines in Fig. 2 which lead to $E°$ values ± 0·7 mv. from the correct value on the assumption of ionic diameters which are ± 1 A in error. In applying this method of extrapolation, therefore, it is desirable to try several ionic diameters and to find not only the one which gives the most linear extrapolation but also the two which give rise to curvature in opposite directions.

Fig. 3 contains three curves corresponding to ionic diameters of 4·5, 5·0 and 5·5 A, the E'_{25} values being obtained from the experimental results up to 0·13 M, together with the data of Scatchard and Tefft.[6] These E'_{25} values are shown as circles of diameter 0·1 mv., those of Scatchard and Tefft as crossed circles. Selection of the $E°_{25}$ value depends now on the weight assigned to the three results below 0·008 M. If these are neglected on the grounds of unreliability of the cells, then the curves in Fig. 3 for 4·5 and 5·5 A clearly exhibit curvature in opposite directions, whilst a value of 5·0 A gives a good linear extrapolation to $E°_{25} = 0·9848_5$ v. for the standard potential of the cell. The standard potential of the Ag-AgCl electrode[10] being 0·22239 v. that of the zinc electrode must be $0·7624_6$ v. The error in this determination should be not more than ± 0·1 mv. It has been assumed that the Zn electrode has the same potential as zinc amalgam.

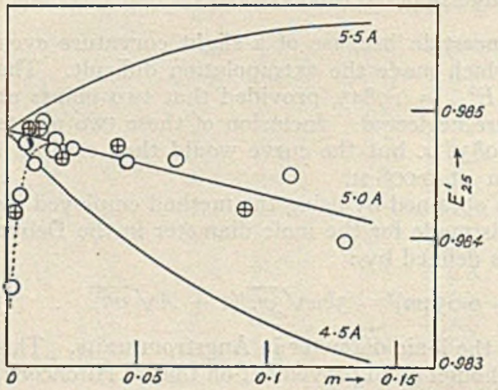

FIG. 3.—Extrapolation of the $E°_{25}$ value.
○ E'_{25} values from data of Scatchard and Tefft.
⊕ from present data, using three ionic diameters.

On the other hand, if one has faith in the reliability of the three points at the lowest concentrations then extrapolation, shown by the dotted line, leads to a considerably lower $E°_{25}$ value. In this case the hump in the curve must be explained either by incomplete dissociation or by the extended terms of the Debye equation. The hump cannot be accounted for by hydrolysis, unless the hydrolysis is considerably greater than is indicated by the data in the literature; Prytz[11] found a hydrolysis constant of the order of 10^{-9}; this would affect the E'_{25} values only a few units in the fifth decimal place.

By taking into consideration the extended terms of the Debye equation,[12] using a diameter of 3·8 A, it may be shown that the data of Scatchard and Tefft at 0·002941, 0·007814 and 0·01236 M lead to $E°_{25}$ values of 0·9837, 0·9838 and 0·9836 v. From the present data at 0·003151, 0·005082, 0·007354 and 0·01040 M values of $E°_{25} = 0·9831$, 0·9835,

[10] Harned and Ehlers, *J. Amer. Chem. Soc.*, 1933, **55**, 2179.

[11] *Z. anorg. Chem.*, 1931, **200**, 139.

[12] Gronwall, LaMer and Sandved, *Physikal. Z.*, 1928, **29**, 558; LaMer, Gronwall and Greiff, *J. Physical Chem.*, 1931, **35**, 2245.

0·9838, and 0·9834 v. are obtained. Unfortunately the theory is not applicable above these concentrations, and it cannot be determined whether the data at higher molalities would give similar E°_{25} values.

The hypothesis of incomplete dissociation with a higher ionic diameter has an effect similar to the incorporation of the extended terms. Using a value of 0·25 for the equilibrium constant of the reaction :

$$ZnCl^+ \rightleftharpoons Zn^{++} + Cl^-,$$

and an ionic diameter of 5 A, the method of Harned and Fitzgerald,[2] applied to the above data, gives an excellent linear extrapolation to $E^\circ_{25} = 0{\cdot}9841$ v. We are reluctant, however, to ascribe incomplete dissociation to this salt at such high dilutions from three e.m.f.'s in the most doubtful concentration region, especially as conductivity measurements [13] indicate that this salt is a strong electrolyte. An examination of the extrapolation curves for ZnI_2, given by Bates,[1] also shows that, below 0·008 M, there is a tendency for the e.m.f. data to fall below the line he used for extrapolation. As there can be little doubt that ZnI_2 approximates closely to a strong electrolyte, even up to 0·8 M, the anomalous behaviour exhibited below 0·008 M must be ascribed to the difficulty of obtaining correct results with the zinc amalgam electrode at high dilutions. This will also be true for $ZnCl_2$ solutions and we therefore consider the linear extrapolation of Fig. 3 the more reliable.

In Table II are collected the determinations of the standard potential of zinc from different sources. The data for the Zn-Hg $\mid$ $ZnCl_2$ $\mid$ HgCl, Hg cell were recalculated, using Bates' method of extrapolation to give a value of approximately 1·0308 v.

TABLE II.—STANDARD ELECTRODE POTENTIAL OF ZINC AT 25°.

Cell.		E°_{25}.		E°_{25}(Zn).
Zn-Hg	$ZnCl_2 \mid AgCl, Ag$.	0·9848$_5$	Ag, AgCl = 0·22239[10]	0·7625
Zn-Hg	$ZnBr_2 \mid AgBr, Ag$[14]	0·8339	Ag, AgBr = 0·0713[15] .	0·7626
Zn-Hg	$ZnI_2 \mid AgI, Ag$[1] .	0·6105$_5$	Ag, AgI = 0·1522[16] .	0·7627
Zn-Hg	$ZnCl_2 \mid HgCl, Hg$[17] .	1·0308	Hg, HgCl = 0·2679[18] .	0·7629
Zn-Hg	$ZnBr_2 \mid HgBr, Hg$[19]	0·9019	Hg, HgBr = 0·1391[20, 14]	0·7628

The standard potentials at other temperatures were evaluated by a different method. Expressing the terms in equation (2) as functions of the temperature at constant molality :

$$E'_t = E'_{25} + a'(t - 25) + b'(t - 25)^2, \quad . \quad . \quad (3)$$

$$E = E_{25} + a(t - 25) + b(t - 25)^2, \quad . \quad . \quad (4)$$

$$k \log 4 = 0{\cdot}01780 + 0{\cdot}6 \times 10^{-4}(t - 25), \quad . \quad . \quad (5)$$

$$3k \log m = 3k_{25} \log m + a_1(t - 25), \quad . \quad . \quad . \quad (6)$$

$$3k\mu\sqrt{3m}/(1 + A\sqrt{3m}) = f(25^\circ) + a_2(t - 25) + b_2(t - 25)^2 \quad . \quad (7)$$

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[13] Connell, Hamilton and Butler, *Proc. Roy. Soc. A*, 1934, **147**, 418.

[14] Parton and Mitchell, *Trans. Faraday Soc.*, 1939, **35**, 758.

[15] Owen and Foering, *J. Amer. Chem. Soc.*, 1936, 58, 1875.

[16] Owen, *ibid.*, 1935, **57**, 1526.

[17] Brüll, *Gazz. chim. ital.*, 1934, 64, 261.

[18] Gerke, *J. Amer. Chem. Soc.*, 1922, 44, 1684 ; Randall and Young, *ibid.*, 1928, **50**, 989.

[19] Ishikawa, Ferui and Takai, *Bull. Inst. Phys. Chem.* (Tokyo), 1936, **15**, 339

[20] Gerke and Geddes, *J. Physical Chem.*, 1927, **31**, 886. The more recent determination of the Hg, HgBr potential = 0·1397 (Larson, *J. Amer. Chem. Soc.*, 1940, **62**, 764), reduces the Zn potential to 0·7622.

where $k = 2{\cdot}303\ RT/2F$, μ and A are functions of the temperature and $f(25°)$ designates the value of the Debye term at 25°. The constants in equations (6) and (7) may be evaluated without reference to the present experimental work, and thus by equating coefficients of like powers of $(t - 25)$, the constants of equation (3) can be evaluated. The necessary data are given in Table III; a is read off at round concentrations from a plot of the experimental values of a (Fig. 4) and a' calculated from

TABLE III.—EVALUATION OF STANDARD POTENTIAL OF ZINC BETWEEN 10° AND 40°.

m.	$-a \times 10^4$.	$-a_1 \times 10^4$.	$-a_2 \times 10^4$.	$-a' \times 10^4$.
0·005	0·72	6·848	0·47	7·44
0·01	1·44	5·952	0·61	7·40
0·02	2·15	5·056	0·79	7·40
0·03	2·55	4·532	0·90	7·38
0·05	2·99	3·872	1·06	7·32
0·10	3·50	2·976	1·28	7·16

$$a' = a + 0{\cdot}6 \times 10^{-4} + a_1 - a_2.$$

The constant, $a°$, of the equation:

$$E°_t = E°_{25} + a°(t - 25) + b°(t - 25)^2 \quad . \quad . \quad (8)$$

is obtained by extrapolation of a plot of a' against m, giving

$$a° = -\ 7{\cdot}45 \times 10^{-4}.$$

$b°$ is obtained by direct extrapolation of b against m, giving

$$b° = -\ 3{\cdot}8 \times 10^{-6},$$

(Fig. 4a.) Table IV gives the $E°$ values of the cell between 10° and 40°, the $E°$ values of the Zn electrode, using the Ag-AgCl potentials of Harned and Ehlers[10] and, for comparison, similar data given by Bates.[1]

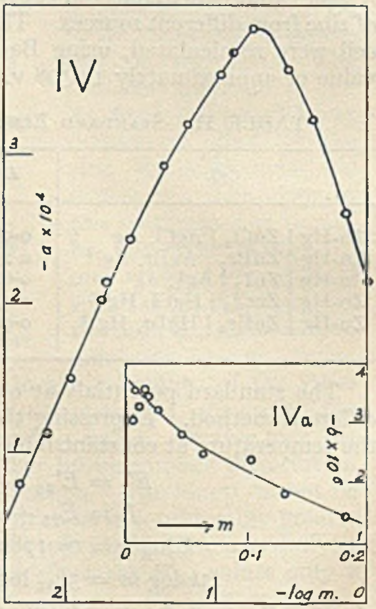

FIG. 4 and 4a.—Constants of equation (1).

TABLE IV.—STANDARD POTENTIALS BETWEEN 10° AND 40°.

$t°$.	Cell $E°$.	$E°$(Zn). Present Work.	$E°$(Zn). Bates.
10	0·99617	0·76391	0·76415
15	·99192	·76345	·76370
20	·98849	·76298	·76322
25	·98485	·76246	·76275
30	·98103	·76193	·76226
35	·97702	·76139	·76176
40	·97281	·76081	·76117

The Activity Coefficient of Zinc Chloride.

E_{25} values at round concentrations were obtained by plotting E'_{25} against m, the requisite E'_{25} values at round concentrations were then calculated back to E_{25} values. This is a more accurate method of extrapolation than a direct graphing of E_{25} against a function of m. Interpolation of a and b values at round concentrations in Figs. 4 and 4a yielded E values at other temperatures. Activity coefficients were then calculated from $E = E_0 - RT/2F \log 4m^3\gamma^3$.

TABLE V.—Activity Coefficients of Zinc Chloride.

m.	10°.	15°.	20°.	25°.	30°.	35°.	40°.
0·005	0·794	0·792	0·791	0·789	0·787	0·785	0·783
·01	·737	·735	·733	·731	·728	·726	·723
·02	·673	·671	·669	·667	·663	·660	·657
·03	·635	·633	·631	·628	·625	·621	·617
·05	·587	·585	·582	·579	·575	·571	·566
·07	·556	·554	·551	·547	·543	·538	·532
·1	·525	·523	·520	·515	·510	·504	·497
·2	·476	·470	·465	·459	·452	·443	·434
·3	·453	·447	·439	·430	·419	·407	·393
·5	·433	·422	·409	·394	·379	·363	·347
·7	·415	·401	·384	·367	·349	·331	·313
1·0	·394	·376	·357	·337	·318	·298	·280
1·49	—	—	—	·306	—	—	—
2·83	—	—	—	·282	—	—	—

As a check on the e.m.f. data some isopiestic vapour pressure measurements were made at 25°. The following molalities (Table VI) of $ZnCl_2$

TABLE VI.

0·1085,	0·1502 ;	0·1086,	0·1494 ;	0·1161,	0·1608 ;	0·1431,	0·1982 ;
0·1571,	0·2181 ;	0·1935,	0·2703 ;	0·1986,	0·2762 ;	0·2480,	0·3466 ;
0·3383,	0·4728 ;	0·3855,	0·5407 ;	0·4098,	0·5743 ;	0·4881,	0·6815 ;
0·5116,	0·7182 ;	0·5828,	0·8141 ;	0·6323,	0·8724 ;	0·6681,	0·9179 ;
0·8884,	1·206 ;	0·9078,	1·223 ;	1·036,	1·380 ;	1·251,	1·634 ;
1·440,	1·856 ;	1·632,	2·096 ;	2·045,	2·622 ;	2·149,	2·752 ;
2·182,	2·807 ;	2·539,	3·306 ;	3·035,	4·028 ;	3·187,	4·291.

and KCl respectively, were found to correspond to isopiestic solutions, and the activity coefficients at 25° were calculated (Table VII).

TABLE VII.

m .	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	
γ .	·513	·458	·429	·410	·394	·381	·369	·357	
m .	0·9	1·0	1·2	1·4	1·6	1·8	2·0	2·5	3·0
γ .	·348	·338	·321	·309	·300	·294	·289	·284	·287

The Relative Partial Molal Heat Content and Heat Capacity.

By combining the Gibbs-Helmholtz equation with the equation relating the e.m.f. to the free energy increment, the relative partial molal heat content is obtained in the form :

$$\overline{L}_2 = -2F(E_{25} - E^\circ_{25}) - \mathrm{T}_{25}(a - a^\circ) + T^2_{25}(b - b_0) - T^2(b - b_0)$$

where $T_{25} = 298{\cdot}1$ and T is the temperature in degrees absolute. Hence the heat content data in Table VI are obtained. The relative partial molal heat capacity is given by:

$$\Delta\bar{C}_p = \left(\frac{\partial \bar{L}_2}{\partial T}\right)_{p,\,m};$$

the temperature coefficient of the latter is beyond the accuracy of these experiments, so it will suffice to record, in the last column of Table VIII, the heat capacity at 25°. The heat data are expressed as cal. per mol and cal. per degree per mol respectively.

TABLE VIII.—RELATIVE PARTIAL MOLAL HEAT CONTENT AND HEAT CAPACITY OF ZINC CHLORIDE.

	$\bar{L}_2$.							$\Delta\bar{C}_p$.
m.	10°.	15°.	20°.	25°.	30°.	35°.	40°.	
0·005	185	202	219	237	255	273	292	4
·01	214	248	282	316	351	386	422	7
·02	211	276	339	403	468	534	602	13
·03	228	312	398	485	574	664	756	18
·05	249	380	510	644	779	918	1060	27
·07	301	469	639	812	988	1170	1350	35
·1	326	540	754	981	1210	1440	1670	45
·2	461	810	1170	1530	1890	2260	2650	73
·3	1020	1490	1960	2450	2940	3440	3950	98
·5	2440	2940	3460	3990	4520	5060	5610	106
·7	3360	3880	4320	4970	5520	6080	6660	110
1·0	4500	5030	5560	6110	6660	7230	7800	110

A graph of $\bar{L}_2$ against $\sqrt{m}$ shows that a limiting slope of 2900 (cal. units) is reached below 0·07 M.

Summary.

The standard electrode potential of zinc at 25°, derived from measurements of the cell: Zn-Hg | $ZnCl_2$ | AgCl, Ag, is found to be 0·7625 v. in good agreement with values derived from other zinc halide cells.

The standard potentials found at temperatures between 10° and 40° are within 0·3 mv. of those deduced from the zinc iodide cell.

Activity coefficients, partial molal heat contents and partial molal heat capacities have been calculated.

We wish to record our thanks to Messrs. Imperial Chemical Industries (Australasia) Ltd. for a substantial monetary grant towards the cost of the potentiometer.

Auckland University College,
New Zealand.

THE CRYSTAL STRUCTURE OF CONJUGATED HYDROCARBONS AT LOW TEMPERATURES.
(I) BUTADIENE.

By C. J. Birkett Clews.

Received 7th May, 1940.

The molecular structure of butadiene has been studied theoretically by Lennard-Jones [1] and by Penney [2] on account of its importance as the simplest molecule with conjugated double bonds. An experimental investigation of its structure is also of technical interest because on polymerisation a material with properties similar to those of natural rubber is produced. It is this aspect of the problem with which this note is concerned. Although the properties of rubber and rubber-like substances have been extensively investigated, there are a number of problems still unsolved; among the more important of these are the nature of the linkages between the polymerised chains (main valence chains) in the material, the reason for the peculiar elastic properties, and the apparent ordering of the crystallites during the stretching process exemplified by the X-ray diagrams.[3]

A structure based on X-ray photographs (which must not, however, be looked upon as more than a close approximation to the true structure), has been proposed for stretched natural rubber,[4] and work is now in progress on other rubber-like polymers, more particularly those of butadiene and chloroprene. In view of the many difficulties involved in making a more exact X-ray analysis of such complex structures, it seemed to be a matter of some interest to study the structures of the building units of the polymerised chains: the monomeric hydrocarbons, butadiene, chloroprene, and isoprene. A brief account of this work has already been published,[5] but the data for butadiene will now be considered in more detail.

Experimental.

The butadiene (C_4H_6) used in these experiments was a pure sample from Imperial Chemical Industries Limited. At normal temperatures butadiene is a gas. The boiling-point is − 4·75° C. and the melting-point is − 108·7° C. In order to obtain useful information from an X-ray study it is necessary to work with the substance in the solid state, for example, at liquid oxygen temperature.

Powder photographs were taken in a Debye-Scherrer camera of 57 mm. radius. The butadiene, contained in a thin-walled glass or cellophane capillary tube, was continuously cooled by a stream of liquid oxygen. The X-ray source was a 5 kw. tube with a rotating copper anticathode, operating at 100 ma. Under such conditions satisfactory photographs were obtained in 30-60 minutes.

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[1] Lennard-Jones, *Proc. Roy. Soc. A*, 1937, **158**, 280.

[2] Penney, *ibid.*, 306.

[3] Schoszberger and Iguchi, *Kautschuk*, 1936, **12**, 193.

[4] Lotmar and Meyer, *Sitzber, Akad. Wiss. Wien, IIb*, 1936, **145**, 721; Clews, *Proc. Rubber Tech. Conference*, 1938, p. 955.

[5] Clews, *Nature*, 1938, **141**, 513.

Results and Discussion.

The diagrams show thirty-four measurable lines. These are listed in Table I, with their visually estimated intensities and the corresponding spacings calculated from the Bragg relation. The intensity scale is self-explanatory.

TABLE I.—BUTADIENE. CU Kα RADIATION. TEMPERATURE : – 170° C.

No. of Line.	Intensity.	Observed Spacing.	d_{hkl} (calculated).	Indices.
1	m	5·85	5·92	120
2	ms	4·66	4·67	220
3	s	4·23	4·23	002
4	s	4·08	4·07	221
5	s	3·87	3·85	112
6	ss	3·55	3·56	202
7	ss	3·47	3·44	212
8	s	3·30	3·30	400
9	s	3·19	3·20	140
10	mw	2·97	2·99	411
11	mw	2·88	—	—
12	mw	2·78	2·78	241, 322
13	mw	2·73	2·73	113
14	w	2·57	2·57	150, 412
15	www	2·49	2·49	511
16	www	2·42	$2{\cdot}41_5$	422
17	ww	2·35	2·34	303, 133, 251
18	ms	2·27	2·27	350
19	m	2·22	2·22	233, 512
20	www	2·17	2·17	160
21	w	2·13	2·12	004, 333
22	s	2·08	2·08	260
23	www	1·99	1·99	124
24	w	1·95	1·95	360, 301
25	w	1·93	$1{\cdot}93_5$	224
26	w	1·90	1·89	700
27	w	1·86	1·87	622, 550
28	mw	$1{\cdot}76_5$	1·77	404
29	m	$1{\cdot}74_5$	$1{\cdot}73_5$	414, 334
30	www	1·70	1·69	005, 231
31	www	1·57	1·57	135
32	www	1·54	1·54	235, 401
33	ww	1·49	1·49	145, 335, 822
34	ww	1·42	1·41	006

As is well known, powder photographs are not easily interpreted unless the crystalline material belongs to a crystal class of high symmetry, and at the time of writing the preliminary note [5] it had not been possible to do more than calculate the spacings. The data have since been re-examined, and by making use of the Hull diagrams for the interpretation of powder photographs it now seems that the crystal has a simple tetragonal lattice. The strong lines No. 3 and No. 8 are taken to correspond to the second order reflection from (001) and the fourth order from (100), respectively. The axial ratio, c/a, is thus 0·64, and the unit cell : $a = b = 13{\cdot}20$ A, $c = 8{\cdot}46$ A. The other spacings calculated from the appropriate quadratic formula

$$d_{hkl} = \frac{a_0}{\sqrt{h^2 + k^2 + (l/c)^2}}$$

are shown in the table for comparison, and the corresponding indices (*hkl*) given. Where more than one set of indices is given to a single reflection the calculated spacing is a mean value. It has been possible to assign indices to all the lines except one; it will be seen that the agreement between the observed and calculated spacings is very satisfactory, although perhaps fortuitous in the case of some of the short spacings. The exception is the weak line No. 11; this reflection could not be indexed, but in view of the satisfactory indexing of all the other lines there seems to be no justification for supposing that the cell chosen is incorrect. It is possible that this line is not a reflection from butadiene at all but from some part of the apparatus, but it has not been possible to confirm this.

