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THE VISCOSITY OF SUSPENSIONS IN NON-AQUEOUS LIQUIDS.

By E. W. J. Mardles.

Received 14*th March*, *Revised* 12*th July*, 1940.

In this investigation the viscosity of suspensions over a wide range of concentration of (*a*) a finely powdered solid in several organic liquids, and (*b*) different solids in one liquid, has been determined, avoiding low rates of shear. In this way it has been found, and some results are recorded in this paper, that the ratio η/η_0, where η is the viscosity of the suspension and η_0 the viscosity of the dispersion medium, for one solid at any particular concentration in different liquids, varies considerably with the viscosity of the medium, being higher for the more viscous liquids. When the kind of the dispersed solid was varied and the dispersion medium kept the same considerable differences in the viscosity behaviour were observed, the ratio being low, for example, with graphite and high for silica, zinc oxide or carbon black.

The conditions of experiment were chosen under which low rates of shear were avoided and the " shearing strength " of the systems small in comparison with the acting force.

Capillaries of bore less than 0·1 cm. were usually avoided because of the tendency with some of the suspensions to give high flow readings if not actual chokage, due to bridging of the tube by aggregates and clots. One of the characteristic features of thixotropic systems is the relationship which exists between their apparent setting time and the cross-section of the vessel in which they are contained, being very rapid in small tubes because of the smaller degree of structure required.[1]

For the sake of simplicity, the term " viscosity " has been used, although with suspensions of marked anomalous viscosity behaviour the term " consistency " is sometimes used.

Experimental.

The method used, unless otherwise stated, was by the use of a simple form of capillary tube plastometer in which up to 25 ml. of the suspension were forced by pressure through a capillary from 0·5 mm. in diameter and up to 10 cm. in length.[2]

The rate of flow of the suspensions was kept about the same by using suitable pressures ; with a tube of 5 cm. length and diameter bore of 0·165 cm., for example, rates of flow less than 0·3 ml./second were avoided because, as shown in Fig. 1A, the apparent viscosity of several suspensions at lower rates of flow is high. With increase in the rate of shear the apparent viscosity falls to a minimum. The viscosity values for the different

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[1] J. Pryce Jones, *J. Oil Colr. Chem. Assn.*, 1934, 17, 305.

[2] E. Mardles, *ibid.*, 1935, 18, 26.

suspensions were obtained in this region of minimum viscosity; unnecessarily high rates of shear were avoided. Eirich, Margaretha and Bunzl[3] have shown with glass rod suspensions that with increasing rates of shear the viscosity goes through a minimum.

In Fig. 1B are shown some viscosity results obtained with suspensions of kaolin of different concentrations in linseed oil at different rates of shear, and it will be seen that at the three higher rates the values fall on the same curve, whilst at the low rate the viscosity coefficient is nearly doubled. Summaries of investigations on the complex viscosity behaviour of suspensions are given in the literature.[4, 5, 6, 7]

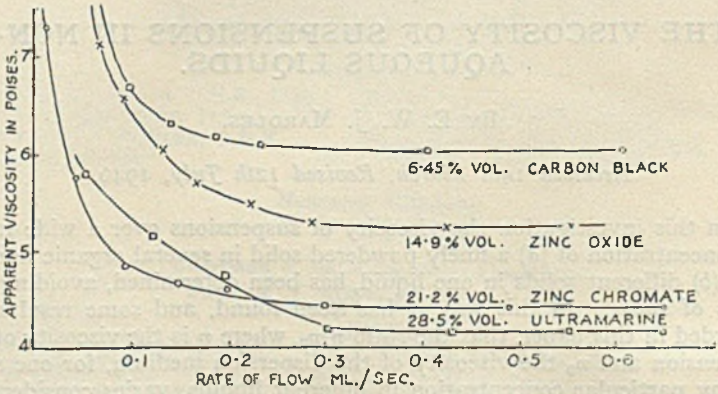

FIG. 1A.—Apparent viscosity at different rates of shear of suspensions in linseed oil, using a tube of bone (diameter) 0·165 cm. and length 5 cm.

In Fig. 1C are shown results obtained with different sized capillaries using the same pressure, and it will be seen that with capillaries below 0·1 cm. diameter bore unreliable results were obtained when the concentration increased to a certain point due to a bridgework structure of solid particles.

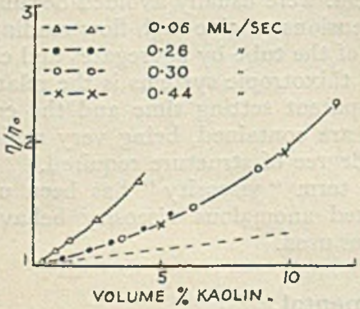

FIG. 1B.—Viscosity coefficients at different rates of flow for kaolin in linseed oil; chain line — $\eta = \eta_0 (1 + 2{\cdot}5\ V)$, Einstein.

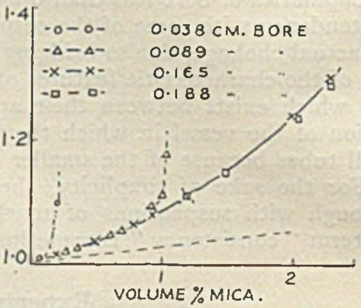

FIG. 1C.—Viscosity coefficients with different diameter capillaries for mica in alcohol.

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[3] F. Eirich, H. Margaretha and M. Bunzl, *Koll. Z.*, 1936, **75**, 20.

[4] E. Hatschek, 1st *Report on Colloid Chemistry, D.S.I.R.*, 1917, 2.

[5] E. Hatschek, *Viscosity of Liquids*, Messrs. Bell & Sons, London, 1928.

[6] G. Scott Blair, *Introduction to Industrial Rheology*, J. & L. Churchill Ltd., London, 1938.

[7] Wo. Ostwald, *Koll. Z.*, 1929, **47**, 176.

It was found advisable, especially with the use of narrow bore tubing, in measuring the flow of suspensions to make frequent check readings with the dispersion medium as occasionally deposits on the walls of the tube are liable to collect and alter the time of flow slightly.

The procedure of obtaining viscosity data was to use several capillaries at different pressures. In this way the minimum values were obtained and accepted when repeatable, using different capillaries.

Considerable differences were observed in the viscosity behaviour of the suspensions; thus, for example, as shown in Fig. 1A, for linseed oil suspensions, carbon black of concentration 6·45 vol. % gave a minimum viscosity of more than 6 poises, while with 28·5 vol. % ultramarine it was 4·2. Similarly, it will be seen from Figs. 1B and 1C that the viscosity values obtained with kaolin in linseed oil at a concentration of 1 or 2 % volume are a little less than twice the Einstein theoretical values, while with mica in ethyl alcohol they are about three times as great.

The suspensions were made by grinding the powders in a ball mill with the liquid to form a thin paste and the concentration was varied by dilution. With graphite, aluminium powder, mica, etc., where grinding was unnecessary the powders were dispersed by using a pestle and mortar. The flow measurements were usually made on the freshly prepared suspensions: values obtained after ageing usually showed some change within ± 10 %.

Unless otherwise stated, the viscosity measurements were made at 20° C.

Lower Concentrations.

Investigations have been carried out on the flow of suspensions and colloidal solutions at low concentrations from the standpoint of the Einstein equation $\eta = \eta_0 (1 + 2{\cdot}5V)$, where V is the volume in parts of a c.c. of the dispersed solid in the form of spheres.[8] The equation was deduced strictly from fundamental equations of hydrodynamics, and assumes that the spheres do not influence one another, and so is true only for low concentrations. It has been recorded that at low concentrations fair agreement has been obtained with dispersions of glass spheres, gamboge and sulphur,[9, 5] yet a higher concentration function than that indicated by the Einstein equation is often obtained; thus, for example, Duclaux and Sachs,[10] working with carborundum of particle size 0·2 to 0·3 μ, found a mean value of 19·2 instead of 2·5 of the Einstein equation, and with lamellar grains of lead iodide a value of 4·6 to 5·9. Sachs,[11] found a value of 35 for the coefficient with a gold hydrosol of concentration 2·5 to 14·6 grams per litre.

In Fig. 2 are given data at low concentrations for (*a*) kaolin in a light mineral oil, (*b*) kaolin in benzyl alcohol, (*c*) kaolin in toluene, and (*d*) graphite in a mixture of equal volumes of hexane and oleic acid. The viscosity ratios found with the suspensions of kaolin in mineral oil and toluene were relatively high, and with kaolin in benzyl alcohol intermediately so, compared with those for the graphite suspension.

It will be seen that the readings appear to fall on a straight line at low concentrations, but assume a decided curvilinear form above 1 % volume concentration when the mutual interference of the particles increases progressively.

The slope of the line for kaolin in toluene at low concentrations is

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[8] H. Mark and R. Simha, *Nature*, 1940, **145**, 571.

[9] F. Eirich, M. Bunzl, and H. Margaretha, *Koll. Z.*, 1936, **74**, 275.

[10] J. Duclaux and D. Sachs, *J. chim. physique*, 1931, **28**, 511.

[11] D. Sachs, *ibid.*, 1932, **29**, 280.

approximately four times that for the Einstein equation, and the value 10 instead of 2·5 was about the highest value obtained in this investigation.

These divergencies at low concentration from values in accord with the theoretical equation of Einstein are of considerable interest in that they are some sort of measure of the disturbance of laminar flow by the precessional motion of the dispersed particles,[12, 13] Eirich and co-workers have shown that with increasing rate of shear minimum apparent viscosity occurred when rod-shaped particles were lying along the stream lines. Lawrence[12] has pointed out in general with suspensions of rigid aniso-dimensional particles that the increase in rate of shear increases orientation, thereby decreasing the number at any moment lying across the velocity gradient and therefore the apparent viscosity. In a suspension flowing through a tube orientation occurs only in an annular region whose thickness increases with rate of flow but never reaches that of the radius of the tube.

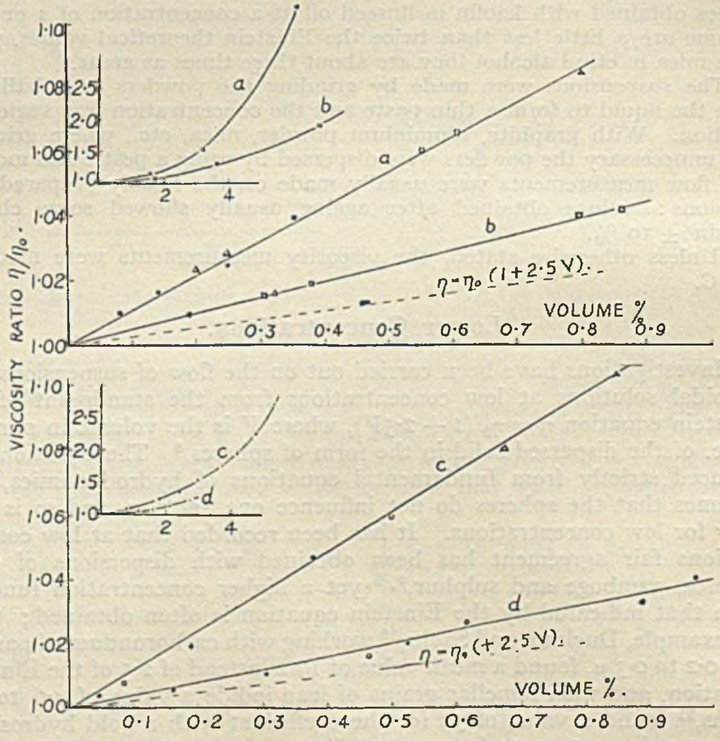

FIG. 2.—Viscosity ratios at low concentrations (inset—higher concentrations) for
(*a*) Kaolin in light mineral oil,
(*b*) Kaolin in benzyl alcohol,
(*c*) Kaolin in toluene,
(*d*) Graphite in hexane (1 vol.), oleic acid (1 vol.).

With non-rigid particles and clots which can be stretched by flow there can be a very large elastic recoil. Goodeve,[14] has discussed at

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[12] A. S. C. Lawrence, *Proc. Roy. Soc.*, *A*, 1937, 163, 324.
[13] J. R. Robinson, *ibid.*, 1939, 170, 519.
[14] C. F. Goodeve, *Trans. Faraday Soc.*, 1939, 35, 342.

some length this phenomenon, first described by Lawrence, and has pointed out that when a system is sheared the links in a clot of aggregated particles stretch, and when broken give rise to a series of impulses transferring momentum from a moving layer to a neighbouring layer.

High viscosities at higher concentrations were always obtained with suspensions well known for exhibiting thixotropy such as, for example, with zinc oxide dispersed in toluene, yet it was found that at lower concentrations, below 1 % volume, with these thixotropic suspensions the viscosity was not unusually high and was practically a linear function of concentration. It would appear that the structural viscosity effect does not become predominant until a volume concentration between 1 and 2 % is reached : some light is thrown on the problem by a study of the differences found in the viscosity and settling behaviour with (*a*) a highly thixotropic suspension of zinc oxide in toluene, and (*b*) zinc oxide dispersed in a mixture of equal volumes toluene and linseed oil, the latter system remaining fluid at high concentrations.

In Fig. 3 the viscosity ratios for concentrations up to 4 % volume are given : with the thixotropic toluene suspension the values obtained up to 1 % volume concentration fall on a line with a slope two and a half times that of the Einstein equation. Divergencies from the linear relationship began at about 1 % volume, and became marked when about 2 % volume was reached.

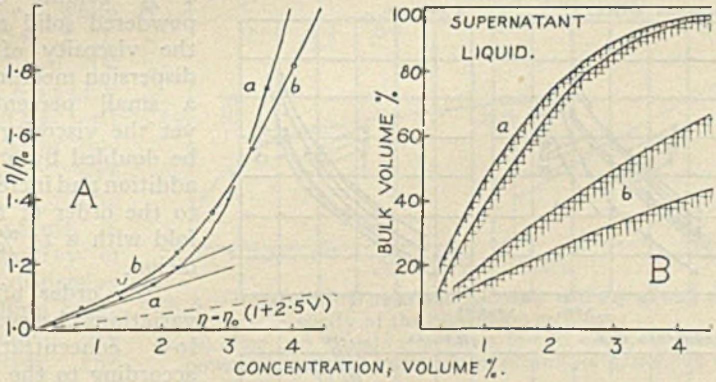


FIG. 3.—Viscosity and settling at different concentrations of (*a*) thixotropic suspension of zinc oxide in toluene and (*b*) zinc oxide in equal volumes of toluene and linseed oil.

3A.—Viscosity.

3B.—Settling after 2 and 24 hours showing boundary of supernatant liquid.

With the second suspension exhibiting no obvious thixotropy, the curve obtained was flatter and divergencies from a straight line of slope three and a half times that of the Einstein equation began at a slightly higher concentration, namely about 1½ % instead of 1 %.

The rate of settling of thixotropic suspensions is small because of the structure, and with concentrations above 2 % volume the rate of settling of the thixotropic zinc oxide suspension in tubes of diameter 1·2 cm. is very small, as shown in Fig. 3B, but is relatively rapid at concentrations below 2 % and in the toluene-linseed oil medium.

Lawrence,[12] in his study of the precessional movement of a suspended aniso-dimensional particle, uses the suggestion of Staudinger that the particle when rotating occupies an effective volume much larger than itself and equal to $\pi(l/2)^2b$, where l is their length and b breadth, and points out that the mean space occupied by an oscillating particle is a double cone, the solid angle of which increases with orientation until it approaches 180°.

If the total effective volume of all the particles is equal to the volume of the solution, then any further addition will cause particle interference and the viscosity-concentration curve becomes steep as found with higher concentrations. It would appear from the data shown in Fig. 3A that particle interference and the mutual interference between the fields of flow associated with neighbouring particles begin at a concentration as low as 2 %, for it will be seen that with the non-thixotropic suspension the curve relating viscosity and concentration begins to become steep at this point.

Higher Concentrations.

The viscosity divergencies observed at low concentrations became increasingly exaggerated with rise of concentration; the addition of 1 % volume of a powdered solid raises the viscosity of the dispersion medium by a small percentage, yet the viscosity can be doubled by a 5 % addition and increased to the order of fifty-fold with a 15 % addition.

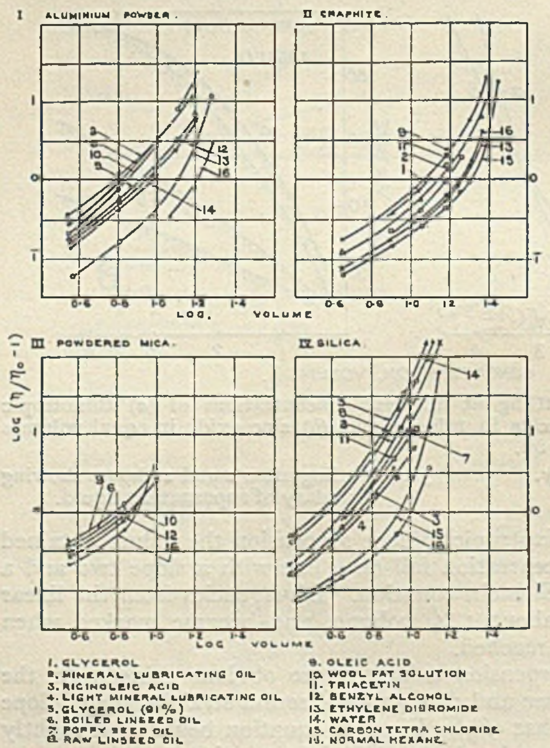


FIG. 4.—The viscosity of suspensions in different liquids; relationship between log $(\eta/\eta_0 - 1)$ and log percentage volume.

The order of the variations observed at low concentrations, according to the solid dispersed and the dispersion medium used, was usually found to be repeated at higher concentrations; thus kaolin in toluene which at low concentrations yields approximately four times the theoretical viscosity values becomes very viscous at concentrations above 7·5 % volume, while kaolin in benzyl alcohol which at low concentrations gives about twice the theoretical viscosity values becomes viscous not until a concentration well above 15 % volume was reached.

A measure of these divergencies at higher concentrations allows of a simple comparison of the flow behaviour of different solids in one dispersion medium or one solid dispersed in various liquids.

In Fig. 4 are given graphs relating log $(\eta/\eta_0 - 1)$ and log percentage volume for aluminium powder, graphite, mica and silica, at different concentrations in various liquids, and it will be seen at a glance by the position of the graphs that the lowest viscosity ratios have been obtained with each of the four solids dispersed in the liquid of lowest viscosity, normal hexane, and highest in the liquids of high viscosity, glycerol and lubricating oil, while intermediate viscosities were obtained with suspensions in liquids of intermediate viscosity such as benzyl alcohol or triacetin.

In Fig. 5 the relationship between the viscosity ratio and viscosity of the dispersion medium in poises is shown in some detail; Fig. 5 I shows the viscosity ratio for several solids in some dispersion media of different viscosity, while in Figs. 5 II, III, and IV viscosity ratios of solids in one liquid are shown, the variations in viscosity of the dispersion medium being obtained by altering the temperature, as shown, for example, in Table I for zinc oxide in linseed oil.

It will be seen that in general the sensitivity is large below a viscosity of 0·1 poises, while above 1 poise the effect becomes relatively small and of negligible value with viscous liquids.

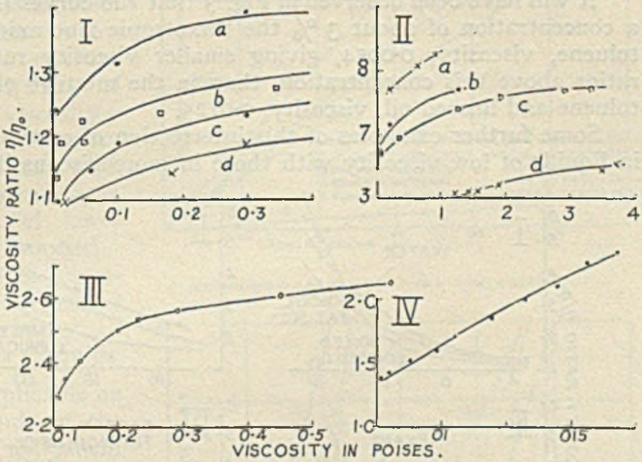


FIG. 5.—Relationship between viscosity ratio η/η_0 and the viscosity of the dispersion medium:

I. (*a*) Mica (3·6 % vol.); (*b*) silica (2·3 % vol.); (*c*) aluminium powder (3·6 % vol.) and (*d*) graphite (4·4 % vol.) in various liquids.

II. (*a*) Ultramarine (28·5 % vol.) in linseed oil; (*b*) kaolin (14·8 % vol.) in meta cresol; (*c*) silica (8·8 % vol.) in mineral lubricating oil; (*d*) graphite (16·7 % vol.) in mineral lubricating oil.

III. Zinc oxide (5·1 % vol.) in linseed oil.

IV. Zinc oxide (4·0 % vol.) in a mixture of equal volumes of toluene and linseed oil.

TABLE I.—VISCOSITY RATIOS FOR 5·1 % VOL. ZnO IN LINSEED OIL.

T (° C.) .	17·5°	25°	40°	50°	60°	70°	80°	93°
η . .	0·62	0·45	0·29	0·23	0·20	0·14	0·12	0·11
η/η_0 . .	2·66	2·61	2·56	2·54	2·50	2·41	2·35	2·29

There appear to be exceptions to the rule that the viscosity ratios are in order of the viscosity of the dispersion medium; thus, for example, silica dispersed in ricinoleic acid of viscosity at 20° C. of 9·75 gave lower ratios than in linseed oil of viscosity 0·52. It was thought that this might possibly be due in some way to the lubricating qualities of the ricinoleic acid, but it was found that the viscosity ratios of silica in a set of lubricating oils, including castor oil, of different "oiliness," taken under conditions of equal viscosity, were closely similar. The anomaly is to be traced to the polar character of the dispersion medium and the stabilisation of the suspension by adsorption of molecules of the dispersion medium by the solid particle.

Considerable help in explaining the phenomenon of the dependence of the viscosity ratio of a suspension on the viscosity of the dispersion medium is afforded by a study of viscosity ratios over a wide range of concentration and of the anomalous viscosity of the suspensions.

It will have been observed in Fig. 3 that the curves (*a*) and (*b*) cut at a concentration of about 3 % the thixotropic zinc oxide suspension in toluene, viscosity, 0·0054, giving smaller viscosity ratios and higher ratios above this concentration, than in the mixture of equal volumes toluene and linseed oil, viscosity, 0·0125.

Some further examples of this intersection of curves for suspensions in liquids of low viscosity with those in more viscous liquids are given

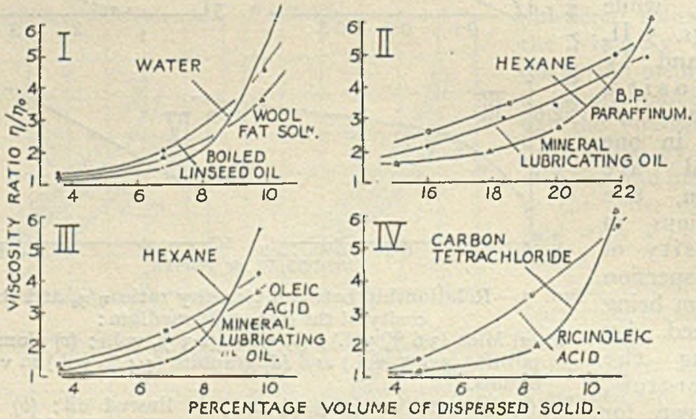


FIG. 6.—The viscosity ratios of I, aluminium powder; II, graphite; III, mica, and IV, silica in liquids of high and low viscosity.

in Fig. 6. It would appear that considerably less particle interference occurs in the viscous liquids at higher concentrations than in the thin liquids.

This is borne out by an examination of the anomalous viscosity behaviour of suspensions in viscous and low viscosity liquids respectively.

Anomalous Viscosity.

A convenient method of examining the anomalous viscosity of suspensions is by the use of the rotating cylinder viscometer, Stormer type, in which a cylinder is set in motion in a cup holding the suspension, by a weight acting over a pulley. It was found that anomalous viscosity occurred to a far greater extent with suspensions in liquids of low viscosity than in viscous liquids; thus, for example, a straight line relationship was obtained between the force acting and the rate of revolution for suspensions in glycerol or mineral lubricating oil, while in water or benzyl alcohol there was a decided curvilinear relationship and a decided rigidity. In liquids of intermediate viscosity flat curves were obtained which passed through or near the origin ; these differences are shown in Fig. 7.

It was found possible to prepare a set of curves showing a progressive change from the straight line passing through the origin to a curve with a "yield value," simply by decreasing the viscosity of the dispersion medium.

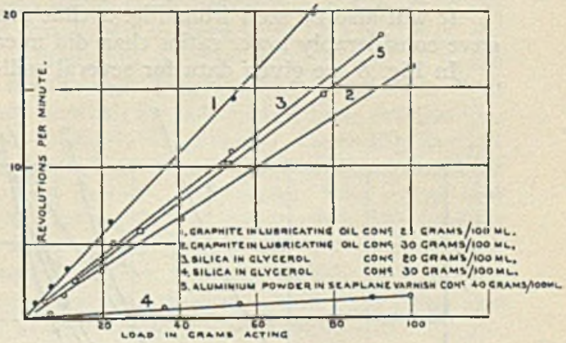
The three characteristic differences observed in the viscosity behaviour of suspensions in viscous and low viscosity liquids respectively, namely :

(*a*) smaller divergencies from the Einstein coefficient at low concentrations for liquids of lower viscosity ;
(*b*) higher viscosity ratios at high concentrations in liquids of lower viscosity ; and
(*c*) less marked anomalous viscosity behaviour in viscous liquids,

appear to be explicable on the same grounds of the more sluggish movement of the dispersed particles in the more viscous liquids.

At low concentrations, say below 1 %, the mutual interference of particles is small and the contribution to high viscosity is due to the turbulence caused by particles lying across the Newtonian layers of flow. If when flow begins the particles take up quickly positions of streamline flow, then the viscosity tends to a minimum, but if as in a viscous medium the time taken by the particle to rotate into a streamline position is comparable with the time taken to pass through the capillary tube, a higher viscosity results.

1. SUSPENSIONS IN VISCOUS LIQUIDS.



2 SUSPENSIONS IN LIQUIDS OF RELATIVELY LOW VISCOSITY.

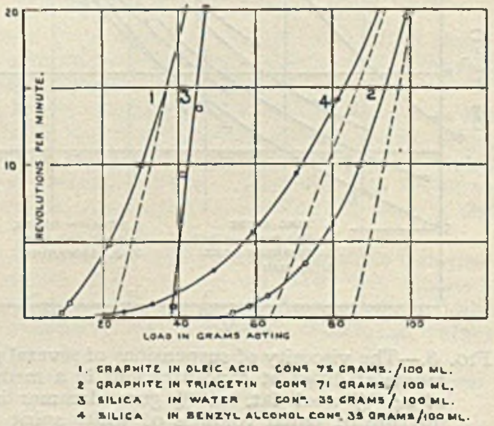


FIG. 7.—Viscosity results obtained with the rotating cylinder viscometer (Stormer type).

Osborne Reynolds found that with the more viscous liquids there was less tendency to form eddies during flow than with low viscosity liquids and a similar behaviour is found with suspensions in viscous liquids, only more so.

In viscous liquids, the movement of the dispersed particles being more sluggish, there is a consequent decrease in interference at higher concentrations ; this would account for the flatter curves obtained in viscous media relating the viscosity ratios and concentration and also for the less pronounced anomalous viscosity of suspensions in viscous liquids.

Viscosity Ratios with Different Solids.

It has already been shown in Fig. 1 that carbon black and zinc oxide suspensions in linseed oil gave considerably higher viscosity ratios than did ultramarine. Duclaux and Sachs[10] found a concentration coefficient of 19·2 for carborundum but 4·6 to 5·9 with lamellar grains of lead iodide.

It will also be seen from Fig. 4 that graphite in the various liquids gave considerably lower ratios than did mica or silica.

In Fig. 8 are given data for several well-known pigments in a resin-hardened wool fat varnish medium. Zinc oxide gave the highest and ultramarine the lowest viscosity ratios, and it will be seen that some of the curves are steeper than others and cut each other, indicating that at higher concentrations particle interference is greater with some solids. The same or similar order of viscosities was obtained with the pigments when other dispersion media were tried.

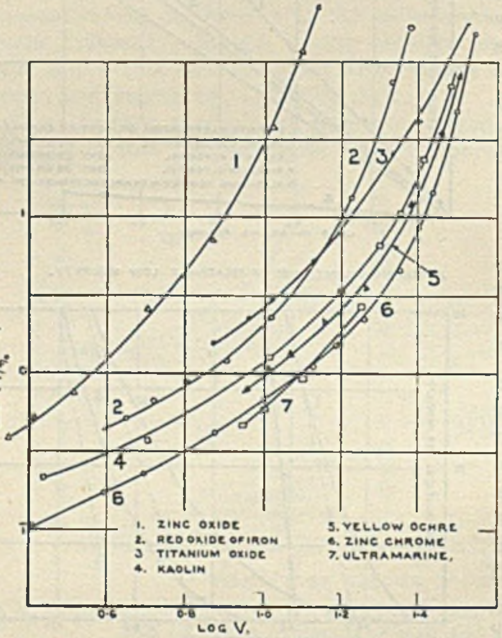


FIG. 8.—The viscosity of suspensions of several pigments at different concentrations in a medium of 24 % wool fat, 16 % gum dammar in a mixture of equal volumes of white spirit and solvent naphtha.

The wide variations in the viscosity ratios obtained with the different solids are of considerable interest in that since they are due to various degrees of aggregation and mutual particle interference and to differences in the amount of disturbance to the laminar flow by these particles turning over or rocking, it should be possible to obtain some idea of the general configuration of the dispersed particle when other means fail.

Viscosity ratios are highest with anisometric particles which tend to cluster by reason of aggregation and entanglement while, on the other hand, the ratios approach a minimum with spheres and lamellar grains, especially at low concentrations, when aggregation and interference become a minimum. Carbon black and zinc oxide, which at low concentrations gave high viscosities, appear from optical examination to consist mainly of anisometric particles, including threelings and burr or starlike particles and clusters. McDowell and Usher,[15] from a micro-

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[15] C. M. McDowell and J. Usher, *Proc. Roy. Soc.*, *A*, 1931, 131, 564.

scopic examination of carbon black dispersed in various organic liquids, concluded that the suspensions were highly aggregated, loosely packed arboriform masses with patches of clear liquid present. The mica suspensions which also give high viscosities showed streaks of silky lustre when shaken, a sign that the particles are decidedly anisometric.[16] Lamellar grains of lead iodide and graphite flakes which give low viscosity values assume relatively stable positions during flow by reason of their configuration, the longer axis coinciding with the direction of flow; their thin edges are less likely to disturb laminar flow than the edges of thick particles and less likely to turn over or rock than the thicker irregular particles. Aluminium powder in the form of flakes gave viscosity ratios much higher than graphite but a little less than silica or mica. When watched beneath the microscope their precessional motion was accompanied by considerable spinning, especially in thin liquids such as turpentine; in linseed oil of higher viscosity the rotational movement was considerably less marked. The flakes were rough and irregular, but for the most part moved singly, only occasionally could a small cluster of particles be seen. The flakes during flow did not seem to be orientated in any marked degree, but the smaller ends of the irregular particles pointed upstream for the most part, this being the position of greatest stability against rotation and rocking.

Summary.

Viscosity measurements have been made, avoiding low rates of shear, of suspension of kaolin, graphite and other solids, over a wide range of concentration, in several organic liquids. It has been found that :—

1. The ratio η/η_0, where η is the viscosity of the suspension and η_0 the viscosity of the dispersion medium, was found to vary with the latter value, being relatively high for viscous liquids such as glycerol, and low for liquids of low viscosity, such as normal hexane. The ratio was found to decrease with rising temperature and consequent fall in the viscosity of the dispersion medium.

2. Although with graphite in liquids of low viscosity the data obtained at low concentrations approached those in accord with the Einstein equation $\eta = \eta_0 (1 + 2{\cdot}5V)$, yet with kaolin in a light mineral oil or mica in alcohol, for example, approximately four times the theoretical values were obtained at low concentrations.

3. Anomalous viscosity was found to be less pronounced with suspensions in viscous liquids than in those of low viscosity.

4. With different solids in one dispersion medium large variations were found, the viscosity being low for graphite and high for silica.

Viscosities of suspensions, higher than the theoretical, appear to be due mainly to the disturbance of laminar flow by the precessional movement and the mutual interference of the dispersed particles, alone or in aggregates. Differences in viscosity behaviour of suspensions in viscous and thin liquids are ascribed to the more sluggish rotational movement of the particles in viscous liquids than in liquids of low viscosity.

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[16] H. Freundlich and F. Juliusburger, *Trans. Far. Soc.*, 1934, **30**, 333.

THE STRUCTURE OF COMPOUNDS CONTAINING S—O AND S—Cl BONDS PART I. INTRODUCTION AND DERIVATIVES OF THE $[SO_4]^{-2}$ AND $[S_2O_3]^{-2}$ RADICALS.

By Archibald Clow, Harry M. Kirton and James M. C. Thompson.

Received 11*th June*, 1940.

In a previous communication by the authors [1] it was not possible to discuss the structures of a large number of sulphur compounds, as the necessary theoretical data for the method used [2] were still lacking. These compounds were principally the oxy-acids of sulphur, the potassium salts of a number of which were examined by Farquharson in this laboratory,[3] and related compounds such as sulphoxides, sulphones, and halogen derivatives of sulphur. In order to extend the above method of interpretation to these compounds it is necessary to know the residual charges due to the unequal sharing of bond electrons for such links as S—O, S=O, S→O, S—Cl, etc., and the diamagnetic bond depressions Δ_{S-O} etc., for these links. For a full account of the method of calculating the diamagnetic susceptibilities of sulphur compounds as well as for the numerical data concerned, reference should be made to the previous communication of the authors on organic sulphur compounds [1] of which this is an extension to a wider field.

For ease of reference the interatomic distances in Ångstrom units determined in the classes of compounds to be discussed are given in Table I.

TABLE I.

Bond.	SO_3.[4]	$[SO_4]-2$.[5]	Me_2SO_2.[6, 7]	SCl_2.[4]	S_2Cl_2.[4]	$SOCl_2$.[4]	SO_2Cl_2.[4]
S—O .	1·43	1·50	1·43	—	—	1·45	1·43
S—Cl .	—	—	—	1·99	1·99	2·01	1·99
C—S . .	—	—	1·82	—	—	—	—

The S—O distances in these compounds are shorter than the sum of the normal double bond radii which is 1·52 A. This is surprising in view of the formulæ usually assigned to these compounds which do not imply double bonds. According to Palmer [4] such a contraction indicates that excited structures involving a degree of double and perhaps triple bonding must make a considerable contribution to the normal state of the molecule being more important in $SOCl_2$ and SO_2Cl_2 than in SO_2 and SO_3. These effects will be considered separately under each relevant

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[1] Clow and Thompson, *Trans. Faraday Soc.*, 1937, **33**, 894.

[2] Gray and Cruickshank, *ibid.*, 1935, **31**, 1491.

[3] Farquharson, *Phil. Mag.*, 1932, **14**, 1003.

[4] Palmer, *J.A.C.S.*, 1938, **60**, 2360.

[5] Pauling and Brockway, *ibid.*, 1937, **59**, 13 and 1223.

[6] Brockway and Jenkins, *ibid.*, 1936, **58**, 2056.

[7] Lister and Sutton, *Trans. Faraday Soc.*, 1939, **35**, 495.

compound. It is still doubtful if the length of any purely co-ordinate bond in a sulphur containing molecule is known, although dimethyl sulphone has been discussed as such by Lister and Sutton.[7]

A sufficient number of bond moments for the bonds involved have now been determined, and although their derivation depends on certain not entirely valid assumptions, they can be used for determining the residual charges necessary for calculating the diamagnetic susceptibilities of these compounds, provided they are of the right order. These bond moments are given in Table II.

TABLE II.

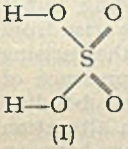
	Ph_2SO_2,[8] Ph_2SO.[8]	Me_2SO_2.[9]	SO_2Cl_2,[9] $SOCl_2$.[9]
S—O .	2·6	2·5	2·16
S—Cl .	—	—	0·61

The bond moments for SO_2Cl_2 and $SOCl_2$ depend on the assumption that these molecules are regular tetrahedra and that the bond moments of S—O and S—Cl are the same in $SOCl_2$ and SO_2Cl_2. These assumptions introduce an element of crudity into the derived results, but, as will be seen later, if the *order* of the bond moments is correct they are sufficiently accurate to yield usable diamagnetic susceptibilities.

Calculation of the Residual Charges in the S—O and S—Cl Bonds.

As the bond moment for S—O bonds is known to be between 2·2 D and 2·6 D, in the sequel the moment will be taken as 2·4 D. Similarly, the S—O interatomic distance for the greater number of the compounds investigated is 1·43 A. Two chlorine compounds give the S—Cl moment 0·61 D, and the S—Cl interatomic distance in several compounds lies between 1·99 and 2·01 A. Using these values, the residual charges for the S—O and S—Cl bonds are ± 0·352 and ± 0·063 respectively. The magnitude of the errors introduced by the use of these average values will be considered later.

It now remains to decide the nature of these bonds. Subsequently, it will become evident that the value of the diamagnetic bond depression determines whether or not the SO bonds in different compounds are of the same nature. Moreover, if it were assumed that H_2SO_4 had the structure (I), then, as may be seen from the calculation on page 1021, no matter how wide a range of probable residual charges be used, the resulting bond depressions for the S—O and S=O bonds are much smaller than would be expected by analogy with similar bonds. Thus the residual charge ± 0·35 cannot correspond to that upon a double bond, but if the above double bonds are replaced by co-ordinate bonds the whole range of compounds considered becomes interpretable. An alternative to co-ordinate bonds would be single bonds in resonance with bonds of a degree of multiplicity greater than two. As, however, an accurate estimate of the degree of such multiple bond formation is not possible magnetically, or by any other means, the bond on which the residual charge is ± 0·35 will be regarded as a co-ordinate bond with the oxygen atom at the negative end of the dipole. Thus we have $S\overset{+0\cdot352}{\text{——}}O^{-0\cdot352}$ for $S \rightarrow O$. Therefore the residual charge in an ordinary covalent bond would be $S\overset{-0\cdot648}{\text{——}}O^{+0\cdot648}$, and by analogy with other links the residual charge in the double bond would be $S\overset{-2}{=}O^{+2}$.



(I)

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[8] Hampson, Farmer and Sutton, *Proc. Roy. Soc., A*, 1933, 143, 147.

[9] Coop and Sutton, *Trans. Faraday Soc.*, 1939, 35, 505.

This residual charge is higher than any recorded value, but it must be borne in mind that even the residual charges in the covalent S—O bond exceed all those involving carbon atoms, the highest 0·61 being that for C≡N. This may result from sulphur not being subject to the octet rule as were all the atoms discussed by Gray and Cruickshank, and the success resulting from the utilisation of this residual charge in the sequel confirms the acceptability of this apparently unusually high value.

In $SOCl_2$ and SO_2Cl_2, the two compounds used to obtain the constants for the S—Cl bond, the S—Cl bond is almost indubitably a normal co-valency, although Varadachari [10] has suggested other structures which will be examined in detail later. In this bond the chlorine forms the negative end of the dipole.

TABLE III.

RESIDUAL CHARGES.

+ −		+ −	
H—C	0·04	S→O	0·35
H—S	0·13	O=S	2·0
C—S	0·15	S—Cl	0·064
O—S	0·65	—	—

It is important to determine the influence which alterations in the bond moment and interatomic distances have upon the foregoing residual charges and the consequent degree of uncertainty introduced in the atomic susceptibility constants.

The interatomic distance used for the S—O bond was 1·43 A, being the value observed by Palmer [4] in SO_3, $SOCl_2$ and SO_2Cl_2, and by other experiments in Me_2SO_2, the corresponding residual charge being $\mathrm{S}\overset{+0\cdot35}{\text{——}}\mathrm{O}^{-0\cdot35}$. Pauling and Brockway,[5] however, indicate that the interatomic distance in the sulphate ion is 1·5 A. This being so, the residual charge on the S and O atoms would be $\mathrm{S}\overset{+0\cdot335}{\text{——}}\mathrm{O}^{-0\cdot335}$, and to obtain the influence of this charge on the calculated susceptibility of a molecule, it must be converted into the corresponding molecular susceptibility constant (Table IV).

TABLE IV.

Bond Length.	Bond Moment.	Residual Charge.	Σ Susc. const. for S and O Atoms.
1·43 A	2·4 D	± 0·352	31·03
1·50 A	2·4 D	± 0·335	31·06

Thus an alteration in the length of the bond of the order of 5 % results in a variation in the atomic susceptibility constants of the atoms involved of about 0·1 % per S—O bond. Such small variations in the length of bonds have been widely interpreted by Pauling, Sutton, etc., as resulting from different types of bonding, but it is evident that such small changes in susceptibility constants as arise from different bonds lengths are of an altogether lesser order than that arising from the different depressions of diamagnetism due to the presence of bonds of different multiplicity. Even a small degree of double bonding will lower the molecular susceptibility constant more than an alteration in the bond lengths of an extent even greater than the variations between the bond lengths derived from different molecules, or the experimental errors involved.

A second possible source of error might arise from inaccuracies in the bond moments. In the determination of the above residual charges a mean of 2·4 D was taken for the moment of the S—O bond. The moment in sulphoxides and sulphones is, however, considerably higher, and that in $SOCl_2$ and SO_2Cl_2 correspondingly lower. Table V compares the upper value with the mean.

This variation in the final result is not greater than the experimental

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[10] Varadachari and Subramanam, *Proc. Ind. Acad. Sci.*, *A*, 1936, 3, 428.

error, indicating conclusively that, provided the interatomic distance and the bond moment are of the correct order, they can be relied upon to yield atomic susceptibility constants whose uncertainty will be less than the experimental error, thus permitting a discussion of the causes of deviations between molecular susceptibility constants and experimental susceptibilities. The same is true of the S—Cl bond; in both cases the variations are too small to explain any deviation of the experimental susceptibilities from those calculated for simple Lewis structures. Where deviations exist they must result from such causes as quantum mechanical resonance or a varying degree of multiple bonding.

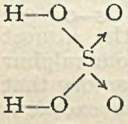
TABLE V.

Bond Length.	Bond Moment.	Residual Charge.	Σ Susc. consts. for S and O Atoms.
1·43	2·4	± 0·352	31·03
1·43	2·6	± 0·374	30·97

Derivation of the Bond Depressions.

(*a*) The S—O and S→O Bond Depressions.

Unlike the bond depressions which have been discussed previously, it is not possible to obtain a compound in which the only unknown factor is $\Delta_{\mathrm{S-O}}$. Several compounds are known, however, in which S—O and S→O bonds occur together, and following Gray and Cruickshank, if $\Delta_{\mathrm{S\to O}}$ is assumed to be about one-fifth of $\Delta_{\mathrm{S-O}}$, knowing the number of these bonds in the molecule and the total depression arising from them, it is possible to solve the equation for $\Delta_{\mathrm{S-O}}$, and hence also derive $\Delta_{\mathrm{S\to O}}$. Such compounds are H_2SO_4, Me_2SO_4 and Et_2SO_4. Consider H_2SO_4 first. It is probable that pure H_2SO_4 is represented by the structure (II), the two H—O bonds being covalencies. For this molecule the residual charges and Pauling atomic susceptibility constants are as in Table VI.



(II)

From this can be deducted $2\Delta_{\mathrm{H-O}} = 1·34$, which leaves 60·57 for the susceptibility of the molecule neglecting the bond depressions in the four sulphur-oxygen bonds. Subtraction of the experimental susceptibility of H_2SO_4 from this latter figure then leaves 21·57, which is equal to the sum of the unknown bond depressions, *i.e.* $2\Delta_{\mathrm{S-O}} + 2\Delta_{\mathrm{S\to O}}$ or $2·4\Delta_{\mathrm{S-O}}$, which gives for $\Delta_{\mathrm{S-O}}$ 8·96 and $\Delta_{\mathrm{S\to O}}$ 1·79. Pauling and Brockway[5] give 1·5 A as the interatomic distance for the S—O bonds of a sulphate, a distance less than either the sum of the single bond radii (1·70) or the double bond radii (1·53), but this difference is not sufficiently large to change appreciably the bond depressions derived above. Alternatively, H_2SO_4 might have been assumed to have the structure (I), 2·4 now being the

TABLE VI.

No. of Atoms.	Fractions of Time.	Corresponding Pauling Atomic Susceptibility Constants.
2 Hydrogen .	31 % in H^{+1} 69 % in H°	3·27
2 Oxygen .	34 % in O^{+1} 66 % in O°	13·96
2 Oxygen .	35 % in O^{-1} 65 % in O°	15·78
1 Sulphur .	60 % in S^{-1} 40 % in S°	28·90
		Total 61·91

moment of the S=O bond, while the interatomic distance and residual charge remain as before. The resulting molecular susceptibility constant, neglecting the depressions in the SO bonds, is 60·57, which now leaves, on subtracting the experimental susceptibility of H_2SO_4, 21·57 to represent $2\Delta_{S—O} + 2\Delta_{S=O}$, a figure whose smallness makes it extremely improbable that the above is the structure of H_2SO_4.

Similar bond depressions can be obtained from the experimental susceptibilities of Me_2SO_4 and Et_2SO_4 and these, together with the values from H_2SO_4, are shown in Table VII.

TABLE VII.

Substance.	Experimental Susceptibility.	Σ Pauling Constants $- \Sigma$ Known Δ_{x-y}.	$\Delta_{S—O}$.	$\Delta_{S\rightarrow O}$.
H_2SO_4 . .	39·00	60·57	8·96	1·79
Me_2SO_4 . .	62·20	83·51	8·88	1·78
Et_2SO_4 . .	86·90	107·35	8·53	1·70
			Mean 8·79	1·76

The agreement of the depressions derived from the three different substances is good, and justifies the assumption made earlier, that the H—O bond in pure H_2SO_4 is a covalency. The revised covalent radii which have been published by Pauling and Brockway [5] since the C—S bond depression was determined by the authors,[1] do not have an appreciable effect on the C—S bond depression used in the calculation of $\Delta_{S—O}$ from Me_2SO_4 and Et_2SO_4. These two bond depressions are of the utmost importance in the discussion of a wide range of compounds from sulphur oxy-acids to organic sulphoxides and sulphones, and it is satisfactory that the bond depressions derived from different compounds are in excellent agreement and are not dependent on the individual nature of the substances used for their determination.

(*b*) The Bond Depression for the S=O Bond.

According to Cross and Brockway,[11] SO_2 can be represented by the structure $O{=}S\rightarrow O$. Even if there is resonance between the single and double bond, taken over a sufficiently long period, the result will be equivalent to one co-ordinate covalency and one double bond. If this is correct, SO_2 can be used to give the depression for the S=O bond, that for the $S \rightarrow O$ bond already having been determined from H_2SO_4, etc.

The corresponding constants are given in Table VIII :—

TABLE VIII

Substance.	Σ Pauling Atomic Suscept. Consts.	Σ Known Δ_{x-y}.	Σ Pauling $- \Sigma$ Known Δ_{x-y}.	Expt. Suscept.	$\Delta_{S=O}$.
SO_2 . .	48·18	1·76	46·42	18·25	28·17

The value used subsequently will be $\Delta_{S=O} = 28{\cdot}0$.

(*c*) The Depression for the S—Cl Bond.

The experimental susceptibilities of S_2Cl_2 and SCl_2 have been measured. Reference to Table IX shows that two somewhat discrepant values for SCl_2 exist in the literature, and particular care was taken to obtain a

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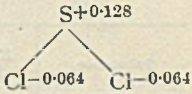
[11] Cross and Brockway, *J. Chem. Physics*, 1935, **3**, 821.

reliable value. The experimental susceptibility obtained is in excellent agreement with that given by Varadachari.[10] The existing susceptibility for S_2Cl_2 was confirmed. Both S_2Cl_2 and SCl_2 have been the subject of extensive investigations. It has been confirmed by Naik and Jadhov [11A] that SCl_2 is a definite chemical entity, and, further, its structure is given by Palmer [1] as the result of electron diffraction experiments. Thus its constitution being beyond doubt, it is a convenient substance to use in the derivation of $\Delta_{\mathrm{S—Cl}}$. The value of this depression will depend to a certain extent on the bond moment obtained by Coop and Sutton,[9] which in turn is derived on the assumption that SO_2Cl_2 and $SOCl_2$ are regular tetrahedra, and further that the S—O and S—Cl bond moments do not change on passing from compound to compound. This evaluation is, it must be admitted, not as accurate as might be desired, but at the same time the value for the S—O bond moment agrees with that deduced from independent measurements on dimethyl sulphone and dimethyl sulphide. This, to a certain extent, adds greater certainty to the bond moment for the S—Cl bond. From it, 0·61 D, and the S—Cl interatomic distances determined in SCl_2, S_2Cl_2, $SOCl_2$ and SO_2Cl_2, we get the residual charge $= \pm 0·064$ which gives the SCl_2 molecule the residual charges shown.



For this molecule Σ Pauling susceptibility constants = 70·13, and subtracting the experimental susceptibility 47·97, we obtain 22·16, representing the bond depression for two S—Cl bonds, *i.e.* $\Delta_{\mathrm{S—Cl}}$ is 11·08.

Had the constitution of S_2Cl_2 not been in doubt, it might have been used to give an independent determination of the S—Cl bond depression, the S—S bond depression being known. In the circumstances it is preferable to use the S—Cl bond depression just determined to discuss the various constitutions which have been suggested for S_2Cl_2.

Experimental.

The diamagnetic susceptibilities were measured at 18° C. with the modified Curie-Chéneveau magnetic balance.[23] The utmost care was taken

TABLE IX.

EXPERIMENTAL SUSCEPTIBILITIES.

Substance.	Experimental Susceptibility.				
	This Laboratory.		Pascal.	Kido.	Varadachari.
	Authors.	Farquharson.			
Sulphur dioxide	—	—	18·25	—	—
Sulphur trioxide	—	28·54	23·12	—	—
Hydrogen sulphate	—	39·00	—	—	—
Dimethyl sulphate	—	—	62·20	—	—
Diethyl sulphate	—	—	86·90	—	—
Potassium sulphate	—	65·00	—	—	—
Potassium ethyl sulphate	77·32	—	—	—	—
Sodium thiosulphate	—	—	—	58·23	—
Potassium thiosulphate	—	75·88	—	—	—
Sodium ethyl thiosulphate	78·77	—	—	—	—
Sulphur monochloride	62·32	—	—	62·23	—
Sulphur dichloride	47·97	—	—	49·4	48·09
Chlorsulphonic acid	—	—	—	46·60	—

[11A] Naik and Jadhov, *J. Ind. Chem. Soc.*, 1926, **3**, 260.

in the purification of the samples measured. Throughout the discussion the susceptibilities have been multiplied by -10^{+6}.

Discussion.

The Constitution of Sulphur Trioxide.

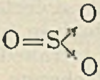
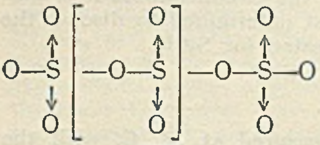
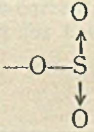
On the assumption that the constitution of SO_3 could be represented as  $O{=}S\overset{O}{\underset{O}{\lessdot}}$ or a resonance hybrid it could be used to determine the $S{=}O$ bond depression (Table X).

TABLE X.

Substance.	Σ Pauling Atomic Suscept. Consts.	Σ Known Δ_{x-y}.	Diff.	Expt. Susc.	$\Delta_{S=O}$.
SO_3 . .	53·56	3·52	50·04	23·12	26·82

This bond depression is in moderately good agreement with that obtained using the experimental susceptibility of SO_2. There are, however, two considerably different values for the experimental susceptibility of SO_3, that of Pascal used above and one determined by Farquharson (28·54). The probable explanation is that SO_3 has not the simple structure represented above. It is known to exist in three forms [12] and although neither Pascal nor Farquharson took special precautions to determine the susceptibility of any single form, it is probable that from his method of introducing it into the measuring tube of the Curie-Chéneveau magnetic balance, Farquharson measured the β-form. Existing data concerning the constitution of SO_3 have been reviewed by Hägg [13] who suggested that the β-form was made up of chains of SO_3 groups (III).


(III)

The chains of this modification will be constituted by a repetition of the unit within the brackets. The susceptibilty of the  $-O-\overset{\overset{O}{\uparrow}}{\underset{\underset{O}{\downarrow}}{S}}$ group can be calculated thus :

1 S with residual charge −0·6 giving Pauling constant = 28·90
1 O with residual charge +1·3 giving Pauling constant = 4·89
2 O with residual charge −0·35 giving Pauling constant = 15·68

∴ Σ Pauling atomic susceptibility constants = 49·47

If the bonds are as represented, from this has to be subtracted $2\Delta_{S\rightarrow O} + 2\Delta_{S-O}$ (*i.e.* 21·10), leaving 28·37 a calculated molecular susceptibility which is in complete agreement with Farquharson's experimental value (28·54).

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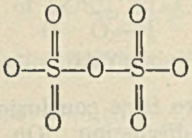
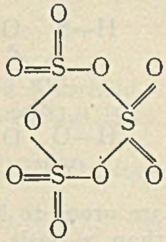
[12] Schultz and Sellack, *Bull. Soc. Chim.*, 1870, (2) 14, 154, and many subsequent papers.

[13] Hägg, *Z. physik. Chem.*, *B*, 1932, 18, 199.

As the result of Raman spectrum investigation, Gerding and Moerman [14] suggested for the β-form the same chain structure as Hägg but with doubly bound oxygen atoms (IV), and for the γ (ice-like) form the ring structure (V).

Despite the discrepancy between Pascal's and Farquharson's results, they both eliminate the possibility of such doubly bound structures, but it is probable that the structures postulated by Gerding and Moerman are valid if co-ordinate links between the S and O atoms are substituted for the double bonds. Magnetically it is impossible to distinguish between the above chain and ring structures as they are both built of the same unit component.


(IV)


(V)

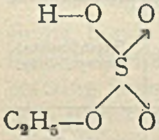
Derivatives of $[SO_4]^{-2}$.

These may be classified :—

(*a*) Metallic sulphates, etc., *e.g.*, H_2SO_4, K_2SO_4.
(*b*) Metal R sulphates, $M[RSO_4]$, *e.g.*, $KEtSO_4$.
(*c*) Di-R sulphates, *e.g.*, Me_2SO_4 and Et_2SO_4.

Several sulphates have already been employed in the development of the present theory. It remains to deal with inorganic sulphates and metal R sulphates. When the molecular susceptibility constant for H_2SO_4 was calculated the H—O bonds were assumed to be covalencies. The formation of K_2SO_4 is accompanied by two changes in the molecule, the substitution of two hydrogen atoms by two K atoms and an alteration in the nature of the bonds under discussion. The experimental susceptibility of H_2SO_4 is 39·00 and that of K_2SO_4 65·00, so that the increment of diamagnetism, 26·00, represents the change in susceptibility arising from the above substitution, or 13·00 per H—O to K—O bond. This increment will be used throughout for the calculation of the susceptibility of potassium salts. Its validity may be checked in the case of $KEtSO_4$.

Following the previous treatment $EtHSO_4$ will be as (VI), with a calculated molecular susceptibility constant of 62·85. This molecule, however, is not suitable for physical measurements, as according to Abdul Hamid [15] it is impossible to isolate the free acid in a state of purity. The potassium salt is quite stable and its calculated susceptibility, 75·85, is in reasonable agreement with that found experimentally, 77·32. Although the coincidence is not as close as that usually found, it does definitely preclude the possibility of the SO bonds being multiple bonds.


(VI)

Derivatives of $[S_2O_3]^{-2}$.

These may be classified as in the case of $[SO_4]^{-2}$ but no simple di-substituted organic derivatives are available.

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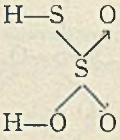
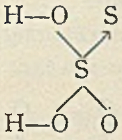
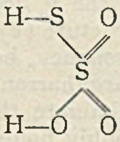
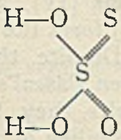
[14] Gerding and Moerman, *Z. physik. Chem.*, *B*, 1937, **35**, 216.
[15] Abdul Hamid, *J.C.S.*, 1926, 1098.

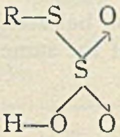
Both sulphates and thiosulphates can be formed from sulphites by the action of oxygen and sulphur respectively, and this has been used as an argument in favour of similar structures. Such analogies are prone to lead to false conclusions and should not be used as more than a basis for discussion. On this assumption several structures are possible for thiosulphates (VII, VIII), the former being in general more probable. Ray,[16] and Ray and Manlik,[17] from chemical evidence, are in favour of an electronic isomerism between (IX) and (X). As neither the free acid nor simple disubstituted organic derivatives are available recourse has to be made to the salts $M_2[S_2O_3]$ and $M[RS_2O_3]$. In the latter there will be two possible additional constitutions resulting from position isomerism of the R group, *i.e.*, from the first of the previous structures there will arise (XI) and (XII), etc.

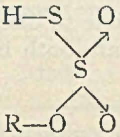

(VII)


(VIII)


(IX)


(X)


(XI)


(XII)

The experimental susceptibilities of $K_2S_2O_3$, $Na_2S_2O_3$ and $NaEtS_2O_3$ are known and enable one to make quite definite pronouncements about the constitution of thiosulphates. First consider the structures (VII) and (VIII). These, for the sodium and potassium salts, have the calculated susceptibility constants given in Table XI.

TABLE XI.

Salt.	Structure.		Experimental Susceptibility.
	(VII).	(VIII).	
$K_2S_2O_3$.	76·83	87·73	75·88
$Na_2S_2O_3$.	58·23	69·13	58·20

It is evident that structure (VIII) is ruled out, leaving (VII) as the constitution of the thiosulphates. The molecular susceptibility constant of the sodium salt was calculated by taking the difference —9·3 between the ionic susceptibilities of the K^+ ion = —18·5 and the Na^+ ion = —9·2 as given in the International Critical Tables. The results also seem to eliminate definitely Ray's idea of an electronic isomerism.

TABLE XII.

Salt.	Structure.		Experimental Susceptibility.
	(XI).	(XII).	
$NaEtS_2O_3$.	75·91	78·52	78·77

The salt $M[RS_2O_3]$ may be represented by (XI) or (XII); the calculated and experimental susceptibilities are as in Table XII.

There is not a large difference between the molecular susceptibility

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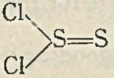
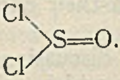
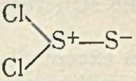
[16] Ray, *J. Ind. Chem. Soc.*, 1931, 8, 307; 1933, 10, 655.
[17] Ray and Manlik, *Z. anorg. Allgem. Chem.*, 1931, 199, 356.

constants of the two structures, but the experimental susceptibility gives an indisputable indication that (XII) is the constitution of sodium ethyl thiosulphate.

The Structure of Sulphur Monochloride.

The Raman spectrum has been studied by Matossi and Alderhold[18] who have also studied the spectra of $SOCl_2$, SO_2Cl_2 and $SO_2(OH)Cl$, and as a result postulate  $Cl_2{>}S{=}S$ as the constitution of S_2Cl_2 in analogy to  $Cl_2{>}S{=}O$. Venkateswaren[19] has studied S_2Cl_2 and $SOCl_2$ and further evidence in favour of this structure is that of Meyer[20] who also decides against the constitution Cl—S—S—Cl. On the other hand, Palmer[4] concludes that the compound is indeed built up of single co-valencies and that the S—S—Cl angle is 103°.

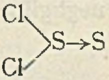
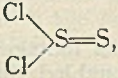
From a chemical point of view the problem was attacked by Giacomello[21] in order to decide between the two constitutions (XIII) and (XIV). He concluded that S_2Cl_2 consists of an equilibrium mixture of two molecules having the constitutions (XIII) and (XIV), the molecule containing the co-ordinate bond being the more reactive. Thus three constitutions have been postulated and mixtures of these as well.


$Cl_2{>}S^{+}{-}S^{-}$

(XIII)

Cl—S—S—Cl

(XIV)

Magnetically there are two approaches to the problem. The first is to assume that S_2Cl_2 has the constitution suggested by Palmer and to use it as above to determine Δ_{S-Cl}. If the bond depression so attained is in agreement with that derived from SCl_2 there is a strong presumption that both compounds have the same type of bonding. Alternatively, the bond depression already derived from SCl_2 may be used to calculate the molecular susceptibility constant for the constitution  $Cl_2{>}S{\rightarrow}S$ and if necessary  $Cl_2{>}S{=}S$, and this calculated susceptibility then compared with the experimental susceptibility of the monochloride. Considering the former alternative, if the constitution is made up of single bonds the residual charges will be $\mathrm{Cl}\overset{-0{\cdot}064}{\text{—}}\mathrm{S}\overset{+0{\cdot}064}{\text{—}}\mathrm{S}\overset{+0{\cdot}064}{\text{—}}\mathrm{Cl}^{-0{\cdot}064}$ for which formula Σ Pauling susceptibility constants is 95·16. Subtracting from this Δ_{S-S} and the experimental susceptibility we obtain $2\Delta_{S-Cl} = 22{\cdot}76$ or $\Delta_{S-Cl} = 11{\cdot}38$, which is in good agreement with the other value obtained for Δ_{S-Cl} from SCl_2. It is therefore highly probable that the constitution of S_2Cl_2 is that suggested by Palmer.[4]

The constitution of S_2Cl_2 has also been investigated magnetically by Varadachari and Subramanam,[10] who, while they obtained the same experimental susceptibility as the authors (62·23 against 62·32), decided

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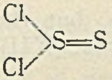
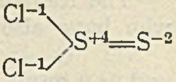
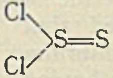
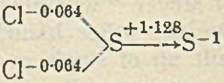
[18] Matossi and Alderhold, *Z. Physik*, 1931, 68, 683.
[19] Venkateswaren, *Ind. J. Physics*, 1931, 6, 275.
[20] Meyer, *Z. anorg. Allgem. Chem.*, 1931, 203, 146.
[21] Giacomello, *Atti. Accad. Lincei*, 1935, 21, 36.

in favour of the constitution  as a result of a different method of interpretation. Varadachari and Subramanam use ionic susceptibility constants derived by Kido[22] of the following value :—

$$Cl^{-1}\ 22{\cdot}1,\ S^{-2}\ 27{\cdot}4,\ S^{+4}\ 4{\cdot}6,$$

giving a calculated susceptibility of 67·0 for the structure  which does not in itself even give a good agreement with their experimental susceptibility.