The volume V of the unit cell is 1474 A^3, and the molecular weight of butadiene M is 54, so that on substituting in the formula for the density

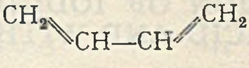
$$\rho = \frac{n \times M \times 1{\cdot}65 \times 10^{-24}}{V}$$

where n is the number of molecules in the cell and $1{\cdot}65 \times 10^{-24}$ gm. is the mass of the hydrogen atom, we get $\rho \sim 0{\cdot}06n$. Now for a hydrocarbon in the solid state $\rho \sim 0{\cdot}5 - 1{\cdot}0$ g./cm.^{3}, usually nearer the upper limit. Thus $n \sim 9 - 16$, but for a tetragonal lattice $n = 2, 4, 8, 16$, etc., so that there are probably 16 molecules in the unit cell, although the possibility of there being only 8 is not entirely excluded. Assuming 16 molecules in the cell, the calculated density is 0·967 g./cm.^{3}; if there are only 8 molecules, the solid would have the abnormally low value 0·483, lower in fact than the density of the liquid near its boiling-point. The former, more probable value may appear high, but we may perhaps compare it with the density of a polymerised hydrocarbon, isoprene; the density of unstretched pure rubber is 0·906 and the highest value quoted in the literature for stretched rubber is 0·965. The density of a very impure specimen of polymerised butadiene was found to be approximately 0·987.

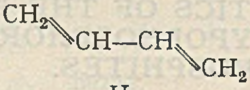
1·3 Butadiene is a relatively simple molecule,

$$CH_2 \overset{B}{=} CH \overset{A}{-} CH \overset{B}{=} CH_2,$$

or if we take into account the two possible modifications, *cis* and *trans*, these may be represented as I and II respectively. Penney suggests



I



II

that it is a staggered chain molecule, that is, it exists in the *trans* rather than the *cis* form, and this is borne out by the work of Price and Walsh [6] on the ultra-violet absorption spectra of conjugated dienes. These authors were unable to find any evidence for the presence of *cis*-butadiene, although according to Mulliken the absorption spectra indicate the presence of about 20 % of this isomer. Penney gives the length of the A linkage as 1·43 A and of the B linkages 1·34 A, both much shorter than would be expected for a simple structure built up with alternate single and double bonds. The shortening of the linkages is due to resonance.

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[6] Price and Walsh, *Proc. Roy. Soc. A*, 1940, 174, 220.

[7] Wood, *Proc. Rubber Tech. Conference*, 1938, p. 933.

In view of the simplicity of the molecule, it is somewhat surprising that the unit cell should be so large and contain so many molecules. From other work on hydrocarbons, a cell with four molecules would seem more probable. It may be that an explanation can be found in a tendency of the molecules to associate, forming groups of two, or possibly four molecules; and that, instead of having four molecules in the unit cell, the building unit is a group of four molecules, there being four such groups of molecules. Such a hypothesis is not unreasonable when the readiness with which the molecules join together to form polymerides is considered, but this is, of course, quite a different phenomenon. There is also evidence that molecules with resonance do tend to show association. Although a tentative explanation is given for the large number of molecules and the correspondingly large unit cell, it must be pointed out there is no *a priori* reason why the molecules should not exist in the cell as separate units and not in groups as postulated in this discussion.

In conclusion, 1·3 butadiene in the solid state crystallises with a tetragonal lattice, the dimensions of the unit cell at − 170° C. being $a = b = 13{\cdot}20$ A, $c = 8{\cdot}46$ A. There are probably sixteen C_4H_6 molecules in the cell, giving a density 0·967 g./cm.^{3} The present data do not permit of any further elucidation of the structure. The number of molecules in the cell can be definitely fixed as soon as the density of the solid has been estimated, but for any more accurate knowledge of the structure of the crystal it would be necessary to produce a single crystal for examination by X-ray and optical methods. Such an investigation would present many technical difficulties.

I am indebted to Dr. W. J. S. Naunton of Imperial Chemical Industries Limited for supplying the butadiene, and to Sir William Bragg and the Managers of the Royal Institution for the facilities they afforded me. My thanks are due to Mr. Smith of the Royal Institution for his valuable assistance.

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KINETICS OF THE REACTION OF IODINE WITH HYPOPHOSPHOROUS ACID AND WITH HYPOPHOSPHITES.

By R. O. Griffith, A. McKeown, and R. P. Taylor.

Received 24*th April*, 1940.

The reaction between hypophosphorous acid and iodine in acid solution has been fairly thoroughly investigated by Mitchell,[1] and a study of the corresponding reaction with bromine by Griffith and McKeown [2] confirmed the mechanism originally proposed by Mitchell. For the bromine reaction the experimental observations were satisfactorily accounted for by the scheme :—

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[1] Mitchell, *J.C.S.*, 1920, **117**, 1322 ; 1921, **119**, 1266 ; 1922, **121**, 1624.
[2] Griffith and McKeown, *Trans. Faraday Soc.*, 1934, **30**, 530.

$$\begin{tikzcd}
H^+ + H_2PO_2^- \arrow[d, "Br_2"', "+ H_2O"] & \rightleftharpoons & H_3PO_2 \text{ (normal)} & \overset{H^+}{\underset{H^+}{\rightleftharpoons}} & H_3PO_2 \text{ (active)} \arrow[d, "\text{Bromine} + H_2O"] \\
H_2PO_3^- + 2HBr & & & & H_3PO_3 + 2HBr
\end{tikzcd}$$

Reaction of the $H_2PO_2^-$ ion with iodine had not been detected by Mitchell, and one object of the present investigation was to investigate the kinetics of this process. During the course of the work, a publication by Nylén[3] indicated that Mitchell's reaction (α), H_3PO_2 (normal) $\rightleftharpoons$ H_3PO_2 (active), is not only catalysed by hydrogen ion but is also subject to general acid catalysis. He attempted (but without complete success) to make his experimental conditions such that the sole rate-determining step was reaction (α), and he did not further discuss the reaction mechanism. We have repeated and extended Nylén's work on this acid-catalysed reaction under conditions which permit a more comprehensive analysis of the complete reaction mechanism to be effected.

A. The $H_2PO_2^-$ — I_2 Reaction.

Previous work having failed to detect the occurrence of this reaction at ordinary temperatures, tests were first made at 50° and 60° and with all the hypophosphite present as the ion (phosphate, arsenate and phthalate buffers with *p*H 6 to 8). Under such conditions reaction was found to occur at convenient speed, the rate being independent of $[H^+]$ and inversely as $K_3 + [I^-]$, where K_3 is the tri-iodide equilibrium constant.

TABLE I.—Phosphate Buffers.

$[Na_2HPO_4]/[KH_2PO_4]$.	$[KH_2PO_4]_0$.	$[\Sigma I_2]_0$.	$[KI]_0$.	$2k_0K_3 \cdot 10^4$.
temp. = 60°; μ = 2·05; K_3 = ·00285.				
0·1/0·1	0·051	0·002	0·005	52·9
0·2/0·02	·245	·0133	·2	52·9
0·2/0·02	·245	·0133	·1	51·8
*0·2/0·02	·248	·0133	·2	52·8
0·05/0·05	·026	·0013	·0027	52·8
0·05/0·15	·051	·002	·005	52·5
0·2/0·01	·244	·0133	·2	52·7
0·05/0·05	·051	·002	·005	50·3
0·15/0·05	·244	·0133	·1	52·3
temp. = 50°; μ = 2·05; K_3 = ·00232.				
0·15/0·05	0·245	0·0133	0·1	13·3
0·05/0·05	·051	·002	·005	13·1
0·2/0·01	·246	·0133	·2	13·0
0·2/0·02	·246	·0133	·2	13·0
temp. = 30°; μ = 1·15; K_3 = ·00155.				
0·1/0·015	0·247	0·017	0·04	0·498
0·1/0·015	·815	·013	·032	0·514
0·1/0·01	·244	·01	·024	0·507
0·1/0·03	·244	·01	·024	0·506

* For this experiment, an arsenate buffer $\frac{[Na_2HAsO_4]}{[KH_2AsO_4]} = \frac{0·2}{0·02}$ was used.

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[3] Nylén, *Z. anorg. Chem.*, 1937, 230, 385.

TABLE II.—PHTHALATE BUFFERS.

[NaKPh]/[KHPh].	$[KH_2PO_2]_0$.	$[\Sigma I_2]_0$.	$[KI]_0$.	$2k_0K_3 \cdot 10$
temp. = 60° ; μ = 1·1 ; K_3 = 0·00285.				
0·2/0·05	0·245	0·0133	0·2	41·0
0·2/0·02	0·245	0·0133	0·2	40·0

A reaction between the $H_2PO_2^-$ ion and the free iodine molecule analogous to, but much slower than, that previously found between $H_2PO_2^-$ ion and Br_2 is thus indicated.

The reaction was followed by running samples into excess of standard sodium arsenite solutions and back-titrating with iodine. Under the present conditions the slow measured reaction :—

$$H_2PO_2^- + I_2 + H_2O \xrightarrow{k_0} H_2PO_3^- + 2HI$$

is followed by the very rapid oxidation :—

$$H_2PO_3^- + I_2 + H_2O \longrightarrow H_2PO_4^- + 2HI$$

so that effectively two molecules of iodine disappear per molecule of $H_2PO_2^-$. Hence :—

$$-\frac{d[\Sigma I_2]}{dt} = 2k_0 \cdot \frac{K_3}{K_3 + [I^-]} \cdot [H_2PO_2^-][\Sigma I_2], \quad . \quad . \quad (1)$$

and values of k_0K_3 have been computed on this basis. Even in the pH range of 6 to 8, however, the acid-catalysed reaction is not entirely suppressed, and corrections of from 1 to 4 per cent. have been subtracted from the observed values of $-\frac{d[\Sigma I_2]}{dt}$, such corrections being based on the data of Section B. All measurements were carried out at one or other of the ionic strengths $\mu = 1{\cdot}1$ or $2{\cdot}0$, obtained by addition of KNO_3 as neutral salt. The values of $k_0\left(\frac{\text{litre}}{\text{mole-min.}}\right)$ deriving from the data are as follows : at 60° and $\mu = 2{\cdot}05$, $k_0 = 0{\cdot}92$; at 60° and $\mu = 1{\cdot}10$, $k_0 = 0{\cdot}71$; at 50° and $\mu = 2{\cdot}05$, $k_0 = 0{\cdot}282$; at 30° and $\mu = 2{\cdot}05$, $k_0 = 0{\cdot}0163$. These yield a critical increment for the reaction

$$H_2PO_2^- + I_2 + H_2O \longrightarrow H_2PO_3^- + 2HI$$

of 25,200 calories. The reaction is compared with analogous reactions of iodine and of bromine in the succeeding paper.

B. The Acid-Catalysed H_3PO_2 — Iodine Reaction.

Before presenting our experimental data for this reaction, it will be convenient to describe the reaction mechanism on the basis of which the experimental findings are to be analysed.

The work of Mitchell[1] and of Griffith and McKeown[2] has shown that the oxidation of H_3PO_2 by halogens, as catalysed by H^+, can formally be interpreted in terms of the reciprocal transformations of two tautomeric forms of H_3PO_2, both brought about by the intermediacy of H^+ ions, with only one of these forms, the " active " form, capable of oxidation by the halogen. Expressing the normal and active modifications of H_3PO_2 by HR and RH respectively the part-processes thus envisaged are :—

$$\mathrm{HR} \underset{\text{catalysed by } H^+}{\overset{\text{catalysed by } H^+}{\rightleftarrows}} \mathrm{RH} \xrightarrow[+ H_2O]{+ \text{ halogen}} \text{Resultants.}$$

The work of Nylén,[3] and more particularly the present investigation show, however, that catalysis is effected, not by H^+ alone, but by acids in general, and a closer consideration of the nature of prototropic change shows that *direct* acid catalysis of the reciprocal transformations $\mathrm{HR} \rightleftarrows \mathrm{RH}$ is unlikely. Instead, each of these reactions must go either *via* an intermediate complex (HRH^+) of the acid and H^+ ion or *via* the R^- ion, the primary stage in the first path being subject to general acid catalysis and the second stage to general basic catalysis, and *vice versa* when the ion R^- is the intermediary. A complete prototropic reaction scheme of this type is one analogous to that suggested by Pedersen,[4] Fig. 1.

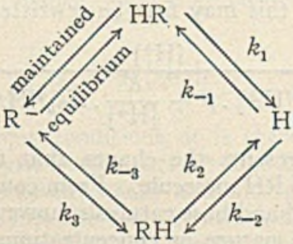

Fig. 1.

Here HR can capture a proton by collision with H_3O^+, H_2O or any other acid HA, the velocity coefficients of these processes being respectively k_1°, k_1^w and k_1^a; the resulting complex HRH^+ may then lose its proton by collision with the conjugate bases H_2O, OH^- or A^-, the velocity coefficients of these reversals being k°_{-1}, k^w_{-1} and k^a_{-1} respectively. Analogous definitions apply to the k_2 and k_{-2} processes. In the alternative route from HR to RH *via* R^-, the reciprocal processes $\mathrm{HR} \rightleftarrows R^-$ in the present case represent the ionisation of the normal form of H_3PO_2, and therefore constitute a rapidly maintained equilibrium (ionisation constant K), while processes k_3 and k_{-3} indicate how by acid and basic catalysis respectively the active form of the acid derives from or gives the $H_2PO_2^-$ ion. We now assume that the reactive form RH is always present in small amount compared with the normal form HR, and that the kinetics of the reaction of RH with iodine to give the resultant H_3PO_3 are formally represented by :—

$$+\frac{d[H_3PO_3]}{dt} = -\frac{d[\Sigma R]}{dt} = k'[RH][\Sigma I_2], \quad . \quad . \quad (2)$$

where $[\Sigma R]$ represents the gross concentration of hypophosphorous acid (*i.e.* hypophosphorous acid + hypophosphite). It is then possible, on the basis of pseudo-stationary state concentrations of HRH^+ and RH, to deduce the following expression for the rate of formation of H_3PO_3 in terms of $[\Sigma R]$, the concentrations of catalysing acids and bases, and the velocity coefficients k_1, k_{-1}, k_2, k_{-2}, k_3, k_{-3} of the part-processes :—

$$-\frac{d[\Sigma R]}{dt} = \frac{[\Sigma R]}{K + [H^+]} \,.\, k'[\Sigma I_2]$$
$$.\,\frac{[H^+] \,.\, \Sigma k_1{}^a[HA] \,.\, \Sigma k^a{}_{-2}[A^-] + K \,.\, \Sigma k_3{}^a[HA]\{\Sigma k_1{}^a[HA] + \Sigma k^a{}_{-2}[A^-]\}}{\Sigma k^a{}_{-1}[A^-] \,.\, \Sigma k^a{}_2[HA] + \{\Sigma k^a{}_{-1}[A^-] + \Sigma k^a{}_{-2}[A^-]\}\{\Sigma k^a{}_{-3}[A^-] + k'[\Sigma I_2]\}}.$$

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[4] Pedersen, *Trans. Faraday Soc.*, 1938, 34, 237.

If now we redefine the observed rate of reaction in terms of free H_3PO_2 as reactant as follows :—

$$-\frac{d[\Sigma R]}{dt} = k_{b1}[H_3PO_2][\Sigma I_2] = k_{b1}\frac{[H^+]}{K+[H^+]}[\Sigma R][\Sigma I_2]$$
$$= k_{obs}[\Sigma R][\Sigma I_2], \qquad (3)$$

it follows from a comparison of these equations that :—

$$\frac{1}{k_{b1}} = \frac{1}{k'}\cdot\frac{\Sigma k_{-1}[A^-]\,.\,\Sigma k_2[HA] + \Sigma k^a{}_{-3}[A^-]\{\Sigma k^a{}_{-1}[A^-] + \Sigma k^a{}_{-2}[A^-]\}}{\Sigma k_1{}^a[HA]\,.\,\Sigma k^a{}_{-2}[A^-] + \frac{K}{[H^+]}\,.\,\Sigma k_3{}^a[HA]\{\Sigma k^a{}_{-1}[A^-] + \Sigma k^a{}_{-2}[A^-]\}}$$
$$+\frac{[\Sigma I_2]}{[H^+]}\cdot\frac{\{\Sigma k^a{}_{-1}[A^-] + \Sigma k^a{}_{-2}[A^-]\}[H^+]}{\Sigma k_1{}^a[HA]\,.\,\Sigma k^a{}_{-2}[A^-] + \frac{K}{[H^+]}\,.\,\Sigma k_3{}^a[HA]\{\Sigma k^a{}_{-1}[A^-] + \Sigma k^a{}_{-2}[A^-]\}}.$$

This complicated expression for $1/k_{b1}$ is fortunately capable of very considerable simplification. In the first place, the expression multiplying $1/k'$ on the right hand side can easily be shown to be just the reciprocal of the equilibrium constant $K_t = [RH]_e/[HR]_e$ of the tautomeric equilibrium $HR \rightleftarrows RH$, so that the first term on the right hand side reduces to $1/k'K_t$. As regards the factor multiplying $[\Sigma I_2]/[H^+]$ in the second term, this may first be rewritten in the form :—

$$\frac{[H^+]}{\Sigma k_1{}^a[HA]\,.\,\beta + \frac{K}{[H^+]}\,.\,\Sigma k_3{}^a[HA]}, \text{ where } \beta = \frac{\Sigma k^a{}_{-2}[A^-]}{\Sigma k^a{}_{-1}[A^-] + \Sigma k^a{}_{-2}[A^-]};$$

β represents the chance that the HRH^+ complex reacts to form the active RH molecule. From considerations based on the Brönsted theory of acid and base catalysis, however, it can be shown that β is independent of the nature or concentrations of the catalysing bases present in the system, being equal to $\frac{G_{-2}}{G_{-1}+G_{-2}}$, where the G's are the factors in the Brönsted relations

$$k^a{}_{-1} = G_{-1}\left(\frac{1}{K_A}\right)^v \quad\text{and}\quad k_{-2} = G_{-2}\left(\frac{1}{K_A}\right)^v.$$

There are no available means of evaluating β, so we have for simplicity assumed it equal to unity, the value it would have if the k_2, k_{-2} reactions in the above scheme effectively constituted a maintained equilibrium. We therefore write :—

$$\frac{1}{k_{b1}} = \frac{1}{k'K_t} + \frac{[\Sigma I_2]}{[H^+]}\cdot\frac{[H^+]}{\Sigma k_1{}^a[HA] + \frac{K}{[H^+]}\,.\,\Sigma k_3{}^a[HA]}. \qquad (4)$$

It follows from this equation that when for any experiment the values for each time interval of $\frac{1}{k_{b1}}$ are plotted against the corresponding values of $\frac{[\Sigma I_2]}{[H^+]}$, the intercept of the resulting plot on the $\frac{1}{k_{b1}}$ axis should be a constant (at constant temperature) independent of the nature and composition of the reaction mixture. It may be said at once that this prediction of the theory is completely verified by our experimental results covering a range of catalysing acids from HCl to $H_2PO_4^-$.

It may be noted that $k'K_t$ is the limiting value which k_{b1} assumes when equilibrium between HR and RH is effectively maintained, so that reaction (k') of RH with iodine provides a very slight drain on the concentration of RH. This condition is approached experimentally only at very low concentrations of iodine. Again, the second term on the right hand side of equation (4) represents the value of $\frac{1}{k_{b1}}$ when reaction k' is very fast compared with the reversals

$$\begin{tikzcd}[column sep=small, row sep=small] & HRH^+ \arrow[dr] & \\ RH \arrow[ur] \arrow[dr] & & HR. \\ & R^- \arrow[ur] & \end{tikzcd}$$

When this condition is fulfilled, the measured reaction should obviously be compounded of the processes $HR \rightarrow HRH^+$ and $R^- \rightarrow RH$, which is in agreement with the form of this second right-hand term. This condition is approached experimentally at very high concentrations of iodine.

Writing equation (4) in the form :—

$$\frac{1}{k_{b1}} = \text{Intercept} + \frac{[\Sigma I_2]}{[H^+]} \cdot \text{slope}, \qquad (5)$$

it is seen that the slope of the plot of $\frac{1}{k_{b1}}$ against $\frac{[\Sigma I_2]}{[H^+]}$ is given by :—

$$\frac{1}{\text{slope}} = \frac{1}{[H^+]} \cdot \Sigma k_1{}^a[HA] + \frac{K}{[H^+]^2} \cdot \Sigma k_3{}^a\,[HA]. \qquad (6)$$

From the values of the slope under various conditions, it is therefore possible to derive the values of the catalytic coefficients $k_1{}^a$ and $k_3{}^a$ of the catalysing acids H_3O^+, H_3PO_2 (the reactant itself) and any other acid HA. In the majority of our experiments the concentrations of H^+ and of the catalysing acids present remained sufficiently constant during a run to give practically linear plots of $\frac{1}{k_{b1}}$ against $[\Sigma I_2]/[H^+]$, and accordingly the slope of each such plot was correlated with the average values of $[H^+]$, $[H_3PO_2]$ and [HA] in the run.

There are no *a priori* grounds for predicting the relative rates of the paths $HR \rightarrow HRH^+ \rightarrow RH$ (k_1 reaction) and $HR \rightarrow R^- \rightarrow RH$ (k_3 reaction) for any given set of conditions, but from equation (6) it is clear that the k_3 path is favoured by low values of $[H^+]$ the k_1 path by high values of $[H^+]$. Actually our results admit of interpretation on the assumption that the k_3 path is negligible for values of $[H^+]$ greater than about $4\cdot10^{-4}$, and we have been able to evaluate k_3 only for the acid $H_2PO_4^-$ (using $H_2PO_4^-$—HPO_4^{--} buffers) and the acid $H_2AsO_4^-$ (using $H_2AsO_4^-$—$HAsO_4^-$ buffers). For all the stronger catalysing acids investigated the k_1 terms predominate in equation (6).

In deducing the above equations, the rate of oxidation of the active RH by the halogen is formally expressed by $k'[RH][\Sigma I_2]$. The question whether the iodine participates in this reaction solely as I_2, or solely as I_3^-, or as both forms reacting simultaneously can obviously be decided by investigating the dependence of the intercept $\frac{1}{k'K_t}$ upon the concentration of iodide in the system. We find that the "intercept," and therefore k', is practically independent of $[I^-]$ for values of this greater than 0·05, which corresponds to over 97 per cent. of the iodine present as the tri-iodide ion. With progressive reduction of $[I^-]$, however, the "intercept" steadily decreases, that is, k' increases. Writing

$$k' = k'_{I_2} \cdot \frac{K_3}{K_3 + [I^-]} + k'_{I_3^-} \cdot \frac{[I^-]}{K_3 + [I^-]} \quad . \quad . \quad (7)$$

where k'_{I_2} and $k'_{I_3^-}$ are the velocity coefficients of reaction of I_2 and I_3^- respectively with RH, it follows that the free iodine is the more reactive of the two, and the data permit the evaluation of the relative reactivities $k'_{I_2}/k'_{I_3^-}$ of the two species.

Experimental.

The catalytic effects of the following acids on the hypophosphorous acid-iodine reaction have been studied: H_3O^+, H_3PO_2, H_3PO_3, H_3PO_4, HSO_4^-, $CH_2Cl . COOH$, $CH_2OH . COOH$, citric acid, $(COOH)_2$, CH_3COOH, $H_2AsO_4^-$ and $H_2PO_4^-$. The kinetic measurements have been carried out mainly at 30°, with a few observations at 40°, 50° and 60°.

The procedure used in following the reaction depended to a large extent upon the acidity of the system. For $p\text{H} < 3$, the rate of further oxidation of the resultant H_3PO_3 by iodine is insignificant relative to that of the primary oxidation $H_3PO_2 \rightarrow H_3PO_3$, that is

$$-\frac{d[\Sigma H_3PO_2]}{dt} = -\frac{d[\Sigma I_2]}{dt}.$$

Under these conditions, samples of reaction mixture were run into excess of iced water and immediately titrated with thiosulphate. For $p\text{H} > 6$, on the other hand, the phosphite—iodine reaction is so rapid that two molecules of iodine disappear per molecule of hypophosphorous acid. For experiments in this range the experimental procedure was therefore similar to that used in Section A. In the intermediate range of acidity, incomplete oxidation of the phosphite to phosphate takes place, and it was therefore necessary to estimate both the concentration of iodine and that of hypophosphite at the beginning and end of each time interval. To do this, duplicate samples of reaction mixture were withdrawn at various times, and the iodine content of one estimated by titration with thiosulphate. The other sample was run into excess of cold saturated $NaHCO_3$ solution in a stoppered flask and the mixture allowed to stand for one or two hours at room temperature, so that all phosphite present might be oxidised to phosphate without further oxidation of the hypophosphite. From the iodine remaining in the mixture the concentration of hypophosphite in the sample could then be computed, and hence by use of the equation :—

$$-\frac{\Delta[\Sigma H_3PO_2]}{t_2 - t_1} = k_{\text{obs}}[\Sigma H_3PO_2]_m[\Sigma I_2]_m$$

the value of k_{obs} in the time interval $t_2 - t_1$ inferred. It must further be noted that correction of the observed rate of reaction for the concomitant $H_2PO_2^- - I_2$ reaction (*cf.* Section A) was in most cases necessary. In acid media ($p\text{H} < 3$) this correction does not exceed 2 per cent., but it becomes increasingly significant with increasing $p\text{H}$ and in the most alkaline range ($p\text{H} > 6$) this reaction becomes the dominant process, accounting in some cases for 80 per cent. of the total. The accuracy with which the residual acid-catalysed process could be estimated is correspondingly poor in this range.

For most experiments the initial concentration of hypophosphite (the potassium salt) was greater than that of the iodine. The former was varied between 0·36 and 0·0067 M ; the latter from 0·0067 M downwards. Except in the experiments designed to evaluate the relative reactivities of I_2 and I_3^-, the initial concentration of potassium iodide was usually 0·1 or

0·2 M. For the most part no effort was made to control the ionic strength which usually lay between 0·1 and 0·6. Additions of KNO_3 in individual cases to vary the μ between these limits showed little effect on the rate of reaction beyond that attributable to alteration of the hydrogen ion conconcentration of the system. Certain observations at $\mu = 1{\cdot}2$ and $2{\cdot}2$ (by addition of KCl) were designed to explore the effect of large ionic strengths on the reaction.

The major difficulty in the treatment of the experimental results lies in the estimation of the concentrations of hydrogen ion, of free hypophorous acid, and of free HA for use in equations (4)-(6), because of uncertainties in the values of the ionisation constants (K_c) of the various acids. Even when the concentration of hydrogen ion is reasonably well known, as in KH_2PO_2—HCl mixtures with low concentrations of KH_2PO_2 where the concentration of H^+ is practically equal to that of the added HCl, it is clear from equation (3) that the evaluation of k_{b1} always requires a knowledge of K, the (concentration) ionisation constant of the hypophosphorous acid itself. The thermodynamic ionisation constant of hypophorous acid does not appear to have been determined, but Kolthoff [5] from conductivity measurements finds that at 18° K_c increases from 0·01 to 0·06 between $v = 1000$ and 20 litres. Again Nylén [3] from electrometric measurements finds

$$K' = \frac{a_{H^+} \times [H_2PO_2^-]}{[H_3PO_2]} = 0{\cdot}076 \text{ at } 20° \text{ and } \mu = 2.$$

From these it may at best be surmised that K_c at ordinary temperatures lies between about 0·05 and 0·1 at ionic strengths between 0·1 and 2. We have attempted by the Lugg method [6] outlined in the succeeding paper to obtain more precisely the value of K_c at different temperatures and ionic strengths (added KCl) with the following results :—

	16°				30°				45°
μ	0·16	0·57	1·13	2·13	0·16	0·57	1·13	2·13	0·57
$K = K_c$	0·096	0·106	0·094	0·071	0·075	0·079	0·074	0·056	0·06

The values of K_c of H_3PO_2 employed have accordingly been based on the above determinations. For certain other acids, namely H_3PO_3 (1st ionisation), H_3PO_4 (1st ionisation) and HSO_4^-, we have similarly determined K_c (see succeeding paper) : for the remaining acids employed as catalysts values of K_c are obtainable from the literature, except for citric acid (1st ionisation). For this acid the thermodynamic ionisation constant at 30° is about $8{\cdot}10^{-4}$, while we find that a value of $K_c = 12{\cdot}10^{-4}$ at $\mu = 0{\cdot}26$ is consistent with our kinetic data.

The k_1 Reaction.

The mode of analysis of the kinetic data in order to obtain the catalytic coefficient of an acid for the k_1 reaction is exemplified by the following experiment in which phosphoric acid was employed as catalyst.

Using the ionisation constants given at the head of Table III, values of $[H^+]_m$ were calculated for each time interval, and hence values of $\frac{[\Sigma I_2]_m}{[H^+]_m}$ and of $\frac{1}{k_{b1}} = \frac{[H^+]}{k_{obs}\{K + [H^+]\}}$ for each time interval. It is now found that the plot of $1/k_{b1}$ against $[\Sigma I_2]/[H^+]$ is linear, with an intercept of 0·043 and 1/slope = 1·187. Substituting this value of 1/slope in the equation :—

$$\frac{1}{\text{slope}} = \frac{1}{[H^+]} \cdot \Sigma k_1^a[HA] = k_1^\circ + k_1^{H_3PO_2} \cdot \frac{[H_3PO_2]}{[H^+]} + k_1^{H_3PO_4} \cdot \frac{[H_3PO_4]}{[H^+]}$$

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[5] Kolthoff, *Rec. trav. Chim.*, 1927, 46, 350.
[6] Lugg, *J. Am. Chem. Soc.*, 1931, 53, 2554.

derived from equation (6) by neglecting the k_3 reaction, it is possible when $k_1{}^\circ$ and $k_1{}^{H_3PO_2}$ are known, to evaluate $k_1{}^{H_3PO_4}$.

Values of $k_1{}^\circ$ were determined from the data of kinetic experiments in which the catalysing acid was HCl and the hypophosphite concentration kept low. Under such conditions the catalyst is solely the oxonium ion, and its catalytic coefficient $k_1{}^\circ$ is given directly by the value of 1/slope in the plot of $1/k_{bl}$ against $[\Sigma I_2]/[H^+]$. Experiments at various temperatures, ionic strengths and hydrogen ion concentrations have been carried out. The results are very briefly summarised in Table IV, each $k_1{}^\circ$ and $1/(K_tk')$ given being the mean of two to seven determinations at various values of $[H^+]$.

TABLE III.

Temp. = 30° ; $\mu = 0{\cdot}25$
$K_{H_3PO_2} = 0{\cdot}077$; $K_{H_3PO_4} = 0{\cdot}0125$.

$$\text{Initial concentrations}\left\{\begin{array}{ll}[KH_2PO_2] & = 0{\cdot}008208\\ [KH_2PO_3] & = 0{\cdot}000065\\ [KI] & = 0{\cdot}200\\ [H_3PO_4] & = 0{\cdot}2018\\ [\Sigma I_2] & = 0{\cdot}006671\end{array}\right.$$

Time (min.)	$t_2 - t_1$.	$[\Sigma I_2]\,.\,10^3$.	$[\Sigma H_2PO^-{}_2]\,10^3$.	$k_{obs.}$	$[H^+]_m\,.\,10^2$.	$\frac{[\Sigma I_2]_m}{[H^+]_m}$.	$\frac{1}{k_{bl}}$.
0·00		6·263	7·800				
	8·25			2·306	4·348	·1347	·1565
8·25		5·449	6·986				
	10·25			2·646	4·440	·1127	·1382
18·50		4·560	6·097				
	12·15			3·108	4·538	·0909	·1193
30·65		3·694	5·231				
	14·30			3·583	4·632	·0710	·1048
44·95		2·888	4·425				
	17·70			4·275	4·720	·0532	·0889
62·65		2·131	3·668				
	26·95			5·208	4·808	·0362	·0738
89·60		1·353	2·890				
	42·35			6·428	4·889	·0208	·0604
131·95		0·685	2·222				
	64·20			7·718	4·951	·0095	·0507
196·15		0·259	1·796				

TABLE IV.

$[KI] = 0{\cdot}1$; $[H^+] = 0{\cdot}005 - 0{\cdot}1$.

Temp.	K			$1/k'K_t$			$k_1{}^\circ$		
	$\mu = {\cdot}15$	1·15	2·15	$\mu = {\cdot}15$	1·15	2·15	$\mu = {\cdot}15$	1·15	2·15
30	·075	·074	·056	·0400	·0369	—	·349	·414	—
40	·062	·062	·047	·0159	·0145	·0133	1·03	1·20	1·49
50	·053	—	—	·00650	—	—	2·73	—	—
60	·045	—	—	·00254	—	—	7·07	—	—

The values of $1/(k'K_t)$ are the intercepts of the above-mentioned plots (*cf.* equations (4) and (5)) ; they are slightly dependent on ionic strength, but at constant temperature and constant μ are found to be independent of the composition of the reacting system, except for an effect of $[I^-]$, which, however, only becomes of significance for values of $[I^-]$ less than 0·05. Thus, under all circumstances, and in presence of all catalysing acids, with $[H^+]$ varying between 10^{-1} and $5 \cdot 10^{-4}$, it is found at 30° with μ between 0·15 and 1·15 and $[KI] = 0 \cdot 1$ or greater that constant intercepts of between 0·036 and 0·045 are obtained, in agreement with the values found under the conditions of Table IV. In terms of our mechanism this means that the velocity coefficient k' of the reaction between the active form of H_3PO_2 and iodine is independent of $[H^+]$ or the concentration of other catalysing acid. From the values of $1/(k'K_t)$ at 30°, 40°, 50° and 60° the average critical increment $E_{k'K_t}$ is found to be 18,000 cal. It is, of course, not possible to infer how much of this "critical increment" belongs to the heat of the reaction

$$H_3PO_2 \text{ (normal)} \rightarrow H_3PO_2 \text{ (active)},$$

and how much to the k' reaction itself.

The values of $1/\text{slope} = k_1°$ in Table IV are found to be quite independent of $[H^+]$ over the range $[H^+] = 0 \cdot 1 - 0 \cdot 005$. From this we infer that the term containing k_3 in equation (6) is negligible under the present conditions compared with the term containing k_1. In other words, the values of 1/slope in the Table represent the velocity coefficients ($k_1°$) of the reaction :—

$$H_3PO_2 + OH_3^+ \rightarrow H_3PO_2 \, . \, H^+ + H_2O.$$

These $k_1°$ values increase slightly with increasing ionic strength, and yield a critical increment $E_{k_1°} = 20{,}000$ cal. This is somewhat higher than previous estimates (Mitchell,[1] 19,000 cal.; Griffith and McKeown,[2] 18,200 cal.).

The catalytic coefficient of H_3PO_2 itself was next determined by rate measurements in systems containing up to 0·36 M hypophosphite (see Table V).

TABLE V.

Temp. = 30° ; [KI] = 0·1.

$[KH_2PO_2]_0$.	[HCl].	μ.	$[H^+] \cdot 10^3$.	$\frac{[H_3PO_2]_m}{[H^+]_m}$.	1/slope.
0·365	0·0158	0·49	3—5	4·42	0·825
·245	·0158	·35	4—7	2·95	·726
·123	·0096	·23	4—8	1·44	·533
·083	·0238	·20	13—19	·90	·487
·041	·0187	·16	14—22	·45	·420
·0165	·0357	·15	32—40	·15	·371
·0083	·0596	·17	57—67	·06	·353
·0066	·0772	·19	75—84	·04	·349

For these experiments equation (6), after neglecting the k_3 reaction, takes the form :—

$$\frac{1}{\text{slope}} = k_1° + k_1^{H_3PO_2} \, . \, \frac{[H_3PO_2]}{[H^+]}.$$

Hence, plotting 1/slope against $[H_3PO_2]/[H^+]$ should yield a linear plot from which $k_1°$ and $k_1^{H_3PO_2}$ may be determined. In this way we find :—

$$\left.\begin{aligned} k_1° &= 0 \cdot 353 \\ k_1^{H_3PO_2} &= 0 \cdot 126 \end{aligned}\right\} \text{at } 30° \text{ and } \mu = 0 \cdot 2 - 0 \cdot 5.$$

These values are used in interpreting the results of experiments in which, besides free H^+ and free H_3PO_2, another catalysing acid is simultaneously present. Under such circumstances we have :—

$$\frac{1}{\text{slope}} = k_1{}^{\circ} + k_1{}^{H_3PO_2} \cdot \frac{[H_3PO_2]}{[H^+]} + k_1{}^{a} \cdot \frac{[HA]}{[H^+]},$$

and hence $k_1{}^a$, the catalytic coefficient of the acid HA can be derived. Table VI contains a summary of the results obtained in this way at 30° for the acids H_3PO_3, H_3PO_4, $HSO_4{}^-$, $(COOH)_2$, $CH_2ClCOOH$, $CH_2(OH)COOH$, citric acid and acetic acid.

TABLE VI.

Temp. = 30° ; [KI] = 0·1 (or 0·2* or 0·05+).

Acid.	No. of Expts.	K_A.	μ.	[ΣHA].	Range of [H+].	Range of $k_1{}^a$.	$k_1{}^a$ (mean).	Intercept. (mean).
H_3PO_3 .	1	·080(7)	·2	·21	·10	—	·237	—
H_3PO_4 .	8	·0125(8)' (7)	·24–·29	·08– ·32	·03 –·08	·224 –·246	·236	·043*
HSO^-_4 .	7	·025–·054(7)	·18–·59	·04– ·23	·03 –·10	·207 –·258	·233	·040
$(COOH)_2$.	3	·074–·077(8)	·12–·18	·1 – ·3	·06 –·12	·237 –·280	·253	·038+
$CH_2ClCOOH$	4	(2·0–2·13) . 10^{-3}(9)	·14–·20	·2 –1·2	·016 –·05	·033 –·037	·0354	·040
Citric . .	7	1·2 . 10^{-3}	·26	·1 – ·58	·011 –·028	·053 –·074	·0594	·040*
$CH_2OHCOOH$	6	(2·56–2·62) . 10^{-4}(10)	·29–·42	·12– ·74	·0009–·009	·0098–·0128	·0118	·040
CH_3COOH .	12	(2·9–3·2) . 10^{-5}(11)	·15–·43	·5 –1·1	·0004–·04	·0032–·0051	·0042	·042

In the above Table the third column gives the value of K_A (the ionisation constant of the acid) used, together with a reference to its source. All the reaction mixtures contained KH_2PO_2, I_2 and KI, together with the acid alone or the acid and HCl or the acid and its Na (or K) salt. The fifth column gives the total concentration of catalysing acid (*i.e.* acid + salt). The last two columns give respectively the mean $k_1{}^a$'s and intercepts obtained. The catalytic coefficients derived from Tables V and VI are in fair accord with the requirements of the Brönsted relation between catalytic coefficient and ionisation constant, *viz.*

$$\log\left(\frac{k_1{}^a}{p}\right) = x \log\left(\frac{q}{p}K_A{}^{\circ}\right) + \log G_1 \quad . \quad . \quad . \quad (8)$$

Table VII shows the extent of this agreement. The fifth column of this Table gives the thermodynamic ionisation constants of the various acids derived from the literature. The $K_A{}^{\circ}$ values for H_3PO_2 and H_3PO_3 have not been determined ; the values in the Table are rough estimates. The values of log $(k_1{}^a/p)$ (calc.) in the last column were calculated from equation (8), with $x = 0{\cdot}529$ and $\log G_1 = -0{\cdot}025$. The agreement between observed and calculated coefficients is reasonably good for all the acids, with the exception of $OH_3{}^+$, for which the observed catalytic

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[7] Griffith and McKeown, *succeeding paper in this Journal.*

[8] Dawson and co-workers, *J.C.S.*, 1929, 1884, 2530 ; 1930, 79 ; Griffith, McKeown and Winn, *Trans. Faraday Soc.*, 1932, **28**, 518.