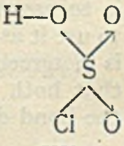
If we apply the method used throughout the present discussion we get the residual charges shewn, which gives 96·11 for the sum of the Pauling atomic susceptibility constants, from which the sum of the bond depressions $2\Delta_{S-Cl} + \Delta_{S\rightarrow S} = 24{\cdot}46$ has to be subtracted, leaving 71·65 for the molecular susceptibility constant. This is not in agreement with the experimental susceptibility nor is the structure  tenable either, thus eliminating all the structures except Cl—S—S—Cl.



The value of Δ_{S-Cl} will be taken as the mean of the values deduced from SCl_2 and S_2Cl_2, *i.e.* $\Delta_{S-Cl} = 11{\cdot}23$.

The Structure of Chlorsulphonic Acid.

Chlorsulphonic acid is usually represented as (XV), a structure in which the only point likely to be open to discussion is the degree of double bonding, if any, in the S—O bonds. The experimental susceptibility is 46·60 while the molecular susceptibility constant for the above structure is 47·04, indicating that any degree of double bonding is negligible.



(XV)

Summary.

The publication of values for the dipole moments and interatomic distances of the links S→O and S—Cl has enabled the method of calculating diamagnetic susceptibilities given by Gray and Cruickshank[2] to be extended to compounds containing such links. The bond depressions Δ_{S-O}, $\Delta_{S\rightarrow O}$, $\Delta_{S=O}$ and Δ_{S-Cl} are calculated and the structures of sulphur trioxide, sulphur monochloride, chlorsulphonic acid and derivatives of $[SO_4]^{-2}$ and $[S_2O_3]^{-2}$ are discussed.

The authors wish to express their thanks as follows : A. C. to the Carnegie Trustees for the Universities of Scotland for a Teaching Fellowship; H. M. K. to the Robbie Fund of the University of Aberdeen for a research scholarship.

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[22] Kido, *Sci. Rpts. Tohoku. Imp. Univ.*, 1933, **22**, 835.
[23] Gray, Clow and Cruickshank, *J. Scient. Instr.*, 1936, 13, 13.

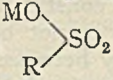
Department of Chemistry,
Marischal College, Aberdeen.

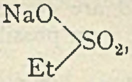
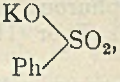
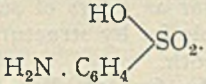
THE STRUCTURE OF COMPOUNDS CONTAINING S—O AND S—Cl BONDS. PART II. DERIVATIVES OF THE $[SO_3]^{-2}$ AND $[S_2O_2]^{-2}$ RADICALS.

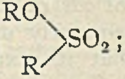
By Archibald Clow, Harry M. Kirton and James M. C. Thompson.

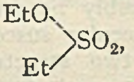
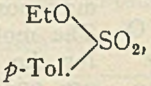
Received 11*th June*, 1940.

The preceding paper by the authors discusses the derivation of the necessary data for applying the Gray-Cruickshank method to the study of compounds containing S—O and S—Cl bonds and contains a discussion of derivatives of the $[SO_4]^{-2}$ and $[S_2O_3]^{-2}$ radicals, while the present communication extends the discussion to derivatives of $[SO_3]^{-2}$ and $[S_2O_2]^{-2}$. These may be classified :

(*a*) Metallic Sulphites, M_2SO_3 ; *e.g.*, K_2SO_3.
(*b*) Di-R sulphites, R_2SO_3 ; *e.g.*, Me_2SO_3, Et_2SO_3.
(*c*) Salts of R sulphonic acids,  $\begin{matrix}\mathrm{MO}\\ \mathrm{R}\end{matrix}>\mathrm{SO_2}$;

e.g.,  $\begin{matrix}\mathrm{NaO}\\ \mathrm{Et}\end{matrix}>\mathrm{SO_2}$,  $\begin{matrix}\mathrm{KO}\\ \mathrm{Ph}\end{matrix}>\mathrm{SO_2}$,  $\begin{matrix}\mathrm{HO}\\ \mathrm{H_2N\,.\,C_6H_4}\end{matrix}>\mathrm{SO_2}$.

(*d*) Esters of R sulphonic acids,  $\begin{matrix}\mathrm{RO}\\ \mathrm{R}\end{matrix}>\mathrm{SO_2}$;

e.g.,  $\begin{matrix}\mathrm{EtO}\\ \mathrm{Et}\end{matrix}>\mathrm{SO_2}$,  $\begin{matrix}\mathrm{EtO}\\ p\text{-}\mathrm{Tol.}\end{matrix}>\mathrm{SO_2}$,

with the corresponding thio-derivatives excepting metallic thiosulphites.

Experimental.

As in the preceding communication, the diamagnetic susceptibilities were measured at 18° C. with the modified Curie-Chéneveau magnetic balance, great care being taken in the preparation of samples free from impurity. Throughout the discussion the susceptibilities have been multiplied by -10^{+6}.

TABLE I.

Experimental Susceptibilities.*

Potassium sulphite . . .	63·7	K
Dimethyl sulphite . . .	54·18	A
Diethyl sulphite . . .	77·02	A
Dimethyl thiosulphite . .	62·26	A
Diethyl thiosulphite . .	86·22	A
Sodium ethyl-sulphonate . .	64·06	A
Potassium phenyl-sulphonate .	96·28	A
Sulphanilic acid . . .	90·07	A
Sodium *p*-tolyl-thiosulphonate .	113·8	A
Ethyl ethyl-sulphonate . .	81·80	P
Ethyl *p*-tolyl-sulphonate . .	114·9	A
p-Tolyl *p*-tolyl-thiosulphonate .	156·7	A

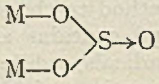
* A = Authors ; P = Pascal ; K = Kido.

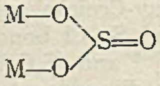
Discussion.

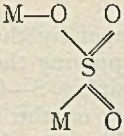
(*a*) Sulphites and Thiosulphites.

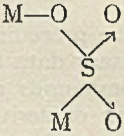
As indicated above there arise from the $[SO_3]^{-2}$ radical and the $[S_2O_2]^{-2}$ radical derived from it, in all seven classes of inorganic and organic derivatives whose structures have formed one of the central problems of the constitution of the simple sulphur derivatives.

The physical evidence for the structure of the sulphite ion and its metallic and organic derivatives has been discussed by Hägg[1] and may be summed up as follows. An X-ray investigation of sodium sulphite reveals that the sulphite radical is pyramidal with the three oxygens at the corners and the sulphur atom slightly above the plane of the oxygen atoms, and according to Hägg structure (I) is the most probable structure :—


(I)

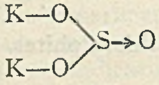

(II)

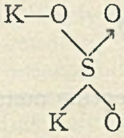

(III)


(IV)

On the other hand, Stelling[2] suggests structure (III) and insists, moreover, that organic and inorganic sulphites cannot be represented as having the same constitution. It is quite obvious that the esters of organic sulphites cannot be represented by (III) or (IV) as these formulæ have already been assigned to the esters of sulphonic acids so that, so far as esters of sulphurous acid are concerned, they must be accountable for by structures (I) or (II), or a possible resonance hybrid of them both.

Consider first of all potassium sulphite. This compound is easily oxidised and consequently difficult to obtain free from the sulphate[3] with the result that its experimental susceptibility, which is 63·70, may possibly be somewhat inaccurate. The molecular susceptibility constants for the two structures (V) and (VI) are 60·61 and 61·81. Although the difference between these molecular susceptibility constants is not large the experimental susceptibility is in favour of the latter structure, and one can at least say definitely that the constitution as proposed by Stelling is incorrect as it stands, but can be brought into line by the replacement of the double bonds by co-ordinate bonds. The same modification brings into line the constitution put forward by Strecker and Spitaler,[4] as the result of a comparative study of the refractive indices of sulphates, organic and inorganic sulphites and sulphones. This, of course, cannot be the constitution of the organic sulphites, but as both Stelling and Strecker suggest different constitutions for the organic and inorganic sulphites, this constitution for the inorganic sulphites is in agreement with their findings.


(V)


(VI)

Turning now to organic derivatives of sulphurous acid, these, as pointed out above, cannot have the same constitution as that assigned to the inorganic sulphites. Consequently, their structures must be represented by (I) or (II) or a resonance hybrid. Two sulphites of this class have been investigated, dimethyl- and diethyl-sulphite, whose

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[1] Hägg, *Z. physik. Chem.*, *B*, 1932, **18**, 199.

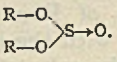
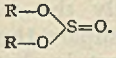
[2] Stelling, *Diss. Lund*, 1927.

[3] Zachariasen and Buellv, *Physic. Rev.*, 1931, **37**, 1295.

[4] Stecker and Spitaler, *Ber.*, *B*, 1926, **59**, 1754.

experimental susceptibilities together with the calculated molecular susceptibility constants for structures (I) and (II) are given in Table II.

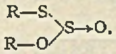
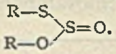
TABLE II.

Sulphite.	Experimental Susceptibility.			Resonance Hybrid.
Me_2SO_3	54·18	58·56	49·53	54·05
Et_2SO_3	77·02	82·28	73·01	77·69

It is immediately apparent that neither the methyl nor ethyl derivatives can be represented by structure (I) or (II), but on the other hand if these organic sulphites are resonance hybrids made up equally of the two possible constitutions then there is an excellent agreement between the experimental susceptibilities and the calculated molecular susceptibility constants.

It is interesting and instructive to extend the field of enquiry to thiosulphites, it being recollected that thiosulphates were derived from sulphates by the replacement of an oxygen atom by a sulphur atom giving in the thiosulphate a sulphydryl and hydroxyl radical in place of two hydroxyls in the sulphate. To compare with Stelling's structure for the sulphite there are unfortunately no simple inorganic thiosulphites, but dimethyl and diethyl thiosulphite were prepared, following the method of Meuwsen,[5] *i.e.*, by the action of sodium alk-oxide upon sulphur monochloride in petrol ether. The experimental susceptibilities and calculated molecular constants for these thiosulphites are as in Table III.

TABLE III.

Thiosulphite.	Experimental Susceptibility.			Resonance Hybrid.
$Me_2S_2O_2$	62·26	68·30	56·09	62·19
$Et_2S_2O_2$	86·22	90·78	78·57	85·18

Apparently therefore, the thiosulphites have constitutions represented by a resonance hybrid of the above possible constitutions.

This, however, does not exhaust the possibilities. From its mode of formation it was assumed by Meuwsen that his compound would have the constitution (VII). The calculated molecular susceptibility constant for this structure is 69·62 which quite definitely eliminates it as a possible interpretation of the product resulting from the above reaction. Metal R sulphites were not investigated, as they all decompose readily.

$$CH_3—O—S—S—O—CH_3.$$

(VII)

(*b*) Salts and Esters of Sulphonic and Thiosulphonic Acids.

Having thus been able to assign constitutions to organic and inorganic sulphites, and organic thiosulphites, having molecular susceptibility constants in agreement with their experimental suscepti-

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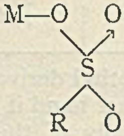
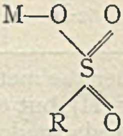
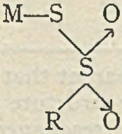
[5] Meuwsen, *Ber.*, *B*, 1935, 68, 121.

bilities, it is possible to consider the remaining classes of compounds derived from $[SO_3]^{-2}$ and $[S_2O_2]^{-2}$, *i.e.*, the salts and esters of sulphonic and thiosulphonic acids. One of these classes is of particular interest, as compounds which were formerly regarded as disulphoxides were shown chemically to correspond to the thiosulphonate constitution.[6] Consider firstly the salts of R-sulphonic acids. Although it is not possible to compare these with the isomeric salts of R-sulphurous acids it is almost certain that the salts of the sulphonic acids will have constitutions represented by either (VIII) or (IX), and the corresponding salts of thiosulphonates by (X) or (XI). Several derivatives of this type have been investigated magnetically and are shown in Table IV with the appropriate molecular susceptibility constants :—


(VIII)

or


(IX)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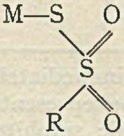
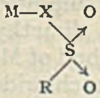

(XI)

TABLE IV.

Salt of Sulphonic or Thiosulphonic Acid.	Experimental Susceptibility.	Molecular Susceptibility Constant for 
Sodium ethyl sulphonate . . .	64·06	60·37
Potassium phenyl sulphonate . . .	96·28	95·70
Sulphanilic acid	90·07	90·65
Sodium *p*-tolyl thiosulphonate . .	113·8	110·9

On the whole the agreements are reasonable, those in particular for potassium phenyl sulphonate and sulphanilic acid being excellent. Even despite the greater variation in the other compounds it is possible to eliminate other structures. The same is true of the esters of R-sulphonic acids, two of which have been examined, ethyl ethyl sulphonate and ethyl *p*-tolyl-sulphonate, whose experimental and calculated susceptibilities are respectively 81·80 against 81·53 and 114·9 against 118·21.

To this group belong also the interesting aldehyde and keto-bisulphite compounds which, according to Raschig and Prahl,[7] are salts of hydroxy-R-sulphonic acids rather than mono-ester metal oxy-R-sulphites. An attempt was made to investigate several examples of these compounds, but their instability when subjected to the rigorous purification preparatory to the measurement of their diamagnetic susceptibilities made it impossible to obtain results which would have been of any value.

Simple esters of simple thiosulphonic acids are not easily prepared and recourse was taken to the *p*-tolyl ester of *p*-tolyl thiosulphonic acid.

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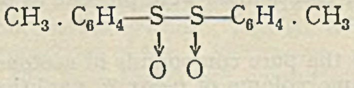
[6] Smiles, *J.C.S.*, **125**, 176.

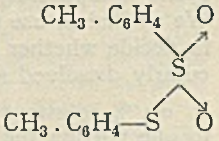
[7] Raschig and Prahl, *Lieb. Ann.*, 1926, 448, 265 ; Schraeter, *Ber.*, 1926, **59**, 2341 ; 1928, **61** 1616.

As a disulphoxide and as a thiosulphonate it would be (XII) and (XIII) respectively. Unfortunately the molecular susceptibility constants of both these structures are almost identical and magnetism can contribute nothing to the physical confirmation of Smiles's chemical investigations.



$$CH_3\,.\,C_6H_4-\underset{O}{\underset{\downarrow}{S}}-\underset{O}{\underset{\downarrow}{S}}-C_6H_4\,.\,CH_3$$

(XII)



(XIII)

Summary.

The diamagnetic bond depressions for the bonds involving sulphur and oxygen atoms derived in the preceding paper are used to discuss the structures of derivatives of $[SO_3]^{-2}$ and $[S_2O_2]^{-2}$, *viz.*, metallic and organic sulphites, organic thiosulphites, salts and esters of sulphonic and thiosulphonic acids.

Further discussions of compounds in which the sulphur is in a lower state of valency are in preparation.

One of us (A. C.) wishes to thank the Carnegie Trustees for the Universities of Scotland for a Teaching Fellowship.

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THE FLUORESCENCE OF HYDROCARBONS AND OF THEIR MIXTURES WITH NAPHTHACENE.

BY F. WEIGERT.

Received 8th July, 1940.

The blue fluorescence of anthracene crystals is almost completely quenched by minute amounts of naphthacene when it is excited by the ultraviolet beam. The fluorescence light becomes yellow-green, and instead of the anthracene bands in the short wavelength portion of the spectrum two to four separate bands in the green which belong to the naphthacene molecule are apparent. On the other hand, the solution of the mixture in acetone, benzene, etc., exhibits the fluorescence spectrum of pure dissolved anthracene. Solid naphthacene fluoresces only faintly, while the fluorescence spectrum of its solution shows the typical green bands. The well-known influence of small amounts of naphthacene on the anthracene fluorescence is interpreted as follows: In the mixed solution the line Hg-3660 is much more strongly absorbed by the anthracene molecules, which are present in excess, than by the naphthacene molecules, and therefore the blue anthracene fluorescence prevails almost completely. In the mixed crystals the energy absorbed by the anthracene releases an "exciton."[1] This is transferred to the naphthacene molecules and excites their green fluorescence bands.

[1] J. Frenkel, *Physik. Z. Sov. Un.*, 1936, 9, 138.

We have studied the analogous phenomena with various condensed cyclic compounds, which interested us for their biological properties. We wished to use the blue and green fluorescence as an easy colour test to decide whether the compounds were present as crystals or in a molecularly dissolved state.

0·1 % solutions of the pure compounds in acetone were prepared, and to one portion the same volume of 0·001 % naphthacene in acetone was added. 1 c.c. each of these acetone solutions was mixed with 50 c.c. of water and the acetone allowed to evaporate at room temperature. Thus microcrystalline " colloidal " suspensions of the pure and mixed compounds were formed. The specimens were excited in tubes of ordinary glass by the beams from a mercury arc which had been filtered through black NiO-glass and the colour and the spectrum of the fluorescence noted.

(1) We found with 1.2-Benzanthracene, 1.2,-5.6-Dibenzanthracene 10-Methyl-1.2-benzanthracene, 5.6-Cyclopenteno-1.2-benzanthracene, 6-Isopropyl-1.2-benzanthracene the same phenomena as with anthracene, *i.e.* the blue fluorescence of the pure hydrocarbons is unaltered in the solution by adding 1 % of naphthacene, but completely quenched in the crystals. These hydrocarbons belong therefore to the " Anthracene-type."

(2) The solutions of 9.10-Dibenzanthracene, 1.2,-5.6-Dibenzacridine (the only non-hydrocarbon tested), 3.4-Benzphenanthrene, 1.2-Benzfluorene, 2-Methyl-3.4-benzphenanthrene flouresce blue without and with added naphthacene. But a blueish green fluorescence which shows the blue bands of the main component as well as the green bands of the naphthacene is emitted by the suspensions of the mixed crystals.

(3) With Fluorene, Dibenzfluorene, Phenanthrene, 1.9-Dimethyl phenanthrene we observed faint blue fluorescence in the pure systems and faint blueish green when mixed. There is no great difference apparent between the solution and suspensions. Since these hydrocarbons do not absorb the near ultraviolet radiations to a great extent, the weak fluorescence may be due to our experimental arrangement which excludes the ultraviolet by the use of ordinary glass. Some unknown impurities may also play a rôle.

(4) The colloidal suspensions of 3.4-Benzphenanthrene, 5.6-Cyclopenteno-1.2-benzanthracene, 2-Methyl-3.4-benzphenanthrene proved to be light sensitive. During the taking of the fluorescence spectrograms the green fluorescence faded away quickly and the blue fluorescence of the main component was left. It was necessary to change frequently the exposed area to get a good record of the spectra. A certain light sensitivity, although to a much less degree, is apparent with all mixed colloidal suspensions. It is apparently due to a sensitised oxydation of the naphthacene.

(5) Three hydrocarbons : 3.4-Benzpyrene, Cholanthrene and Methylcholanthrene exhibited fluorescence phenomena which were distinctly different from those noted under (1)-(3). The fluorescence spectra of the acetone solutions without and with added naphthacene were blue with the typical band structures of the main components. The pure colloidal suspensions exhibited one broad band from green to orange which became brighter by adding naphthacene. The typical narrow naphthacene bands in the green were not apparent. The fluorescence colour was yellow in all cases.

(6) This " Benzpyrene-type " of fluorescence was studied in detail with benzpyrene itself.[2] We found that it was associated with the colloid microcrystallinic state of the hydrocarbon which we termed, owing to its yellow fluorescence, BP-y and with the original yellow crystals of benzpyrene. They are needle-shaped, and belong to the monoclinic system, but their fluorescence spectrum is different from that of the colloidal suspension.

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[2] J. Iball, *Z. Kryst.* (*A*), 1936, 94, 7.

It exhibits in the pure state a broad symmetrical band with its maximum in the green, and we called it therefore BP-gr. With added naphthacene the broad band shifts toward the yellow. There exists still a third solid modification of benzpyrene which is unstable below 66°. It was called BP-bl owing to its bright blue fluorescence. Its lattice belongs, according to Iball,[3] to the orthorhombic system. This BP-bl has exactly the same properties as the hydrocarbons of the " Anthracene-type " (1) *i.e.* on addition of naphthacene the blue bands are completely quenched and the naphthacene bands appear in fluorescence. The naphthacene bands may therefore be used as a fluorescence "label" for the blue fluorescing modification of benzpyrene. They allow the easy detection of minute quantities of BP-bl, even when the blue bands of the pure hydrocarbon are very faint. This method helped indeed greatly to outline the fields of stability of the various solid forms of benzpyrene. It is a remarkable fact that the orthorhombic BP-bl belongs to the Anthracene type while anthracene itself belongs to the monoclinic crystal system. Preliminary experiments point to similar phenomena with cholanthrene and methylcholanthrene.

(7) The above-mentioned interpretation of the change of fluorescence by adding naphthacene to the compounds of the anthracene type takes into account the free moving around of the " exciton " inside the undisturbed crystal lattice. Therefore, the quenching of the blue bands of the main component and the excitation of the green naphthacene bands ought to be the more pronounced the more perfect and the larger the crystals are. This could be established by the preparation of very finely dispersed colloidal suspension by adding the acetone solutions of the hydrocarbons to water in presence of gelatine which served as a protective colloid. The fluorescence of anthracene + 1 % naphthacene was now blueish green, and the blue anthracene bands appear in the spectrum. With the blue fluorescing form of benzpyrene + naphthacene the change of fluorescence from green to blue in the presence of gelatine was still more striking.

(8) Our aim was to test by the fluorescence colour in presence of naphthacene, whether the compounds are present in dissolved or solid state. According to (7) this aim was not reached without restriction. The test is of use with the compounds and the special modifications which belong to the anthracene type, if the crystals are not too small. But the absence of the naphthacene bands *does not exclude* the presence of crystals in a highly dispersed state.

(9) In a series of biological experiments we left fresh muscle tissue in contact with colloidal suspensions of the compounds mentioned under (1), (2) and (5) with an addition of 1 % naphthacene. In all these cases we established a complete disappearance of the green and yellow fluorescence after a couple of hours. This indicates that the relatively large particles of the suspensions have disappeared. Since with benzpyrene and the cholanthrenes the typical fluorescence bands of the solution developed gradually with the disappearance of the yellow bands, it is probable that also the other compounds which have been tested enter the tissue cells in a state of molecular solution. Some biological conclusions from these observations will be drawn in due course.

The author is indebted to the British Empire Cancer Campaign for financial help, to Dr. F. C. Mottram for valuable discussions, and to Professor Ingold and Dr. Goodeve from University College, London, for the loan of a spectrograph.

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[3] Weigert and Mottram, *Nature*, 1940, 145, 895.

THE SPARK IGNITION OF MIXTURES OF ASYM.-DIMETHYLHYDRAZINE AND NITRIC OXIDE.

By Daphne A. Bamford and C. H. Bamford.

Received 18th July, 1940.

In a previous paper[1] it has been shown that hydrazine vapour, under suitable pressure conditions, undergoes explosive decomposition when sparked. It was suggested that NH_2 and N_2H_3 radicals participate in the chain, the former being produced by the initial sparking, and also by the rupture of the N—N link of hydrazine molecules on collision with " hot " molecules present. If nitric oxide is present a very exothermic reaction occurs between this gas and amino radicals,[2] with the result that the branching of the chain is increased, and the explosion region between the upper and lower pressure limits is widened.

We now describe a similar investigation of asym.-dimethylhydrazine, rupture of the N—N link of which would produce $(CH_3)_2N$ radicals.[3] Thus an additional check on the mechanism proposed for the hydrazine decomposition might be obtained. Pure dimethylhydrazine vapour does not explode when sparked, but does so if NO is present. A small amount of the latter can effect the decomposition of a much larger amount of dimethylhydrazine, the NO acting as sensitiser. The ignition is considerably less violent than in the case of hydrazine, and there is no appreciable emission of visible light. In this case also there exist critical upper and lower pressure limits of explosion, the region of explosion between them being widened by an increase in the initial temperature.

From the results it is concluded that dissociation of the molecule into $(CH_3)_2N$ and NH_2 radicals is an essential step in the decomposition. At the comparatively high temperatures reached during the ignition the $(CH_3)_2N$ radicals do not behave in the manner previously observed at 100°; instead they appear mainly to react with NO. As in the case of hydrazine NH_2 radicals participate in the chain. It is difficult to envisage any purely radical mechanism by which branching may occur, but a branching energy chain resulting from the interaction of radicals and NO may be readily constructed. It appears, therefore, that the explosion is ultimately thermal in character, that is to say, heat liberated in the reaction is responsible for, and not a result of the ignition.

Experimental.

1. Preparation of Materials.

Asym.-dimethylhydrazine was prepared by the reduction of dimethylnitrosamine by means of Zn dust and acetic acid according to the method described in *Organic Syntheses*, Vol. XVI, page 22. The substance was purified by two distillations over solid potassium hydroxide, followed by refluxing with barium oxide and fractionation in an inert atmosphere. The product boiling between 61·5° and 64° was submitted to further

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[1] Bamford, *Trans. Faraday Soc.*, 1939, **35**, 1239.
[2] *Ibid.*, 568.
[3] See Bamford, *J. Chem. Soc.*, 1939, 12.

fractionation *in vacuo* and kept in an evacuated tube shielded from light. Before use the vapour was passed through a tube packed with BaO.

Nitric oxide, prepared by Winkler's method, was purified by passing through concentrated KOH solution and a trap at − 80° to remove higher oxides of nitrogen. After condensation in liquid air and fractionation *in vacuo* the gas was stored in a glass bulb.

2. Apparatus and Method.

The apparatus used was essentially the same as that employed in the study of hydrazine.[1] A pyrex reaction vessel was used, internal diameter 35 mm., length 6·6 cm., heated in a furnace to a temperature uniform to within 1° over the whole vessel. Two tungsten electrodes were sealed into the walls, and formed a spark gap of about 2 mm. situated near the middle of the reaction vessel. As in the earlier experiments the outlet tube of the latter communicated with a Hg seal, which served to isolate the reaction vessel and to measure the pressure. The connecting tubes and also the upper part of the Hg column nearest the vessel were maintained at about 100° by means of a heating coil to prevent condensation of the dimethylhydrazine. The volume of the dead space was only about 5 % of the effective volume of the reaction vessel at 150°.

The method of introducing the reactants has been described before. They were allowed to stand for 15 minutes in the reaction vessel before sparking, to attain homogeneity. After explosion the products were separated as far as possible by fractionation. After removal of the permanent gases the substances remaining were HCN, NH_3, H_2O, unused dimethylhydrazine, and in some cases small amounts of methylamine and hydrazine. This mixture was distilled into a weighed tube containing solid KOH to remove HCN and H_2O. The total weight of these bodies was thus obtained, and the former was estimated with N/20 $AgNO_3$, using Liebig's method. From the mixture remaining after the treatment with KOH the NH_3 was distilled off between − 95° and − 100°, at which temperatures the other constituents are not appreciably volatile. However, the vapour density of the NH_3 was determined to ascertain the presence or absence of methylamine. The latter was distilled off at − 80°; its vapour density was recorded, and it was identified by its vapour pressure and reactions. The unchanged dimethylhydrazine was divided into a number of fractions and the vapour density of each determined. In some cases the final fraction had lower vapour density and vapour pressure than dimethylhydrazine, the vapour density corresponding to a molecular weight of approximately 32. These facts were considered to indicate the presence of a small quantity of hydrazine among the products, and this was in agreement with the vigorous reaction produced on adding a little solid potassium permanganate to the final fraction. This reaction is given by hydrazine but not by dimethylhydrazine.

3. Results.

The analytical results for a number of experiments performed under different conditions of initial temperature and composition are given in Table I.

In each case the sum of the volumes of CO and H_2O formed is equal to the volume of NO used. The oxygen balance is thus satisfactory, the whole appearing as CO and H_2O. On attempting to establish a C, H, N balance, however, it will be found that there are small deficiencies in these elements, of approximately equal magnitude. This is evidently connected with the deposition of a brown polymer on the exit tube of the reaction vessel, which was noticed after each ignition. This substance is similar in appearance to the polymers of HCN produced by adding ammonia to liquid HCN. It is reasonable to suppose that polymerisation of HCN on the walls is induced by the presence of NH_3, or, more probably, NH_2

radicals. The polymerisation and the C, H, N deficiencies were greater when more ammonia was present (experiments 1, 6). On warming the polymer it evolves HCN.

TABLE I.*

Expt.	T° C.	Initial Pressures mm. (DH)	Initial Pressures mm. (NO)	Volumes Reacted c.c. (DH)	Volumes Reacted c.c. (NO)	Products in c.c.										
						H_2	CH_4	N_2	CO	C_2H_4	C_2H_6	NH_3	HCN	H_2O	$MeNH_2$	N_2H_4
1 (7)	170	130	46	38·0	12·1	22·2	23·1	16·5	0·6	4·0	4·5	20·0	20·2 (33·7)	11·5	1·5	0·2
2 (2)	230	123	136	8·7	4·9	8·1	5·1	4·9	0·2	1·0	0·2	2·7	6·3 (9·6)	4·9	—	—
3 (2)	285	131	140	7·9	4·5	7·5	4·6	4·8	0·3	1·0	0·3	2·1	5·9 (8·3)	4·5	—	—
4 (2)	80	90	195	10·3	8·1	9·6	5·2	7·2	0·6	1·0	0·5	2·7	8·0 (11·6)	7·6	—	—
5 (3)	245	90	182	9·9	7·7	10·8	4·8	6·7	0·7	1·0	0·3	2·2	7·0 (11·7)	7·0	—	—
6 (2)	240	264	36	16·6	2·6	10·8	9·8	5·7	0·3	2·1	2·1	10·2	5·7 (14·0)	2·2	0·4	0·3

* In the majority of the experiments the products from a number of runs were combined to facilitate analysis. This number is indicated by the figure in brackets under the number of the experiment. DH in the table represents dimethylhydrazine. The total volume of HCN formed, allowing for polymerisation, is given by the figure in parentheses in the column headed HCN.

The decomposition of the dimethylhydrazine is never complete. The extreme values obtained (after allowing for the small amount of the substance present in the dead space) are 83 % and 71 % in experiments 5 and 6 respectively. Thus increasing the pressure of NO increases the percentage combustion. The figure for experiment 4 is 80 %; a comparison of this with experiment 5 suggests that a decrease in the initial temperature causes a small decrease in the percentage combustion.

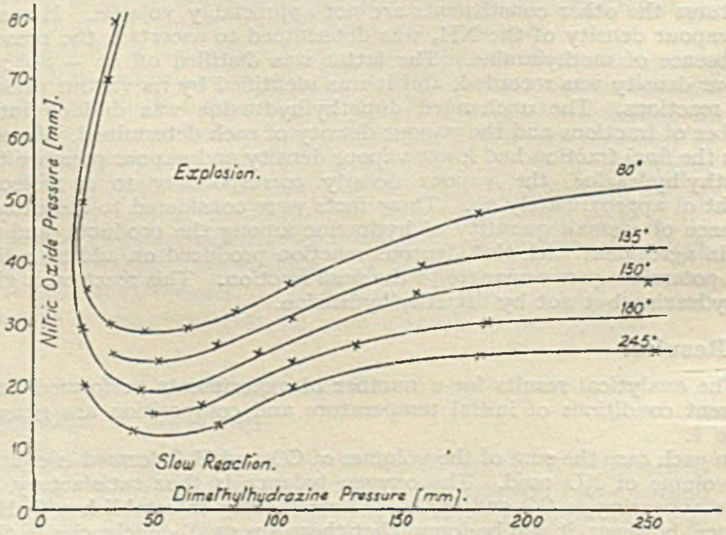

FIG. 1.—Explosion limits.

Fig. 1 shows the disposition of the explosion limits for a number of temperatures. The limiting pressures of nitric oxide are plotted against dimethylhydrazine pressures. The curve representing the upper limit is initially very steep, and with the present apparatus it is impossible to follow it further.

Discussion.

As mentioned previously, it may be considered that the initial sparking of dimethylhydrazine vapour forms, among other products, $(CH_3)_2N$ and NH_2 radicals—

$$(CH_3)_2NNH_2 \rightarrow (CH_3)_2N + NH_2 - 23\ \text{Cal.}^* \quad . \quad . \quad (1)$$

This is reasonable, since the N—N link is much weaker than any other in the molecule.

The amino radicals liberated may enter into reaction with NO or dimethylhydrazine. The reaction between NH_2 and NO mentioned on page 1036 is

$$NH_2 + NO \rightarrow N_2 + H_2O + \text{ca. } 100\ \text{Cal.} \quad . \quad . \quad (2)$$

When little NO is present, NH_3 is a major product; the yield of NH_3 falls off, however, as the pressure of NO is increased. This is consistent with the view that NH_3 is formed from amino radicals, probably by a simple disproportionation reaction—

$$NH_2 + (CH_3)_2NNH_2 \rightarrow NH_3 + [C_2H_7N_2] \quad . \quad . \quad (3)$$

The relative importance of (2) and (3) thus depends on the ratio nitric oxide/dimethylhydrazine. A small fraction of the amino radicals diffuses to the walls with formation of hydrazine—

$$NH_2 \rightarrow \tfrac{1}{2}N_2H_4 \quad . \quad . \quad . \quad . \quad (4)$$

Methane is always a major product, even when a large excess of NO is present. Thus it is improbable that the CH_4 is mainly formed from CH_3 radicals. The decomposition of the $C_2H_7N_2$·radical formed in (3) above may give CH_4 according to (5). Small amounts of methylamine

$$C_2H_7N_2 \rightarrow CH_4 + HCN + NH_2 + 22\ \text{Cal.} \quad . \quad . \quad (5)$$

may result from the dehydrogenation of $C_2H_7N_2$, *e.g.* by another $C_2H_7N_2$ or

$$\left.\begin{aligned} C_2H_7N_2 &\rightarrow \tfrac{1}{2}(CH_3)_2NNH_2 + \tfrac{1}{2}CH_3NH_2 + \tfrac{1}{2}HCN + 35\ \text{Cal.} \quad (a) \\ NH_2 + C_2H_7N_2 &\rightarrow NH_3 + CH_3NH_2 + HCN \quad . \quad (b) \end{aligned}\right\} \ . \quad (6)$$

NH_2 (equations (6)). Some of the amine formed probably decomposes during ignition[4] (equation (7)). Ammonia is also decomposed in the

$$CH_3NH_2 \rightarrow HCN + 2H_2 \quad . \quad . \quad . \quad (7)$$

flame (8), as is also the case in the explosive decomposition of hydrazine.

$$NH_3 \rightarrow \tfrac{1}{2}N_2 + \tfrac{3}{2}H_2 \quad . \quad . \quad . \quad . \quad (8)$$

It is now necessary to consider the behaviour of the $(CH_3)_2N$ radicals formed in reaction 1. It has been shown[3] that these radicals produced photochemically from dimethylnitrosamine do not react with NO at 100°, but disproportionate among themselves forming dimethylamine and a divalent radical. It seems that in the present case, at the high

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* The heats of reaction given in this discussion are estimated from Bichowsky and Rossini's figures in *Thermochemistry of the Chemical Substances.*

[4] See *e.g.* Emeleus and Jolley, *J. Chem. Soc.*, 1935, 929.

temperatures reached during ignition, reaction occurs between the radicals and NO—

$$(CH_3)_2N + NO \rightarrow 2HCN + H_2O + H_2 + 54 \text{ Cal.} \qquad (9)$$
$$(CH_3)_2N + NO \rightarrow HCN + CO + H_2 + NH_3 + 56 \text{ Cal.} \qquad (10)$$

Alternatively these reactions can be regarded as due to the splitting off of CH_3 from $(CH_3)_2N$, followed by reaction of the former with NO—

$$CH_3 + NO \rightarrow H_2O + HCN \qquad (9a)$$
$$CH_3 + NO \rightarrow CO + NH_3 \qquad (10a)$$

These reactions have already been suggested previously.[5] The residue CH_3N is known to decompose into H_2 and HCN at elevated temperatures,[4] so that this latter scheme leads to the same products as 9 and 10. On this view methylamine can be formed by union of CH_3 and NH_2 radicals. Some methyls will be hydrogenated to CH_4 by dimethylhydrazine or hydrogen (since reaction between CH_3 and H_2 occurs readily above about 150°).[6] It may also be considered that CH_3 radicals are formed by a decomposition of $C_2H_7N_2$ (alternative to (5)) into CH_3, NH_3, HCN. The introduction of free CH_3 complicates the scheme of reactions, and does not assist in the interpretation of the results. For this reason reactions 6, 9, 10, which do not involve free methyl, are preferred to the later scheme.

In order to account for the relative yields of N_2 and HCN, it is necessary that some of the N from the $(CH_3)_2N$ part of the dimethylhydrazine molecule should appear as the free gas. The following reactions are thus suggested to account for the formation of ethane and ethylene—

$$(CH_3)_2N \rightarrow C_2H_6 + \tfrac{1}{2}N_2 + 46 \text{ Cal.} \qquad (11)$$
$$(CH_3)_2NNH_2 \rightarrow C_2H_4 + N_2 + 2H_2 + 13 \text{ Cal.} \qquad (12)$$

As the pressure of NO is increased (9) and (10) will predominate over (11), and the yield of C_2H_6 will diminish, as observed experimentally. The yield of C_2H_4 does not vary appreciably with the NO pressure, and for this reason its formation from dimethylhydrazine, rather than from $(CH_3)_2N$ radicals, is suggested above.

From Fig. 1 it may be deduced that as the total pressure is reduced, the value of the ratio NO/dimethylhydrazine at the lower explosion limit increases. Since the effect of reducing the pressure is to facilitate diffusion of active centres to walls, it must be concluded that these centres can be formed by a reaction involving NO. It is difficult to see what this can be, other than reaction (2) followed by the dissociation of dimethylhydrazine molecules on collision with excited molecules of the products, according to equation (1). Reaction (2) liberates sufficient energy to permit (thermodynamically) the dissociation of about four dimethylhydrazine molecules. Thus a branching chain mechanism may be constructed.

We can now show that reactions (1)-(12) can account satisfactorily for the volumes of the various products. Let a and b represent the extents in c.c. to which reactions (2) and (8) occur respectively in any experiment. Then the two equalities below may be deduced—

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[5] Davis, Jahn, and Burton, *J. Amer. Chem. Soc.*, 1938, 60, 10; Bamford, *J. Chem. Soc.*, 1939, 17.

[6] Taylor and Rosenblum, *J. Chem. Phys.*, 1938, 6, 119.

$$N_2 = C_2H_4 + \tfrac{1}{2}C_2H_6 + a + \tfrac{1}{2}b \quad . \quad . \quad . \quad (13)$$

$$(DH) = C_2H_4 + C_2H_6 + (NO) - a + \tfrac{1}{2}[NH_3 + b - CO + CH_4] \quad (14)$$

(DH) and (NO) represent the volumes of dimethylhydrazine and NO which react respectively, and other formulæ represent the yields of the various products in c.c. Equations (13) and (14) determine a and b, and from these the extents to which reactions (1)-(12) occur in any experiment can be calculated. These are set out in Table II. (In these calculations equation (6a) has been used.) The calculated volumes of H_2 and HCN are given in the two columns on the right of the table, and may be compared with the figures in Table I. The volumes of all other products are used in constructing Table II. In experiments in which much NO is present (2)-(5), it will be seen that reaction (6) (producing methylamine) is negligible—probably on account of the rapid decomposition of $C_2H_7N_2$ according to equation (5) at the high temperature produced. Thus reactions (3), (5) occur equally, and since the extent of (3) is known, that of (5), *i.e.* the yield of methane, can be predicted in these cases.

TABLE II.—EXTENTS TO WHICH REACTIONS (1)-(12) OCCUR, IN C.C.

Expt.	Ratio NO/DH initial	(DH) used.	Reaction No.												H_2	HCN calc.
			1	2	3	4	5	6	7	8	9	10	11	12		
1	0·35	38·0	9·6	7·0	25·7	0·4	23·1	2·6	~0	6·3	4·5	0·6	4·5	4·0	22·6	34·0
2	1·11	8·7	2·6	2·5	5·1	0·0	5·1	0·0	0·0	2·6	2·2	0·2	0·2	1·0	8·3	9·7
3	1·07	7·9	2·4	2·4	4·3	0·0	4·6	0·0	0·0	2·5	1·8	0·3	0·3	1·0	7·8	8·8
4	2·16	9·9	4·2	4·4	5·0	0·0	5·2	0·0	0·0	2·9	3·1	0·6	0·5	1·0	10·0	12·0
5	2·02	9·9	4·1	3·9	4·7	0·0	4·8	0·0	0·0	3·2	3·1	0·7	0·3	1.0	10·6	11·7
6	0·14	16·6	3·4	1·3	12·3	0·6	9·8	2·5	0·9	2·4	1·0	0·3	2·1	2·1	10·9	14·3

According to Table II, the initial temperature has comparatively little effect on the relative probabilities of the various reactions. (Compare, for example, experiments (2), (3), and (4), (5).) This is not surprising, since a high temperature is reached during ignition, and the nature of the products will not be appreciably affected by the initial temperature. The latter, however, will be expected to alter the explosion limits to some extent as is, in fact, the case.

An alteration in the ratio NO/dimethylhydrazine produces a marked change in the relative probabilities of the reactions. This is brought out by a comparison of experiments (5) and (6). For equal volumes of dimethylhydrazine reacting, the number of amino radicals reacting with NO is about five times as great in the former, in which the NO pressure is much greater. Many more hot molecules are thus produced by reaction (2), with the result that the percentage of the total dimethylhydrazine decomposed which is dissociated according to (1) is larger in (5) than in (6). The values of this percentage are 41 and 21 in experiments (5) and (6) respectively. In the latter, the chain reaction of equations (3), (5) predominates, while in the former (1), (2), (9) are also important. The relative importance of reactions (2) and (3) mentioned on page 1039 is shown by Table II to vary markedly with the ratio NO/dimethylhydrazine.

Conclusion.

The explosion of mixtures of dimethylhydrazine and NO has been shown to be thermal in character. The fact that pure dimethylhydrazine vapour will not explode shows that the chain reaction given in equations (3) and (5) must be supplemented by a branching mechanism involving NO. This is considered to be reaction (2), followed by the dissociation of fresh dimethylhydrazine molecules by the energy liberated in this reaction. Reaction (9) may also act in the same way as (2). These conclusions are similar to those reached in the case of the explosive decomposition of hydrazine, except for the fact that with hydrazine the chains may branch without the intervention of NO. The explosive reactions of the hydrazines would appear to be due to the ease with which the N—N link breaks on collision with excited molecules.

Summary.

Continuing the study of the explosive decomposition of hydrazines, the ignition which occurs on sparking mixtures of asym.-dimethylhydrazine and nitric oxide has been investigated. A mechanism is proposed which accounts for the products of combustion, and it is concluded that the ignition is thermal in origin, and due to the heating up of the system by very exothermic reactions between radicals and nitric oxide.

One of the authors (C. H. B.) wishes to express his thanks to Trinity College, Cambridge, for a Fellowship, during the tenure of which this work was carried out.

Laboratory of Physical Chemistry,
Cambridge.

THE ELECTROPHORESIS OF CERTAIN HYDROCARBONS AND ALIPHATIC ESTERS AS A FUNCTION OF *p*H.

By G. C. Williams.

(*Communicated by* W. C. M. Lewis.)

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A considerable amount of work has been performed on the electrophoresis of dispersed particles, the object being usually to correlate the electrophoretic mobility with the ionic composition of the aqueous phase. Attempts to relate the mobility to the chemical composition of the dispersed phase, however, have been much less numerous. Alty and Johnson [1] studied the electrophoretic behaviour of paraffin wax, alone and with the surface coated with aliphatic acids, amides and alcohols. They found that as the water soluble group was changed in the order —$CONH_2$, —COOH, —CH_2OH, the mobility progressively decreased. They also found that the mobility was decreased by lowering the *p*H of the aqueous phase.

[1] Alty and Johnson, *Phil. Mag.*, 1935, 20, 129.

The present paper describes an attempt to determine the effect on the mobility, (*a*) of the physical state of the dispersed phase, and (*b*) of the chemical constitution of certain aliphatic esters.

Experimental.

The electrophoresis measurements were carried out macroscopically in the moving-boundary apparatus described by Price and Lewis,[2] and by Roberts.[3] The apparatus is capable of accurate temperature control, and measurements have been made at various temperatures ranging from 25° to 40° C. The data obtained are accurate to approximately 4 %. In general, the movement is towards the anode, *i.e.* the particles are negatively charged. The *p*H values were determined by a glass electrode in an oil thermostat at 25° C. for values up to *p*H 9. The results are accurate to ± 0·01 *p*H unit for buffered solutions and also for unbuffered solutions up to *p*H 5 ; for unbuffered solutions between *p*H 5 and 7 the error is ± 0·05. For *p*H values greater than 9, a hydrogen electrode was used, the results being accurate to 0·01 *p*H unit.

Three methods were employed for the preparation of dispersions, of which only the first is applicable to a substance in the solid state.

(1) 0·5 g. of the substance was dissolved in 10 ml. of hot absolute alcohol, and the resulting solution poured into 1 litre of boiled distilled water at 90° C.

(2) This method is applicable only to substances which melt below 50° C. One gram of the substance was floated on the surface of 1 litre of boiled distilled water at room temperature (in the case of liquids), or at a temperature 2° C. above the melting-point (in the case of solids melting between 15° and 50° C.), and steam at a pressure of 1½ metres of water was blown through a jet 1 mm. in diameter, situated at the oil-water interface. Rapid dispersion of the " oil " was effected.

(3) This method is applicable only to substances which melt below 95° C. One g. of the substance and 1 litre of boiled distilled water at room temperature (or at a temperature 5° C. above the melting-point in the case of substances melting above room temperature) were together passed several times through a mechanical homogeniser.

In all cases the dispersion was allowed to stand overnight before any electrophoretic mobility determinations were made. Dispersions prepared by all three methods had identical mobilities and contained from 0·03 to 0·05 % of the dispersed substance.

As is well known, mobilities are dependent on the ionic composition of the aqueous phase, and it is important, therefore, to maintain this constant as far as possible throughout the *p*H range. In this work all mobilities have been determined in the presence of 0·01 N sodium ion. Between *p*H 2 and 7 both dispersion and supernatant liquid contained 0·01 N sodium chloride, varying amounts of hydrochloric acid being added to alter the *p*H. Above *p*H 7 it is necessary to use a buffer to ensure that dispersion and supernatant liquid shall be exactly matched as regards *p*H ; 0·01 M sodium diborate was employed. In all cases the dispersion contained 2 % A.R. sucrose. This is necessary in order to increase the density, an essential requirement for the production of clear boundaries ; Northrop and Cullen [4] have shown that this small amount of sucrose does not affect the mobility.

Experimental Material.

Hydrocarbons.—A sample of dodecane was supplied by Fraenkel and Landau, Berlin. It was purified by repeated shaking with concentrated

[2] Price and Lewis, *Trans. Faraday Soc.*, 1933, **29**, 775.

[3] Roberts, *ibid.*, 1936, **32**, 1705.

[4] Northrop and Cullen, *J. Gen. Physiol.*, 1922, **4**, 635.

sulphuric acid to remove unsaturated compounds and subsequently washed, dried, and fractionally distilled. The final product was a colourless liquid, b.p. 78·6° C. (5 mm.). The ultimate criterion of purity was constancy of electrophoretic mobility.

A sample of octadecane from the same source was purified by Ham and Dean[5] in this laboratory.

Esters.—Samples of ethyl myristate, caproate and heptylate were supplied by Fraenkel and Landau, a sample of amyl acetate by Kahlbaum, and one of octyl acetate by B.D.H., Ltd. All these esters were liquids, and were purified by shaking with A.R. K_2CO_3 solution to remove acids followed by washing, drying and fractional distillation. The boiling-points of the final products were :—

Ethyl myristate,	146° C. (4 mm.).
Ethyl caproate,	166·4° C. (760 mm.).
Ethyl heptylate,	188° C. (760 mm.).
Amyl acetate,	139·2° C. (760 mm.).
Octyl acetate,	80° C. (4 mm.).

The remaining esters, with the exception of ethyl laurate and cetyl palmitate, which were kindly supplied chemically pure by Dr. T. Malkin of the University of Bristol, were synthesised by the writer.

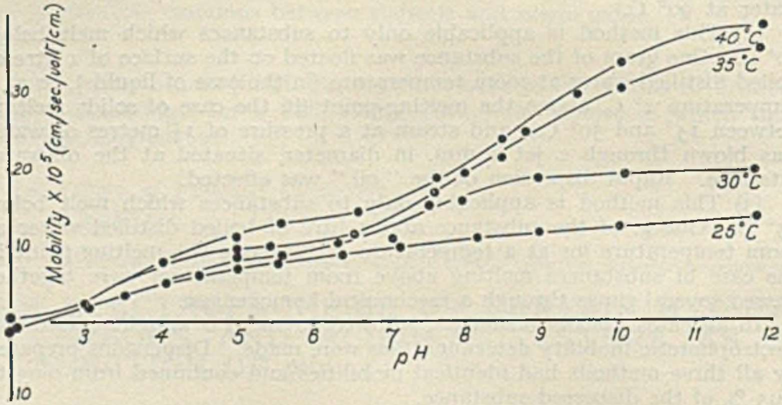

FIG. 1.—Octadecane (solid and liquid) at various temperatures.

Cetyl and octyl stearates were prepared by the method described by Whitby[6] from silver stearate and the alkyl halide. Cetyl and octadecyl acetates and ethyl stearate were made by condensing the appropriate acid and alcohol in the presence of hydrogen chloride.

After purification the products obtained had the following melting-points : cetyl stearate 56·9° C. ; octyl stearate 32·0° C. ; ethyl stearate 33·1° C. ; cetyl acetate 19·0° C. ; octadecyl acetate 32·8° C.

The Effect of the Physical State of the Dispersed Phase.

Figs. 1, 2 and 3 show the mobility — *p*H curves obtained for octadecane, dodecane and ethyl stearate at various temperatures. Octadecane (Fig. 1) is a solid hydrocarbon, m.p. 28° C. The lowest curve, therefore, represents the behaviour of the solid, and the other three that of the liquid hydrocarbon. The differences between these curves cannot be ascribed solely to alteration in the viscosity of the aqueous medium

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[5] Ham and Dean, *Trans. Faraday Soc.*, 1940, **36**, 52.
[6] Whitby, *J.C.S.*, 1926, 1458.

as the temperature is raised, for although this supposition would satisfactorily explain the small difference between the 35° and 40° C. curves, it fails to explain the much larger differences between the lower three curves.

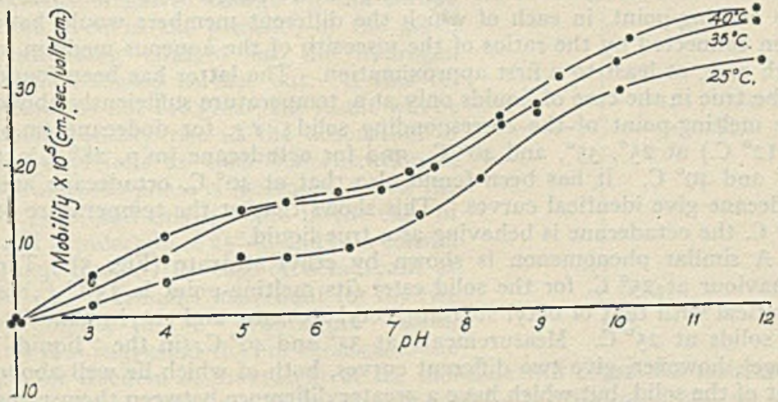

FIG. 2.—Dodecane (liquid) at various temperatures.

It has been suggested by many workers that in the process of fusion molecules do not pass over into a state which remains unchanged with increase in temperature until the boiling-point is reached, but that the

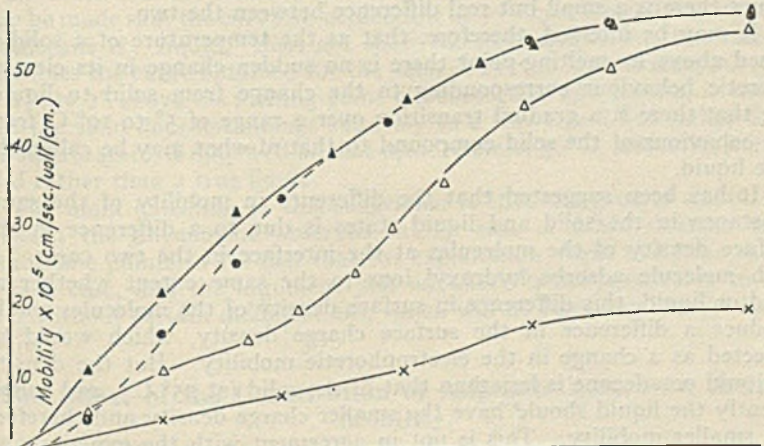

FIG. 3.

× Ethyl stearate (solid), 25° C.
△ Ethyl stearate (liquid), 35° C.
▲ Ethyl stearate (liquid), 40° C.
● Ethyl myristate (liquid), 40° C.

process of fusion represents but a partial breakdown of the crystalline structure. The results shown in Figs. 1 and 3 clearly bear out this idea. If, for the moment, the reason why the mobility of the liquid should be higher than that of the corresponding solid is ignored it is seen that as the temperature is raised past the melting-point there is no abrupt change from one type of curve to the other. It might have been expected that if the process of fusion represented a sudden definite transition from one physical state to another, then two distinct types of curve would have been obtained for the temperature ranges below and above the melting-point, in each of which the different members would have been connected by the ratios of the viscosity of the aqueous medium in each case, at least to a first approximation. The latter has been found to be true in the case of liquids only at a temperature sufficiently above the melting-point of the corresponding solid; *e.g.* for dodecane (m.p. — 12° C.) at 25°, 35°, and 40° C., and for octadecane (m.p. 28° C.) at 35° and 40° C. It has been found also that at 40° C. octadecane and dodecane give identical curves. This shows that at the temperature of 40° C. the octadecane is behaving as a true liquid.

A similar phenomenon is shown by ethyl stearate (Fig. 3). The behaviour at 25° C. for the solid ester (its melting-point is 33·1° C.) is identical with that of octyl stearate, cetyl stearate, and cetyl palmitate, all solids at 25° C. Measurements at 35° and 40° C. (in the "liquid" range), however, give two different curves, both of which lie well above that of the solid, but which have a greater difference between themselves than can be accounted for purely by alteration in viscosity of the medium. Ethyl myristate (m.p. 10·5° C.) was also investigated at 40° C. (Fig. 3), it being assumed that this ester was then sufficiently above its melting-point to behave as a true liquid. The resulting curve is identical with that of ethyl stearate over the range *p*H 6 to 12, although at lower *p*H values there is a small but real difference between the two.

It may be inferred, therefore, that as the temperature of a solid is raised above its melting-point there is no sudden change in its electrophoretic behaviour corresponding to the change from solid to liquid, but that there is a gradual transition over a range of 5° to 10° C. from the behaviour of the solid compound to that of what may be called the true liquid.

It has been suggested that the difference in mobility of the same substance in the solid and liquid states is due to a difference in the surface density of the molecules at the interface in the two cases. If each molecule adsorbs hydroxyl ions to the same extent whether as solid or liquid, this difference in surface density of the molecules would produce a difference in the surface charge density, which would be reflected as a change in the electrophoretic mobility. But the density of liquid octadecane is less than that of the solid (at 25° C.), and consequently the liquid should have the smaller charge density and therefore the smaller mobility. This is not in agreement with the experimental findings. Other possibilities present themselves (including streaming in the liquid droplet, cybotaxis and surface rearrangement), but none of them appear to afford an explanation of the behaviour observed.

The results for dodecane and octadecane may be considered from another point of view, namely the nature of the residual charge on the group projecting into the aqueous phase. The curve for solid octadecane at 25° C. which was obtained by Dickinson [7] in this laboratory, exhibits a slow, gradual rise throughout the *p*H range, the mobility never reaching a large value. This is the type of curve which would be expected. The end-group of the hydrocarbon has residual charges distributed as in

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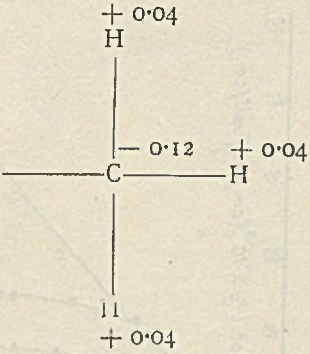
[7] Dickinson, Ph.D. Thesis, Liverpool, 1940.

(A),[8] and the net residual charge on the end-group is zero. There will, therefore, be no particular tendency for hydroxyl ions to be adsorbed at the surface, and indeed they will be likely to be repelled to some extent by the localised negative charge on the carbon atom even in the presence of the small neutralising charges on the hydrogen atoms situated further out. If this repulsion is not too great, the result will be a slow, steady rise in the adsorption of hydroxyl ions as their concentration in the aqueous phase is increased, *i.e.* as the *p*H rises, and this is found in the case of solid octadecane at 25° C. and to a certain extent also in the case of octadecane at 30° C. It remains to account for the rise in mobility in the "true liquid" state, and it is suggested that in these cases the greater freedom of movement of the molecule will cause less resistance to be offered to the repulsive force exerted by the hydroxyl ions on the carbon atom, and consequently the carbon atom may retract and leave in effect only the terminal hydrogen atoms in contact with the aqueous phase. This would mean an increase in the adsorption of hydroxyl ions, and so an increase in the primary charge density, which would be reflected as an increase in the mobility as is found by experiment. The objection may be made that the curve for octadecane at 30° C., at which temperature octadecane is "liquid," does not show the same behaviour, but rather resembles the curve obtained for the solid at 25° C. This is true, but 30° C. is only 2° above the melting-point of octadecane, and bearing in mind that the solid does not change suddenly to a true liquid but rather to a cybotactic state, it may well be that octadecane at 30° C. resembles a true solid rather than a true liquid.



(A)

The main objection to this suggestion is that the general similarity between the phenomena observed in the case of ethyl stearate and octadecane points to the fact that the explanation ought to be the same in each case, and the argument just advanced is not applicable to an ester without certain modifications, which will be considered in the next section.

The Effect of the Constitution of Aliphatic Esters on their Mobility.

The esters examined are of three types, classifiable according to the nature of their mobility—*p*H curves as follows :—

Type I.—Esters whose mobility—*p*H curves are depressed throughout the entire *p*H range (Figs. 4 and 5). These are cetyl palmitate, cetyl stearate, octyl stearate, the curves for which are indistinguishable, and octadecyl acetate—all solids at 25° C., to which temperature the foregoing statement particularly applies.

Type II.—Esters whose mobility —*p*H curve remains fairly flat in the acid region, but shows a sudden sharp rise in the weak alkaline region, the mobility eventually reaching the same figure at high *p*H values as in the case of esters of Type III (Figs. 4 and 6). The esters of

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[8] Eucken and Meyer, *Physikal. Z.*, 1929, 30, 397.

this type which have been investigated are amyl and octyl acetates, and ethyl caproate and heptylate. They are all liquid at 25° C.

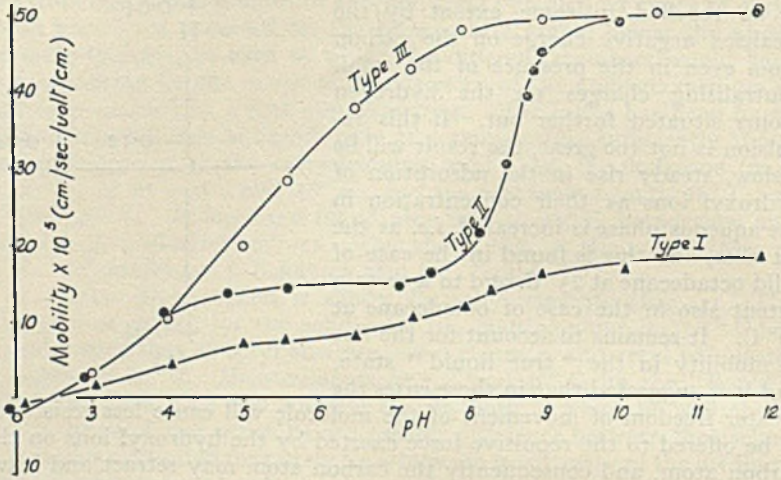

FIG. 4.

○ Ethyl laurate (liquid).
● Amyl acetate (liquid).
▲ Cetyl palmitate (solid).

Type III.—Esters whose mobility — *p*H curve rises steadily as the *p*H increases from 2 to 12, the mobility approaching a maximum of about 50 units (Figs. 4 and 7). Ethyl laurate and myristate are of this type. They also are liquid at 25° C.

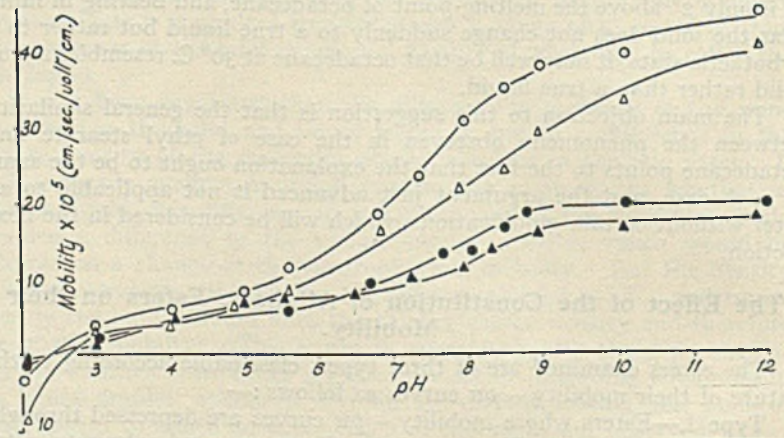

FIG. 5.