[9] Wright, *J. Am. Chem. Soc.*, 1934, **56**, 314 ; Dawson and Key, *J.C.S.*, 1929, 1239.

[10] Nims, *J. Am. Chem. Soc.*, 1936, **58**, 987 ; Larssen and Adell, *Z. physik. Chem. A*, 1931, **157**, 342.

[11] Harned and Murphy, *J. Am. Chem. Soc.*, 1931, **53**, 8.

coefficient is over twenty times too small. Nylén [3] has previously determined at 20° the catalytic coefficients of OH_3^+, H_3PO_4 and citric acid. He found $k_1^a/k_1^\circ = 0{\cdot}85$ and 0·23 for phosphoric acid and citric acid respectively, compared with 0·67 and 0·17 in the present work. The ratios are thus in fair agreement with those found here, and confirm the anomalous value of k_1°, the catalytic coefficient of the oxonium ion. It should further be noted that we have found that the k_1° value in the acid-catalysed H_3PO_3—I_2 reaction is also abnormally low (*cf.* succeeding paper), though at present the cause of these discrepancies is not apparent.

TABLE VII.

Acid.	p.	q.	k_1^a.	K_A°.	$\log\left(\frac{k_1^a}{p}\right)$ (obs.)	$\log\left(\frac{k_1^a}{p}\right)$ (calc.)
OH^+_3 . .	1	1	0·353	55·5	— 0·452	+ 0·898
H_2PO_2 . .	1	2	·126	$2{\cdot}5 \,.\, 10^{-2}$(?)	— 0·900	— 0·713
H_3PO_3 . .	2	2	·237	$2{\cdot}10^{-2}$(?)	— 0·926	— 0·924
H_3PO_4 . .	3	2	·236	$7{\cdot}15 \,.\, 10^{-3}$	— 1·104	— 1·254
$(COOH)_2$ . .	2	2	·253	$5{\cdot}70 \,.\, 10^{-2}$	— 0·898	— 0·683
HSO_4^- . .	1	4	·233	$1{\cdot}13 \,.\, 10^{-2}$	— 0·633	— 0·736
$CH_2Cl \,.\, COOH$.	1	2	·0354	$1{\cdot}33 \,.\, 10^{-3}$	— 1·451	— 1·388
Citric . .	3	2	·0594	$8{\cdot}30 \,.\, 10^{-4}$	— 1·703	— 1·748
$CH_2OH \,.\, COOH$	1	2	·0118	$1{\cdot}48 \,.\, 10^{-4}$	— 1·928	— 1·892
CH_3COOH .	1	2	·00418	$1{\cdot}75 \,.\, 10^{-5}$	— 2·379	— 2·382

The k_3 Reaction. Acid Catalysis in $H_2PO_4^- - HPO_4^{--}$ and $H_2AsO_4^- - HAsO_4^{--}$ Buffers.

It has been mentioned in Section A that an acid-catalysed reaction takes place (together with the direct hypophosphite ion-iodine reaction) in phosphate buffers. It has been possible to measure this acid-catalysed part of the net process at 30° in phosphate and arsenate buffers, though the reaction is slow and it is not possible to isolate it from the direct ion reaction. Under our experimental conditions the ion reaction amounted to between 15 and 75 per cent. of the total reaction; consequently the accuracy with which the acid-catalysed process has been measured is not very high, but it is probably sufficiently good to justify the main conclusion drawn in this section.

We have seen that in media with $p\text{H} < 3{\cdot}4$ the acid-catalysed reaction may be satisfactorily interpreted on the basis that the transformation HR → RH takes place entirely *via* the k_1k_{-2} route (*i.e. via* HRH^+). In phosphate and arsenate buffers of pH about 6, however, our results indicate that the alternative path, *via* the k_3 reaction, is the dominant part of the acid-catalysed process, though apparently some reaction *via* HRH^+ is still detectable.

From equations (3) and (4) it follows that :—

$$\frac{1}{k_{\text{bi}}} = \frac{[H^+]}{k_{\text{obs}}\{K + [H^+]\}} = \frac{1}{k'K_i} + \frac{[\Sigma I_2][H^+]}{[H^+] \,.\, \Sigma k_1^a[HA] + K \,.\, \Sigma k_3^a[HA]} \quad . \qquad (9)$$

Under present conditions $[H^+]$ is negligible compared with K, and also $k_1[HA]$ (where $HA = H_2PO_4^-$ or $H_2AsO_4^-$) must be much greater than either $k_1{}^{\circ}[H^+]$ or $k_1{}^{H_3PO_2}[H_3PO_2]$. Similar remarks apply to the corresponding k_3's.

Equation (9) thus reduces to :—

$$\frac{1}{k_{bi}} = \frac{[H^+]}{k_{obs} \, . \, K} = \frac{1}{k'K_t} + \frac{[\Sigma I_2][H^+]}{[HA]\{k_1{}^a[H^+] + k_3{}^a K\}} \quad . \qquad (10)$$

in which k_{obs} is the k_{obs} defined by equation (3) after correcting for the concomitant hypophosphite ion-iodine reaction. It will be seen from equation (10) that for large values of $[\Sigma I_2]$, the rate of reaction, which is proportional to k_{obs}, tends to become independent of $[H^+]$ at constant [HA] if the k_3 reaction predominates. On the other hand, when the k_3 reaction is negligible (as, for example, in CH_3COOH—CH_3COONa buffers of *p*H 3·4) the rate of reaction at high enough values of $[\Sigma I_2]$ tends to be proportional to $[H^+]$ at constant [HA]. In phosphate and arsenate buffers we find a slight increase in k_{obs} on increasing $[H^+]$ at constant [HA], from which it is concluded that the main reaction path is *via* the k_3 process.

With phosphate buffers, seven experiments were carried out at 30° and $\mu = 1·15$ the experimental conditions being : $[KH_2PO_2] = 0·25$; $[\Sigma I_2] = 0·01 - 0·017$; $[KI] = 0·2$; $[Na_2HPO_4] = 0·1$; $[KH_2PO_4] = 0·2 - 0·5$. To evaluate $[H^+]$ in these systems, the values of $K_{H_2PO_4^-}$ employed were those found in the succeeding paper. Interpreting the data of these experiments on the basis of equation (10), and putting $1/(k'K_t) = 0·0369$, the mean value of $k_3{}^a$ (for $H_2PO_4{}^-$) found was $3·0 \, . \, 10^{-6}$, while the $k_1{}^a$ was about 0·027. Five experiments with arsenate buffers under similar conditions gave $k_3{}^a$ (for $H_2AsO_4{}^-$) $= 4·3 \, . \, 10^{-6}$ and $k_1{}^a =$ about 0·05. The inferred values of $k_3{}^a$ should be of moderate accuracy, but the $k_1{}^a$'s are subject to extremely large errors, and we would therefore lay no stress on them, especially as they appear to be about 100 times greater than the values to be anticipated on the basis of the acid strength. It is possible that the $k_3{}^a$ values are also somewhat too great, as they would imply that the $k_3{}^a$ reaction should be detectable in acetate buffers of $[H^+] = 4·10^{-4}$, which seems not to be the case. Thus, though no definite quantitative conclusions can be drawn from the experiments of this section, they seem to establish the occurrence of a k_3 process in phosphate and arsenate buffers.

Experiments at Low [I⁻].

There remains to be mentioned the experiments with lower concentrations of iodide from which the ratio of the velocity coefficients $(k'_{I_2}/k'_{I_3^-})$ of the reactions of I_2 and $I_3{}^-$ with the active form of hypophosphorous acid may be derived. From equation (7) it follows that :—

$$\frac{1}{\text{Intercept}} = K_t\left\{k'_{I_2} \cdot \frac{K_3}{K_3 + [I^-]_\infty} + k'_{I_3^-} \cdot \frac{[I^-]_\infty}{K_3 + [I^-]_\infty}\right\} \quad . \qquad (11)$$

where $[I^-]_\infty$ is the concentration of free iodide ion at the end of the experiment. The kinetic experiments were carried out at 30°, using H_3PO_4 as the catalysing acid, and with KNO_3 added to keep μ constant at 0·25. Table VIII gives the results.

The values of the intercepts in the last column are calculated from equation (11) on the basis that :—

$$K_t k'_{I_2} = 79·0 \, ; \quad K_t k'_{I_3^-} = 22·76 \, ; \quad \frac{k'_{I_2}}{k'_{I_3^-}} = 3·47 .$$

The agreement between observed and calculated intercepts shows that the data are quantitatively accounted for on the assumption that the specific rate of reaction with RH of I_2 is about 3·5 times that of I_3^-.

TABLE VIII.

Temp. = 30° ; $\mu = 0{\cdot}25$; $K_3 = 0{\cdot}00155$.

$[\Sigma H_2PO_2^-]_0 = 0{\cdot}0049$; $[\Sigma I_2]_0 = 0{\cdot}001$.

$[KI]_0$.	$[I^-]_\infty$.	$\left\{\frac{[I_2]}{[\Sigma I_2]}\right\}_\infty$.	Intercept (obs.).		Intercept (calc.).
			$[\Sigma H_3PO_4] = {\cdot}0807$.	$[\Sigma H_3PO_4] = 0{\cdot}321$.	
·002	·0040	0·274	0·0255	0·0275	0·0260
·020	·0220	·0643	·0365	·0390	·0378
·200	·2133	·0074	·0426	·0445	·0432

This result is nearly identical with that found in the succeeding paper for the ratio of the rates of interaction of I_2 and I_3^- with the active form of phosphorous acid.

General Discussion.

The reactions measured in Section B have been the prototropic change H_3PO_2 (normal) $\rightarrow$ H_3PO_2 (active), catalysed by various acids, either *via* the k_1 route or *via* the k_3 route, together with the reactions of this active form with I_2 and I_3^-. It is reasonably certain that the prototropic change is bound up with a change in valency of the phosphorus atom in the acid molecule from five to three. There is no detectable reaction of iodine with the normal form of H_3PO_2 (pentavalent P), while the active form (tervalent P) reacts readily, the reaction being accompanied by the reversal to the normal form. It cannot be concluded, however, that the hypophosphite ion must also have its phosphorus atom in the tervalent condition before it can react with iodine. It has been shown in Section A that this ion reacts directly with iodine, and in Section B that it also reacts *via* the prototropic k_3 reaction which first transforms it into the active acid (tervalent phosphorus).

It is to be noted that in practically all prototropic reactions hitherto studied the substrate is an exceedingly weak acid. In the present case, and in that of H_3PO_3 studied in the following paper the substrates are very strong acids, which, however, must both exhibit some basic properties. The active form of each acid (RH) must even be a stronger acid than the substrate itself, and the intermediate HRH^+ be a still stronger acid. It is possible that the anomalous catalytic coefficient of OH_3^+, which is considerably smaller than expected for the prototropic changes of both H_3PO_2 and H_3PO_3, is connected in some way with the high strengths of these acids.

Part of the data for the two reactions are summarised below :—

Reaction.	k_1° (30°).	$E_{k_1^\circ}$ (cal.).	$k'K_t$ (30°).	$E_{k'K_t}$ (cal.).
H_3PO_2—I_2 .	0·35	20,000	25	18,000
H_3PO_3—I_2 .	0·001	22,500	0·038	21,400

It is seen that both $k_1°$ and $k'K_t$ are smaller for the phosphorous acid reaction than for the hypophosphorous acid reaction, and also that for each of these constants the change in critical increment accounts roughly for the magnitude of the difference. The critical increment of the k_3 reaction for hypophosphite has not been measured ; it is probably, however, of the same order of magnitude (25,000 cal.) as E_{k_0}, the critical increment of the direct *non-catalysed* reaction between hypophosphite and iodine.

Summary.

The reaction between hypophosphorous acid and iodine in aqueous solution has been investigated at temperatures between 30° and 60° over a range of pH from 1 to 8. The reaction scheme

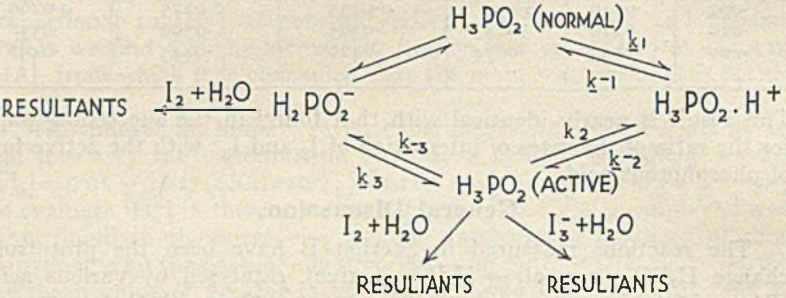

FIG. 2.

embraces all the experimental findings. The reaction *via* H_3PO_2 (active) which presumably contains a tervalent phosphorus atom is subject to general acid and basic catalysis. The catalytic coefficients of a number of acids for the k_1 reaction have been determined ; they satisfy the Brönsted relation, except that of OH_3^+. The k_3 process has not been quantitatively studied. $H_2PO_2^-$ ion also reacts directly with iodine. The critical increments of some of the above processes have been determined, and a short discussion of the results is given.

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KINETICS OF THE REACTION OF IODINE WITH PHOSPHOROUS ACID AND WITH PHOSPHITES.

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The reaction between H_3PO_3 and I_2 in aqueous solution has been studied by several workers, but certain anomalies remain for further investigation. The work of Mitchell[1] satisfactorily accounted for the main features of the process in acid solution. He showed that, as in the case of hypophosphorous acid, phosphorous acid also exists in two tautomeric forms whose reciprocal transformations are catalysed by H^+.

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[1] Mitchell, *J.C.S.*, 1923, **123**, 2241.

In solutions with sufficiently high values of $[H^+]$ the reaction with I_2 takes place entirely *via* :—

$$\underset{\text{(normal form)}}{H_3PO_3} \underset{H^+}{\overset{H^+}{\rightleftarrows}} \underset{\text{(active form)}}{H_3PO_3} \xrightarrow{I_3^- + H_2O} H_3PO_4 + 2H^+ + 2I^-.$$

In less acid solutions there is concomitant oxidation which is retarded by H^+, and Mitchell found that for this process the retardation by H^+ is greater than can be accounted for on the assumption that the actual reactant is $H_2PO_3^-$ ion. Finally, Mitchell appears to have considered that in the process catalysed by H^+ the sole reacting form of the iodine is the I_3^- ion, while in the process retarded by H^+ it is the I_2 molecule. Further work, apparently in ignorance of Mitchell's, was carried out by Berthoud and Berger,[2] who studied the reaction both in acid media and in a more alkaline range (acetate buffers), but without adding anything essential to our knowledge of the mechanism. Recently the reaction has again been investigated by Nylén.[3] He showed that the reaction in weakly acid media ($p\text{H} = 3{\cdot}2 - 6{\cdot}8$) is one between HPO_3^{--} and iodine. The first and second ionisation constants of H_3PO_3 according to Nylén, are $pK_1 = 0{\cdot}97$ and $pK_2 = 6{\cdot}18$ at $\mu = 1{\cdot}0$. The fact that over the above mentioned range of pH, over the greater part of which the concentration of $H_2PO_3^-$ is much greater than that of HPO_3^{--}, the velocity of reaction is found to be proportional to $\frac{1}{(K_1 + [H^+])(K_2 + [H^+])}$ means that if $H_2PO_3^-$ reacts at all with iodine then its specific rate is many times smaller than that of HPO_3^{--}. Nylén further concluded that both I_2 and I_3^- react with HPO_3^{--}, the specific rate of the former being about a thousand times that of the latter. Finally, he attempted to determine whether or not the reaction in acid media (catalysed by H^+) is subject to general acid catalysis and decided that it was not. The one experiment attempted to test this point was, however, not well chosen.

We have now re-investigated the process both in presence of acids and also in various buffers covering a range of pH from 0·5 to 9. Our results are in general agreement with Mitchell's and with Nylén's, but differ in certain respects. We find, in disagreement with Nylén, that the reaction catalysed by H^+ is also catalysed by acids in general, and we have determined the catalytic coefficients for a few moderately strong acids. Further, we find that both I_2 and I_3^- react with the active form of H_3PO_3, and have determined their relative rates. Finally, we have confirmed Nylén's conclusion that for the reaction retarded by H^+ the reacting entities are the HPO_3^{--} ion, and (mainly) the I_2 molecule, but we consider that Nylén's value of the much slower reaction between HPO_3^{--} and the I_3^- ion is an over-estimate, and in fact are doubtful whether this reaction is fast enough to be detected at all.

Experimental.

The phosphorous acid used contained from 8 to 15 per cent. phosphoric acid but no appreciable H_3PO_2. All other chemicals were of A.R. quality. Blank tests showed that under all our experimental conditions the rate of disappearance of iodine in absence of the phosphorous acid was negligibly slow. Reaction mixtures were contained in blackened glass-stoppered

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[2] Berthoud and Berger, *J. Chim. physique*, 1928, **25**, 568.

[3] Nylén, *Z anorg. Chem.*, 1937, **230**, 385.

flasks maintained in thermostats regulated to ± 0·03°. Samples withdrawn from time to time were run into ice-cold water (containing excess H_2SO_4 when necessary) and the iodine at once titrated with thiosulphate solution.

A. The Reaction in Feebly Acid and Neutral Solutions ($p_H = 2 - 9$).

Kinetic experiments have been carried out at temperatures between 0° and 30° in the presence of the following buffers: CO_3^{--}—HCO_3^-, $H_2BO_3^-$—H_3BO_3, HPO_4^{--}—$H_2PO_4^-$, $HAsO_4^{--}$—$H_2AsO_4^-$, CH_3COO^-—CH_3COOH, CH_2ClCOO^-—$CH_2ClCOOH$, and also at 45° in the presence of low concentrations of $HClO_4$. The reaction was found, under these conditions, to be unimolecular with respect to each reactant, *viz.* total phosphite (ΣH_3PO_3) and total iodine (ΣI_2). Values of k_{obs} were calculated from the equation:

$$k_{\text{obs}} = \frac{1}{t_2 - t_1} \cdot \frac{1}{[\Sigma H_3PO_3]_0 - [\Sigma I_2]_0} \ln \frac{[\Sigma I_2]_1 \cdot [\Sigma H_3PO_3]_2}{[\Sigma I_2]_2 \cdot [\Sigma H_3PO_3]_1}. \quad (1)$$

With low initial concentrations of reactants ($[\Sigma I_2]_0$ usually 0·0025 M or less; $[\Sigma H_3PO_3]_0 > [\Sigma I_2]_0$, but usually less than 0·01 M) and with moderate concentrations of buffers and of iodide, values of k_{obs} were found to be constant in each run. In Table I the results of most of these experiments

TABLE I.

Expt. No.	Temp.	$[I^-]_m$.	$[HA]_m/[A^-]_m$.	μ.	k_{obs}.	k.
(i) $NaHCO_3$—Na_2CO_3 buffers.						
12	0·17	0·201	0·076/0·024	0·38	1·32	355
23	0·14	0·201	0·026/0·242	0·98	1·265	340
24	0·13	0·201	0·014/0·118	0·60	1·32	355
40	10·00	0·101	0·030/0·090	0·41	14·3	1515
29	10·00	0·201	0·103/0·097	0·60	6·88	1445
27	10·00	0·201	0·014/0·118	0·60	7·04	1480
30	10·00	0·201	0·014/0·118	0·80*	6·53	1375
31	10·00	0·201	0·014/0·118	1·00†	6·18	1300
33	10·00	0·201	0·014/0·118	0·80‡	7·08	1490
39	10·00	0·201	0·033/0·087	0·80§	7·14	1500
32	10·00	0·400	0·014/0·118	0·80	3·44	1440
35	20·00	0·201	0·101/0·099	0·60	33·4	5460
34	20·00	0·400	0·014/0·118	0·80	16·65	5390
(ii) KH_2PO_4—Na_2HPO_4 buffers.						
25	0·11	0·201	0·013/0·120	0·60	1·265	340
37	10·00	0·201	0·301/0·100	0·81	2·69	566
38	10·00	0·201	0·102/0·099	0·81‡	4·85	1020
28	10·00	0·201	0·102/0·099	0·61	4·88	1025
26	10·00	0·201	0·014/0·119	0·59	6·70	1410
(iii) CH_3COOH—CH_3COONa buffers.						
18	30·00	0·101	0·212/0·194	0·31	5·05	329
17	30·00	0·201	0·212/0·094	0·31	1·25	161
16	30·00	0·201	0·212/0·194	0·41	2·71	350
19	30·00	0·201	0·109/0·194	0·41	5·30	684
(iv) $CH_2ClCOOH$—$CH_2ClCOONa$ buffer.						
22	30·00	0·050	0·083/0·120	0·25	0·196	6·44

* 0·2 M $NaNO_3$ added; † 0·4 M $NaNO_3$ added.
‡ 0·2 M KNO_3 added; § 0·3 M KNO_3 added.

are summarised, the sixth column giving mean values of k_{obs} in litres/(moles-min.). The subscript m indicates mean concentration during the run and the column headed $[HA]_m/[A^-]_m$ gives the mean concentrations of acid and alkaline components of the buffer, after correction for the small amounts of phosphite (and phosphate) present.

Discussion.

From Table I it is seen that the addition of the neutral salt KNO_3 has no effect on the reaction rate (*cf.* expts. 27 and 33, 10 and 11, 38 and 28). On the other hand, increase of μ by addition of $NaNO_3$ diminishes the rate slightly (*cf.* expts. 27, 30 and 31). The effect of iodide (studied over the range $[KI] = 0{\cdot}1$ to $0{\cdot}4$) is given approximately by $k_{\text{obs}} \propto 1/[I^-]$ (*cf.* expts. 27 and 32, 16 and 18), which indicates that the reactant is the I_2 molecule. Hence, on this basis, the velocity constant for the reaction between ΣH_3PO_3 and I_2 is $k = k_{\text{obs}} \dfrac{K_3 + [I^-]}{K_3}$, where K_3 is the constant for triodide formation. The values in the last column are those of this k; they have been calculated on the basis that

$$K_3 = 1{\cdot}40 \times 10^{-3} \text{ at } 25^\circ,$$

and that the heat of the reaction $KI + I_2 = KI_3$ is 4180 cal.[4] Comparison of the k's of experiments with varying iodide but at the same acidity and temperature shows satisfactory agreement, so that for the present we may assume that iodine reacts only as I_2.

Considering next the effect of pH on the reaction rate, it is seen from Table I that in general for a given buffer increase in alkalinity increases the value of k. In $NaHCO_3$—Na_2CO_3 buffers, however, there is no increase with increasing $[Na_2CO_3]/[NaHCO_3]$, except that which might be due to ionic strength effects. Since for these buffers the pH is 9–10, the phosphite exists entirely as HPO_3^{--}, and this result is in agreement with Nylén's conclusion that HPO_3^{--} is the actual reactant. This is completely borne out by the results with other buffers. Remembering that K_2 for phosphorous acid is of the same order of magnitude ($\approx 10^{-7}$) as the second ionisation constants of phosphoric and arsenic acids, it follows that in HPO_4^{--}—$H_2PO_4^-$ and in $HAsO_4^{--}$—$H_2AsO_4^{--}$ buffers appreciable fractions of the phosphite exist as $H_2PO_3^-$, from which it follows that the k in these buffers should be smaller than in HCO_3^-—CO_3^{--} buffers, and further that k should fall with an increasing ratio $[HA]/[A^-]$. Finally, in acetate buffers, in which nearly all the phosphite is present as $H_2PO_3^-$, the rate is practically inversely proportional to $[HA]/[A^-]$, again indicating that it is the HPO_3^{--} ion which is the actual reactant. Even in chloracetate buffers (expt. 22) with $[H^+]$ about 100 times that in acetate buffers (expt. 19) there is still no evidence of any sensible amount of reaction of $H_2PO_3^-$ with iodine.

The values of k listed for the experiments in $NaHCO_3$—Na_2CO_3 buffers are identical with k_{true}, the velocity coefficient which is defined by the equation :—

$$-\frac{d[\Sigma I_2]}{dt} = k \,.\, [\Sigma H_3PO_3] \,.\, [I_2] = k_{\text{true}}\, [HPO_3^{--}][I_2], \qquad . \quad (2)$$

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[4] Latimer and Zimmermann, *J. Am. Chem. Soc.*, 1939, 61, 1554.

since in these buffers the phosphite exists entirely as HPO_3^{--}. For any other buffer within the pH range of 3 to 9 it is readily seen that :—

$$k_{\text{true}} = k\left\{1 + \frac{[H^+]}{K_2}\right\} = k\left\{1 + \frac{K}{K_2} \cdot \frac{[HA]}{[A^-]}\right\}, \quad \cdot \quad \cdot \quad (3)$$

where K and K_2 are the ionisation constants of HA and $H_2PO_3^-$ respectively, expressed in terms of concentrations. It has not, however, been considered profitable to attempt to evaluate k_{true} values for the experiments of sections (ii), (iii) and (iv) of Table I, since to do this would require pre-knowledge of the variations of the ionisation constants K and K_2 with ionic strength. It was thought preferable to carry out a few series of measurements at constant ionic strength ($\mu = 0{\cdot}4$ or $1{\cdot}15$) from which could be inferred (*a*) the value of k_{true}, and (*b*) the value of K/K_2 at the ionic strength in question. The results of these measurements are given in Table II. The values of k_{true} and K/K_2 in the last two columns were obtained as follows. From equation (3) it is seen that a plot of $1/k$ against $[HA]/[A^-]$ should be linear (provided that K/K_2 is independent of $[HA]/[A^-]$ at constant μ), with an intercept equal to $1/k_{\text{true}}$ and a slope equal to $K/K_2 \,.\, 1/k_{\text{true}}$.

TABLE II.

TEMPERATURE = 20° C. ; $[KI]_0 = 0{\cdot}2$.

Expt. No.	$[HA]_m/[A^-]_m$.	k_{obs}.	k.	K/K_2.
(vi) KH_2AsO_4—Na_2HAsO_4 buffers ; $\mu = 0{\cdot}40$.				
43	0·1004/0·0326	12·95	2105	0·560
44	0·0805/0·0394	16·35	2660	
41	0·0508/0·0492	22·25	3625	
45	0·0212/0·0588	29·30	4765	
(vii) KH_2PO_4—Na_2HPO_4 buffers ; $\mu = 0{\cdot}40$.				
47	0·1004/0·0326	14·60	2375	0·457
46	0·0805/0·0394	18·30	2975	
42	0·0508/0·0492	24·10	3920	
48	0·0014/0·0653	34·75	5650	
(viii) KH_2PO_4—Na_2HPO_4 buffers ; $\mu = 1{\cdot}15$.*				
54	0·401/0·100	8·85	1430	0·735
50	0·301/0·100	11·45	1850	0·682
51	0·151/0·100	18·45	2980	0·591
55	0·101/0·099	22·20	3585	0·566
49	0·002/0·099	34·60	5595	—
(ix) CH_3COOH—CH_3COONa buffers ; $\mu = 1{\cdot}15$.*				
53	0·199/0·211	1·05	170	34·2
52	0·097/0·211	2·15	347	33·1

* By addition of KNO_3.

This linearity actually holds good for the data of Sections (vi) and (vii) referring to arsenate and phosphate buffers respectively at $\mu = 0{\cdot}4$. The intercept is the same in both cases, and equal to 0·000175 giving $k_{\text{true}} = 5710$, which is in substantial agreement with the value obtained at 20° in $NaHCO_3$—Na_2CO_3 buffers (*cf.* expts. 34 and 35 of Table I ; the slightly lower value of k_{true} in these cases probably corresponds to the depressing effect of sodium salt). On the other hand, the plot of $1/k$ against $[H_2PO_4^-]/[HPO_4^{--}]$ for the five experiments of section (viii) for which $\mu = 1{\cdot}15$ is not linear, the value of $1/k$ increasing more rapidly with increasing $[H_2PO_4^-/[HPO_4^{--}]$ than equation (3) demands. Nevertheless, the limiting value of $1/k$ as $[H_2PO_4^-/[HPO_4^{--}] \rightarrow 0$ is 0·000177, or $k_{\text{true}} = 5650$, in good agreement with the value of k_{true} given by phosphate and arsenate buffers at $\mu = 0{\cdot}4$. Since the main difference between series (vi) and (vii) on the one hand, and series (viii) on the other lies in the potassium ion content, it seems certain, as already inferred from Table I, that the addition of potassium salts does not alter appreciably the intrinsic rate of reaction between HPO_3^{--} and I_2. The non-linearity of the plot of series (viii) must therefore be referred to a progressive increase of K/K_2 with increasing value of $[H_2PO_4^-]/[HPO_4^{--}]$ throughout the series. The values of K/K_2 given in the last column have been deduced from equation (3) on the assumption that in each case k_{true} equals the limiting value of k, *viz.* 5650. The ratio K/K_2 is practically a linear function of $[H_2PO_4^-]$, *viz.*

$$K/K_2 = 0{\cdot}505 + 0{\cdot}58[H_2PO_4^-].$$

Since $[HPO_4^{--}]$ is constant in the series, it is not possible to say whether K/K_2 is a function of [phosphate] alone or also of $[H_2PO_4^-]/[HPO_4^{--}]$ also. It is perhaps significant, however, that in series (vii) where the total range of concentration of phosphate is smaller, no appreciable variation of K/K_2 is observed. It is, of course, impossible to say with certainty whether the variation of K/K_2 in series (viii) relates to a variation of K or of K_2 or of both with changing environment, but since the concentration of phosphite is exceedingly small (and μ remains constant) it is probable that the bulk of the variation of K/K_2 is due to variation of K, the second ionisation constant of phosphoric acid, with changes in the concentration of total phosphate and in the ratio in which this is distributed between $H_2PO_4^-$ and HPO_4^{--}. This variation of K is in the same sense and of the same order of magnitude as that found by Cohn[5] for the dependence of $K' = \dfrac{a_{H^+} \cdot [HPO_4^{--}]}{[H_2PO_4]}$ upon total phosphate and phosphate ratio.

The values of k for the two experiments of series (ix) with acetate buffers at $\mu = 1{\cdot}15$, taken in conjunction with $k_{\text{true}} = 5650$, the limiting value obtained with phosphate buffers at this same ionic strength, permit the ratio of K_{acetic}/K_2 at $\mu = 1{\cdot}15$ and 20° to be calculated. The two values 34·2 and 33·1 for K_{acetic}/K_2 are reasonably consistent. Using now $K_{\text{acetic}} = 2{\cdot}7 \times 10^{-5}$ for the temperature and ionic strength indicated,[6] it follows that K_2 for phosphorous acid at 20° and $\mu = 1{\cdot}15$ equals 8×10^{-7}. A similar estimation of K_2 at 30° and $\mu = 0{\cdot}4$ can be made from experiments 16 and 19 of Table I. Combining the k's of these experiments with a $k_{\text{true}} = 19{,}750$, obtained from $k_{\text{true}} = 5710$ at 20° and a temperature coefficient (*cf.* Table IV) of 3·38, it follows that $K_{\text{acetic}}/K_2 = 52$ at 30° and $\mu = 0{\cdot}4$. Using $K_{\text{acetic}} = 3{\cdot}1 \times 10^{-5}$ under these same conditions, K_2 for phosphorous acid is $5{\cdot}9 \times 10^{-7}$. The difference between these two estimates of K_2 at 20° and 30° respectively, must be almost entirely due to the different ionic strengths concerned

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[5] Cohn, *J. Am. Chem. Soc.*, 1927, 49, 173.

[6] Harned and Murphy, *J. Am. Chem. Soc.*, 1931, 53, 8.

and not to the difference in temperature. They may be compared with Nylén's value[3] of $K'_2 = \frac{a_{H^+} . [HPO_3^{--}]}{[H_2PO_3^-]} = 6{\cdot}6 \times 10^{-7}$ at 0° C. and $\mu = 1$, and with Kolthoff's value[7] of K_2 ($\mu = 0$) $= 2 \times 10^{-7}$ at 18° C.

Using $K_2 = 5{\cdot}9 \times 10^{-7}$ at $\mu = 0{\cdot}4$, the data of series (viii) combined with $K_2 = 8 \times 10^{-7}$ at $\mu = 1{\cdot}15$ give

$$10^7 . K_{H_2PO_4^-} = 4{\cdot}04 + 4{\cdot}64[H_2PO_4^-].$$

Although we have not attempted to use the method systematically, it is clear that this reaction affords a means of evaluating the (concentration) ionisation constants of acids in the range $K_c = 10^{-4} - 10^{-8}$.

In Table I the experiment for which $[H^+]$ has the highest value is expt. 22 (chloracetate buffer), for which $[H^+]$ is about $1{\cdot}5 \times 10^{-3}$, and it has already been pointed out that the observed rate in this experiment is entirely accounted for by the reaction between HPO_3^{--} and I_2, and that no trace of a reaction between $H_2PO_3^-$ and I_2 is here detectable. In order to explore further for a possible $H_2PO_3^- - I_2$ reaction a few experiments at still lower *p*H have been carried out. These were effected with mixtures of $HClO_4$ and H_3PO_3 and—to obtain conveniently measurable rates—with low concentrations of NaI at 45° C. The results are summarised in Table III.

TABLE III.

Temp. = 45°; $\mu = 0{\cdot}56$; $[\Sigma H_3PO_3]_0 = 4\text{—}8{\cdot}10^{-3}$
$[\Sigma I_2]_0 = 2{\cdot}10^{-3}$; $[HClO_4] = 7{\cdot}5\text{—}30{\cdot}10^{-3}$; $[NaI]_0 = 5\text{—}10{\cdot}10^{-3}$.

Expt. No.	$[H^+]_m$.	$[I^-]_m$.	k_{obs} (corr.).	k.	k_{true}.
56	0·01247	0·0103	0·690	3·95	98,400
57	0·01942	0·00988	0·421	2·33	98,000
58	0·01959	0·00525	0·686	2·34	99,300
59	0·03630	0·00528	0·308	1·055	98,600
				Mean	. 98,600

The values of k_{obs} were corrected for the concomitant acid-catalysed reaction between H_3PO_3 and iodine, the necessary data for this correction deriving from Part B of this paper. The magnitude of this correction varied with the experimental conditions, but was usually less than 5 per cent. The values of k_{true} in the last column have been calculated on the assumption that the sole ion reaction taking place is one between HPO_3^{--} and I_2, that is, from the equation :—

$$k_{true} = k \times \frac{K_1 + [H^+]}{K_1} \times \frac{K_2 + [H^+]}{K_2}$$

using for K_1 (the first ionisation constant of H_3PO_3) the value 0·07 (see Part B) and for K_2 the value $5{\cdot}9 \times 10^{-7}$. On this basis k_{true} should be constant, as is found to be the case. We must therefore infer that even when $[H^+] = 0{\cdot}036$, that is when $[H_2PO_3^-] = 1{\cdot}5 \times 10^{+5}\ [HPO_3^{--}]$, the rate of a possible $H_2PO_3^- - I_2$ reaction is less than one or two per cent. of that of the $HPO_3^{--} - I_2$ reaction, so that the intrinsic rate of the

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[7] Kolthoff, *Rec. trav. Chim.*, 1927, 46, 350.

$H_2PO_3^-$ — I_2 reaction (if it occurs) is less than about 10^{-7} of that of the HPO_3^{--} — I_2 reaction. It may be noted that the corresponding intrinsic rates of reaction of HPO_3^{--} and $H_2PO_3^-$ with Br_2 have both been determined,[8] the latter being about $2 \cdot 10^{-7}$ times the former. Doubtless a reaction between $H_2PO_3^-$ and I_2 does take place, but its rate is too slow for detection. It is not possible to test for its occurrence at still higher values of $[H^+]$ than those of Table III since the acid-catalysed reaction of H_3PO_3 and I_2 then becomes the dominant process.

The value 98,600 for k_{true} at 45° obtained from the experiments of Table III is in good agreement with that inferred from Table I. Thus we calculate, using the data of Table I, that k_{true} at 45° and $\mu = 0{\cdot}4$ should be about 102,000. The latter figure refers to an environment for which $[K^+] = 0{\cdot}2$ and $[Na^+] = 0{\cdot}2$, while the value 98,600 refers to an environment in which $[Na^+] = 0{\cdot}56$. The practical constancy of k_{true} over a range of iodide ion concentration from 0·4 to 0·005 implies that even when $[I_3^-]/[I_2] = 400$ any reaction between HPO_3^{--} and the I_3^- ion is insignificant compared with that between HPO_3^{--} and the free I_2 molecule. Nylén [3] has deduced from his experiments that the ratio of the intrinsic rates of reaction of HPO_3^{--} with I_3^- and with I_2 is about 1 : 1000, but although it is difficult to distinguish salt effects from a possible slight dependence of k_{true} upon $[I^-]$, our own results would certainly suggest that the I_3^- ion is even less reactive than Nylén has stated. Thus, in experiments 32 and 33 of Table I (which are as nearly as possible comparable as regards ionic environment) the values of $[I_3^-]/[I_2]$ are about 400 and 200 respectively. Accepting Nylén's ratio of the intrinsic reactivities of I_3^- and I_2, it follows that k for expt. 32 should be about 17 per cent. *greater* than that for expt. 33, whereas it is actually 3 per cent. *less.*

From Table I and other experiments not listed the temperature coefficient or activation energy E_k of the reaction between HPO_3^{--} and I_2 may be derived. The results are summarised in Table IV. The weighted mean value of E_k is 22,050 cal., but there is a tendency for it to fall with increasing temperature. The value of E_k is very high when the absolute magnitude of k itself is taken into consideration, and the reaction between HPO_3^{--} and I_2, when treated on the basis of the simple collision theory of a bimolecular reaction, belongs to the category of reactions with abnormally high values of P in the equation

$$k = P \cdot Z \cdot e^{-E/RT},$$

the factor being about 3×10^7. Actually many reactions of the halogens in aqueous solution exhibit the same abnormality, and, as less attention seems to have been paid to these very fast bimolecular reactions than to

TABLE IV.

No. of Detns.	Temp. Interval.	Temp. Coeff. of k.	E_k (cal.).
4	0-10°	4·30	22,400
3	10-20°	3·74	21,740
1	20-30°	3·38	21,460

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[8] Griffith and McKeown, *Trans. Faraday Soc.*, 1933, 29, 611.

the abnormally slow ones, we present in Table V the data for several such cases the kinetics of which we have investigated in recent years. In the first column of the table are listed the actual reactants, in the next two columns the value of the bimolecular coefficient k in the units litre/mole-minute at the temperature indicated, in the fourth column E_{obs}, the apparent critical increment derived from the Arrhenius equation $d \ln k/dT = E_{\text{obs}}/RT^2$, and in the last two columns values of P as deduced from the two alternative collision formulæ :—

TABLE V.

Reactants.	k_{obs}.	temp. °C.	E_{obs}.	P_1.	P_2.
HPO_3^{--}—I_2 . .	5·7 × 10^3	20	22,050	2·7 × 10^7	1·9 × 10^6
HPO_3^{--}—Br_2(8) .	9·6 × 10^7	20	11,400	4·8 × 10^3	6·6 × 10^2
$H_2PO_3^-$—Br_2(8) .	25	20	15,100	0·7	0·1
$H_2PO_2^-$—I_2(9) .	0·92	60	25,200	4·7 × 10^3	3·2 × 10^2
$H_2PO_2^-$—Br_2(10) .	47	10	21,000	1·1 × 10^5	8 × 10^3
NO_2^-—I_2(11) . .	0·44	60	27,000	3 × 10^4	3 × 10^3
NO_2^-—Br_2(12) . .	1·2 × 10^3	30	18,700	4·7 × 10^3	3·9 × 10^2
$HC_2O_4^-$—HOI(13) .	2 × 10^3	45	18,500	1·7 × 10^3	1·6 × 10^2
$HC_2O_4^-$—HOBr(14)	2 × 10^4	21·5	15,400	8 × 10^2	1 × 10^3
$HC_2O_4^-$—HOCl(15) .	4 × 10^2	15	15,000	12	1·5

$$k = P_1 . Z . e^{-E_1/RT}$$

and

$$k = P_2 . Z . \left(\frac{E_2}{RT} + 1\right) . e^{-E_2/RT}.$$

The first of these formulæ assumes that only the energy associated with two squared terms (*e.g.* the relative kinetic energy along the line of centres) can be utilised as activating energy, whereas the second presumes that all the relative kinetic energy of the reactants can be so utilised. In the first case the true critical increment is given by $E_1 = E_{\text{obs}} - \frac{1}{2}RT$, in the second case by $E_2 = E_{\text{obs}} + \frac{1}{2}RT$. In carrying out the calculations R^2_{AB} the square of the distance of closest approach of centres in a collision has been taken as 10^{-15} cm.^{2} in every case.

(B) The Reaction in Acid Media ($p_{\text{H}} < 1$).