▲ Cetyl palmitate, cetyl stearate, octyl stearate (solids), 25° C.
△ Cetyl acetate (liquid), 25° C.
○ Octadecyl acetate (liquid), 35° C.
● Octadecyl acetate (solid), 25° C.

The esters of Type I will be considered first. These are represented by cetyl palmitate and stearate, octyl stearate and octadecyl acetate.

It has been shown by Eucken and Meyer [8] and by Smyth [9] that for esters in non-polar solvents the strong interaction of the polar groups prevents free rotation about the C—O bond, and only one configuration, the *trans*, is possible, whereas Alexander and Schulman,[10] working with films of esters on water, found that the aqueous substrate so

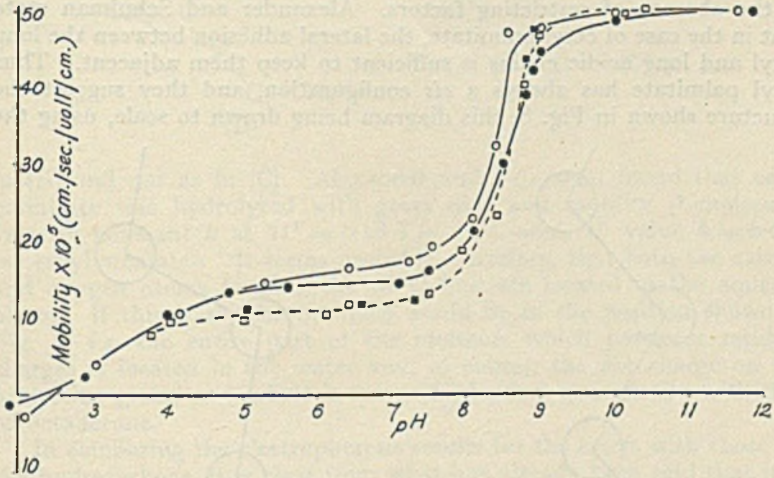

FIG. 6.

● Amyl acetate (liquid), 25° C.
○ Octyl acetate (liquid), 25° C.
■ Ethyl caproate (liquid), 25° C.
☐ Ethyl heptylate (liquid), 25° C.

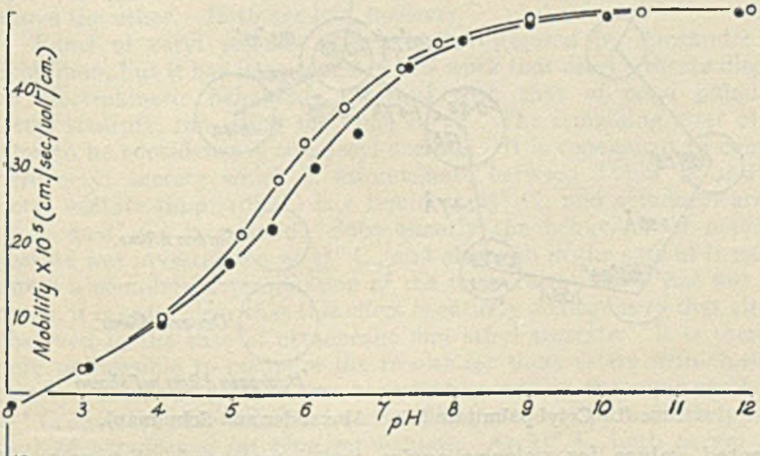

FIG. 7.

○ Ethyl laurate (liquid), 25° C.
● Ethyl myristate (liquid), 25° C.

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[9] Smyth, *J. Amer. Chem. Soc.*, 1931, 53, 527.

[10] Alexander and Schulman, *Proc. Roy. Soc.*, *A*, 1937, 161, 115.

decreased the interaction that both the *cis* and the *trans* configurations may exist, other factors such as the constitution of the ester and the film pressure being the determining conditions.

The same possibility of *cis* and *trans* forms exists in the present work in the absence of restricting factors. Alexander and Schulman state that in the case of cetyl palmitate, the lateral adhesion between the long alkyl and long acidic chains is sufficient to keep them adjacent. Thus cetyl palmitate has always a *cis* configuration, and they suggest the structure shown in Fig. 8, this diagram being drawn to scale, using the accepted values for valency angles and inter-atomic distances. Its probability is supported by the fact that, as pointed out by Alexander and Schulman, the calculated vertical component of the dipole moment (7 milli debyes) is in close agreement with the observed value (zero).

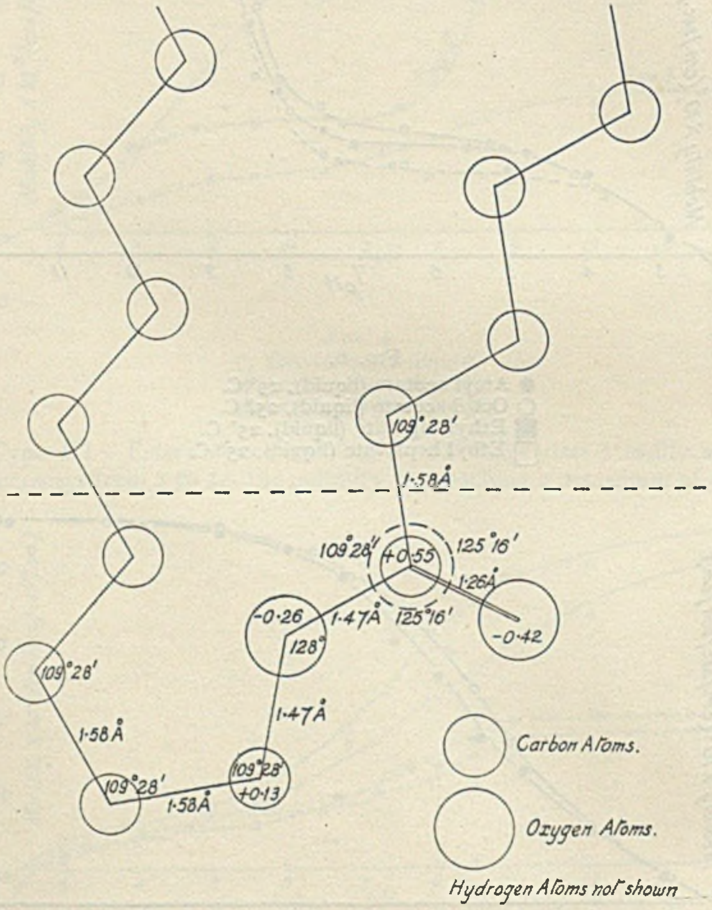

FIG. 8.—Cetyl palmitate (after Alexander and Schulman).

It should be noted that this comparison of the calculated value with the observed value determines only the inclination of the ester molecule to the water surface, and does not define their exact relative positions.

It has been shown by Polanyi and Szabo [11] by the use of isotopes of

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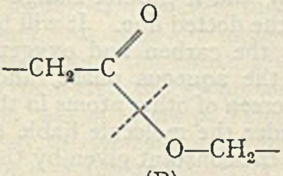
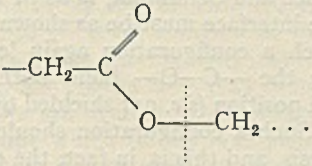
[11] Polanyi and Szabo, *Trans. Faraday Soc.*, 1934, 30, 508.

oxygen that in the saponification of an ester the break occurs as shown



(B)



(C)

in (B) and not as in (C). Alexander and Schulman found that cetyl palmitate was hydrolysed with great ease and rapidity (bimolecular velocity constant *k* at 21° = 0·18 l./g. mol./min., *cf.* value *k* = 0·005 for ethyl stearate). It seems probable, therefore, that both the carbon and oxygen atoms forming the C—O link are located in the aqueous phase. If this is so, the interface would be in the position shown in Fig. 8, *i.e.* the entire part of the molecule which possesses residual charges is located in the water and, of course, the net charge on the projecting group as a whole is zero, *i.e.* identical numerically with that of octadecane.

In comparing the electrophoresis results for the esters with those for the hydrocarbons, it is clear from what has already been said that it is only legitimate to make comparison between solid esters and solid octadecane (at 25° C.), and between liquid esters and dodecane at 25° C. In particular, therefore, the curve for cetyl palmitate (m.p. 54° C.) must be compared with that for octadecane at 25° C. When this is done, it is seen that, although the net residual charge on the end-group is apparently the same in each case (zero), the curve for cetyl palmitate lies slightly above the other. Both are low, however.

Films of cetyl stearate were not investigated by Alexander and Schulman, but it has been found in this work that cetyl stearate displays an electrokinetic behaviour identical with that of cetyl palmitate. Octyl stearate, too, gives the same curve. The remaining ester of this type to be considered is octadecyl acetate. It is convenient to consider here cetyl acetate which is intermediate between Types II and III. Cetyl acetate (m.p. 19° C.) is a liquid at 25° C., and octadecyl acetate (m.p. 32·8° C.) is a solid. Subsequently the behaviour of octadecyl acetate was investigated at 35° C., and although in the case of these two esters a complete determination of the temperature effect has not been made, it is quite clear that this effect is entirely analogous to that already observed in the case of octadecane and ethyl stearate. It is therefore only permissible to compare the results for these esters with those for the hydrocarbons at the same temperature and in the same state. At 25° C. the curve for octadecyl acetate lies 7·0 units approximately above that of octadecane (at high *p*H values). At 35° C. both curves have changed but the acetate still lies approximately 6 units higher than the hydrocarbon, and it may be expected that at higher temperatures a somewhat larger difference will be found, since at 35° C. octadecyl acetate is only 2·2° C. above its melting-point. It is seen also that at 25° C. the acetate curve lies approximately 2·5 units above that of cetyl palmitate. The difference between the curves for octadecyl acetate and cetyl palmitate is so small, as probably to be caused by some difference in shielding effect and not by a change in the net charge on the group projecting, *i.e.* zero as a whole.

The structure of the end-group in octadecyl acetate, as deduced by Alexander and Schulman, is as in Fig. 9, and if the net charge is to be zero the interface must be as shown by the dotted line. It will be noted that such a configuration again leaves the carbon and oxygen atoms forming the —C—O— bond both in the aqueous phase, and in an exposed position (*i.e.* not shielded by a screen of other atoms in the molecule). Such a configuration should render the molecule liable to rapid hydrolysis, and this is, in fact, the case, the constant given by the above workers being $k = 0{\cdot}15$. A reason is still required, however, why the electrophoretic mobility should be higher than that of cetyl palmitate, and higher still than that of octadecane. In this case there is no strain in the molecule, although the high local concentrations of positive and negative charges are the same as before. It must be assumed, therefore, that these two effects act in opposite directions. It is reasonable that local concentrations of charges should increase the electrophoretic mobility to a small extent, since the high positive charge on the carbon atom will probably exert an influence on hydroxyl ions even in the presence of the other neutralising charges, but it is not clear why the strain in the molecule should reduce the mobility. Cetyl acetate behaves somewhat similarly to octadecyl acetate, but as it is not known whether this substance is a true liquid at 25° C., or is still in the intermediate stage, too much reliance has not been placed on the shape of the curve.

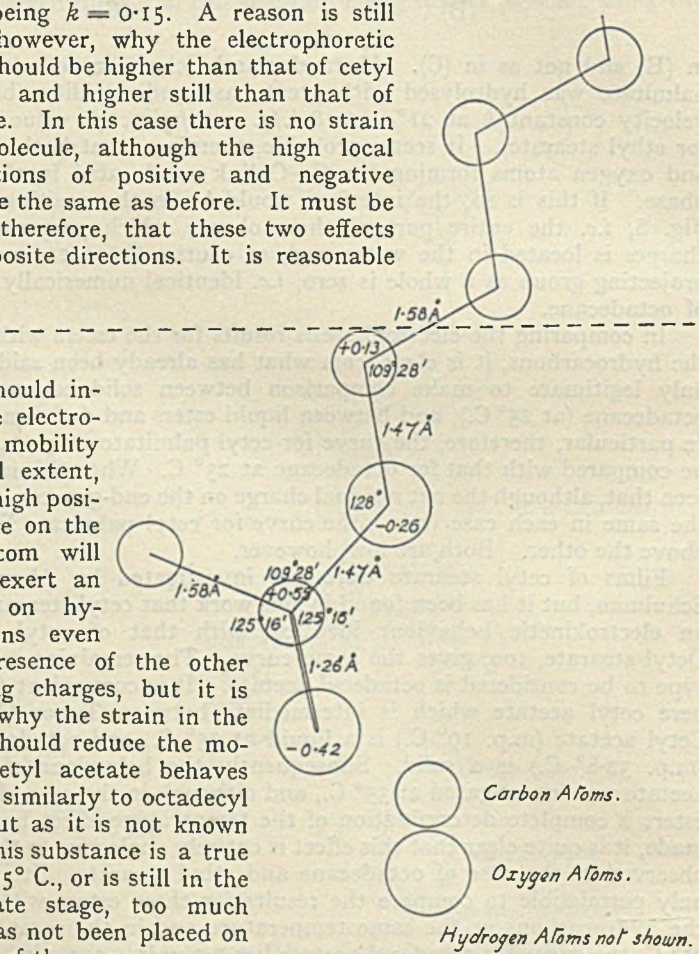


Fig. 9.—Octadecyl acetate (after Alexander and Schulman).

The high limiting value of the electrophoretic mobility exhibited by esters of Type III, *i.e.* ethyl laurate and ethyl myristate, strongly suggests the possession of a positive net residual charge on the projecting group, and furthermore, since the curves for ethyl myristate and laurate approach the same limiting mobility at high pH values as do the esters of Type II, it is probable that the numerical value of the charge is the same in the limit in both types. Whether we are to regard the Type III esters as *cis* or *trans*, however, is by no means clear on the existing evidence.

Thus, according to Adam,[12] the esters of Type III form condensed films on water at 25° C., and hence they will be of the *trans* type. It may be suggested, however, that these esters also exist in the *cis* form *when liquid*, but that the oxygen atom (— 0·26) remains in the ester phase throughout the entire *p*H range, thus leaving only the —C=O group in the water, this group carrying the charge of + 0·13 as required.

In the case of esters of Type II, we are dealing with configurations which lead to electrophoretic behaviour which in the acid region and up to *p*H = 8 resembles esters of Type I, the mobility then rapidly increasing with increase in *p*H, so that finally the behaviour is indistinguishable from esters of Type III. It would not seem possible to offer any satisfactory explanation of such behaviour until more is known regarding the connection between orientation and mobility in the case of the two " extreme " types denoted by I and III. It may be remarked, however, that the esters of Type II are of relatively low molecular weight, and consequently the possibility of change from one configuration to another as a function of *p*H cannot be excluded. At the same time, the degree of surface penetration of the ester by the aqueous phase and the alteration in degree of penetration with *p*H may play a greater part in the case of such esters than occurs in the more massive esters of Types I and III.

Summary.

The electrophoretic mobilities of various purified paraffin hydrocarbons and aliphatic esters have been determined in the presence of 0·01 N sodium ion over the range *p*H 2 to 12.

The difference in mobility produced by the change of state from solid to liquid cannot be ascribed to the difference in surface densities of the molecules produced by the change of state. The solid compounds on melting do not pass immediately to the true liquid state. It is suggested that an intermediate cybotactic state is involved.

Three different types of curve are obtained for aliphatic esters. These do not admit of any simple explanation, but certain considerations involving the residual charge on the group projecting into the aqueous phase is partly successful in explaining the results obtained.

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[12] Adam, *Physics and Chemistry of Surfaces*, 2nd ed., 1938.

VARIATION OF BOND STRENGTH WITH INTERNUCLEAR DISTANCE IN A GROUP OF HOMOLOGOUS DIATOMIC MOLECULES.

By R. F. Barrow.

Received 29th July, 1940.

In a preliminary note on the lengths and strengths of atomic bonds, Wrinch and Harker[1] draw attention to the regular variation of bond strength with internuclear distance for certain pairs of atoms, and refer

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[1] D. Wrinch and D. Harker, *J. Chem. Physics*, 1940, 8, 502.

also to the curves prepared by Fox and Martin[2] which exhibit the interrelation of these quantities in compounds containing the C—C bond.

The smooth variation discussed by these authors is not confined to bonds formed at different distances by the same pair of atoms. In a group of homologous diatomic molecules in which the bonds may be assumed to be of identical, though unspecified, nature throughout, a similar lowering of the bond strength with increasing internuclear distance is also found. This is clearly illustrated in the group of oxides, sulphides, selenides and tellurides of the group-IV(*b*) elements, data for the ground states of which have recently been collected.[3] In Fig. 1 the relation between D_0, the energy of dissociation, and r_e, the equilibrium internuclear distance, for these molecules is compared with the curve for the C—O bond, data on which have been taken from Pauling.[4] It must be emphasised that both curves are tentative. The C—O bond data are accepted uncritically, since further study of these has been promised by Wrinch and Harker. Uncertainties in the derivation of some of the other constants may be rather more serious. Thus, the D_0 values are taken from a smoothed curve of D_0 (obtained by extrapolation using the Morse expression) against reduced mass, and only six values of r_e have been determined by rotational analysis, the remainder being interpolated from a graph of $1/r_e^3$ against ω_e. Further, it is just possible that some of these molecules in the ground state dissociate into excited states of one or both atoms. The observed energy of dissociation would then, of course, no longer represent the chemical bond strength. However, there is some justification for believing that the dissociation products of all these molecules are the respective atoms in their ground states (see, for example, Sponer[5] and Barrow and Jevons[6]) ; the other errors mentioned are probably not large enough to affect the general shape of the curve.

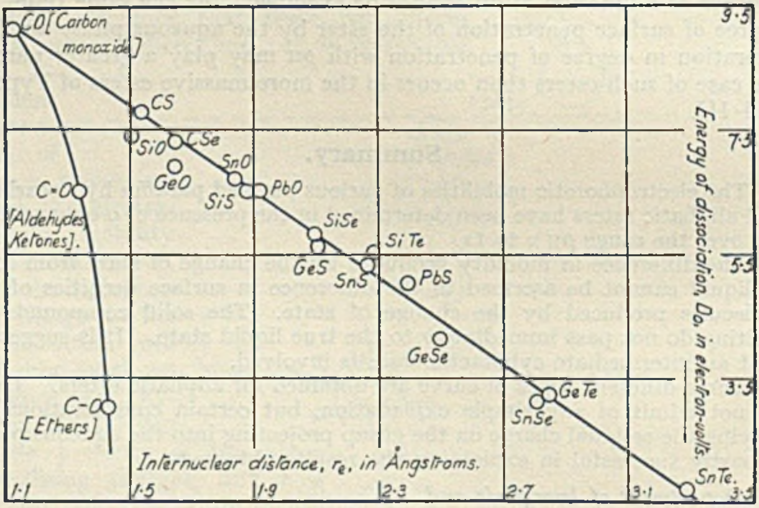

FIG. 1.

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[2] J. J. Fox and A. E. Martin, *J.C.S.*, 1938, 2106.

[3] R. F. Barrow and W. Jevons, *Proc. Physic. Soc.*, 1940, **52**, 534.

[4] L. Pauling, *The Nature of the Chemical Bond*, New York, 1939.

[5] H. Sponer, " *Molekülspektren. I. Tabellen*," Berlin, 1935.

[6] R. F. Barrow and W. Jevons, *Proc. Roy. Soc., A*, 1938, **169**, 45.

Bearing these uncertainties in mind, the close approach to linearity and the rather small departures of the individual points from the line are remarkable in view of the tenfold increase in reduced mass in passing from CO to SnTe, the extreme molecules. Comparison with the curve for the C—O bond makes it seem likely that the type of binding in all members of the series is closely similar to that obtaining in the ground state of carbon monoxide. The data further lends support to the view of Wrinch and Harker that the length of a bond can conveniently be regarded as determining its energy, and interpolation on such a graph may provide a method of evaluating bond strengths when no other means is available.

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ON THE STATISTICAL MECHANICS OF ASSEMBLIES WHOSE ENERGY-LEVELS DEPEND ON THE TEMPERATURE.

By G. S. Rushbrooke.

Communicated by C. A. Coulson.

Received 15*th August*, 1940.

§ 1. Introduction.

At first sight there is little room in the ordinary scheme of statistical mechanics[1] for energy-levels which depend on the temperature; for an energy-level is a primary concept while temperature is a secondary one derived, in some measure, from the energy-levels. It is given by the equilibrium value of a certain "selector-variable". We may think that in the mutual interaction of two parts of an assembly we have a clear case of energy-levels which depend, primarily, on the temperature: the physical state of either part of the assembly will depend on the temperature, and thus so also will its interaction with the other part of the assembly. But the ordinary rules of statistical mechanics are sufficient for dealing with this problem without introducing the concept of an interaction depending on the temperature: we have only to include in the partition-function, or phase-integral, terms from all the possible configurations of the systems of the assembly distributed among two phases.

Nevertheless, the idea of energy-levels which are functions of the temperature is as necessary physically as is, for instance, the crystalline picture of a solid. If we may think of the surface of an adsorbing solid as presenting to a neighbouring gas a definite pattern of sites suitable for adsorption, we may equally legitimately (it is, in fact, equally necessary that we do) say that the energy of adsorption for each of these sites is a certain function of the temperature of the solid. By energy of adsorption, of course, we mean the true energy of adsorption (in the sense of the first law of thermodynamics) and not merely the free-energy

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[1] R. H. Fowler, *Statistical Mechanics*, Cambridge, 1936.

of adsorption. Similarly, whenever we employ the concept of a dielectric medium with a dielectric constant which is a function of the temperature, we are obliged also to regard as explicit functions of the temperature all potential differences, heats of solution, etc., which depend directly upon the numerical value of this dielectric constant. There are other familiar instances in which the idea of energy-levels which depend on the temperature is equally desirable.

Now in dealing with a quasi-physical problem of this kind, in which there are energy-levels dependent on the temperature, we can frequently use methods of thermodynamics, and so avoid the need, real or apparent, for a more general statistical mechanics. An instance of this, for example, is Becker and Brattain's [2] treatment of the evaporation of electrons from a metal, when the work function depends on the temperature and the well-known Clausius-Clapeyron equation [3] is used. But such a combination of statistical and thermodynamical methods is not always either convenient or possible, and in attempts to deal with such problems purely statistically an error is frequently made owing to the lack of a recognised technique. This mistake is to introduce into the partition-function or distribution formulæ for the problem considered Boltzmann factors of the form

$$e^{-E/kT} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

when E is an energy-level (or the difference between two energy-levels) which depends in magnitude explicitly upon the temperature. As a typical example, we may quote Ewell and Eyring's [4] formula:

$$\eta = A \, . \, e^{\Delta E_{\text{vis.}}/kT}, \quad . \quad . \quad . \quad . \quad (2)$$

where η is the viscosity of a liquid, A is a constant, and $\Delta E_{\text{vis.}}$ is an activation energy for viscous flow: this formula is, according to Eyring's [5] theory of viscous flow, of the correct form when $\Delta E_{\text{vis.}}$ is a constant, independent of T; but its use is quite unjustified, and actually incorrect, when $\Delta E_{\text{vis.}}$ varies with the temperature, as it does in the paper of Ewell and Eyring.[4] * There is, indeed, no foundation at all in statistical mechanics for the use of Boltzmann factors of the form (1) when $E \equiv E(T)$.

We shall show below that the correct procedure when an energy-level, E, depends on the temperature is to replace the Boltzmann factor (1), which would be involved were E a constant, by

$$e^{-F(T)/kT}, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where $F(T)$ is the (Helmholtz) free-energy change associated with $E(T)$ by the Gibbs-Helmholtz relation (3)

$$F - T\left(\frac{\partial F}{\partial T}\right)_{V,\,N} = E \quad . \quad . \quad . \quad . \quad (4)$$

This result is not particularly original (*cf.* [1], §§ 6·9 and 8·4; [6] §§ 702 and 908), but it is worth emphasising, perhaps, on account of the frequency with which incorrect formulæ occur in recent papers. In

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[2] J. A. Becker and W. H. Brattain, *Physic. Rev.*, 1934, 45, 694.

[3] E. A. Guggenheim, *Modern Thermodynamics*, Methuen, 1933.

[4] R. H. Ewell and H. Eyring, *J. Chem. Physics*, 1937, 5, 726.

[5] H. Eyring, *J. Chem. Physics*, 1936, 4, 283.

* Table VI of this paper is correct as it stands, owing to a compensating error.

[6] R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics*, Cambridge, 1939.

§ 2 we shall show, by reasoning similar to that customarily employed in the theory of fluctuating forces (see, for example, Onsager's review of the theory of strong electrolytes[7]), how, for a special type of problem, it follows from elementary statistical principles; in § 3 more direct arguments, which the author has not seen elsewhere, suggest that it is of quite general validity.

§ 2. Fundamental Approach to the Problem.

We have shown in the introduction that temperature-dependent energy-levels occur in physical problems when, using physical insight, we short-circuit a full statistical treatment by considering a simpler problem in which the systems of the assembly move in certain average, physically appropriate, fields. Thus, in a rather vague sense, temperature-dependent energy-levels are always the result of some sort of preliminary averaging over the various possible states of the assembly.

Suppose, for instance, that we consider one system of many between which there are interatomic fields (*e.g.* one atom of a dense gas, or an ion in a solution). If we denote the momenta and co-ordinates of this particular system by (p_0, q_0) and those of the other systems, collectively, by (p, q) and $E(p_0, q_0, p, q, V)$ is the energy of the whole assembly, then the probability that q_0 lies between q'_0 and $q'_0 + \Delta q_0$ can be shown (see [7]) to be given by

$$\mathrm{f}(q'_0)\Delta q_0 = \frac{\iiint \mathrm{e}^{-E(p_0, q'_0, p, q, V)/kT}\, \mathrm{d}p_0 \,.\, \mathrm{d}p \,.\, \mathrm{d}q}{\iiiint \mathrm{e}^{-E(p_0, q_0, p, q, V)/kT}\, \mathrm{d}p_0 \,.\, \mathrm{d}q_0 \,.\, \mathrm{d}p \,.\, \mathrm{d}q}\Delta q_0. \qquad (5)$$

If, however, we were, from physical considerations, to say that the system (p_0, q_0) behaved as if it moved in a potential field $w(q_0)$, then we should write

$$\mathrm{f}(q'_0)\Delta q_0 = \frac{\mathrm{e}^{-w(q'_0)/kT}}{\int \mathrm{e}^{-w(q_0)/kT}\mathrm{d}q_0}\Delta q_0, \qquad (6)$$

and comparison of equations (5) and (6) shows that

$$\mathrm{e}^{-w(q'_0)/kT} = \text{const.} \iiint \mathrm{e}^{-E(p_0, q'_0, p, q, V)/kT}\, \mathrm{d}p_0 \,.\, \mathrm{d}p \,.\, \mathrm{d}q. \qquad (7)$$

This implies both that $w(q_0)$ is a function of T and also (since $F = -kT$. log . partition-function) that it has the nature of a free-energy rather than an ordinary energy (in the sense of the first law of thermodynamics).

From equation (7) it is customary to deduce the Einstein-Smolochowski result that $w(q'_0)$ is the potential of the average force-field acting on the particle at q'_0 (averaged over all p_0, p and q). But, for our present purpose, we are more interested in the connection between $w(q'_0)$ and the average energy of the assembly when the particular system in which we are interested is at q'_0. This energy is given by

$$\overline{E}(q'_0) = \frac{\iiint E(p_0, q'_0, p, q, V)\mathrm{e}^{-E(p_0, q'_0, p, q, V)/kT}\, \mathrm{d}p_0 \,.\, \mathrm{d}p \,.\, \mathrm{d}q}{\iiint \mathrm{e}^{-E(p_0, q'_0, p, q, V)/kT}\, \mathrm{d}p_0 \,.\, \mathrm{d}p \,.\, \mathrm{d}q}, \qquad (8)$$

and the first law of thermodynamics is satisfied if we regard this as just the potential energy of the particular system in which we are interested (considered by itself) when at q'_0. Clearly, from (7) and (8)

$$w(q'_0) - T\left(\frac{\partial w}{\partial T}\right)_V = \overline{E}(q'_0),$$

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[7] L. Onsager, *Chem. Rev.*, 1933, 13, 73.

i.e. $w(q'_0)$ is the (Helmholtz) free-energy corresponding to the true potential energy $\overline{E}(q'_0)$.

This result, which we wished to establish, is easily generalised to apply to any assembly which obeys classical statistics and for which the permissible energy-levels are all of the form

$$\epsilon = \epsilon_n + \epsilon(p, q), \quad . \quad . \quad . \quad . \quad (9)$$

where the ϵ_n's form, shall we say, a discrete set * and $\epsilon(p, q)$ stands for a contribution to the energy which depends on the momenta and co-ordinates of certain systems of the assembly. Such assemblies will include, *inter alia*, assemblies of which the systems form two phases, $\epsilon(p, q)$ denoting the total energy of one of these phases. Although, primarily, it is necessary to introduce the momenta and co-ordinates p, q in order to specify the energy-levels we are not interested in them further and shall show, in fact, that we can replace the set of energies $\epsilon(p, q)$ by one temperature-dependent energy $\epsilon(T)$.

For an assembly of this type the partition-function, or phase-integral, is of the form

$$\sum_n \iint e^{-\epsilon_n/kT} e^{-\epsilon(p, q)/kT} \varpi_n . \, dp \, . \, dq \quad . \quad . \quad . \quad (10)$$

i.e.

$$= \sum_n e^{-\epsilon_n/kT} \varpi_n e^{-F(T)/kT}$$

where

$$F(T) = - kT \log \iint e^{-\epsilon(p, q)/kT} \, dp \, . \, dq \quad . \quad . \quad (11)$$

If we write

$$\epsilon(T) = \overline{\epsilon(p, q)} = \frac{\iint \epsilon(p, q) e^{-\epsilon(p, q)/kT} \, dp \, . \, dq}{\iint e^{-\epsilon(p . q)/kT} \, dp \, . \, dq} \quad . \quad . \quad (12)$$

then $\epsilon(T)$ and $F(T)$ are connected by a Gibbs-Helmholtz relation of the form (4), and the important point again is that had we specified the possible total energies of the assembly as

$$\epsilon = \epsilon_n + \epsilon(T) \quad . \quad . \quad . \quad . \quad (13)$$

(which we might equally well have done, having defined $\epsilon(T)$ as the equilibrium value of $\epsilon(p, q)$), then the correct partition-function for the assembly would have been

$$\sum_n e^{-[\epsilon_n + F(T)]/kT} \varpi_n \quad . \quad . \quad . \quad . \quad (14)$$

and not

$$\sum_n e^{-[\epsilon_n + \epsilon(T)]/kT} \varpi_n : \quad . \quad . \quad . \quad . \quad (15)$$

this is the result stated at the end of § 1.