Under these conditions the reaction is catalysed by H^+, as found by Mitchell,[1] and also in general by acids. We shall apply to our data the mechanism of Mitchell modified in an analogous manner to that we have carried out for the $H_3PO_2 - I_2$ reaction (*cf.* preceding paper). Using the same notation as there, but neglecting the k_3 and k_{-3} reactions, we have :—

$$\frac{1}{k_{\text{bi}}} = \frac{[H^+]}{k_{\text{obs}}\{K_1 + [H^+]\}} = \frac{1}{k'K_t} + \frac{[\Sigma I_2]}{[H^+]} \cdot \frac{[H^+]}{\Sigma k_1^a[\text{Acid}]} . \quad (4)$$

[9] Griffith, McKeown and Taylor, *Trans. Faraday Soc.*, *preceding paper*.
[10] Griffith and McKeown, *Trans. Faraday Soc.*, 1934, 30, 530.
[11] Durrant, Griffith and McKeown, *Trans. Faraday Soc.*, 1936, 32, 999.
[12] Clarkson, Griffith and McKeown, *Trans. Faraday Soc.*, 1938, 34, 1274.
[13] Griffith and McKeown, *Trans. Faraday Soc.*, 1932, 28, 752.
[14] Griffith, McKeown and Winn, *Trans. Faraday Soc.*, 1932, 28, 107.
[15] Griffith and McKeown, *Trans. Faraday Soc.*, 1932, 28, 518.

Here k_{obs} is the bimolecular velocity constant with respect to ΣH_3PO_3 and ΣI_2, corrected, when necessary, for the occurrence of the HPO_3^{--} — I_2 reaction, and K_1 is the first ionisation constant of H_3PO_3. Hence, as in the preceding paper, a plot for any experiment of $1/k_{bi}$ against $[\Sigma I_2]/[H^+]$ should yield a straight line (provided that $\Sigma k_1{}^a$ [Acid] remains reasonably constant) with an intercept equal to $1/k'K_t$ and the reciprocal of the slope equal to $\Sigma k_1{}^a[\text{Acid}]/[H^+]$. Fig. 1 reproduces some of these plots pertaining to experiments in H_3PO_3—HCl—I_2 systems; it is seen that in each case a straight line is obtained and that the intercept is common to all the plots.

Experiments have been carried out mainly at 45° to determine the catalytic coefficients ($k_1{}^a$) of OH_3^+, H_3PO_3, H_3PO_4, HSO_4^-, chloroacetic acid, glycollic acid and acetic acid. A few experiments have also been effected at 35° to determine the temperature coefficients of $k_1{}^a$ and $k'K_t$. As found for the acid-catalysed H_3PO_2—I_2 reaction, variation of iodide concentration has also comparatively little effect on the rate of the acid-catalysed reaction between H_3PO_3 and iodine (see p. 779); in most of the experiments the initial concentration of iodide (KI) was 0·25 *M*.

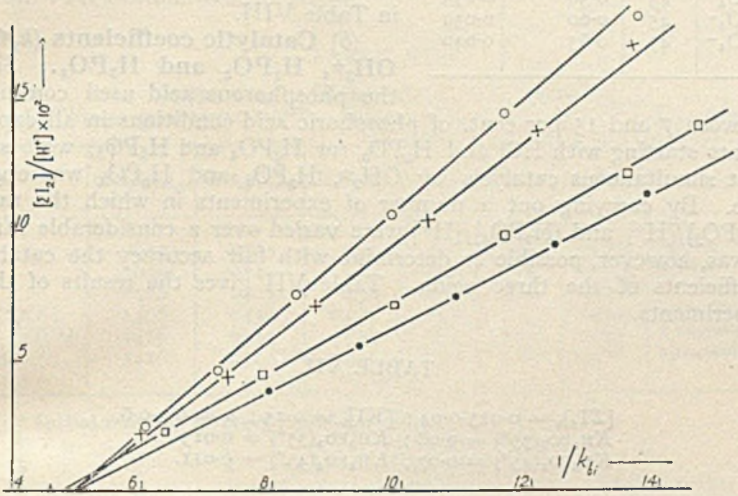

FIG. 1.—Plots of $1/k_{bi}$ against $[\Sigma I_2]/[H^+]$ for the first, second, fourth and fifth experiments of Table VII.

(*a*) **Ionisation constants of H_3PO_3, H_3PO_4, HSO_4^-, $CH_2ClCOOH$, $CH_2OH.COOH$ and CH_3COOH.**—To interpret the kinetic measurements in terms of equation (4) it is necessary to evaluate $[H^+]$ throughout each run, and hence one requires to know the values of K_C, the "concentration" ionisation constants of the various acids present in each reaction mixture. Unfortunately there is no method applicable by which these may be unequivocally determined for the conditions applying in our kinetic experiments, but we have attempted to obtain approximate values of K_c for H_3PO_3 (1st), H_3PO_4 (1st), and HSO_4^- by an E.M.F. method analogous to that used by Lugg.[16] For this purpose we have employed weak solutions of the acid in KCl solutions of the same total

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[16] Lugg, *J. Am. Chem. Soc.*, 1931, 53, 2554.

ionic strength as those used in the kinetic measurements, small corrections being applied when required for liquid-liquid junction potentials. It is recognised that the values of K_c thus derived can at best be only approximately correct, as they will vary with the type of salt present at a given total ionic strength and also with the concentration of undissociated acid. Table VI summarises the values of K_c obtained in this manner. The values for H_3PO_4 at 18° and 45° are both slightly larger than Lugg's estimates of ·0155 and ·0113.

TABLE VI.

Acid.	Temp.	μ.	K_c.
H_3PO_3	18	0·58–0·60	0·098
H_3PO_3	45	0·58–0·60	0·068
H_3PO_4	18	0·56	0·0173
H_3PO_4	45	0·56	0·0133
HSO_4^-	18	0·57	0·077
HSO_4^-	18	0·61	0·075
HSO_4^-	18	0·66	0·088
HSO_4^-	30	0·57	0·053
HSO_4^-	30	0·65	0·062
HSO_4^-	45	0·56	0·035
HSO_4^-	45	0·60	0·039
HSO_4^-	45	0·65	0·040

The values of K_c for the remaining acids used as catalysts were obtained from the literature as indicated in Table VIII.

(*b*) **Catalytic coefficients (k_1^a) of OH_3^+, H_3PO_3 and H_3PO_4.** Since the phosphorous acid used contained between 7 and 15 per cent. of phosphoric acid conditions in all experiments starting with HCl and H_3PO_3 (or H_3PO_4 and H_3PO_3) were such that simultaneous catalysis by OH_3^+, H_3PO_3 and H_3PO_4 was operative. By carrying out a number of experiments in which the ratios $[H_3PO_3]/[H^+]$ and $[H_3PO_4]/[H^+]$ were varied over a considerable range, it was, however, possible to determine with fair accuracy the catalytic coefficients of the three acids. Table VII gives the results of these experiments.

TABLE VII.

$[\Sigma I_2]_0$ = 0·015-0·04 ; $[KI]_0$ = 0·25 ; μ = 0·5-0·6.
$K_{H_3PO_3}(35°)$ = 0·08 ; $K_{H_3PO_4}(35°)$ = 0·013
$K_{H_3PO_3}(45°)$ = 0·07 ; $K_{H_3PO_4}(45°)$ = 0·011.

$[\Sigma H_3PO_3]_m$.	$\frac{[H_3PO_3]_m}{[H^+]_m}$.	$[\Sigma H_3PO_4]_m$.	$\frac{[H_3PO_4]_m}{[H^+]_m}$.	$[H^+]_m$.	Intercept.	1/slope (obsd.).	1/slope (calc.).
			temp. = 45°				
0·122	0·297	0·037	0·106	0·339	4·95	0·0128	0·0125
0·187	0·522	0·051	0·171	0·288	4·75	0·0142	0·0144
0·255	0·823	0·063	0·250	0·240	4·74	0·0168	0·0169
0·321	1·079	0·076	0·318	0·228	4·92	0·0190	0·0190
0·390	1·375	0·087	0·388	0·213	4·98	0·0219	0·0214
0·670	2·356	0·129	0·575	0·214	5·15	0·0285	0·0289
0·329	1·454	0·311	1·860	0·156	4·85	0·0324	0·0325
0·194	0·940	0·530	3·600	0·136	5·00	0·0417	0·0418
0·123	0·623	0·678	4·870	0·128	5·05	0·0491	0·0490
			temp. = 35°				
0·295	0·874	0·071	0·262	0·257	14·1	0·00535	0·00544
0·697	2·240	0·156	0·639	0·231	15·6	0·00879	0·00902
0·195	0·876	0·529	3·395	0·143	15·0	0·01311	0·01256

The penultimate column in this table gives the observed values of 1/slope of the linear plots of $\frac{[H^+]}{k_{obs}\{K_1 + [H^+]\}}$ against $\frac{[\Sigma I_2]}{[H^+]}$. Substituting in equation (4*a*), *viz.* :—

$$\frac{1}{\text{slope}} = k_1^{\circ} + k_1^{H_3PO_3} . \frac{[H_3PO_3]}{[H^+]} + k_1^{H_3PO_4} . \frac{[H_3PO_4]}{[H^+]}, \quad (4a)$$

the data given are then consistent with :—

$k_1^{\circ} = 0·00987$; $k_1^{H_3PO_3} = 0·00634$; $k_1^{H_3PO_4} = 0·00722$ at 45°, and with values of the same constants reduced 3·18 times at 35°. The values of 1/slope (calc.) obtained by substituting these parameters in equation (4*a*) are given in the final column.

(*c*) **Catalytic coefficients of HSO_4^-, glycollic acid, acetic acid and chloroacetic acid.**—A few experiments have been carried out also at 45° to determine the catalytic coefficients of the above acids. Table VIII summarises the results.

TABLE VIII.

Temp. = 45° ; $[KI]_0$ = 0·25 ; μ = 0·56-0·62.
$K_{HSO_4^-}$ = ·038 ; $K_{CH_2Cl\,.\,COOH}$ = 0·0012[17] ; $K_{CH_2OH\,.\,COOH}$ = 2·8 . 10^{-4} [18] ; K_{CH_3COOH} = 3·10^{-5} [6].

Acid.	$[\Sigma H_3PO_3]_m$.	$[\Sigma H_3PO_4]_m$.	$\Sigma[Acid]_m$.	$[H^+]_m$.	Intercept.	1/slope.	k_1^a.
* HSO_4^- . .	·0893	·0325	·276	·351	4·97	·01581	$k_1^{HSO_4}$ = ·00560
† HSO_4^- . .	·1006	·0242	·220	·297	4·84	·01565	$k_1^{HSO_4^-}$ = ·00533
‡ HSO_4^- . .	·1578	·0293	·176	·128	4·60	·02250	$k_1^{HSO_4^-}$ = ·00564
§ CH_2Cl . COOH	·1398	·0430	1·011	·163	—	·02140	$k_1^{CH_2ClCOOH}$ = ·00096
§ CH_2OH . COOH	·1416	·0412	·972	·152	5·08	·0197	$k_1^{CH_2OHCOOH}$ = ·00060
§ CH_3COOH .	·1416	·0412	1·000	·152	5·04	·0180	$k_1^{CH_3COOH}$ = ·00031

* Initial reaction mixture contained $[\Sigma H_2SO_4]$ = ·276.
† ,, ,, ,, ,, $[\Sigma H_2SO_4]$ = ·220
‡ ,, ,, ,, ,, $[\Sigma KHSO_4]$ = ·176
§ ,, ,, ,, ,, also [HCl] = ·072 ; [KCl] = 0·161.

The values of k_1^a in the last column were obtained from equation (4*b*) after substituting the values of k_1°, $k_1^{H_3PO_3}$ and $k_1^{H_3PO_4}$ derived from Table VII. No great accuracy can be claimed for the catalytic coefficients of HSO_4^-, CH_2Cl . COOH, $CH_2OHCOOH$ and CH_3COOH in Table VIII, since in no case was the last term in the equation :—

$$1/\text{slope} = k_1^{\circ} + k_1^{H_3PO_3} . \frac{[H_3PO_3]}{[H^+]} + k_1^{H_3PO_4} . \frac{[H_3PO_4]}{[H^+]} + k_1^a . \frac{[HA]}{[H^+]} \quad (4b)$$

more than 30 per cent. of the observed 1/slope. Indeed, conditions under which the catalytic contribution of a weak acid should predominate over those of H^+ and H_3PO_3 cannot be realised in practice since, for convenient speeds of reaction, it is necessary to have a reasonably large

[17] Wright, *J. Am. Chem. Soc.*, 1934, 56, 314 ; Dawson and Key, *J.C.S.*, 1929, 1239.

[18] Nims, *J. Am. Chem. Soc.*, 1936, 58, 987 ; Larsson and Adell, *Z. physik. Chem. A*, 1931, 157, 342.

concentration of free H_3PO_3 in the system as *reactant*, and this in turn necessitates a moderately high concentration of hydrogen ion. The results are, however, sufficiently accurate to demonstrate the existence of a general acid catalysis, and the values of the k_1^a's of Tables VII and VIII may be used for a rough test of the Brönsted relation between catalytic coefficient and ionisation constant. The pertinent data are collected together in Table IX. The plot of log $\left(\frac{k_1^a}{p}\right)$ against log $\left(\frac{q}{p} \cdot K_A^\circ\right)$ is roughly linear, except for the case of H^+ ion for which k_1^a is abnormally low. The values of log $\left(\frac{k_1^a}{p}\right)$ calculated from a linear relation

$$\log\left(\frac{k_1^a}{p}\right) = 0{\cdot}415 \log\left(\frac{q}{p} \cdot K_A^\circ\right) - 1{\cdot}74$$

are shown in the last column of Table IX.

TABLE IX.

Acid.	p.	q.	k_1^a.	K_A°.	$\log\left(\frac{k_1^a}{p}\right)$ obs.	$\log\left(\frac{k_1^a}{p}\right)$ calc.
OH_3^+ . .	1	1	0·00987	55	$-$ 2·006	$-$ 1·02
H_3PO_3 .	2	2	0·00634	$3{\cdot}7 \times 10^{-2}$	$-$ 2·499	$-$ 2·33
H_3PO_4 .	3	2	0·00722	$5{\cdot}9 \times 10^{-3}$	$-$ 2·619	$-$ 2·74
HSO_4^- .	1	4	0·00552	$8{\cdot}83 \times 10^{-3}$	$-$ 2·26	$-$ 2·34
Chloroacetic	1	2	0·001	$1{\cdot}09 \times 10^{-3}$	$-$ 3·00	$-$ 2·86
Glycollic .	1	2	0·0006	$1{\cdot}44 \times 10^{-3}$	$-$ 3·22	$-$ 3·22
Acetic .	1	2	0·00031	$1{\cdot}67 \times 10^{-5}$	$-$ 3·50	$-$ 3·60

The inner mechanism of this acid-catalysed reaction must evidently be similar to that of the analogous reaction with hypophosphorous acid ; the normal form of H_3PO_3 with the phosphorus atom in the pentavalent state is transformed *via* the complex $H_3PO_3 . H^+$ into the active form of H_3PO_3, whose phosphorus atom is tervalent.

(*d*) **Temperature coefficients of k_1^a and $k'K_t$.**—It was seen from Table VII that, within our experimental error, the k_1^a's have all got a temperature coefficient between 35° and 45° of 3·18. This corresponds to $E_{k1} = 22{,}500$ calories for the critical increment of the acid-catalysed process : $H_3PO_3 + \text{acid} \rightarrow H_3PO_3 . H^+ + \text{base}$. As regards the intercept $\frac{1}{k'K_t}$, its average value at 45° equals 4·95 ; the three estimates at 35° are not very concordant, but their mean value is 14·9. These data yield a temperature coefficient of $k'K_t$ of 3·0 and $E_{k'K_t} = 21{,}400$ cal.

(*e*) **Dependence of k' upon $[I^-]$.**—Under this heading similar remarks apply to the acid catalysed H_3PO_3—I_2 reaction as for the acid-catalysed H_3PO_2—I_2 reaction discussed in the preceding paper. There it was shown that

$$\frac{1}{\text{Intercept}} = k'K_t = K_t\left\{k'_{I_2} \cdot \frac{K_3}{K_3 + [I^-]_\infty} + k'_{I_3^-} \cdot \frac{[I^-]_\infty}{K_3 + [I^-]_\infty}\right\} \quad (5)$$

with k'_{I_2} (the specific rate of interaction of I_2 with the active form of the acid) greater than $k'_{I_3^-}$, and here (for H_3PO_3) the same equation applies. The experimental observations from which $K_t . k'_{I_2}$ and $K_t . k'_{I_3^-}$ may be estimated are summarised in Table X. All the experiments were carried out at 45° and $\mu = 0{\cdot}55$, using NaI as iodide, $HClO_4$ as catalysing acid and $NaClO_4$ as neutral salt.

TABLE X.

Temp. = 45° ; $K_3 = 2{\cdot}18 \times 10^{-3}$.

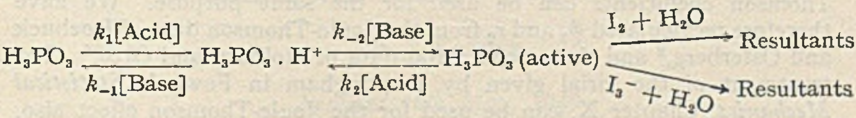
$[H^+]$	0·240	0·133	0·254	0·254	0·275	0·275
$[I^-]_\infty$	0·0090	0·0090	0·0181	0·0282	0·1451	0·3493
Intercept (obs.) .	3·13	3·06	3·72	4·09	4·62	4·84
Intercept (calc.) .	3·10	3·10	3·73	4·06	4·73	4·86

The data are consistent with $K_t . k'_{I_2} = 0{\cdot}818$; $K_t . k'_{I_3^-} = 0{\cdot}202$ and $k'_{I_2}/k'_{I_3^-} = 4{\cdot}05$, as shown by the values of intercept (calc.) in the last row, obtained by substituting these parameters in equation (5). It may be noted that the ratio of the reactivities of I_2 and I_3^- found here is not very different from the corresponding ratio obtained in the acid-catalysed reaction of iodine with hypophosphorous acid.

Summary.

The kinetics of the reaction between phosphorous acid and iodine in aqueous solution have been investigated over a range of pH between 0·5 and 9, and at temperatures between 0° and 45°. In solutions whose pH lies between 2 and 9 the sole detectable process is a reaction between HPO_3^{--} ions and free I_2 molecules. This bimolecular reaction is found to have a very high P factor in the Arrhenius equation ; attention is directed to other reactions of halogens in aqueous solution which also have high P factors.

In acid solutions of pH less than 1 the reaction taking place involves a prototropic change and is subject to general acid-base catalysis. Its mechanism is presumed to be :—



$$H_3PO_3 \underset{k_{-1}[\text{Base}]}{\overset{k_1[\text{Acid}]}{\rightleftharpoons}} H_3PO_3 . H^+ \underset{k_2[\text{Acid}]}{\overset{k_{-2}[\text{Base}]}{\rightleftharpoons}} H_3PO_3\ (\text{active}) \begin{array}{l} \xrightarrow{I_2 + H_2O} \text{Resultants} \\ \xrightarrow{I_3^- + H_2O} \text{Resultants} \end{array}$$

in which H_3PO_3 (active) contains tervalent phosphorus. The catalytic coefficients of a number of moderately strong acids of the k_1 reaction have been determined ; except for that of OH_3^+, whose reactivity is too low, they satisfy the Brönsted relation.

The velocity of the reaction between $H_2PO_3^-$ and I_2 was found to be too small (in comparison with the two above-mentioned processes) to be detectable.

THE INTERACTION BETWEEN NITROGEN MOLECULES.

By J. Corner.

Received 14*th May*, 1940.

The intermolecular potential

$$\phi = 12\phi_0\left\{\frac{1}{12}\left(\frac{r_0}{r}\right)^{12} - \frac{1}{6}\left(\frac{r_0}{r}\right)^{6}\right\}$$

where ϕ_0, r_0 are constants and r is the distance between the centres of the molecules, has been shown to give a good approximation to the second virial coefficient of some simple molecules. Lennard-Jones and Devonshire have interpreted many properties of liquids and solids in terms of ϕ_0 and r_0, whose dimensions are those of energy and length respectively. The parachor $[P]$ can be treated similarly, and by dimensional analysis it appears that $[P]\phi_0^{-1/4}\,r_0^{-5/2}$ should be a constant. This is, in fact, the case except that for neon and hydrogen there are deviations, probably due to quantum effects. Nitrogen shows a deviation in the opposite direction, of magnitude several times the average deviation. The same anomaly can be traced in other properties. For example, the values of r_0 and ϕ_0 given in Fowler's *Statistical Mechanics* (2nd edn., p. 306) lead one to expect too large a critical volume and too large a volume of the solid at the melting-point and at 0° K.

The theory assumes spherically symmetrical molecules and the deviations for nitrogen might be caused by the failure of this assumption. However, it would be disappointing if the theory could not be applied even to nitrogen, whose molecule is much more nearly spherical than most substances of chemical interest.

These force-constants were derived from second virial data. Recently Hirschfelder, Ewell, and Roebuck [1] have shown that low-pressure Joule-Thomson coefficients can be used for the same purpose. We have therefore recalculated ϕ_0 and r_0 from the Joule-Thomson data of Roebuck and Osterberg,[2] and the second virial data of Holborn and Otto.[3] The treatment of the virial given by Buckingham in Fowler's *Statistical Mechanics*, Chapter X, can be used for the Joule-Thomson effect also, instead of the process used by Hirschfelder, Ewell, and Roebuck. This permits both sets of data to be used together, which is an advantage when they are believed to be of equal weight. The data refer to temperatures above 198° K. Hirschfelder, Ewell, and Roebuck have shown that the quantum correction to the Joule-Thomson coefficient of argon at 173° K. is about $\frac{1}{2}$ %, so the correction was omitted in the present case.

The result was

$$\left.\begin{aligned}\phi_0 &= 1{\cdot}307 \times 10^{-14}\\ V_0^* = r_0^3/\sqrt{2} &= 4{\cdot}88 \times 10^{-23}\end{aligned}\right\}$$

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[1] Hirschfelder, Ewell, and Roebuck, *J. Chem. Physics*, 1938, 6, 205.

[2] Roebuck and Osterberg, *Physic. Rev.*, 1935, 48, 450.

[3] Holborn and Otto, *Z. Physik*, 1924, 30, 320.

The values previously accepted were

$$\left.\begin{aligned}\phi_0 &= 1{\cdot}324 \times 10^{-14}\\ V_0^* &= 5{\cdot}14 \times 10^{-23}\end{aligned}\right\}$$

The change in ϕ_0 alters previous theoretical calculations of temperatures, such as the critical temperature, by about 1 % ; the 5 % change in V_0^* brings the properties of nitrogen more nearly into line with those of the inert gases. This is shown in the table, in which $V_0 = NV_0^*$, where N is Avogadro's number.

	Ne	Ar	Kr	Xe	CH_4	N_2
Critical volume/V_0 .	3·33	3·13	3·29	3·05	3·08	3·04
kT_c/ϕ_0 . . .	1·25	1·24	(1·33)	(1·33)	(1·33)	1·32
Lattice distance } obs.	3·20	3·81	3·94	4·33	4·16	4·02
at 0°K., in Å. } calc.	3·13	3·76	(3·94)	(4·33)	(4·16)	4·03
	5·69	5·26	—	—	5·38	5·24

(Brackets indicate that these values were assumed in the calculation of ϕ_0 and r_0.)

I am indebted to Professor Lennard-Jones for his interest in this correction.

Summary.

A recalculation of the interaction of nitrogen molecules, on conventional lines, eliminates some anomalies in the derived observable properties of this substance.

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THE EXPLANATION OF A RULE FOR CRITICAL TEMPERATURES.

By J. Corner.

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The critical temperature of a gas provides a scale of reduced temperature, and so enables its properties to be correlated with those of related gases. This has considerable technical importance. Unfortunately, the determination of critical temperatures is often very difficult. To take an example, the properties of the normal paraffins are of special interest to the oil industry, but with increasing chain length the critical temperatures enter a temperature region where decomposition is rapid, so that they cannot be determined experimentally. Nevertheless, when so-called " critical temperatures " have been obtained by extrapolation or from some more easily observed property they can be used to predict many other properties of long-chain paraffins. For this reason, many rules for predicting critical temperatures have been suggested in the past. In this note we show that a recent theory of liquids (*a*) explains the form of one of the more successful of these empirical rules, and (*b*) shows that T_c/T_B can be correlated with certain other properties, at any rate for the simpler molecules.

Watson's Rule.

Let T_c be the critical temperature, and T_B the boiling-point. Let T_e be the temperature at which the molecular concentration in the vapour is the same as in a perfect gas at N.T.P.; that is, 1 g.-molecule in 22·4 litres. Let V_B be the molar volume at the boiling-point. Watson[1] suggested the empirical equation

$$T_e/T_c = 0{\cdot}283\, V_B{}^{0{\cdot}18} \quad . \quad . \quad . \quad . \quad (1)$$

He tested this on a number of non-polar substances, over a range of V_B from 16 to 190 c.c., and found that the deviations between calculated and predicted values of T_e/T_c were about 2 %. T_e can be derived from T_B by using Hildebrand's rule. The result is

$$\log T_e = 4{\cdot}26\, T_e/T_B - 1{\cdot}82 \quad . \quad . \quad . \quad . \quad (2)$$

Here, and in the rest of this note, the logarithms are to base 10.

That there should be a rule connecting T_e/T_c and V_B can be derived from the theory of liquids due to Lennard-Jones and Devonshire.[2] This assumes that in the liquid the molecules can be treated as spherically symmetrical. The numerical calculations have been carried out for the case when the potential energy of two molecules, whose centres are r apart, is $12\phi_0\left[\frac{1}{12}\left(\frac{r_0}{r}\right)^{12} - \frac{1}{6}\left(\frac{r_0}{r}\right)^{6}\right]$ where ϕ_0 and r_0 depend only on the type of molecule considered. One result has been the following formula for the vapour pressure p (in atmospheres) at temperature T:

$$\log p = \log(\phi_0 r_0{}^{-3}) - 2{\cdot}744\phi_0/kT - 4{\cdot}678 \quad . \quad . \quad (4)$$

This gives the boiling-points of the rare gases to within a few per cent.* It is convenient to introduce a volume $V_0 = N r_0{}^3/\sqrt{2}$, where N is Avogadro's number. V_0 is approximately the volume of a mole of the liquid. Lennard-Jones and Devonshire[4] have proved that the critical temperature is related to ϕ_0 by $\phi_0 = 0{\cdot}75 kT_c$. The vapour can be taken as a perfect gas, so that when $T = T_e$, the vapour pressure is $T_e/273$ atmospheres. Eliminating ϕ_0, $r_0{}^3$, and the vapour pressure, from equation (4) with $T = T_e$, by using their expressions in terms of T_c, V_0, and T_e, it follows that

$$2{\cdot}058\, T_c/T_e - \log {}^{T_c}/_{T_e} = 5{\cdot}403 - \log V_0 \quad . \quad . \quad (5)$$

This can be represented approximately by a formula of type (1), with suitable constants. For V_0 between 18 and 90 c.c., the ratio T_e/T_c, calculated from (5), agrees with the formula

$$T_e/T_c = 0{\cdot}3204\, V_0{}^{0{\cdot}122} \quad . \quad . \quad . \quad . \quad (6)$$

with deviations of about 0·3 %.

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[1] Watson, *Ind. Eng. Chem.*, 1931, 23, 360.

[2] Lennard-Jones and Devonshire, *Proc. Roy. Soc. A*, 1939, 169, 317.

* We are indebted to Professor Lennard-Jones and Dr. Devonshire for the private communication of this unpublished formula. The boiling-point of argon, derived from this formula, has been given in one of their papers.[2] The formula differs considerably from the result of an earlier version of the theory.[3]

[3] Lennard-Jones and Devonshire, *Proc. Roy. Soc. A*, 1938, 165, 1.

[4] *Ibid.*, 1937, 163, 53.

Let V be the molar volume at temperature T. In this theory the behaviour of a liquid is completely determined by the values of V_0 and ϕ_0 for the constituent molecules. In particular, V/V_0 is the same function of ϕ_0/kT for all liquids. The volume of any one liquid varies only slowly with the temperature, so that V/V_0 is, in fact, a slowly varying function of ϕ/kT. Considering variations from liquid to liquid at the boiling-points, it follows that V_B/V_0 is not much affected by the variations of ϕ_0/kT_B. This latter quantity can be found from (4), when we put $p = 1$ atmosphere and $T = T_B$. Differences of $\phi_0 r_0^{-3}$ cause small variations of ϕ_0/kT_B from liquid to liquid, and hence only small variations of V_B/V_0. Thus T_e/T_c which is, according to (6), determined by V_0, will appear to be determined by V_B. This explains the form of Watson's rule.

For the rare gases V_B is about $1{\cdot}2\ V_0$; by (6) this leads to

$$T_e/T_c = 0{\cdot}313\ V_B^{0{\cdot}122} \quad . \quad . \quad . \quad . \quad (7)$$

This does not agree well with the experimental data; even for the rare gases, to which the theory should apply best, the deviations of T_e/T_c are about 10 %. This test is more stringent than the calculation of boiling-points.

The Ratio T_c/T_B.

We may mention two other consequences of the vapour pressure equation (4). At $T = T_B$, $p = 1$ atmos.; ϕ_0 and r_0^3 can be eliminated in favour of T_c and V_c, for Lennard-Jones and Devonshire have shown [4] that $\phi_0 = 0{\cdot}75\ kT_c$ and $Nr_0^3 = 0{\cdot}707\ V_c$.

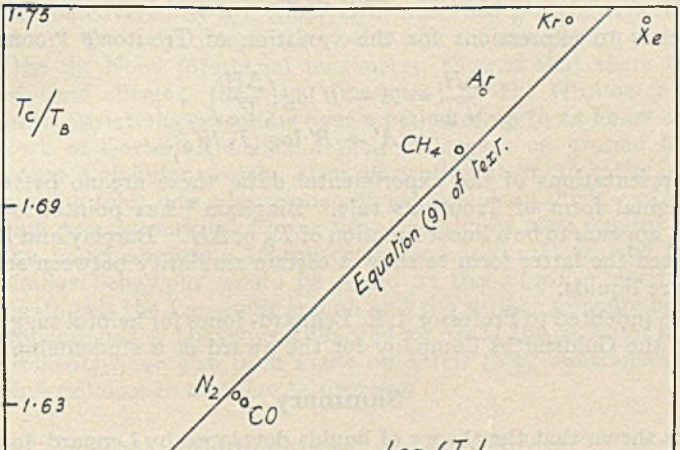

FIG. 1.—The ratio T_c/T_B for the simpler gases.

Hence

$$T_c/T_B = 1{\cdot}597 + 0{\cdot}486 \log (T_c/V_c) \quad . \quad . \quad . \quad . \quad (8)$$

The underlying theory should apply to the inert gases (except the light members neon and helium) and to N_2, CO, and CH_4. Whether the assumptions of the theory are true for other liquids is to be decided by testing its consequences. One such test is an attempt to express experimental results in the form

$$T_c/T_B = A + B \log (T_c/V_c),$$

where A and B are constants. Certainly, as a rule for all liquids, this is not significantly better than $T_c/T_B = \text{constant}$. It is well known that this is only a crude approximation. If, however, we restrict our attention to the substances, listed above, to which the theory should apply best, we find that the best values of the constants are

$$A = 1{\cdot}567\,; \quad B = 0{\cdot}4744 \qquad . \quad . \quad . \quad . \quad (9)$$

Fig. 1 shows that this law fits the observations very well. The agreement in the first term is helped by the fact that in deriving (8) we have used the *theoretical* relation between r_0^3 and V_c. The *experimental* relation increases this term by 0·08. The second coefficient is independent of this uncertainty.

For the family of normal paraffins the constants A, B are

$$A = 1{\cdot}3608\,; \quad B = 0{\cdot}898 \qquad . \quad . \quad . \quad . \quad (10)$$

Best values of T_c and T_B for paraffins up to octane have been selected by Cox.[5] This formula reproduces T_c/T_B with deviations about 0·3 %. This is closer agreement than we have been able to obtain from any other formula for T_c/T_B, containing only two arbitrary parameters.

The molar heat of evaporation ΔH is given in this theory by

$$\begin{aligned} \Delta H &= NkT^2 \frac{\partial}{\partial T}(\log_e P) \\ &= 6{\cdot}19\, \phi_0. \end{aligned}$$

This leads to expressions for the variation of Trouton's "constant."

$$\begin{aligned} \frac{\Delta H}{T_B} &= A + B \log\left(\frac{\Delta H}{V_c}\right) \\ &= A' + B' \log (T_c/V_c). \end{aligned}$$

As representations of the experimental data, these are no better than the original form of Trouton's rule. Bingham[6] has pointed out that $\Delta H/T_B$ appears to be a linear function of T_B or ΔH. Barclay and Butler[7] have used the latter form to show a certain similarity between solutions and pure liquids.

I am indebted to Professor J. E. Lennard-Jones for helpful suggestions, and to the Goldsmiths Company for the award of a studentship.

Summary.

It is shewn that the theory of liquids developed by Lennard-Jones and Devonshire explains the form of Watson's rule for critical temperatures, and also gives the correct form of the variation of the ratio of the critical temperature to the boiling-point, for the simple "permanent gases" and the normal paraffins.

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Cambridge.

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[5] Cox, *Ind. Eng. Chem.*, 1935, 27, 1423 ; 1936, 28, 613.

[6] Bingham, *J. Am. Chem. Soc.*, 1906, 28, 723.

[7] Barclay and Butler, *Trans. Faraday Soc.*, 1938, 34, 1445.

MEASUREMENTS OF THE PRESSURES DUE TO MONOLAYERS AT OIL-WATER INTERFACES.*

By Frederic Anderton Askew and James Frederic Danielli.

Received 14*th May*, 1940.

The study of surface films has already proved its usefulness in relation to biological problems; in numerous papers Adam and his co-workers, and Rideal and his co-workers, have described measurements of the shapes and sizes of large molecules. These studies have hitherto, however, been made at the interface between air and aqueous solutions: the results of measurements at liquid-liquid interfaces would be more valuable for biologists, since this type of interface is of much more frequent occurrence in biological systems. The work described in this paper is an attempt to measure the properties of films of various types (solid, liquid, gaseous) formed at the oil-water interface under conditions analogous to those at the air-water interface, so that the variation in area per molecule and in surface pressure can be measured as the film is compressed.

Danielli and Harvey[1] found that proteins were able to reduce the "i.t." (interfacial tension) between oils and aqueous phases to the order of 1 dyne or less, and that naturally occurring oil-water interfaces must therefore be covered by a monolayer of adsorbed protein molecules. A preliminary investigation of the behaviour of adsorbed protein films using the du Nouy interfacial tensimeter, showed that there are very marked time effects; the "i.t." measured by the tensimeter showed systematic variations extending over a period of up to 24 hours or more.[2] The work of Gorter, Rideal and their colleagues on protein films has shown that a globular protein, after adsorption at an *air-water* interface, ultimately unfolds into a layer one polypeptide chain thick, and that this unfolding process may take place very quickly, or may require a period of many hours according to the conditions used. It seemed probable that similar behaviour would be found at the *oil-water* interface: to investigate this the Langmuir trough and the surface pressure apparatus of Adam and Jessop[3] have been adapted for use at the oil-water interface. Measurements have also been made on a few fatty substances and on trimethyl cellulose in addition to proteins.

Methods and Apparatus.

Since the measurements which it was desired to make were entirely analogous to those made with the Langmuir-Adam trough and surface pressure measuring apparatus at the air-water interface, such an apparatus was taken as a starting-point and the necessary modifications devised.

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* A preliminary account of some of this work was given at the Royal Society Discussion on Surface Phenomena in 1936.

[1] J. F. Danielli and E. N. Harvey, *J. Cell. Comp. Physiol.*, 1934, **5**, 483.

[2] J. F. Danielli, *Cold Spring Harbour Symposia*, 1938, **6**, 191.

[3] N. K. Adam and G. Jessop, *Proc. Roy. Soc. A*, 1926, **110**, 423.

The essential differences are shown schematically in Fig. 1. At the air-water interface, the film-covered surface is divided from the clean surface by a metal float, coated with paraffin wax to prevent it becoming wet. If wet, the float will no longer retain the film. A pressure exerted on the left of the float causes it to move to the right and allows the mirror (M), to which it is attached by a fine silver wire, to tilt forward. This tilt is corrected by twisting the upper torsion wire (T_2), which pulls the float back again by means of a lever and the second silver wire. The pressure is read directly on a pointer and scale attached to the upper torsion wire, and the apparatus is calibrated by hanging weights on a beam (B) and observing the twist necessary to compensate for this. In the interfacial pressure modification of this apparatus, the arrangement is very similar, except that the float is situated in the interface, and is wet by the upper liquid layer, and not by the lower.

In the experiments to be described in this paper, the upper liquid consisted of aqueous buffer solutions, and the lower of brombenzene. The reasons for choosing brombenzene were several: (1) it is almost completely immiscible with water; (2) it has a considerable attraction for the hydrocarbon groups of molecules, as contrasted with the high attraction of water for the polar groups; (3) it has a high density (1·5) and low volatility, which make for convenience in manipulation; (4) it is easy to purify; and (5) it has a high interfacial tension against water, about 40 dynes per cm., a very important point, since this sets an upper limit to the values of interfacial pressure which it can be hoped to measure.

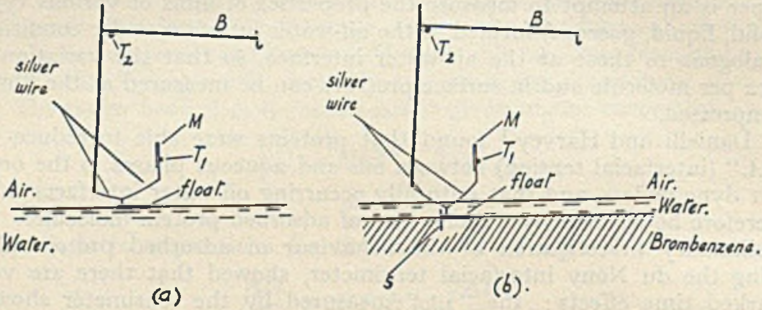

FIG. 1.—Diagram of apparatus for measuring surface pressure, (*a*) at air-water interfaces, (*b*) at oil-water interfaces. B, rigid beam; M, mirror; T_1, mirror suspension; T_2, main torsion wire.

Choice of Materials for the Trough and Apparatus. The choice of materials for the apparatus is a good deal narrower than that available for work in the air-water interface. The condition obtaining in the Langmuir-Adam trough under which efficient sweeping of the surface by "barriers", and retention of the film under observation, are secured is: in the system air/water/trough material, the contact angle in water must be fairly high, about 90°. This enables the trough to be filled a little above the level of the sides, so that when the flat "barriers" are resting on the sides, they form a seal against movement of the film along the water surface. This condition is conveniently satisfied for the air-water interface by coating the trough and barrier surfaces with a high-melting paraffin wax. The wax/water/air contact angle is about 105° in water, and the system works well for water and solutions having surface tensions approaching that of water, as the experiments of many workers have shown.

Similar conditions will evidently apply to the choice of barrier and trough surfaces to work in conjunction with a liquid-liquid interface. In our experiments, brombenzene instead of water forms the lower liquid and aqueous solutions, instead of air, the upper. In order to fulfil the above-mentioned condition the trough material must be such that the contact angle water/trough material/brombenzene is about 90° in brombenzene. Clean glass approximately fulfils these conditions, and was the material used for the inner trough and barriers in the earlier experiments. It was found, however, that water under slight pressure tends to displace brombenzene from the glass surfaces and cause leakage. Brass barriers were tried and found to be more satisfactory, presumably owing to forces of attraction between metal and the halogen of brombenzene.

The thickness of the upper layer of liquid is of some importance, for if it is too thin the layer is unstable, and if the brombenzene surface is exposed by any disturbance, its area increases instead of the break healing; *i.e.* the water flows away, leaving the brombenzene surface exposed. By keeping the thickness of the aqueous layer rather greater than 5 mm. this particular trouble can be avoided.

Form of the Apparatus. The general form of the apparatus consists of two rectangular troughs, one inside the other. The outer one consisted, in our experiments, of a brass or silica surface pressure trough of the usual type, but unwaxed. The inner trough was made of plate glass, also unwaxed, and was 1 cm. deep, fitting loosely inside the outer trough. Short brass barriers, 12 mm. wide and 2 mm. thick, bridged the inner trough and were manipulated with forceps. Clean glass barriers were used, however, to sweep the air-water surface free from drops of brombenzene, which tended to accumulate there during experiments.

The pressure-measuring instrument was that used by Adam and his co-workers to measure surface pressures at the air-water interface, with the following modifications:—

In the standard machine a copper or platinum " float " is used to divide the film-covered from the clean surface, and floats by virtue of the fact that it is coated with paraffin wax, and therefore is not easily wetted by water. In the interfacial-pressure apparatus this float was made of a strip of paper standing perpendicular to the interface, supported by a slip of mahogany veneer approximately 6 cm. long by 1 cm. by 0·05 cm.; this wood was extracted well with water and benzene and kept soaked in water. When mounted in the apparatus, this wooden float was weighted with small brass clips, so that it sank through the aqueous phase, but rested in the interface between this and the brombenzene, by which it was not wetted. A brass clip in the centre was attached to the pressure balance and mirror support of the apparatus in the usual manner, by fine silver wires.