This completes our present discussion of temperature-dependent energy-levels from a fundamental point of view. We have dealt only with a particularly simple type of problem for which the temperature-dependent energy-levels arise, quite straightforwardly, as the result of a preliminary averaging over certain states of the assembly. As we have said above, such energy-levels must always be due, basically, to a preliminary averaging of much of this nature; but the general problem is too complex to be dealt with here. We can see, however, that their introduction is not necessarily an approximation. Even when it is, if

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* This condition, of course, is not essential to the analysis, and is introduced merely for convenience; $\epsilon(p, q)$ might equally well be a discrete set of energies too.

there are such cases, the result of using the temperature-dependent energy-levels correctly in a further statistical analysis will be as exact and justified as the physical picture in which they occur.

§ 3. A Direct Approach to the Problem.

We shall now approach the problem more directly, which means that we shall try to find a self-consistent formal scheme of equations, constituting a statistical mechanics to deal with assemblies whose energy-levels depend on the temperature, which shall

(i) give results compatible with the demands of thermodynamics,
(ii) go over into the ordinary well-established scheme of statistical mechanics when the energy-levels do not depend on the temperature.

The physical validity of the scheme, as of all statistical treatments indeed, must be left to be established *a posteriori*; but if the conditions (i) and (ii) are satisfied we may reasonably suppose that this will follow.

The generating-function (1) for a two-phase assembly when the energy-levels—symbolised, collectively or individually, by ϵ—do not depend on the temperature may be written symbolically as

$$G_A(xz^{\epsilon}) \,.\, G_B(xz^{\epsilon}), \qquad . \quad . \quad . \quad . \quad (16)$$

where x and z are two " selector variables ". The equilibrium properties of the assembly are then found from this generating-function by formulæ of the types

$$\overline{N}_A = \lambda \frac{\partial}{\partial \lambda} \log G_A(\lambda \vartheta^{\epsilon}) \qquad . \quad . \quad . \quad . \quad (17)$$

$$\overline{E}_A = \vartheta \frac{\partial}{\partial \vartheta} \log G_A(\lambda \vartheta^{\epsilon}) \qquad . \quad . \quad . \quad . \quad (18)$$

etc.

where λ and ϑ are equilibrium values of x and z found from the conditions

$$\left.\begin{aligned} \overline{N}_A + \overline{N}_B &= X, \\ \overline{E}_A + \overline{E}_B &= E. \end{aligned}\right. \qquad . \quad . \quad . \quad . \quad (19)$$

Here X is the total number of systems in the assembly, E is its total energy, and the other symbols also have the same meanings that they have in [1]. The formal scheme can be identified with that of thermodynamics if

$$\begin{aligned} & \log \vartheta = -1/kT \\ \text{and} \qquad & \log \lambda = \mu/kT, \end{aligned} \qquad . \quad . \quad . \quad . \quad (20)$$

where μ is a chemical potential. The external reactions of the assembly are given by equations of the form

$$p_A = - \sum_i \overline{n}_{A,i} \left(\frac{\partial \epsilon_{A,i}(V_A)}{\partial V_A} \right)_{T, N_A}, \qquad . \quad . \quad . \quad (21)$$

where $\epsilon_{A,i}$ are the energy-levels accessible to systems of the phase A, etc.

It follows from equations (17) and (18) that

$$\overline{E}_A = \sum_i \overline{n}_{A,i}\, \epsilon_{A,i}\,, \qquad . \quad . \quad . \quad . \quad (22)$$

which is a necessary formula if the first law of thermodynamics is to be obeyed. But this equation could not be deduced if ϵ, in equation (18), were a function of ϑ. This alone shows that the use, in statistical theory, of Boltzmann factors of the form

$$\mathrm{e}^{-E(T)/kT}$$

is not thermodynamically sound.†

The whole formal scheme implicit in the use of generating-functions has to be modified when the energies involved depend on the temperature.

A suitable modification can be obtained as follows. Instead of starting from a generating-function of the form (16) we start now with one of the form

$$G_{\mathrm{A}}\left(x\mathrm{e}^{-\int_z^{z_0}\frac{\epsilon(z)}{z}\mathrm{d}z}\right)G_{\mathrm{B}}\left(x\mathrm{e}^{-\int_z^{z_0}\frac{\epsilon(z)}{z}\mathrm{d}z}\right), \quad . \quad . \quad (23)$$

where $\epsilon(z)$ and the given energies $\epsilon(T)$ are connected through the relation

$$\log z = -1/kT,$$

and z_0 is a constant; see § 4 below. Then we can retain equations of the types (17) and (18) and equation (22) follows, as a necessary consequence, as before. In fact, the new statistical scheme is again formally identical with the scheme of thermodynamics, provided only that now the formulæ for the external reactions are replaced by formulæ of the type

$$p_{\mathrm{A}} = \sum_i \bar{n}_{\mathrm{A},i}\, kT\frac{\partial}{\partial V_{\mathrm{A}}}\left[-\int_T^{T_0}\frac{\epsilon_{\mathrm{A},i}(V_{\mathrm{A}},T)}{kT^2}\mathrm{d}T\right]_T \quad . \quad . \quad (24)$$

And it can be shown indeed that this change would be expected from purely thermodynamical arguments, *i.e.* an appropriate Carnot cycle.

Since the new generating-function goes over into the old one when all the ϵ's involved are constants (independent of T), and all the other formulæ then have their normal well-known forms, it appears that we have, by starting from the new generating-function (23), constructed a scheme of statistical mechanics which obeys the requirements (i) and (ii) above.

The argument could be given in more detail and with greater generality, but to do so would not add anything essentially new to it. It remains to be added here only that

$$\mathrm{e}^{-\int_z^{z_0}\frac{\epsilon(z)}{z}\mathrm{d}z} = \mathrm{e}^{-\int_T^{T_0}\frac{\epsilon(T)}{kT^2}\mathrm{d}T} = \mathrm{e}^{-F(T)/kT}, \quad . \quad . \quad (25)$$

where $F(T)$ is the free-energy change associated with $\epsilon(T)$ by the equation

$$F - T\left(\frac{\partial F}{\partial T}\right)_{V,N} = \epsilon(T).$$

This is the result described at the end of the introductory paragraph, and justified for certain particular temperature-dependent energy-levels by the more analytical arguments of § 2. The arguments of the present section suggests that it is of quite general validity.

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† See also "The Thermodynamic Derivation of Langmuir's Isotherm," by G. S. Rushbrooke and C. A. Coulson.[8]

[8] G. S. Rushbrooke and C. A. Coulson, *Proc. Camb. Phil. Soc.*, 1940, **36**, 248.

§ 4. An Example.

We conclude with an example of the statistical methods outlined in §§ 2 and 3. It provides an opportunity for considering the correct choice of limits in the integrals in formulæ (24) and (25).

It is customary (see [1]) to derive Langmuir's isotherm formula for the adsorption of a perfect monatomic gas by combining together the three formulæ

$$\theta = \lambda e^{W/kT}/[1 + \lambda e^{W/kT}] \quad . \quad . \quad . \quad (26)$$

$$(X - N) = \lambda\frac{\partial}{\partial\lambda}\left[\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\lambda V\right] \quad . \quad . \quad (27)$$

and

$$pV = (X - N)kT \quad . \quad . \quad . \quad . \quad (28)$$

Here θ is the fraction of surface covered by adsorbed gas atoms, N is the number of atoms adsorbed, X is the total number of gas atoms adsorbed or not adsorbed, W is the heat of adsorption, and p, V, and T are the pressure, volume and temperature respectively of the gas phase. Combining the equations gives

$$\theta = \frac{p}{p + \left(\frac{2\pi m}{h^2}\right)^{3/2}(kT)^{5/2}e^{-W/kT}}, \quad . \quad . \quad (29)$$

which is Langmuir's isotherm formula.

Now the second of these formulæ, (27), expresses the fact that a gas atom which is not adsorbed can be in any of the energy states accessible to an atom of a perfect gas enclosed in a volume V. The expression enclosed by square brackets is the partition-function for all these energy states. But the average (equilibrium) value of the energy of an atom of a perfect monatomic gas at temperature T is well-known to be

$$3/2 \, . \, kT.$$

So we might equally well say that the adsorbable atoms of the assembly are either

(i) adsorbed: energy $-W$,
(ii) in an energy-level of height $3/2 \, . \, kT$, and degeneracy proportional to V.

We have here an example of an energy-level whose value depends on the temperature, and we can deal with the problem by the methods which we have outlined.

Equations (26) and (28) remain unchanged, but equation (27) is now replaced by

$$\begin{aligned}(X - N) &= \lambda\frac{\partial}{\partial\lambda}\left[\lambda V e^{-\int_T^{T_0}\frac{3}{2}kT\frac{dT}{kT^2}}\right] \quad . \quad . \quad (30)\\ &= \lambda V\left(\frac{T}{T_0}\right)^{3/2}.\end{aligned}$$

Using this equation instead of (27) gives

$$\theta = \frac{p}{p + \left(\frac{T}{T_0}\right)^{3/2}kTe^{-W/kT}},$$

which is equation (29) again except that the constant $\left(\frac{2\pi mk}{h^2}\right)^{3/2}$ therein is replaced by the unknown constant $T_0^{-3/2}$.

We can give no general rule for fixing the upper limits of the integrals in formulæ (24) and (25). The ambiguity has its counterpart in the use of the Gibbs-Helmholtz equation to derive free-energy, F, from true energy, E. We need to know, for instance, the entropy of the substance at some one particular temperature. There is, however, one simple class of problems for which the upper limit, T_0, can be fixed at ∞. If it is possible to formulate exactly the same problem, physically, but with the stipulation that the energy-level no longer depends on the temperature, then we must fix this limit, T_0, at ∞ in order that the solution involving

$$e^{-\int_T^{T_0}\frac{E(T)}{kT^2}dT}$$

may go over into the solution involving simply $e^{-E/kT}$ when the dependence of $E(T)$ on T is ignored.

Summary.

The well-known formalism of statistical mechanics is extended to apply to assemblies for which the permissible energy-levels depend on the temperature.

If an energy E, occurring in a partition-function, depends on the temperature, then the corresponding Boltzmann factor $e^{-E(T)/kT}$ must always be replaced by $e^{-F(T)/kT}$, where $F(T)$ is the Helmholtz free-energy related to $E(T)$ by a Gibbs-Helmholtz relation. This is necessary in order that the statistical scheme may conform to the demands of thermodynamics.

Finally, I have to thank Professor R. H. Fowler, F.R.S., and Dr. E. A. Guggenheim for stimulating correspondence and their kind interest in the paper, and the Council of University College, Dundee, for a research grant enabling me to work at Dundee.

THE OCCURRENCE OF NEGATIVE IONS IN THE GLOW DISCHARGE THROUGH OXYGEN AND OTHER GASES.

By R. Winstanley Lunt and A. H. Gregg.

Received 4th June, 1940.

Whilst there are numerous experiments establishing the existence of negative ions in weakly ionised gases, there are comparatively few establishing the existence of such ions in considerable concentration in the much more intense ionisation of the cold cathode glow discharge.[1, 6, 9, 12, 22, 23, 24] The presence of negative ions in oxygen discharges is of importance in relation to the mechanism of the formation of ozone in such discharges. It has been suggested that the energy liberated in the recombination of negative with positive ions is avail-

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[1] Spencer-Smith, *Phil. Mag.*, 1934, 19, 806.

able for effecting the synthesis of ozone;[2] if this is the case, the rate of formation of ozone should be related to the stationary concentration of negative ions. On the other hand, the data for the photo-reaction[3] together with the statistical theory of discharge reaction[4] suggest that ozone formation in discharges is not likely to be connected with the occurrence of negative (or positive) ions.

This paper describes an attempt to identify, and to determine the stationary concentration relative to that of the electrons, of the negative ions present in cold cathode glow discharges through oxygen at pressures of about 1 mm. Hg. Cylinder electrolytic oxygen (containing 0·2 % of hydrogen) was used because ozone formation from this gas had been extensively investigated in other experiments in this laboratory to be published elsewhere. Negative ions were sought for in a gas stream emerging from the tube containing the discharge, the magnetic technique of Spencer-Smith[1] being used for their detection and identification. Within the sensitivity of the apparatus no negative ions were detected in the negative glow or the Faraday dark space; but in the positive column negative atomic ions were found in concentrations comparable with those of the electrons.

These results appear at first sight to support the view that the formation of ozone is connected with the existence of negative ions because Brewer and Westhaver[2] reported that, under conditions of pressure and current density comparable with those in the experiments now reported, the formation of ozone is detectable in the positive column only. A more detailed analysis of the problem, to be published elsewhere, leads, however, to the conclusion that the observed stationary concentrations of negative ions are inadequate to account for more than an insignificant fraction of the observed rates of ozone formation.

Experimental.

The apparatus was constructed in two main parts which are represented diagrammatically in Fig. 1, the discharge tube *Y* and the analysing chamber *Z*; these are joined together by a taper joint sealed with picein wax. (In Fig. 1, *Z* is shown partly withdrawn from *Y*.)

The discharge tube, *Y*, was constructed in pyrex glass and contained a parallel electrode system, *AC*, mounted on a cage made of pyrex rod, the electrodes being movable in a vertical plane by the winch *W*. The thermionic filament *X* was inserted in a side tube to provide a beam of electrons necessary for an adjustment of the apparatus to be described later. For the range of pressures in which the apparatus was found to function, a positive column did not develop using the electrodes *A* and *C*. In order to investigate positive column conditions the filament was removed from the side tube, and the side tube was extended to a convenient distance, an auxiliary cathode being sealed in the remote end. Oxygen or other gas under investigation was admitted through a needle valve and side tube *H*; an auxiliary connection from *J* led through a liquid air trap to a Macleod gauge, and also to a pump for initial evacuation of the tube.

The hollow probe electrode *P* served to withdraw a beam of negatively charged particles from the discharge to the analysing chamber; this consisted of a brass bolt through which was drilled a channel 0·075 mm. in diameter, and which was securely mounted in a hollow soapstone cylinder which fitted tightly over the arm *M* of the analysing chamber. Electrical

[2] Brewer and Westhaver, *J. Physic. Chem.*, 1930, 34, 1280.
[3] Bonhoeffer and Harteck, *Photochemie*, Leipzig, 1933.
[4] Emeléus and Lunt, *Trans. Faraday Soc.*, 1936, 32, 1504.

connection to *P* was effected by a glass sheathed lead which was carried through the wall of the analysing chamber by an insulated vacuum tight bushing *B*. The end of the arm *M* was closed except for a small central orifice *Q* of diameter 0·125 mm. which served to focus the beam of negatively charged particles entering the chamber, and for a series of holes, *O*, which were drilled in the outer rim facing *P* in order to facilitate the evacuation of the space between *Q* and *P*. The distance between *Q* and the near side of *P* was 5 mm.

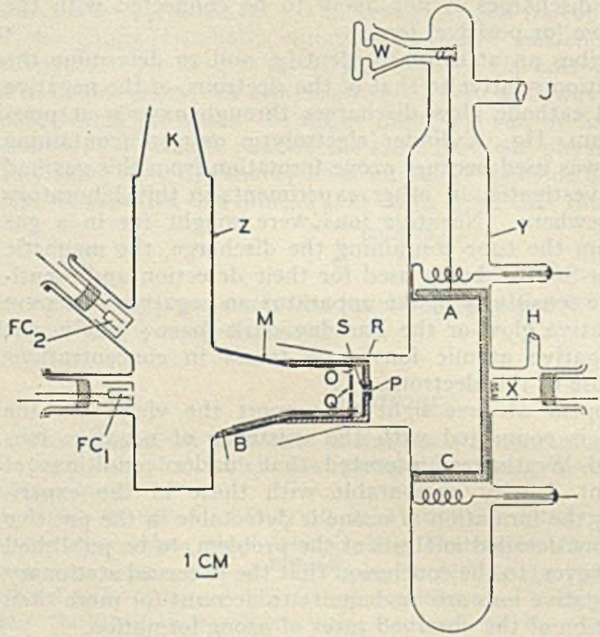

FIG. 1.

The analysing chamber, *Z*, was constructed entirely in brass, the Faraday cylinders FC_1 and FC_2 being mounted on glass valve stems sealed in with picein. It was directly connected at *K* to a large oil diffusion pump, and it was thus possible to maintain a pressure of less than 10^{-4} mm. in *Z*, and so ensure a very small probability of collision for ions traversing *Z* on their path to the collecting electrode. The size of the orifice in *P*, the capacity of the diffusion pump, and the necessity for low pressures in *Z*, restricted the maximum pressure in the discharge tube to about 0·7 mm.

Auxiliary Apparatus and Method of Assembly.

In order to minimise stray magnetic fields the tube was assembled in a position as far removed as possible from steel clamps, gas and water pipes, and other magnetic material, all the supports for the apparatus being of wood.

The inconvenience of balancing out the horizontal component of the earth's field was avoided by placing the axis of the analysing chamber along the line of action of this field.

Two horizontal coils, one below, and one above the analysing chamber and two smaller horizontal coils above and below *M* were used to counteract the vertical component of the earth's field. For uniformity the small coils were of such a size and distance apart that they gave the same maximum field as the larger coils for the same current.

In addition to the coils compensating the earth's field two vertical coils of 40 turns and 10 cm. diameter were placed on each side of the analysing chamber. These gave a horizontal field by which the electrons could be bent in a vertical plane and thus be deflected to the upper Faraday cylinder FC_2. The much larger fields necessary to deflect any ions were obtained from an electromagnet whose poles were placed in the centre of the two vertical coils and as close to the analysing chamber as possible. The method used to calibrate the magnet will be described later. When the magnet was in use it was necessary to shield the discharge tube completely with Mu-metal shields to prevent distortion of the discharge by the large magnetic field.

The current for the main discharge was produced by a 4000 volt motor generator and was regulated by a saturated diode; and the necessary potentials for the probe and accelerating electrodes were derived from accumulator batteries.

The currents to the Faraday cylinders were measured by means of a quadrant electrometer, all leads and connections to the Faraday cylinder and electrometer being carefully screened.

Experimental Procedure.

1. Detection of Negative Ions.

Before the commencement of a run the pressure in the apparatus was maintained at 10^{-7} mm. Hg for at least an hour, all the glass parts being warmed with a hand blow-pipe in order to remove occluded gas as far as possible; the reduction valve was then adjusted to admit gas (usually oxygen) and the pressure allowed to attain a constant value, when the discharge was switched on. It was found that after the discharge had been running for about 15-20 minutes the pressure was constant and the discharge fairly steady.

After the space potential had been determined approximately as in the experiments of Spencer-Smith,[1] the potential of the probe was adjusted to 5 volts positive to the space potential. Q was maintained at 60 volts positive to P except in the experiments to determine the mass of the negative ions.

After the current in the compensating coils had been adjusted to the standard value, the total current, I, to the collector FC_1 was then determined. Any electrons in the beam to FC_1 were then deflected by allowing a suitable current to flow in the vertical deflecting coils; the residual current to FC_1, I_i, is then due to negative ions, and the ratio of negative ions to electrons in the sampling beam is then given sensibly by I_i/I.*

No attempt was made to determine the absolute value of the currents I, I_i, but the electrometer leak, which varied somewhat with the atmospheric humidity, excluded the detection of currents smaller than about $10^{-4}I$; the apparatus was thus unable to detect negative ions in the sampling beam unless these were present in amount exceeding about 10^{-4} of that of the electrons.

In order to estimate the relative stationary concentration of ions and electrons in the discharge itself from the beam intensities, it is necessary to take account of the fact that, on account of their much greater mobility, electrons are preferentially attracted to the probe, P. It is difficult to make any exact allowance for this effect, but since it is known that the mobility of negative ions is of the same order as that of similar positive ions, it follows that electrons are preferentially attracted by a factor of the order of 10^2. Since the lower limit of the relative concentration of ions to electrons in the beam detectable by the apparatus is about 10^{-4}, it follows that the lower limit of the relative stationary concentration *in the discharge itself* which can be detected is about 10^{-2}.

2. The Identification of the Negative Ions.

For any given conditions in which negative ions were detected in the ion beam from Q to FC_1, the ratio of the charge to the mass of the ions,

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* Strictly, the ratio of the two beams should be taken as the ratio of the constant negative ion current to the difference between the total current and the constant negative ion current; the error introduced by using the ratio I_i/I is, however, less than 5 % (*cf.* Table I).

e/m, was determined by measuring the current I_m through the magnet coils, which determines the field required to deflect the ion beam from FC_1 to FC_2; such measurements were carried out for a series of values of the potential between P and Q, V_{PQ}.

If the ion beam from Q to FC_1 were extremely narrow and homogeneous in kind and velocity, there would be a critical value of I_m necessary to deflect the beam from FC_1 to FC_2, and the curve relating the ion current I_i' reaching FC_2 to I_m would show a single sharp maximum. Since the actual ion beam has a finite width, and is not quite homogeneous in velocity,† the curves describing I_i' as a function of I_m show a maximum which is broadened to an extent determined by these factors. If there is more than one species of ion present, there will be a corresponding number of maxima; in the special case that two ions are present, the e/m values of which are but slightly different, the curve for I_i' as a function of I_m will be equivalent to the superposition of two curves with closely placed maxima, and the broadening of each maximum from the causes mentioned above may be so large that the individual maxima in the curve for the total ion current to FC_2 are not distinguishable.

The relation between e/m and the magnet field at which I_i' is a maximum follows from classical theory. A particle of velocity v cm. sec.$^{-1}$, charge e e.s.u., and mass m g., moving in a uniform magnetic field H will follow a path the curvature, ρ, of which is given by

$$mv^2/\rho = Hev. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Apart from any small energy the ions may have in the discharge before entering the channel in P, the energy of the ions in the beam emerging from Q is V_{PQ} electron volts, and hence their velocity v is given by

$$v = (2 \times 10^8 V_{PQ}/m)^{0\cdot5}. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The distances x_1, and y_1, between Q and FC_1, and between FC_1 and FC_2 respectively, are such that the curvature of the path of an ion from Q to FC_2 is in any case large; to a close approximation it then follows that

$$d^2y/dx^2 = 1/\rho \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

and hence

$$y_1 = \iint (eH/mv) \, . \, dx \, . \, dx$$

or, evaluating the numerical term, and substituting for v from (2),

$$y_1 = 7{\cdot}07 \times 10^{-5} \, (e/m)^{0\cdot5} \, . \, V_{PQ}^{-0\cdot5} \iint H \, . \, dx \, . \, dx. \quad . \quad . \quad (4)$$

When the integral in (4) is evaluated, and y_1 is known from the mechanical dimensions of the apparatus, e/m may at once be evaluated.

In the present case the field H was not uniform, and hence it became necessary to evaluate the integral in (4) graphically. This was accomplished by measuring the intensity of the field as a function of the distance x from Q to FC_1; and from these values $\int H \, . \, dx$ was computed as a function of x. The area of the curve giving this integral as a function of x between the limits $x = 0$ (at Q) and $x = x_1$ (at FC_1) then gives the required integral, $\iint H \, . \, dx \, . \, dx$. This procedure was carried out for a series of values of I_m, and a curve was constructed giving the values of $\iint H \, . \, dx \, . \, dx$ as a function of I_m; from this curve the value of the integral in (4) corresponding to the value of I_m at which the ion current to FC_2 attained its maximum value was read off, and hence, knowing y_1, the corresponding value of e/m was evaluated.

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† An inhomogeneity of the beam may arise if the ions in the discharge before they enter the channel in P have an energy distribution; since the mean energy of the ions in the discharge is almost certainly less than 1 volt, the inhomogeneity is small provided that V_{PQ} is large compared with this value.

Experimental Results.

Using the electrodes A and C in oxygen at pressures from 0·1 to 0·7 mm. Hg, and with discharge currents of 1, 5, and 8 milliamps., it was found that no negative ions could be detected when the position of the electrode system was adjusted so that the probe P was adjacent to either the cathode glow or the Faraday dark space. The stationary concentration of negative ions of any kind in these zones is therefore less than about 10^{-2} of that of the electrons. Furthermore, it follows that no detectable amounts of negative ions are formed in the channel through the probe electrode P.

In order to investigate the negative ions present in the positive column, the electrodes A and C were connected in parallel as an anode, and the auxiliary (cold) electrode in the side tube facing the probe was placed at a conveniently remote position, and was used as the cathode. In oxygen, at pressures from 0·4 to 0·7 mm., and with discharge currents from 1 to 9 milliamps., a visually uniform positive column was obtained. Under these conditions a fairly well-defined maximum was found in the curves representing the dependence of I_i' on I_m'; from these the values of I_m' corresponding with the maximum could be read with an estimated uncertainty of 10 % or less. A single maximum was found indicating that only a single species of negative ion was present; the magnetic fields used were large enough to have detected O_2^- ions if present, but not O_3^-.

The relative magnitudes of the ion currents reaching FC_1 varied from about 5 % of that of the electron current to about 0·04 %, depending on the pressure and the discharge current. These data are given in Table I below. At the pressure 0·45 mm. and for a discharge current of 1·5 milliamps., the ratio of the electric force in the positive column to the gas pressure, Xp^{-1}, was about 80 ± 20 volts cm.$^{-1}$ mm. Hg^{-1}; at the higher pressures Xp^{-1} was somewhat smaller, and at all pressures diminished somewhat with the current.*

TABLE I.

I_i/I, THE RATIO OF THE ION TO ELECTRON CURRENTS DRAWN FROM THE POSITIVE COLUMN.

Expt. No.	p (mm.)	Discharge Current, m.a.	I_i/I
10	0·40	1·5	0·048
17	0·45	1·3	0·0095
11	0·45	1·3	0·023
16	0·45	1·5	0·022
15	0·45	2·0	0·019
13	0·45	2·4	0·014
14	0·45	2·6	0·013
12	0·45	2·7	0·010
18	0·50	0·5	0·022
19	0·55	1·0	0·0125
20	0·55	1·5	0·0080
22	0·55	1·55	0·0067
21	0·55	3·8	0·00042
5	0·75	1·1	0·024
4	0·72	1·1	0·016
1	0·66	1·5	0·019
2	0·68	2·9	0·0059
6	0·70	2·9	0·0012
3	0·68	9·0	0·0005

It will be seen from Table I that the relative concentration of negative ions to electrons in the sampling beam is highest at the lowest pressures

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* The importance of measuring Xp^{-1} precisely was not realised at the time the experiments were carried out; the values are approximate estimates based on the electrode potential under these conditions, and those of the previous paragraph when the positive column was small or absent.

investigated; the value in experiment 10 may, however, be fortuitously high, because other experiments at comparable current densities, for example, Nos. 11, 16, 20, 21, and 1, suggest that the dependence on gas pressure is not very large. In each of the three ranges of pressure it is clear that the relative concentration diminishes markedly as the discharge current is increased.

When considered in conjunction with the factor 10^{-2} discussed on page 1065, the fact that the relative concentration in the sampling beam is about 10^{-2} shows that in the discharge itself the concentrations of negative ions and electrons were about the same.

The Identity of the Ions in Oxygen.—The identity of the ions to which Table I relates was determined by finding the value of I_m necessary to deflect the ion beam from FC_1 to FC_2 for a series of values of the potential between P and Q, V_{PQ}, and hence determining e/m from (4). The curves relating I_i' with I_m were not characterised by uniformly sharp maxima, experiments in which the discharge was unsteady giving ill-defined maxima. The data for four experiments in which relatively sharp maxima were obtained together with the corresponding values of e/m and M, the atomic weight assuming unit charge on the ion, are given in Table II.

The mean molecular weight found for the negative ions, 17·2, strongly suggests that the ions are O^- and that the numerical discrepancy arises from experimental inaccuracies. It is, however, pertinent to consider the following facts which make this inference somewhat uncertain. Firstly, it is well known that water is readily formed from mixtures of hydrogen and oxygen in discharges, and it has already been mentioned that the electrolytic oxygen used contained 0·2 % of hydrogen. Secondly, Smyth and Mueller[5] have shown that OH^- ions (but not H_2O^- ions) are readily formed from water vapour; Bradbury [7 (a)] has given theoretical reasons for supposing that singlet molecules such as water do not form negative ions. There is thus the possibility that, despite the fact that the gas consists of 99·8 % oxygen in the present experiments, the negative ions observed might be OH^- having the molecular weight 17. In order to resolve this uncertainty, similar experiments were carried out on water vapour, oxygen containing appreciable amounts of water vapour, ammonia, and hydrogen chloride; in these gases it is known from independent experiments that negative ions are formed by the passage of a discharge.[6, 7 (b), 7 (c), 12, 14, 20, 21, 22, 24]

TABLE II.

e/m AND M FOR THE IONS IN OXYGEN.

V_{PQ}	$\iint H\,.\,dx\,.\,dx$	e/m (e.m.u.)	M
60 volts	$0·98\,.\,10^4$	$5·5\,.\,10^2$	17·4
90 ,,	1·15	6·0	15·9
120 ,,	1·37	5·6	17·1
180 ,,	1·75	5·2	18·3
	mean	5·6 ± 0·2	17·2 ± 0·7

Negative Ions in other Gases.—The introduction of water vopour, carefully purified by distillation at low pressure, into the type of positive column discharge to which the experiments on Tables I and II relate, gave a single broad maximum in the curve connecting I_i' with I_m'; for comparable values of V_{PQ} the value of I_m' corresponding with the maximum, and hence also the value of M, were found to be slightly in excess of the corresponding values for oxygen. The maximum was so ill-defined,

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[5] Smyth and Meuller, *Physic. Rev.*, 1933, 43, 116.

[6] J. J. and G. P. Thomson, *Conduction of Electricity through Gases*, Cambridge, 1933, Vol. I, 80.

[7] (*a*) Bradbury, *J. Chem. Physics*, 1934, 2, 840; (*b*) *ibid.*, 1934, 2, 835; (*c*) *ibid.*, 1934, 2, 827.

however, that no very precise values of e/m and M could be determined; the average of a number of determinations gave the value $M = 18 \pm 1{\cdot}5$. Furthermore, this broadness of the maximum persisted for many hours of running the discharge if oxygen was admitted to the apparatus in place of water vapour.

Since H_2O^- ions have never been detected, and since their formation is theoretically improbable, [7 (a), 12] it is reasonable to conclude that the value $M = 18$ corresponds with OH^- ions. It then follows that the ions to which Tables I and II relate are O^-; and that the persistence of a broad maximum for oxygen containing a little water vapour is most probably attributed to the coexistence of maxima, corresponding with O^- and OH^-, which are too close to be resolved by the apparatus; and that the experimental determinations of M are too high by about 1 unit in this range of M. Such an error is possible because of the uncertainty in the correction that should be applied to V_{PQ} for the initial energy of the ions entering the channel in P, and because of the experimental difficulty in determining precisely the variation of H with x, and hence of the value of $\iint H \, . \, dx \, . \, dx$.

Using ammonia of purity greater than 99·99 %, two species of negative ions were found in the positive column discharge; the principal maximum in the curves relating I_i' with I_m occurred at values of I_m slightly less than the corresponding values for oxygen, and the average of several experiments led to the value $M = 16{\cdot}5 \pm 1$. The subsidiary maximum was small and not well defined; it corresponded to a value of M of about 1·5.

Again, since NH_3^- ions have never been detected, and since their formation is theoretically improbable, [7 (a), 12, 14] it is probable that the value $M = 16{\cdot}5$ corresponds to either NH^- or NH_2^- ions, or to a mixture of both. It is well known that NH molecules are formed in considerable amount by discharges through ammonia, and since such molecules are iso-electronic with oxygen atoms they may be expected to exhibit similar properties; it is therefore likely that the ions found are[8] NH^-. Despite the uncertainty as to whether NH_2^- ions are present in addition, the value of M found is consistent with the identifications suggested by the data for oxygen and water vapour, and with the view that the errors in the determinations lead to values of M which are too high by about one unit. The other species present in small relative amount and having a value of M of about 1·5 must be either H_2^- or H^-, or a mixture of these ions.

When the positive column discharge in carefully refractionated hydrogen chloride was likewise examined for negative ions, only one species was found for discharge currents greater than 1 milliamp.; at much lower currents of about 0·1 milliamp. a second species of ion of much smaller mass and in small relative amount appeared in addition, and it is noteworthy that this lighter ion could no longer be detected if V_{PQ} were increased beyond 120 volts. In this gas the probe P was surmounted by an anode glow under all conditions, and the potential across this glow affects the velocity of the ions entering the channel in P; in addition the discharge was so unsteady that the values of I_m for which I_i' attained its maximum could not be determined. The magnetic fields necessary to deflect the ions to FC_2 were, however, of the magnitude expected from previous data to be those corresponding to HCl^- or Cl^- ions, and to a very light ion having an M of about 2.

Discussion of Results.

The most striking results of the experiments in oxygen are :—

(1) In the positive column, for pressures about 0·5 mm. Hg, for current densities of about 0·5 ma. cm.$^{-2}$ and for values of Xp^{-1} about

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[8] McNeill, *Ph.D. Thesis*, Belfast, 1937; *Phil. Mag.*, 1938, **25**, 471.

80, the stationary concentration of negative atomic ions is about the same as that of the electrons, but tends to diminish as the current density is increased; under these conditions no negative molecular ions were detected, and the sensitivity of the apparatus was such that it may be inferred that their stationary concentration must have been less than about 1 % of that of the electrons.

(2) In the negative glow and Faraday dark space, for the same range of pressures and current densities, no negative ions were detected and hence the stationary concentration of both atomic and molecular ions must have been less than about 1 % of that of the electrons.

It is interesting to consider these results in relation to the characteristic properties of the various zones of the cold cathode glow discharge,[4, 9, 10] and to the data for the information of negative ions in oxygen in other ways.[11, 12]

Bradbury[11] has determined the attachment constant, h, for an electron swarm drifting in a uniform electric field so that the current density is low, and over a range of Xp^{-1} from about 1 to 20; the mechanism of the attachment has been discussed by Bloch and Bradbury[13] who conclude that negative molecular ions are formed. Bradbury[11] found that h fell rapidly from an initial value of about $3 \cdot 10^{-4}$ at $Xp^{-1} = 0{\cdot}5$ to a minimum of about $0{\cdot}5 \,.\, 10^{-4}$ at $Xp^{-1} = 2$ and after passing through a maximum of about $4 \cdot 10^{-4}$ at $Xp^{-1} = 8$, again diminished as Xp^{-1} was further increased. The relation between h and β, the current efficiency of the electron collision process concerned as defined by Emeléus and Lunt for the case of an electron swarm moving through a gas under the influence of a uniform electric field is given by :—[14]

$$\beta p^{-1} = 1{\cdot}32 \times 10^{15} \,.\, Xp^{-1} \,.\, W^{-2} \,.\, h,$$

where W cm. sec.$^{-1}$ is the drift velocity of the electrons. Hence R, the rate of electron collision resulting in attachment, per cm.^{3} per sec., follows from expression (4) of Emeléus and Lunt as :—[4]

$$R = 1{\cdot}32 \times 10^{15} \,.\, p \,.\, I_e \,.\, Xp^{-1} \,.\, W^{-2} \,.\, h,$$

where I_e is the electron drift current density, which may be approximately identified with the total current density as measured by experiment.[4] Now it is known that in oxygen the term $(Xp^{-1} \,.\, W^{-2})$ diminishes as Xp^{-1} increases; [15] hence if h diminishes as Xp^{-1} is increased, R diminishes much more rapidly. Thus, if the progressive diminution in h observed by Bradbury[11] in the range of Xp^{-1} from 8 to 20 extends to the range concerned in the present experiments, about 80, which appears probable on theoretical grounds,[13] it is to be expected that R for the formation of negative molecular ions will be small; for example, if for $Xp^{-1} = 80$, h is assumed to be 10^{-4}, then[15] since $W = 2{\cdot}85 \,.\, 10^7$, and taking for the present experiments the values $p = 0{\cdot}5$ and $I_e = 3 \cdot 10^{15}$, we find $R = 2 \cdot 10^{13}$.

In a similar way, if we suppose that the value of Xp^{-1} in the negative glow and Faraday dark space is about 1, corresponding[11] to which

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[9] Darrow, *Electrical Phenomena in Gases.*

[10] Greeves and Johnson, *Phil. Mag.*, 1936, 21, 659.

[11] Bradbury, *Physic. Rev.*, 1933, 44, 883.

[12] Massey, *Negative Ions*, Cambridge, 1938.

[13] Bloch and Bradbury, *Physic. Rev.*, 1935, 48, 689.

[14] Bailey and Duncanson, *Phil. Mag.*, 1930, 10, 145.

[15] Brose, *ibid.*, 1925, 50, 536.

$h = 10^{-4}$ and[15] $W = 0{\cdot}22 . 10^7$, we find the slightly greater value $R = 4 \times 10^{13}$. This value is not inconsistent with the experimental failure to detect negative molecular ions in these zones because for the closely similar value of R found above for the positive column, such ions were also not detected.

Lozier[16] has investigated the production of negative ions in oxygen resulting from the passage of a homogeneous electron beam through the gas and, for our present purposes, the most significant of his results is that atomic negative ions are formed by electrons having energy in the range 5-10 el.-v.; the mechanism of the process has been discussed by Massey and Smith.[17, 12] By comparison with Lozier's results for carbon monoxide,[16] his data for oxygen lead to the estimate of $0{\cdot}005\pi a_0^2$ for the mean cross-section for negative atomic ion formation in the above energy range. Now Emeléus, Lunt and Meek[18] have shown that, by assuming a Maxwellian electron energy distribution, the cross-section data for simple ionisation by electron impact may be used to calculate the Townsend coefficient of ionisation αp^{-1} (that is, the 'βp^{-1}' for ionisation), in fair agreement with experiment for values of Xp^{-1} as large as 80; it is therefore a reasonable inference that the same distribution function may be used in conjunction with the cross-section estimated from Lozier's data in order to calculate approximately βp^{-1}, and hence R, for the formation of negative atomic ions.* By proceeding in this way we find for $Xp^{-1} = 80$ that $R = 4{\cdot}10^{13}$. It will at once be noticed that, within the accuracy of the calculations, this value of R is sensibly the same as that derived previously for the formation of negative molecular ions in the positive column. Whilst it is difficult to perform a similar calculation for R in the negative glow, the theory[4] considered in conjunction with the electrical data for this zone[10] leads to the expectation that R in the negative glow will be at least of the same order of magnitude as in the positive column.

The experimental results now reported, considered in conjunction with the calculated values of R, thus suggest that in the positive column negative molecular ions are much more readily destroyed than atomic ions, and that in the negative glow both types of ions are very rapidly destroyed. Whilst there are many known ways in which negative ions may be destroyed,[12, 17] the available data appear to be inadequate to estimate the corresponding rates of destruction in the present experiments and thus identify the particular processes concerned.

Although the experiments with ammonia and hydrogen chloride were carried out only to check the value of the ratio of the charge to the mass of the ions found in oxygen, it is interesting to note that the ease with which negative ions were detected in the positive column discharge through these gases is at least consistent with the large values of h, and the trend of these with Xp^{-1}, as reported by Bradbury[7 (c)] and by Bailey and Duncanson[14] in ammonia, and with the dependence of βp^{-1} for attachment on Xp^{-1} in hydrogen chloride.[21] In addition, for

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[16] Lozier, *Physic. Rev.*, 1934, 46, 268.

[17] Massey and Smith, *Proc. Roy. Soc., A*, 1936, 155, 472.

[18] Emeléus, Lunt and Meek, *ibid.*, 156, 394.

* Examples of such calculations of R for various types of electron collisions in hydrogen have been discussed by Lunt and Meek.[19]

[19] Lunt and Meek, *ibid.*, 157, 146.

[20] Bailey and Higgs, *Phil. Mag.*, 1929, 8, 277.

[21] Bailey and Healey, *ibid.*, 1935, 19, 725.

discharges through hydrogen chloride, the experiments of Zimmermann[22] afford ample evidence of the presence of numerous negative ions.

Summary.

In glow discharges through oxygen at pressures of about 0·5 mm., negative atomic ions have been detected in the positive column for values of Xp^{-1} about 80, their stationary concentration being comparable with that of the electrons. Under these conditions no negative ions have been detected in the negative glow or Faraday dark space, and the results show that their stationary concentration cannot have exceeded about 1 % of that of the electrons.

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University College,
London.

Trinity College,
Dublin.

[22] Zimmermann, *Z. Physik*, 1937, 104, 309.

[23] Emeléus and Sayers, *Proc. Roy. Irish Acad., A*, 1938, 44, 7.

[24] Tüxen, *Z. Physik*, 1936, 103, 463.

CHEMICAL REACTION IN ELECTRIC DISCHARGES. PART III. THE MEANING OF Φ, THE ELECTROCHEMICAL ANALOGUE OF THE PHOTO-CHEMICAL QUANTUM YIELD, AND THE FACTORS CONTROLLING Φ IN THE STATIONARY STATE.

By R. Winstanley Lunt and G. E. Swindell.

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The statistical theory of collisions involving electrons and reactant molecules (briefly, "electron-reactant" collisions) of Part I[1] of this series offers a possible quantitative explanation for many characteristics of the kinetics of reactions initiated by the passage of a steady electrical discharge through a system of constant, or nearly constant, composition. This explanation is based on marked similarities frequently observed between the following sets of quantities:—

(1) The rate in collisions per cm.^{3} per sec. of a specified type of electron-reactant collision as computed for some given experimental conditions, and the derived quantities (*cf.* Part I), the current and energy efficiencies for such collisions; and

(2) The rate in molecules per cm.^{3} per sec. of formation of the observed reaction product in the same experimental conditions, and the

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[1] Emeléus and Lunt, *Trans. Faraday Soc.*, 1936, 32, 1504.

derived quantities, or electrical reaction velocity constants, the current and energy efficiencies for the formation of this product (*cf.* Part I).

The explanation is not complete, however, unless the one or more types of electron-reactant collisions concerned are identified together with the immediate products, termed "active species," of such collisions which initiate the chemical processes leading to the formation of the observed product, and the detailed steps by which the active species leads to the observed product. The necessity for these identifications is taken account of by the introduction of the factor Φ: this is defined in Part I as the ratio of the rate of formation of the observed reaction product to the rate of the electron-reactant collisions concerned; alternatively, it is the ratio of the corresponding two current and energy efficiencies. These identifications and the elucidation of the factors controlling Φ are thus the main problem in tracing the mechanism of discharge reaction. In this paper we consider the factors controlling Φ.

It is clear that a parallelism between the corresponding quantities cited in (1) and (2) above arises only when Φ is constant, or sensibly so. It transpires from the analysis developed in this paper that such a constancy of Φ is to be expected only when the rate of generation and the fractional concentration of the active species is small; that is, in general, Φ is likely to depend on all the conditions in any given experiment, and Φ tends to become constant in certain limiting conditions only. Only for the case of reactions involving a branching chain mechanism is a constancy of Φ improbable.

It is mentioned in Part I that the factors controlling Φ must be similar to those controlling the quantum yield in reactions initiated by light absorption but modified by the factors arising in discharges only; and it may be recalled that the quantum yield in photo-reactions is often sensibly constant over a considerable range of experimental conditions. The aim of the present paper can thus be seen to be equivalent to an extension of Leighton's analysis * of the photo-chemical problem [2] to the rather different conditions arising in discharges. For this purpose we have introduced the additional quantity f,† termed the "fractional utilisation of the active species," and which is the fraction of the active species initially produced which is consumed in forming the observed product. The analysis of the factors controlling f shows that the value of λ_a, the fractional concentration of the active species, is of prime importance. It transpires that a discussion of the stationary state of a system in which discharge reaction occurs readily yields formal expressions for the dependence of λ_a on the discharge parameters. The corresponding dependence of f, and hence of Φ, can then be deduced.

A stationary state of a discharge reaction arises when the electrical factors are maintained constant together with the fractional concentrations of the reactants and all other species present, the system being at a constant total pressure or concentration. We restrict considera-

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* In Leighton's notation [2] Φ is the photo-chemical quantum yield; his ϕ is strictly analogous to the ϕ_1 of this paper, and his ρ to the present $f\phi_2$. Thus for photo-reactions Leighton defines Φ as $\rho\phi$; and in this paper Φ for discharge reaction is defined as $f\phi_1\phi_2$.

[2] Leighton, *The Determination of the Mechanism of Photo-Chemical Reaction, Actualités Scientifiques*, No. 655, Paris, 1938.

† In the so-called equilibrium state the product is not removed from the system and is decomposed by the discharge (or decomposes spontaneously) to reform the reactant; an example of this is furnished by the oxygen-ozone reaction.

tion, however, to the class of stationary states that arise when the final product of the reaction is removed at a steady rate which is fast enough to ensure that the fractional concentration of this species is very small;* the requirement of constant total concentration then demands that reactant molecules are fed into the system at a compensating rate. In the stationary state the rate of generation of any one species in any volume element of the system must be equal to the sum of the rates at which it is lost by reaction and by other processes. A knowledge of these latter processes, especially in the case of the active species, is thus essential to a formal statement of the stationary state. When these are known together with the identifications mentioned previously, the fractional concentration of the active (or other) species, λ_a, is the only unknown in the formal statement of the stationary state corresponding with any given experimental conditions. When λ_a is known, the absolute rates at which the species is consumed in the various possible ways can be computed, and the evaluation of f, the fractional utilisation, can then be carried out. Except in the case when branching chain mechanisms are involved, f is the only variable factor controlling the magnitude of Φ; and a knowledge of the dependence of f on the experimental conditions then suffices to completely specify that of Φ.

After stating the other factors controlling the magnitude of Φ and introducing the formal definition of f, we develop convenient formal expressions for the stationary state and for the absolute rates of the principal types of processes by which the active (and other) species are likely to be consumed. This formal treatment relates mainly to the active species, and hence the solution of these expressions leads to values of λ_a. The extension of this analysis to other species is formally very similar, and the necessary modifications are briefly outlined. In all cases attention is directed particularly to the special case when λ_a (or the λ for any other species under consideration) is small compared with unity.

This restriction to the case when the λ's are small for all species other than the reactants derives partly from the earlier restriction on the type of stationary state to be considered, but also from the practical consideration that the necessary auxiliary data for the computation of the absolute rate of electron-reactant collisions according to the theory of Part I effectively limit the application of this theory to gases consisting almost entirely of reactant molecules. The formulation of the expressions for the stationary state in terms of the active species is also based on expedience, and experience gained in attempting to trace reaction mechanisms. For it appears that the rate determining step in the mechanism as a whole is often the primary reaction involving the active species.

The expressions for the stationary state and for the rates of the various processes concerned take special forms depending on the particular discharge zone (*cf.* Part I) concerned. In this paper we consider only the forms appropriate to reaction in the uniform positive column and the negative glow. The fact that the latter zone is characterised by a chemical activity which varies considerably throughout the zone necessitates an approximate treatment of the volume rates of the processes concerned. For this purpose it is assumed that the volume of the zone varies inversely as the total pressure, which is approximately

* See note † on page 1073.

in accordance with experiment. Another model for this zone, recently introduced by Emeléus and Beck[3] is, however, especially convenient for the discussion of diffusion.

The definition of quantities and symbols defined in the earlier papers of this series is avoided as far as possible here.

1. The Quantity Φ and its Component Factors.

This quantity in Part I is defined as the number of molecules of the observed product formed per initial electron-reactant collision of the kind which generates the active species. This definition requires restatement in order that it shall be practically useful in the detailed interpretation of discharge reaction. We state first the idealised case, and then indicate what particular approximations are appropriate in relation to the two discharge zones in which the kinetics of reaction have been extensively examined, the uniform positive column and the negative glow. If the discharge zone in which the active species is generated is isotropic and co-extensive with the reaction zone, and if the system is in a stationary state (*cf.* Introduction) so that the reaction is proceeding steadily, it follows from the above definition that in any volume element

$$\Phi = R_p/R_{er} \quad . \quad . \quad . \quad . \quad (1)$$

where R_p is the rate of formation of the observed product in molecules cm.$^{-3}$ sec.$^{-1}$, and R_{er} is the rate of the relevant electron-reactant collisions cm.$^{-3}$ sec.$^{-1}$. The further discussion of Φ necessitates a consideration of the kind of information which is available for the two discharge zones mentioned above. We consider here only the case of the typical experimental arrangement in which the electrodes are plane and perpendicular to the axis of a cylindrical insulating discharge tube, and discharge conditions such that the negative glow and positive column (if present) extend radially to the wall of the discharge tube.*

For a uniform positive column the electron concentration and drift current density vary radially (*cf.* § 2.45, expression 14.4), but the mean electron energy is practically constant[4] and there is little doubt that the discharge and reaction zones are sensibly co-extensive. From the theory of Part I it then follows that η, the energy efficiency of any given kind of electron-reactant collisions, is independent of position, but that R_{er} varies radially as the current density. The quantity derivable directly from experiment relating to the observed product is, strictly speaking, the radial average value of R_p. It follows that the only characteristic of Φ directly determinable is its radial average value. When, however, the destruction of the active species at the wall is small, which appears to be a case which occurs frequently in practice, diffusion ensures that the radial variation of its concentration is small (*cf.* § 2.45). The radial variation of R_{er} is then unimportant, for the same condition would be reached if it is supposed that the rate of generation of the active species is constant at all points and equal to

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[3] Emeléus and Beck, *Proc. R. Irish Acad.* (*in the press*).

* For the pressure range concerned in practice, upwards of 0·1 mm., the positive space charge sheath separating the positive column and the negative glow from the wall is so small that its volume may be neglected compared with that of the zones themselves. Moreover, its chemical activity is almost certainly extremely small, as is also that of the large zone of positive space charge, the cathode dark space.

[4] Druyvesteyn, *Ann. Physik*, 1933, 81, 571.

the radial average value of R_{er}. Furthermore, when the radial variation of the concentration of the active species is small, it follows that for any product resulting from its homogeneous reaction R_p varies but little radially. With these reservations, then, it is seen that Φ as given by (1) when R_{er} is replaced by its radial average value is likely to be nearly independent of position, or in the notation of Part I

$$\Phi = R_{p,\mathrm{P}}/R_{er} \quad . \quad . \quad . \quad . \quad (1.1)$$

where $\bar{R}_{er}$ now denotes the radial average value; and there is the corresponding relation

$$\Phi = \eta_{p,\mathrm{P}}/\eta \quad . \quad . \quad . \quad . \quad (1.11)$$

where $\eta_{p,\mathrm{P}}$ is radial average energy efficiency for the formation of the observed product as deduced from experiment. These relations derive their importance from the fact that, when the necessary auxiliary data are available, R_{er} and η can be computed by theory (*cf.* Part I).

On the other hand, in the negative glow the electron concentration and mean energy vary markedly in the direction of the discharge tube axis as well as radially. Although diffusion of the active species tends to diminish the dependence of R_p on position, it is not possible to envisage for this zone the approximate uniformity that has been seen to be permissible for the positive column; in addition, it is less certain that the discharge and reaction zones are co-extensive. Then Φ depends on position, but the volume average value for an assumed identity between the discharge and reaction zones is given by

$$\Phi = \bar{R}_{p,\mathrm{N}}/\bar{R}_{er} \quad . \quad . \quad . \quad . \quad (1.2)$$

using the nomenclature of Part I and introducing a bar over the symbols to denote volume averages.

The alternative definition of Φ for this zone is

$$\Phi = \beta_{p,\mathrm{N}}/\beta_f \quad . \quad . \quad . \quad . \quad (1.21)$$

where $\beta_{p,\mathrm{N}}$ denotes the current efficiency as determined by experiment for the formation of the observed product, and β_f is the current efficiency for the relevant electron-reactant collisions (*cf.* Part I). Defined in this way Φ is independent of uncertainties arising from the lack of isotropy and the possibility that the discharge and reaction zones are not co-extensive; from the definitions of the β's (*cf.* Part I) it remains, however, an average quantity. This definition is of importance because the properties of β_f can be deduced from theory (*cf.* Part I) although its absolute magnitude is not usually known from experiment. But the definitions of Φ that are of practical importance in tracing the detailed mechanism of discharge reaction transpire to be those given by (1.1) and (1.2).

We may resolve Φ into three factors so that

$$\Phi = f\phi_1\phi_2\,, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where ϕ_1 is the number of active species which are the immediate product of a single electron-reactant collision of the particular type concerned, and does not depend on any experimental factors. R_a, the rate of production of the active species, is then given by

$$R_a = \phi_1 R_{er} + R_{af}\,, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where R_{af} denotes the rate of formation of the active species in other ways. R_{af} is usually zero, but there are some cases in which it appears to be important. When R_{af} is zero R_a follows the dependence of R_{er} on position; ϕ_2 is the number of molecules of the observed product which are formed per particle of the active species reacting *to give this product only;* that is, it denotes the maximum number of product molecules that can be formed per particle of the active species by the mechanism which is operative. Thus ϕ_2 is a characteristic of the reaction mechanism, and except in the case of branching chain mechanisms, is a constant independent of position and of all experimental factors. In what follows we exclude the consideration of branching chain mechanisms.* The quantity f, conveniently termed "the fractional utilisation" of the active species, takes account of the possibility that the active species may react or be destroyed in processes other than that leading to the formation of the observed product. It is defined as the fraction of the active species which is consumed in forming the observed product, or

$$f = R_{ac}/(R_{ac} + R_{\mathrm{L}}), \qquad . \quad . \quad . \quad . \quad (4)$$

where R_{ac} and R_{L} denote, respectively, the rate at which the species is consumed in forming the observed product and in all other ways. Alternatively, by the same definition, we have

$$R_{ac} = f(\phi_1 R_{er} + R_{af}); \qquad . \quad . \quad . \quad . \quad (4\cdot1)$$

and it is seen that ϕ_2 is expressed formally by

$$\phi_2 = R_p/R_{ac}. \qquad . \quad . \quad . \quad . \quad . \quad (5)$$

It follows that for non-isotropic regions for which R_{ac} and R_{L} must be replaced by their appropriate volume average values f depends on position, and the value given by (4) is then also a volume average value.

From (5) the above expression for f may be written in the form

$$f = 1/(1 + \phi_2 R_{\mathrm{L}}/R_p), \qquad . \quad . \quad . \quad . \quad (4\cdot2)$$

which is sometimes convenient to use; but the form generally useful is that given by (4) or

$$f = 1/(1 + R_{\mathrm{L}}/R_{ac}). \qquad . \quad . \quad . \quad . \quad (4\cdot3)$$

Except in the improbable case that R_{L} is proportional to R_p or R_{ac}, both these expressions show that f, and hence $\Phi = f\phi_1\phi_2$, cannot be expected to be constant over a range of experimental conditions unless R_{L} is unimportantly small, and in this case f is sensibly unity. Now R_{ac}, R_{L}, and R_p are necessarily functions of λ_a, the fractional concentration of the active species; and it follows that a constancy in f is to be expected only for a limited range of values of λ_a. The parallelism between theory and experiment which is revealed by a constancy of Φ in some experiments over a wide range of conditions is thus explicable if f is constant, either because R_{L} is negligibly small, or more improbably, because R_{L}/R_{ac} does not vary.† In either case the detailed interpretation of the experiments must provide for such a constancy in terms of the actual processes consuming the active species and determining the

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[*] The appropriate extension of the present treatment to the case of branching chain mechanisms is, however, easily developed.

[†] The constancy of the quantum yield often observed in photo-chemical reactions arises from similar causes.[2]

absolute magnitudes of R_{ac} and R_L. For this purpose a knowledge of λ_a is essential; and to this quest we now turn by considering the stationary state.

2. The Stationary State in Relation to the Active Species.

The fractional concentration, or partial pressure, of an active species in the stationary state (*cf.* Introduction) when the discharge and reaction zones are co-extensive and isotropic is determined by the condition that in any volume element the rate of formation is equal to the total rate of loss, or

$$\phi_1 R_{er} + R_{af} = R_{ac} + R_L , \qquad . \quad . \quad . \quad (6)$$

all the terms being replaced by the corresponding volume averages when the system is not isotropic. Convenient and typical expressions for the various R's are developed shortly. When the active species, the relevant electron-reactant collisions, and the processes destroying the active species, including the mechanism leading to the observed product, are identified, the only unknown in (6) for any given experimental conditions is λ_a, which may therefore be evaluated. (In the practically important cases of positive column and negative glow reaction it is obvious that the resulting values of λ_a are also volume averages.) It will be seen shortly that for many types of destructive process the rate is a linear function of λ_a; in this case, when also R_{af} is not a function of λ_a or is zero, the solution is linear, or

$$\lambda_a = (\phi_1 R_{er} + R_{af})/A + B), \qquad . \quad . \quad . \quad (6.1)$$

where A and B are equal, respectively, to R_{ac}/λ_a and R_L/λ_a, and are computable in terms of the experimental conditions together with R_{er} and R_{af}.

The importance of the solution of (6) for λ_a is twofold. Firstly, it is explained in the Introduction that in practice the computation of R_{er} is practicable only in the case of a gas consisting almost entirely of reactants; that is, λ_a must be small compared with unity, and the magnitude of λ_a is usually a valuable guide in estimating the fractional concentration of other species involved in the reaction. In addition (*cf. infra*) the expressions for R_{ac} and R_L take simple and convenient forms only when λ_a is small. Secondly, when λ_a is known, the absolute magnitudes of R_{ac} and R_L may be computed, and hence f evaluated according to (4.3). It is then possible to complete the interpretation of the reaction by the demonstration that Φ as computed from $f\phi_1\phi_2$ provides an explanation for the characteristics of Φ as deduced from (1.1) and (1.2).

2.1. The Rate of Electron-Reactant Collisions.

The dependence of this rate on the conditions in any given experiment follows from the theory of Part I. For uniform positive conditions, the radial average value is given by

$$R_{er} = \lambda_A p(Xp^{-1})I_e \eta , \qquad . \quad . \quad . \quad . \quad (7.1)$$

where $\lambda_A p$ is the partial pressure of the reactant A involved, X, the field in the uniform positive column, and I_e the electron borne radial average drift current density in electronic charges cm.$^{-2}$ sec.$^{-1}$; because the motion of the ions is negligible compared with that of the electrons,

I_e may be sensibly identified with the total drift current density, which is the quantity usually measured. For simplicity in the solution of (6) it is convenient to deal with the current density in milliamp. cm.$^{-2}$ sec.$^{-1}$, $I_{ma} = I_e/(6{\cdot}3 \,.\, 10^{15})$, and to introduce a numerical factor $N = 3{\cdot}55 \times 10^{16}$; this is number of particles in 1 cm.^{3} of a gas at unit pressure, 1 mm., and the standard temperature. We then find

$$R_{er} = 0{\cdot}18\, pN\lambda_A(Xp^{-1})I_{ma}\,\eta. \qquad . \qquad . \qquad . \qquad (7.2)$$

The corresponding expressions for negative glow conditions when the volume of this zone can be expressed as Z_o/p, where Z_o is the equivalent volume at unit pressure, are

$$\bar{R}_{er} = p \,.\, I'_e \,.\, \beta_f/Z_o\,, \qquad . \qquad . \qquad . \qquad (7.3)$$

where I'_e is the current in electronic charges sec.$^{-1}$, or in practical units after introducing the same numerical factor N,

$$\bar{R}_{er} = 0{\cdot}18\, pNI'_{ma}\,\beta_f/Z_o\,, \qquad . \qquad . \qquad . \qquad (7.4)$$

where $I'_{ma} = I'_e/(6{\cdot}3 \times 10^{15})$.

2.2. The Production of the Active Species.

It has already been seen that the rate of this process as effected by electron-reactant collisions is simply $\phi_1 R_{er}$ for any single type of such collision; if more than one type is concerned the sum of their rates must be taken.

The possible processes whereby an active species might be formed other than by electron-reactant collisions are too numerous and varied to warrant an attempt to formulate any general expression for their rates, R_{af}. Experience indicates that in comparatively few cases is there reason for thinking that R_{af} is not negligible compared with $\phi_1 R_{er}$.

2.3. The Destruction of the Active Species in the Formation of the Observed Product.

The formulation of R_{ac}, the rate at which the active species is consumed in this way obviously requires a knowledge of the reactions involved; we shall therefore illustrate the way in which R_{ac} must be formulated by making use of hypothetical special cases, using approximate expressions for the collision rates between massive particles both here and in what follows.* The simplest case is one in which the active species reacts bimolecularly with a reactant A which is not necessarily that from which the active species is derived; R_{ac} is then given by *

$$R_{ac} = 4{\cdot}6 \times 10^{23}\, k_{aA}\, \lambda_a\, \lambda_A\, p^2 \qquad . \qquad . \qquad . \qquad (8.1)$$

or

$$= 1{\cdot}3 \times 10^7\, k_{aA}\, N\, \lambda_a\, \lambda_A\, p^2\,. \qquad . \qquad . \qquad (8.2)$$

where $\lambda_A\, p$ is the partial pressure of A, and k_{aA} is the collisional efficiency. If, however, the reaction involves in addition ternary collisions with a second reactant B, R_{ac} is given approximately by *

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* In deriving (8.1) it is assumed that the collision rate for any active species molecule moving in any gas A at atmospheric pressure is 10^{10} per second; and in deriving (8.3) from (8.1) it is further assumed that at atmospheric pressure the fraction of essentially binary collisions which are ternary is 10^{-3}.

$$R_{ac} = 6 \times 10^{17} \, k_{a\mathrm{AB}} \, \lambda_a \, \lambda_{\mathrm{A}} \, \lambda_{\mathrm{B}} \, p^3 \quad . \quad . \quad . \quad (8.3)$$

or

$$= 16 \, k_{a\mathrm{AB}} \, N \, \lambda_a \, \lambda_{\mathrm{A}} \, \lambda_{\mathrm{B}} \, p^3, \quad . \quad . \quad . \quad (8.4)$$

where $\lambda_{\mathrm{B}} \, p$ is the partial pressure of B, and $k_{a\mathrm{AB}}$ is the collisional efficiency.

For some purposes it is more convenient to express R_{ac} in terms of R_p the corresponding rate of formation of the observed product; from (5) the corresponding particular expressions are

in a P.C. $$R_{ac} = 0{\cdot}18 \, pN(Xp^{-1}) I_{ma} \, \eta_{p,\mathrm{P}} / \phi_2, \quad . \quad . \quad (8.5)$$

and in a N.G. $$R_{ac} = 0{\cdot}18 \, p I'_{ma} \, \beta_{p,\mathrm{N}} \, N / (\phi_2 \cdot Z_o). \quad . \quad . \quad (8.6)$$

Although by definition R_{ac} relates only to the homogeneous consumption of the active species in forming the observed product, it is necessary to bear in mind the possibility that part of the active species may react at the wall to give a reaction product which may or may not be identical with the "observed product" which is identified with the homogeneous reaction; this possibility is more conveniently considered in relation to diffusion, *cf* §§ 2.45.