In place of the platinum ribbons which, in the surface pressure apparatus, prevent the film passing the ends of the float strips of filter paper were used. In some of the earlier experiments a tendency was found for the film to leak underneath the float when subjected to pressure, and it was found desirable to continue this paper strip right across the front of the float, and to arrange that it should be depressed into the brombenzene layer. The filter paper strip was held in clips made from brass foil; these clips also served to weight the float so that it sank through the aqueous layer. A wooden " tail " to the float projecting behind the float and at right angles to it served to keep the float level in the surface. The outer ends of the paper strips were held in clips attached to the framework of the pressure measuring apparatus by brackets which rested on the sides of the inner trough and formed leak-proof joints with it. Wire hooks suspended from the frame of the apparatus held the float clear of the outer trough when the apparatus was being assembled.

The best method of filling the trough was found to be to pour the aqueous phase in first, until it filled and completely wetted the inner trough, and then to add the brombenzene through a funnel (the stem dipped well below the water surface), till the brombenzene layer filled the inner trough, displacing the water. This technique has two advantages: (1) prewetting of the glass surfaces by water diminishes the tendency of brombenzene to wet them; (2) if water is poured onto brombenzene, the latter tends to break up into drops, some of which lodge in the air-water interface and are difficult to remove.

To test for leakage of film past barriers, float, etc., talc was injected as an aqueous suspension below the water surface: it then sank to the interface, where it remained and served to indicate the movements of the invisible interfacial films. Leaks were much more frequent in these experiments than they are at the air-water interface, probably owing to the comparatively small difference in wetability of glass by water and brombenzene.

The film-forming substances were introduced into the interface in solution by means of a micrometer pipette. This was provided with a long straight needle, ground square at the end. The position of the tip of the needle with regard to the interface was fairly critical, especially with the protein solutions, so that the pipette was clamped vertically on a stand, and its height adjusted before expelling the solution. For solutions miscible with the aqueous phase, *e.g.* protein solutions, the tip of the pipette was placed just below the interface, so that the small droplets of solution rose and spread at the interface. For solutions easily miscible with the organic phase and not with water, *e.g.* those solutions in $CHCl_3$, the tip was placed above the interface, so that the small drops fell to the interface and spread. Organic solutions lighter than water or miscible with both phases were as far as possible avoided, owing to the difficulty of ensuring that the material was wholly introduced into the interface.

The procedure of an experiment was as follows. The trough being full and level, the interface was swept once or twice with brass barriers, on each side of the float. Since the barriers were necessarily dipped through, and therefore first wet with the aqueous phase, they were wholly immersed in the brombenzene before being lifted gently to the interface near the float and moved with forceps gently back to the other end of the trough. A fresh barrier was used for each sweep. The barriers accumulating at the end of the trough were removed as necessary, rinsed with water and used afresh.

After the preliminary sweeping of the interface, a few drops of talc suspension in water were placed in the interface and a barrier brought from the far end of the trough up to the float, to test for leaks. These, if found, were stopped by the adjustment of the liquid levels, or the position of the paper strip. The interface was then thoroughly swept until as much as possible of the incidental impurities were removed from the surface. The increase of pressure registered when a barrier was brought rapidly from the far end of the trough to within 3 cms. of the float was observed. When spreading proteins this was usually of the order of 1-3 dynes/cm., and was not diminished much below 1 dyne by further sweeping. After a number of experiments had been performed on the trough, this value tended to increase. After many unsuccessful attempts to secure greater cleanliness, it was decided when using proteins to fix the amount of dirt at about 2·5 dynes at 3 cms. and apply a correction (discussed later). When the surface pressure due to dirt (protein not removed from the surface by sweeping) could not be easily brought below and kept below 3 dynes for a length of time corresponding to the duration of an experiment (2-3 minutes) the apparatus was dismantled and cleaned. With substances other than proteins dirt was not allowed to exceed 1·5 dynes per centimetre at 3 cms.

Having obtained a clean interface, the zero position of the float was noted, film-forming substance introduced into the interface and allowed to spread and the pressures developed when the barrier was brought to various positions observed in the usual way.

The brombenzene was purified after each series of experiments by separating it from the aqueous phase, allowing it to stand in contact with solid $Ba(OH)_2$ overnight, and redistilling in vacuo in an all-glass apparatus.

The glass and silica parts of the apparatus were cleaned by water and grease-free alcohol, the brass parts by rubbing with emery powder on cotton wool. Emery paper had to be avoided, since the glue used to fix the emery to the paper forms excellent films at the oil-water interface.

Ovalbumin was prepared by the method of Larosa.[4] Several different preparations were used, all of which were recrystallised four or five times.

Clark and Lubs' buffers were used except over the *p*H range 1-3, where dilute HCl solutions were used. NaCl was added to the HCl solutions to bring the total cation normality to the same value as for the buffers (0·1 N in cation).

Results.

The spreading of ovalbumin was found to be very rapid and complete, when comparison was made with the air-water interface. The protein molecules were completely unfolded to large areas per molecule within a few seconds of ejection from the spreading pipette ; at the air-water interface as much as 24 hours may be needed for spreading to an area comparable with that reached in a few seconds at the oil-water interface.

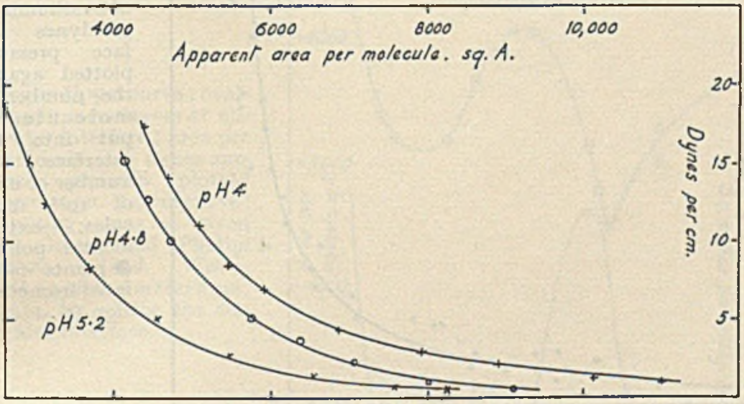

FIG. 2.—Area per molecule of ovalbumin plotted against surface pressure.

Fig. 2 shows several curves of surface pressure plotted against area per molecule (assuming a molecular weight of 35,000). Between 3×10^{14} and 5×10^{14} molecules were placed on the surface. The areas per molecule are much larger than those found at the air-water interface, and the films at low surface pressures appear to be gaseous or semi-gaseous in type. It was usually not possible to compress the films to above 15 dynes pressure without considerable collapse occurring, but between *p*H 4·8 and 5·8 the films were comparatively stable, and in two experiments pressures of 39 dynes were withstood, collapse being quite slow. In addition to the tendency to collapse at high pressures, below 12-15 dynes pressure there is no linear portion of the curve, such as Gorter and his colleagues have found at the air-water interface. It was therefore not possible to obtain reliable measurements of the limiting area of the close-packed film at zero compression.

Relatively accurate measurements of the area per molecule could be made at a standard pressure of 3 dynes/cm. With such measurements it was found that, provided the same total number of protein molecules was put on the surface, the observed area was independent of the concentration of the protein solution from which they were spread ; solutions containing

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[4] A. Larosa, *Chemical Analyst*, 1927, 16, 216.

0·0625 % or 0·000625 % protein gave the same area per molecule.* There was also no significant change in area with time over a period of 40 minutes from spreading the film. But when different total amounts of protein were spread, the area at 3 dynes was the greater the smaller the amount of protein put on. This is shown by Fig. 3, the crosses on which give values for ovalbumin at *p*H 5·2. It will be seen that very large areas were obtained if very small amounts of protein were spread. This was probably caused by dirt on the surface (which was kept at a constant amount). And if large amounts of protein were used, so as to swamp the effect of the dirt, very small areas were found, due to incomplete spreading. To make a correction for incomplete spreading does not appear to be possible, but a correction can be applied for the dirt on the surface if it is kept constant irrespective of the amount of protein spread. Let n be the number of units of 10^{14} molecules which were brought into the interface. Then the observed area A at 3 dynes pressure is given by

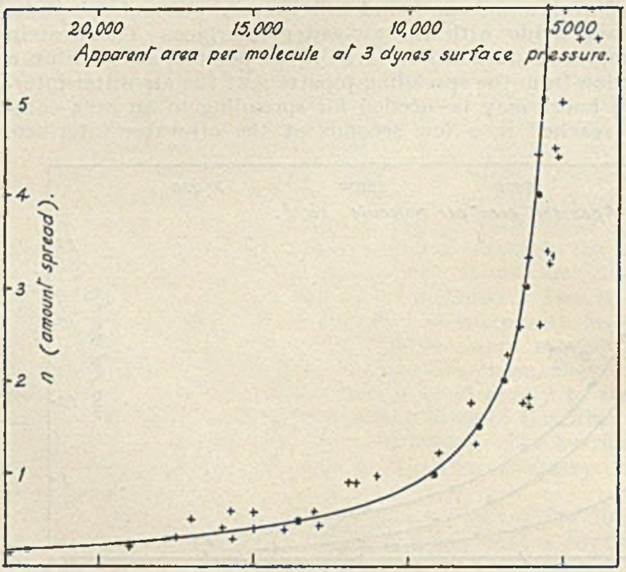

Fig. 3.—Apparent area per molecule at *p*H 5·2 of ovalbumin at 3 dynes surface pressure, plotted against the number of molecules (n) put into the interface. n = number of units of 10^{14} molecules; +, experimental points; ● points calculated from equation (1).

$$A = A' + \frac{A''}{n}, \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (1)$$

where A' is the true area per molecule, and A'' is the area occupied by the dirt, which is approximately constant. When n is very large $A' = A$, so that A tends to the asymptote A'. Thus if A is plotted against n, the resulting curve should have an asymptote which is the true area per molecule. The circles and curve of Fig. 3 represent such a curve fitted to the data for ovalbumin at *p*H 5·2. The curve is $A = 4800 + 4400/n$, *i.e.* the area per molecule at 3 dynes pressure at *p*H 5·2 is $4800\ \text{A}^2$. The curve fits the points reasonably well up to $n = 5$, and then deviates increasingly as n increases. The deviation from the curve for larger values of n may reasonably be ascribed to incomplete spreading. For values of n much greater than 10, incomplete spreading can be detected by the rapid fouling of the surface after cleaning off the spread film. On Fig. 4 are shown values of the areas at 3 dynes surface pressure at various *p*H: the areas we obtained from the experimental results by using equation (1). These

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* Analogous results were obtained by Mitchell at the air-water interface, *Trans. Faraday Soc.*, 1937, 33, 1129.

areas are liable to an error of ± 500 A^2 on the acid side of *p*H 5·2. On the alkaline side of *p*H 5·2 the error may be larger, as the results were more erratic. The variations in area per molecule observed with *p*H variation may quite well be due to incomplete spreading, for we have no proof that the whole of the material intended to spread did, in fact, do so. We are, however, confident that all the molecules which remained in the surface did in fact unroll—it seems quite improbable that most of the molecules would unroll in a few seconds or less, and others take much more than 40 minutes to unroll. The areas given in Fig. 4 must, therefore, be regarded as the minimum possible areas for completely unrolled protein. The variation of the apparent area with *p*H may be complicated by incomplete spreading and must be regarded with suspicion.*

The ovalbumin films were usually liquid at 1 dyne surface pressure, and were markedly elastic at 3-5 dynes.

Type II and Type III pneumococcus antibody globulins (presented by Professor J. R. Marrack) spread excellently, and were markedly elastic at pressures as low as 1-3 dynes. Sturin (presented by Dr. J. Northrop) did not spread; this is not due to lack of surface activity, for the surface tension of a brombenzene interface in contact with a solution containing 0·025 % sturin is reduced to a value of about 20 dynes or less. Evidently sturin is too soluble, or unfolds too slowly, to form a stable monolayer.

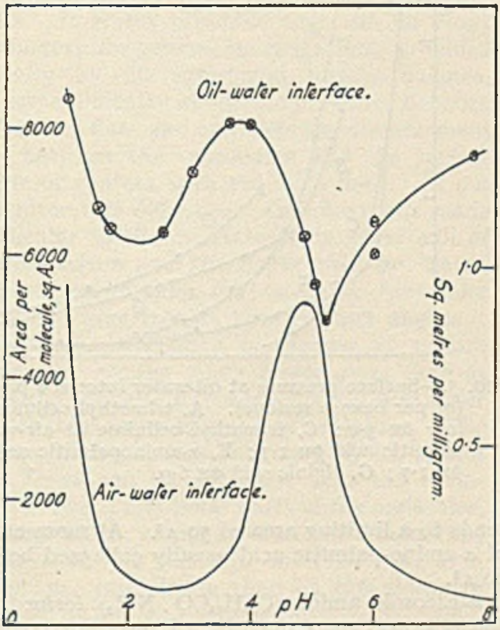

Fig. 4.—Upper curve: ovalbumin monolayers at oil-water interface; area per molecule at 3 dynes surface pressure plotted against *p*H. Lower curve: limiting areas as given by Gorter and Phillipi (*Proc. Akad. Wetenschappen Amsterdam*, 1934, **37**, 3) for the air-water interface.

An attempt was also made to spread ovalbumin films on brombenzene containing sufficient lecithin to reduce the i.t. to about 7 dynes; this was a failure, as it was quite impossible to stop leakage past the barriers.

Non-Protein Substances. Curves for a number of other substances are shown on Fig. 5. All of these substances were kindly provided by Dr. N. K. Adam, with the exception of alginic acid, given by Dr. W. Rose.

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* Langmuir (*Cold Spring Harbour Symposium*, 1938, **6**, 172) and Dervichian (*Nature*, December, 1939, 629) have suggested mechanisms whereby area-*p*H curves of the form obtained by Gorter. These explanations cannot apply to the different form of curve obtained at the oil-water interface. The latter, if not an artifact, may be due to swelling, analogous to that of blocks of gelatin.

Trimethyl cellulose (curves A and B) formed fairly stable films, having a considerably greater area per hexose residue than is found at the air-water interface. The surface pressure curve at the air-water interface (curve C) is given for comparison.[5] Curves D and E are for α-amino-palmitic acid at *p*H 1·7 and 3·6 respectively. The acid was dissolved in warm glacial acetic acid. At large areas per molecule the films are gaseous. In the region of *p*H 4 the film may be compressed to over 30 dynes pressure, and is solid above 6-8 dynes. The surface pressure curve of the solid film tends to a limiting area of 50 A^2. At more acid or more alkaline *p*H films of α-amino-palmitic acid usually collapsed before reaching areas less than 80 A^2.

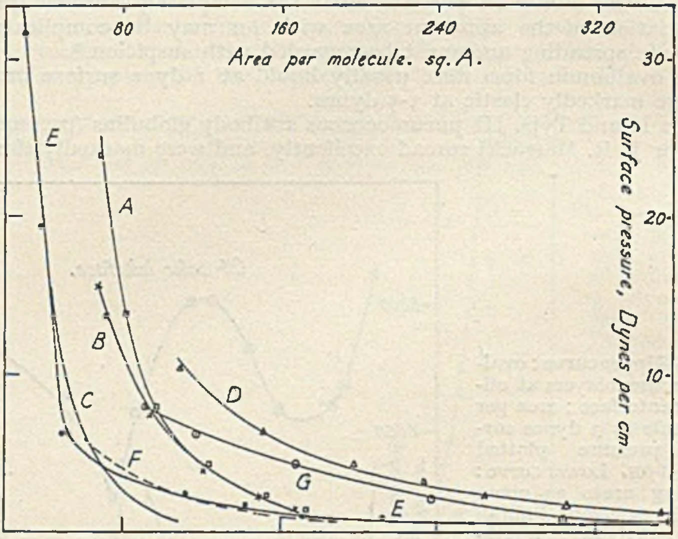

FIG. 5.—Surface pressure at oil-water interface plotted against area per molecule (or per hexose residue). A, trimethyl cellulose *p*H 1·7 ; B, trimethyl cellulose *p*H 3·0 ; C, trimethyl cellulose at air-water interface [5] ; D, α-amino-palmitic acid *p*H 1·7 ; E, α-aminopalmitic acid *p*H 3·5 ; F, *n*-eicosoic amide *p*H 1·7 ; G, alginic acid *p*H 6·9.

n-Eicosoic amide ($C_{19}H_{39}CO \, . \, NH_2$) formed moderately stable films of the gaseous type (curve F). It was not possible to compress these films above 10 dynes/cm. The area per molecule is again much larger than that at the air-water interface.

Alginic acid formed a film which was possibly gaseous, occupying very large areas per hexose residue (curve G).

Discussion.

The method described above is too time-consuming to be of general use. The great defects of the method are that fouling of the interface usually increases much more rapidly with time than at the air-water interface and the barriers frequently develop leaks. It is, however, an essential check on other methods of investigation. The pressure measurements are true surface pressure measurements and measurements may be made at different areas per molecule on the same film. This latter

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[5] N. K. Adam, *Trans. Faraday Soc.*, 1933, 29, 93.

point is an essential one, for, as we have found here, the fraction of the material applied to the interface which has actually spread depends upon the total amount put on the surface. At surface pressures of 5-10 dynes the amount of spreading may be a small fraction of the total amount applied. It is, therefore, impossible to obtain reliable compressibility curves by spreading different amounts of substance and measuring the surface tension with each amount, since with the larger amounts of substance, a considerable part often will not spread. Measurements made without compressing the same film to different areas cannot be regarded as accurate unless checked by compression experiments; and even here, in our experiments, the difficulty of removing dirt from the interface reduces the accuracy to about ± 10 % of the area per molecule at a given surface pressure.

In a recent interesting paper Alexander and Teorell [6] have compared the interfacial surface balance with the du Nouy interfacial tensimeter, with most encouraging results. It seems probable that the du Nouy instrument will be quite satisfactory for general investigations, provided that it is checked occasionally by the interfacial surface balance. Alexander and Teorell found some difficulty at surface pressures between 15 and 20 dynes. They used a mica float and attribute the disagreement they found over this region between the tensimeter and the surface balance to the change in angle of contact with the mica float. In our experiments we did not encounter this difficulty. Our float was made of a paper strip held perpendicular to the interface: the lower half of this strip was wetted by brombenzene and the upper half by water. This arrangement, though more fragile than that used by Alexander and Teorell, is much less likely to give trouble with contact angles.

It will have been observed that the fatty substances at surface pressures of less than 10 dynes/cm. occupy much larger areas than at the air-water interface. The same conclusion was reached by Alexander and Teorell for lecithin, lysolecithin and sodium cetyl sulphate. The same is true of the protein films, both of ovalbumin used by us, and of serum albumin and gliadin. There can be no doubt that the brombenzene breaks down adhesions between non-polar parts of the molecules, literally dissolving the CH_2 chains which, at the air-water interface, tend to hold adjacent molecules together. It was also observed that at a given pressure ovalbumin films are less elastic than at the air-water interface.

It was noteworthy that ovalbumin unfolds much more rapidly at the oil-water than at the air-water interface. It has been pointed out [2] that the hydrocarbon residues of the polypeptide chains will tend to be grouped together in globular proteins, stabilising the globular structure. At the air-water interface this stabilising action will not be completely broken down, but at an oil-water interface all hydrocarbon adhesions will be " dissolved " and it is possible that the more rapid spreading at an oil-water interface is to be attributed to oil " dissolving " these stabilising hydrocarbon-hydrocarbon adhesions.

We are greatly indebted to Dr. N. K. Adam for advice and the loan of apparatus, and one of us (F. A. A.) to the Medical Research Council for a maintenance grant; the other (J. F. D.) to the Department of Scientific and Industrial Research for a Senior Research award.

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[6] A. E. Alexander and T. Teorell, *Trans. Faraday Soc.*, 1939, **35**, 727.

Summary.

The surface balance has been adapted for use at the interface between aqueous solutions and brombenzene. Surface pressure measurements have been made on ovalbumin, alginic acid, trimethyl cellulose, α-amino-palmitic acid and *n*-eicosoic amide.

Substances occupy larger areas per molecule than would be expected at the air-water interface; this is attributable to the brombenzene breaking down the adhesions between the non-polar portions of adjacent molecules. Ovalbumin spreads more rapidly, more completely, and to larger areas than at the air-water interface.

The effect of *p*H on ovalbumin films has been studied between *p*H 1 and 7.

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University College, London.

REVIEW OF BOOK.

A New Dictionary of Chemistry. Edited by Stephen Miall. (Longmans Green & Co. Ltd.; London. Pp. xv + 575. Price 42s. net.)

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The Dictionary meets a real need; before it had been a day on the reviewer's desk a would-be borrower became a buyer! It is excellently printed and strongly bound.

Transactions of the Faraday Society

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