It is to be noted that the above expressions for R_{ac} are independent of whether the active species is charged or not.

2.4. The Destruction of the Active Species other than by the Formation of the Observed Product.

The term R_{L} in (6) which takes account of all these other ways in which the active species may be consumed may be expressed as the sum of a number of terms each representing the rate of loss in a particular way, or

$$R_{\mathrm{L}} = R_{\mathrm{A}} + R_e + R_+ + R_d + R_{\mathrm{D}} + \ldots, \quad . \quad . \quad (6.2)$$

the individual terms being defined below. On account of the numerous possibilities, we do not attempt more than to consider those destructive processes that are usually important in interpreting the data for discharge reaction.

2.41. Radiative Loss.—This loss is represented by the term R_{A} which is zero except when the active species is an excited state; in this latter case

$$R_{\mathrm{A}} = AN\lambda_a p \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where A is the radiative transition probability;[*] for normal excited states A is about 10^8 to 10^7 sec.$^{-1}$, and for metastable states it may be 10^4 or less.

2.42. Destruction by Collisions with Electrons.—The contribution to R_{L} by processes of this type is denoted by R_e; it is convenient to distinguish between the case when the active species is uncharged and when it is charged.

When the active species is uncharged R_e is of the same form as R_{cr} (*cf.* § 2.1), and may be derived from expression (3) of Part I when λ is replaced by λ_a, and when the meaning of $Q(V)$ is changed so that it now denotes the cross-section for destruction of the active species by electron

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[*] When more than one radiative transition is possible, A must be replaced by the sum of the A's concerned.

impact;* for uniform positive column conditions there is then a corresponding η which is denoted by η_r, and we find

$$R_e = \lambda_a p(Xp^{-1}) I_e \eta_r \tag{10.1}$$

or

$$= 0{\cdot}18\, \lambda_a pN(Xp^{-1}) I_{ma} \eta_r \,. \tag{10.2}$$

And similar expressions may be derived for the conditions in a negative glow.

When the active species is positively charged R_e is again of the same form as R_{er} for collisions which result in excitation or further ionisation, which processes usually involve relatively fast electrons. For slow electrons, however, electron capture, or recombination, is likely to be the important process; for this case R_e may be expressed in a form similar to (8.4) when, as is usual, ternary collisions are involved, or

$$R_e = 16\, k_{ae\mathrm{B}}\, n_e\, \lambda_a \lambda_{\mathrm{B}}\, p^2, \tag{10.3}$$

where n_e is the electron concentration and $k_{ae\mathrm{B}}$ is the collisional efficiency. When the active species is negatively charged, R_e is again of the same form as R_{er} for collisions which result excitation or ionisation.

2.43. Destruction by Collision with Positive Ions.—The contribution of this type of process to R_{L} is denoted by R_+, and since fast ions are rarely encountered we may make use of expressions formally similar to (8.1) so that convenient forms for R_+ are

$$R_+ = 1{\cdot}3 \times 10^7\, Nk_{a+}\, \lambda_a \lambda_+\, p^2, \tag{11.1}$$

$$= 1{\cdot}3 \times 10^7\, k_{a+}\, n_+\, \lambda_a\, p, \tag{11.2}$$

and

$$= 4 \times 10^{-10}\, Nk_{a+}\, n_+\, \lambda_a\, p, \tag{11.3}$$

where $n_+ = \lambda_+ Np$ is the concentration of positive ions, and k_{a+} is the collisional efficiency. These expressions are appropriate to the case of an uncharged active species reacting chemically, or exchanging charge, with a positive ion. If the active species is negatively charged, recombination is the process most likely to be important, and since this process involves ternary collisions, we find for R_+

$$R_+ = 6 \times 10^{17}\, k_{a+\mathrm{B}}\, \lambda_a \lambda_+ \lambda_{\mathrm{B}}\, p^3, \tag{11.4}$$

or

$$= 16\, k_{a+\mathrm{B}}\, n_+\, \lambda_a \lambda_{\mathrm{B}}\, p^2, \tag{11.5}$$

or

$$= 4{\cdot}6 \times 10^{-16}\, k_{a+\mathrm{B}}\, Nn_+\, \lambda_a \lambda_{\mathrm{B}}\, p^3, \tag{11.6}$$

where $k_{a+\mathrm{B}}$ is the collisional efficiency.

2.44. Destruction by Collision with Uncharged Particles without any consequent Formation of the Observed Product.—The contribution by processes of this type to R_{L} is denoted by R_d, and may be of many varieties; for example, in the case of an uncharged active species it may react with itself to form an unobserved product, or, if metastable,† it may lose part or all of its excitation energy in collisions in the other species. In general, the active species may be regarded as reacting with some species Q present at the partial pressure $\lambda_{\mathrm{Q}}p$,

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* In general more than one type of destructive process is possible, and then R_e must be replaced by the sum of the individual R_e's concerned.

† It is to be noted that vibrationally and rotationally excited molecules in the ground electronic state are usually metastable, and together with atoms and molecules in electronically metastable states may lose their energy of excitation in collisions.

and R_a has then the same form as R_{ac}. By analogy with (8.1) for the case of a bimolecular process, we find

$$R_a = 4{\cdot}6 \times 10^{23} k_{aQ} \lambda_a \lambda_Q p^2, \quad . \quad . \quad . \quad (13.1)$$

or

$$= 1{\cdot}3 \times 10^7 k_{aQ} N \lambda_a \lambda_Q p^2; \quad . \quad . \quad (13.2)$$

and expressions similar to (8.3) may be derived for ternary processes. When the active species is positively charged, it may sometimes be more convenient to use expressions for R_d similar to those for R_+. In general, there may be several processes simultaneously contributing to the homogeneous destruction of the active species, and in this case it is necessary to replace R_d by the sum of the relevant R_d's for the individual processes.

2.45. Loss by Diffusion and the Stationary State.—For reasons that will be apparent shortly, it is convenient when discussing this process not merely to formulate the rate of loss of the active (or any other) species, as has been done with other types of processes, but to consider this rate directly in relation to the stationary state and to its effect on the fractional concentration of the species, λ_a. Two cases considered in which the problem is tractable are :—*

(*a*) The active (or other) species is destroyed on reaching the wall or other surfaces bounding the reaction zone so that there is no reflection of the species at these boundaries, and

(*b*) Only a very small fraction of the species is destroyed at the boundaries, that is, a large fraction is reflected unchanged.

In what follows we restrict attention to the case of a cylindrical discharge tube, and make considerable use of the analysis of diffusion processes given recently by Emeléus and Beck.[3]

For an indefinitely long tube in which the chemical activity of a discharge is uniform, diffusion is radial only (except near the axial boundaries), and hence R_d, the volume rate of loss of the species by diffusion at the radial distance r from the axis, in particles cm.$^{-3}$ sec.$^{-1}$ is given by [3]

$$R_D = (ND/r)\mathrm{d}/\mathrm{d}r(r\mathrm{d}\lambda_a/\mathrm{d}r), \quad . \quad . \quad . \quad (14.1)$$

where D is the coefficient of diffusion of the species in the reacting gas at unit pressure, 1 mm. If we now denote the sum of the rates of all other losses of the species by R_L^* so that from (6.2) we may write

$$R_L = R_L^* + R_D, \quad . \quad . \quad . \quad . \quad (14.2)$$

and substitute the above expression for R_D in the general expression for the stationary state, we find, after rearranging,

$$(ND/r)\mathrm{d}/\mathrm{d}r(r\mathrm{d}\lambda_a/\mathrm{d}r) + (\phi_1 R_{er} + R_{af}) - (R_{ac} + R_L^*) = 0. \quad (14.3)$$

The solution of this expression for λ_a as a function of r, and of the analogous expressions that may be written for other species (*cf.* § 2.6), is, however, tractable in certain special cases only. In particular, for case (*a*) (above), in which λ_a is zero at $r = r_o$, the radius of the boundary, and provided that $\phi_1 R_{er} + R_{af}$ is independent of r and λ_a, and that $(R_{ac} + R_L^*)$ is a linear function of λ_a, the solution of (14.3) is [3]

$$\lambda_a = \frac{\alpha}{\beta}\left\{1 - \frac{J_o[\iota r\sqrt{\beta/(ND)}]}{J_o[\iota r_o\sqrt{\beta/(ND)}]}\right\} \quad . \quad . \quad . \quad (15)$$

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* It is, of course, possible that the effects of diffusion may be modified by those caused by convection, but for this complication no analysis of the problem appears to have been attempted.

where $\alpha = (\phi_1 R_{er} + R_{af})$, $\beta = (R_{ac} + R_L^*)/\lambda_a$, and J_o denotes the Bessel function of zero order here with an imaginary argument. The restriction on $\phi_1 R_{er}$ is fulfilled when R_{er} is defined by (7.1) or (7.2), which is equivalent to regarding the discharge as approximately uniform radially; but the solution of (15) then yields only a correspondingly approximate value for λ_a†. But even such approximate estimates for λ_a are often valuable: for when λ_a is known it is at once possible to judge whether the arbitrary but practically important requirement (*cf.* Introduction) that this quantity shall not exceed some specified value is fulfilled.* When $\beta/(ND)$ is small compared with unity, which usually arises when $(R_{ac} + R_L^*)$ is relatively small, the estimation of λ_a is simple because (15) then reduces to

$$\begin{aligned}\lambda_a &= 0{\cdot}25\,(\alpha/\beta)r_o^2[\beta/(ND)](1 - r^2/r_o^2)\\ &= 0{\cdot}25\,[\alpha r_o^2/(ND)](1 - r^2/r_o^2)\,; \qquad . \quad . \quad (15.1)\end{aligned}$$

from this it may be seen that the maximum value of λ_a occurs at $r = 0$, or

$$\lambda_{a,\mathrm{max.}} = \alpha r_o^2/(4ND). \qquad . \quad . \quad . \quad (15.2)$$

Since for many discharge tubes r_o^2 is about 4, the following approximate expression is sometimes useful

$$\lambda_{a,\mathrm{max.}} \approx \alpha/(ND), \qquad . \quad . \quad . \quad (15.3)$$

which, when R_{af} is zero, becomes from (7.2)

$$\lambda_{a,\mathrm{max.}} \approx 0{\cdot}2\,p\,\phi_1(Xp^{-1})I_{ma}\,\eta/D. \qquad . \quad . \quad (15.4)$$

Since D is of the order of 10^3, and since $\phi_1(Xp^{-1})I_{ma}\,\eta$ is unlikely to exceed about 10, we reach the approximate relation

$$\lambda_{a,\mathrm{max.}} \overset{\sim}{<} 2 \times 10^{-3}\,p. \qquad . \quad . \quad . \quad (15.5)$$

This relation shows that, for example, λ_a is unlikely to exceed about 0·01 at all pressures below about 10 mm., provided always that $\beta/(ND)$ is small compared with unity.

Again following Emeléus and Beck, we consider next f_w, the fraction of the active species produced which reaches the wall. The rate of this latter process per unit length of tube is given in molecules sec.$^{-1}$ by

$$S_w = -\,2\pi r_o\,ND\,(\mathrm{d}\lambda_a/\mathrm{d}r)_{r=r_o}, \qquad . \quad . \quad . \quad (16)$$

whilst the corresponding rate of production is $\pi r_o{}^2\alpha$, and hence when R_{af} is zero

$$f_w = S_w/(\pi r_o^2 \phi_1 R_{er}). \qquad . \quad . \quad . \quad (16.1)$$

To proceed further $(\mathrm{d}\lambda_a/\mathrm{d}r)_{r=r_o}$ must be evaluated from (15), but the resulting expression becomes tractable only when $\beta/(ND)$ is small compared with unity, for which case it is found that

$$f_w \approx 1 - \tfrac{1}{8}r_o^2[\beta/(ND)]. \qquad . \quad . \quad . \quad (16.2)$$

Since in practice r_o^2 is rarely larger than about 8, this relation shows, for the special conditions assumed, that f_w is close to unity, that is, that

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* In case (*b*) (p. 1082) λ_a is nearly constant (*vide infra*), and the term representing the rate of formation of any intermediate, or final, product by the reaction of the active species is likewise independent of r; that is, when considering such other species, the terms which replaces $\phi_1 R_{er}$ (*cf.* § 2.6) closely conforms to the condition that α in (15) shall be independent of position.

a very large fraction of the active species reaches the walls. Conversely, it may be seen that when $\beta/(ND)$ is not small compared with unity a large fraction of the active species produced will suffer some sort of change or reaction before reaching the wall, but whether this is mainly concerned in forming the observed product or in destructive processes cannot be judged without a more detailed examination of the terms comprising β.

In the other extreme case, (*b*), large wall reflection, (14.2) is still applicable but intractable. It can be seen, however, that in this case the concentration at the wall can differ little from that in the main body of the gas, and thus to a first approximation λ_a may be regarded as independent of position. If k_w denotes the fraction of active species which are not reflected on reaching the wall, it follows that the rate at which they reach the wall per unit length of tube is approximately given by

$$S_w = 2\pi r_o \,.\, 0{\cdot}25\, k_w \lambda_a pNc \quad . \quad . \quad . \quad (17)$$

where c is the mean velocity of their thermal agitation; hence R_{D} the rate of loss in this way per unit volume is given by

$$\begin{aligned} R_{\mathrm{D}} &= S_w/\pi r_o^2 \\ &= 0{\cdot}5\,(k_w/r_o)\lambda_a pNc. \quad . \quad . \quad . \quad (17.1) \end{aligned}$$

Again it transpires that R_{D} is a linear function of λ_a.

Approximate solutions of the corresponding problems for the case of negative glow reaction can be formulated in terms of models which represent approximately the characteristics of this zone. In the first of these, Z, the volume of the zone is taken to be given by Z_o/p where Z_o is the equivalent volume at unit pressure; this model is usually appropriate to the consideration of cases in which the observed product is formed by homogeneous reaction and the loss of the active species by diffusion to the walls is small (*cf.* § 2.1). In the other, recently introduced by Emeléus and Beck,[3] the formation of the active species by electron-reactant collisions throughout the zone is idealised as equivalent to a radially uniform flux of the active species entering the zone at its negative boundary, the rate of formation in the zone then being zero and the extent of the zone towards the anode unspecified. This model is particularly helpful when all the homogeneous reactions of the active species are relatively unimportant and the observed product is formed as a consequence of the diffusion of this species to the walls.

In the first model the wall area bounding the discharge zone is $2Z_o/(pr_o)$, and the wall area per unit volume of the zone $2/r_o$. Neglecting any diffusional loss in the direction of the tube axis, $\overline{R}_{\mathrm{D}}$, the average volume rate of loss of the active species by diffusion, is then $2/r_o$ times the average rate of loss per unit area of wall; hence for case (*a*), no wall reflection, by analogy with (16) we find

$$\overline{R}_{\mathrm{D}} = -(2/r_o)ND(\mathrm{d}\lambda_a/\mathrm{d}r)_{r=r_0} \quad . \quad . \quad . \quad (18.1)$$

where the term involving λ_a denotes the average value over the whole wall bounding the zone. An approximate estimate for this term may be derived by replacing the R's in α and β in (15) by the appropriate $\overline{R}$'s, and then evaluating $\mathrm{d}\lambda_a/\mathrm{d}r$ for $r = r_o$; but, as in deriving (16.2), the computation is simple only when $\beta/(ND)$ is small compared with unity. For case (*b*), large wall reflection, the wall loss per unit area is again given approximately by $0{\cdot}25\,k_w\,\lambda_a\,pNc$ where λ_a is the volume average quantity; and hence, neglecting as before any loss in the axial directions, we find the approximate relation

$$\bar{R}_D = 0{\cdot}5\,(k_w/r_o)\lambda_a\,pNc. \quad . \quad . \quad . \quad (18.2)$$

In the other model of the negative glow S_f, the flux of the active species into the zone from the idealised disc of generation at the negative boundary, in molecules (or atoms) cm.$^{-2}$ sec.$^{-1}$, is given by

$$S_f = (1/\pi r_o^2)\phi_1\,\beta_f\,I_e\,. \quad . \quad . \quad . \quad (19.1)$$

The analysis of Emeléus and Beck[3] shows that the stationary state is then formally expressed by

$$(ND/r)\mathrm{d}/\mathrm{d}r(r\mathrm{d}\lambda_a/\mathrm{d}r) + \alpha(r, z) - \beta(r, z)\lambda_a + ND\mathrm{d}^2\lambda_a/\mathrm{d}z^2 = 0 \quad . \quad (19.2)$$

the z direction being that of the tube axis; in this expression $\alpha(r, z)$ represents R_{af}, and $\beta(r, z) = (R_{ac} + R_L^*)/\lambda_a$. Emeléus and Beck give the solution of this expression for case (*a*), no wall reflection, when there are no generative or destructive homogeneous processes involving the active species (*i.e.*, R_{af}, R_{ac}, R_L^*, are zero); this reads

$$\lambda_a = \frac{r_o S_f}{2ND}\left(\frac{\left(J_o\left(s_o\frac{r}{r_o}\right)\right)}{J_1(s_o)}\right)\mathrm{e}^{-s_o z/r_o} \quad . \quad . \quad (19.3)$$

where $s_o = 2{\cdot}40$ is the first zero of J_o, $J_1(s_o) = 0{\cdot}52$, and the origin of z is taken to be the plane of generation of the active species. The maximum value of λ_a then occurs at the centre of the generating disc, $r = 0$, $z = 0$; hence

$$\lambda_{a,\mathrm{max.}} = r_o\,S_f/(ND).$$

From (19.1) this may be written in the more convenient form, after converting to practical units of current and some simplification (*cf.* § 2.1),

$$\lambda_{a,\mathrm{max.}} = (0{\cdot}18/\pi r_o)\phi_1\,\beta_f\,I'_{ma}/D. \quad . \quad . \quad . \quad (19.4)$$

The importance of this expression, which does not involve the pressure, is that it enables $\lambda_{a,\mathrm{max.}}$ to be computed simply when R_{af} is zero or negligible, which is the case usually encountered. And even if the active species reacts homogeneously $\lambda_{a,\mathrm{max.}}$ is then an upper limit to the fractional concentration of the active species; alternatively, the existence of such homogeneous reaction may be regarded as exerting an effect equivalent to an increase in the diffusion constant D when it is supposed in solving (19.3) that such processes are not operative.

For the same case (*a*) the rate at which the active species reaches the wall per unit length of tube is still given by (16) but when homogeneous destructive processes are absent we find, after evaluating $(\mathrm{d}\lambda_a/\mathrm{d}r)_{r=r_o}$ from (19.2),

$$S_w(z) = 0{\cdot}5\,s_o\,S_f\,\mathrm{e}^{-s_o z/r_o}. \quad . \quad . \quad . \quad (19.5)$$

From (19.1) this yields the simple approximate expression for the practically important case in which r_o is about 2 cm.

$$S_w(z) \approx 0{\cdot}1 \times 10^{-z/r_o} \times \phi_1\,\beta_f\,I'_e \quad . \quad . \quad (19.6)$$

The importance of these expressions in estimating the extent of heterogeneous reactions in discharges is emphasised by Emeléus and Beck.[3]

2.5. Summarising Statement relating to the Active Species in the Stationary State.

The general expression for the fractional concentration of this species follows from (6), (6.1), and (6.2) as

$$\lambda_a = \frac{\phi_1 R_{er} + R_{af}}{(1/\lambda_a)(R_{ac} + R_{A} + R_e + R_d + R_+ + R_D)}; \qquad (6.3)$$

but the considerations advanced in § 2.45 show that this is convenient only when the diffusional loss R_D is small. In this case it happens frequently that R_D and all the other R's in the denominator are linear functions of λ_a; when higher powers of λ_a are involved it is found that only one root of (6.3) is physically significant. Whilst (6.3) is applicable to any point when the discharge and reaction zones are co-extensive, the application of this expression to the conditions of uniform positive column and negative glow reaction necessitates the introduction of the appropriate volume average values for all the R's concerned; the expression then yields approximate volume average values for λ_a. When the diffusional loss of the active species is large, (6.3) may still be used to give a rough estimate for the upper limit to λ_a by omitting R_D in the denominator; alternatively, in certain limited conditions λ_a may be computed from the expressions derived from (15) and (19.3).

2.6. The Stationary State in relation to other Species.

The foregoing analysis for the active species may be regarded as a special case of the stationary state for which the rates of formation and destruction of a species can be specified. To derive λ_i, the fractional concentration of any intermediate species, it is merely necessary to make the following substitutions in all the expressions for λ_a: $\phi_1 R_{er}$ is replaced by R_i, the rate of formation of the intermediate species, R_{ac} by R_{ic}, the rate at which the intermediate species is consumed in forming the observed product by homogeneous reaction, and the individual terms in R_L are changed to relate to the destruction of the species in the various other possible ways. Precisely similar substitutions are appropriate to the derivation of λ_p, the fractional concentration of the observed product, except that $\phi_1 R_{er} + R_{af}$ is to be replaced by R_p, the rate of formation of the product by homogeneous * reaction as deduced from experiment. It is important to note, however, that when the observed product of homogeneous reaction is removed from the system by refrigeration of the discharge tube wall, the conditions correspond closely with case (*a*) (p. 1082) and with the restrictions for which the solutions of expressions (14.3) and (19.2) are available; for homogeneous destruction is then usually unimportant.

Summary.

The individual factors comprising the quantity Φ, the electro-chemical analogue of the photo-chemical quantum yield, are specified. This quantity denotes the number of molecules of an observed product which are formed per electron-reactant collision generating the active species which initiates reaction, and is used to relate the rate of such electron-

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* It is possible that a given active species yields the same observed product by homogeneous reaction and by heterogeneous reaction at the wall of the discharge tube.

reactant collisions to the rate of formation of the observed product. Of these factors the only one that usually depends on the experimental conditions is the fractional utilisation of the active species. From a consideration of discharge reaction proceeding in a steady state, formal expressions are derived for the dependence of the fractional concentration of the active species on the experimental conditions and the rate of the relevant electron-reactant collisions. The corresponding dependence of the fractional utilisation of the active species, and hence that of Φ, is then readily deducible. The extension of this analysis to the conditions in uniform positive column and negative glow reaction, and to other species, is briefly outlined.

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CHEMICAL REACTION IN ELECTRIC DISCHARGES. PART. IV. THE NEGATIVE GLOW REACTION IN HYDROGEN-OXYGEN MIXTURES.

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Kirkby,[1, 2, 3] working in Townsend's laboratory, described the first quantitative experiments on the reaction between hydrogen and oxygen in discharges, and demonstrated the fundamental difference between the chemical activity of the negative glow (N.G.) and the positive column (P.C.). Subsequently, in numerous papers widely divergent views on the mechanism of the reactions have been expressed. In this paper we consider the reaction in the N.G. only. Our purpose is to summarise the existing data, and on the basis of the general theory of discharge reaction given in Part I [23] of this series to interpret them in terms of reaction mechanisms which are consistent with the known physical data for this discharge zone and with the kinetics of the oxidation of hydrogen initiated by light absorption.

In the pioneer work of Kirkby, and in later work, the reaction products were rapidly removed from the reaction zone so that the gas in that zone consisted mainly of reactant molecules, a condition that simplifies the application of the general theory of Part I. It was not

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[1] Kirkby, *Phil. Mag.*, 1904, 7, 223.
[2] *Ibid.*, 1905, 9, 131.
[3] *Ibid.*, 1907, 13, 289.

observed whether the immediate product of the reaction is water or hydrogen peroxide because the phosphorus pentoxide or sulphuric acid sometimes used to remove water from the system must have decomposed any peroxide formed; for this reason the data are discussed everywhere in this paper in terms of the equivalent water formation. Using a reaction vessel refrigerated externally[6] to – 180°, it is reported that one-fifth of the total reaction product is peroxide; but it is not clear whether this originates in the negative glow or in the discharge as a whole including the positive column.

The available quantitative data for the oxidation of hydrogen in the negative glow maintained in hydrogen-oxygen mixtures have been analysed in detail to derive values for the "electrical reaction velocity constants" β and η which the considerations advanced in Part I show to be the significant quantities. β is the equivalent number of water molecules formed in the negative glow per electronic charge carried by the current as measured in the external circuit, and is known as the current efficiency; * η is the energy efficiency in molecules per electron-volt (ev.) * and is equal to β/V_N where V_N is the potential difference required to maintain the negative glow. Strictly speaking, β and η relate to the chemical activity of all the discharge zones, including the negative glow, which are maintained by the electrode potential difference V_N; but since the available data for discharge reaction strongly suggest that of the "negative zones" (*cf.* Part I) the negative glow is mainly responsible for the observed chemical activity, we follow the usual procedure of speaking of "negative glow" reaction. In one or two cases, however, strong evidence is found for attributing part of the observed chemical activity of the discharge to a zone close to the cathode surface. For the most part β and η exhibit the characteristic properties mentioned in Part I. Over a very wide range of conditions in electrolytic gas the results of different investigators present a remarkable uniformity: the individual values of β do not differ from their mean by more than a factor of about 2, and the deviations of the values of η from their mean is even smaller. A detailed examination of these data (*cf.* Table I) strongly suggests that in many cases these deviations from the mean are attributable to specific factors. Of these, the variation of β with the pressure of the reacting gas appears to be the most clearly defined. In the "low pressure" range extending from about 0·3 to 7 mm., the mean value of β is about 8, all values lying between 5·4 and 11. In the "high pressure" range from 30 to 90 mm., the mean value of β is about twice as large as in the low pressure range, but is still practically independent of the pressure; the deviations from the mean are somewhat larger in this range, and it appears that they are to be associated with the metal of the cathode. The few data available for the "intermediate" pressure range strongly suggest that in this range β at first increases before becoming constant again in the "high" range.

In attempting to trace the mechanism of reaction we make use of the formal theory of Part I[23] as extended in Part III,[25] and particularise this by supposing that the particular electron-reactant collisions initiating the oxidation of hydrogen in the negative glow reaction effect the same primary changes as does the absorption of light in the unsensitised

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* For simplicity we omit the subscripts *p,N* which are used in Part I to qualify β and η; similarly, $R_{p,N}$ of Part I becomes R_p, and other changes will be immediately obvious from the text.

and mercury sensitised reaction in hydrogen-oxgen mixtures, namely, the formation of an "active species," respectively, oxygen and hydrogen atoms. In effect, this provides two reaction mechanisms, now termed "A" and "C" respectively, which in any case must occur to some extent. The application of these mechanisms to the detailed explanation of the characteristics of β and η as revealed by typical groups of representative experiments in the three pressure ranges is then explored. After introducing certain plausible and energetically acceptable assumptions specifying the rate of the electron-reactant collisions generating the two active species, the volume of the reaction zone, and the collisional efficiencies of the initial step in the unsensitised photo-reaction, it is found that mechanisms "A" and "C" provide a detailed explanation for the results of these typical experiments. The coherence of the remaining data with those selected for detailed discussion is satisfactory. Furthermore, these same reaction mechanisms have been found by Lunt, Meek and Swindell [26] to provide a quantitative explanation for the oxidation of hydrogen in the original experiments of Kirkby [4] on positive column discharges in electrolytic gas.

A number of other possible reaction mechanisms are considered briefly, and the reasons are outlined why they cannot contribute significantly to the negative glow reaction.

For convenience, the absolute values of the collision rates of the principal steps in the reaction mechanisms are summarised briefly in an Appendix.

As far as possible, quantities and symbols defined in earlier parts of this series are not redefined in this paper.

1. Experimental Data.

The values of β and η which we have derived from the published data for the negative glow reaction in electrolytic gas are given in Table I; and a number of other characteristics of these quantities are summarised later. Kirkby's data [1, 2, 3, 4] show that in the low pressure range these quantities are, to a close approximation, independent of the apparatus, the metal of the cathode, the current density, and the pressure; and that, in contrast with the positive column reaction at pressures above about 4 mm., there is no tendency towards explosion. These characteristics are confirmed by later researches [5, 6, 7, 8, 9, 10, 11, 12, 13] which extend to higher pressures; they reveal, however, the existence of some secondary factors. The fact that β and η are so little dependent on the apparatus and the experimental conditions leads to the deduction that the main reaction in electrolytic gas does not involve the cathode surface, the walls of the reaction vessel, or branching chain mechanisms.

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[13] Finch, *J.C.S.*, 1935, 32.

TABLE I.

FORMATION OF WATER FROM ELECTROLYTIC GAS IN THE NEGATIVE GLOW.

M = cathode metal.
V_N = cathode fall in volts.
I = current, or current range, in ma.
p = pressure, or pressure range, in mm. Hg.
T = temperature of surroundings in ° C. (RT = room temperature).
β = current efficiency in molecules H_2O per electron-charge carried by the current.
η = energy efficiency in molecules H_2O per electron-volt used in maintaining the discharge.

M	p	V_N	I	T	β	$\eta\ 10^2$	Ref.
Mg .	4[a]	430	20[a]	−80[a]	$6{\cdot}4_5$	$1{\cdot}5_0$	8
Al .	4[b]	358	20	−80	$5{\cdot}7_0$	$1{\cdot}5_9$	6
	4[b]	374	30	−80	$6{\cdot}4_8$	$1{\cdot}7_3$	6
	4[b]	386	40	−80	$7{\cdot}3_0$	$1{\cdot}8_9$	6
	4[b]	391	50	−80	$7{\cdot}9_4$	$2{\cdot}0_3$	6
	8[c]	370	20	−80	$6{\cdot}0_8$	$1{\cdot}6_5$	6
	16[c]	372	20	−80	$6{\cdot}2_0$	$1{\cdot}6_7$	6
	16·4[d]	350	25[d]	20	6·0	1·8	11
	16·4[d]	350	25[d]	320	6·0	1·8	11
	4[a]	420	20[a]	−80[a]	5·9	$1{\cdot}4_0$	8
Ca .	4[a]	420	20[a]	−80[a]	$5{\cdot}8_5$	$1{\cdot}3_9$	8
Cr-Fe alloy	4[e]	730	20	−80	8·1	1·1	12
	8[e]	410[f]	40	−80	10·7[f]	$2{\cdot}5_8$[f]	12
	13[e]	424[g]	20	−80	9·2[g]	$2{\cdot}1_8$[g]	12
	16[e]	425[g]	20	−80	$11{\cdot}_1$[g]	$2{\cdot}6_2$[g]	12
	16[e]	387[h]	40	−80	$11{\cdot}_3$[h]	$2{\cdot}8_8$[h]	12
	24[e]	445[g]	20	−80	$13{\cdot}_8$[g]	$3{\cdot}0_6$[g]	12
	24[e]	427[h]	40	−80	$13{\cdot}_7$[h]	$3{\cdot}1_6$[h]	12
Fe .	0·3[b] to 7	1200 to 400	20	−80	$8{\cdot}3_8$	0·7 to 2·74	6
	4[b]	345	10	−80	$5{\cdot}3_8$	$1{\cdot}5_6$	6
	4[b]	397	20	−80	$8{\cdot}3_8$	$2{\cdot}1_1$	6
	4[b]	470	40	−80	$11{\cdot}_5$	$2{\cdot}4_5$	6
	4[a]	480	20	−80	$6{\cdot}9_3$	$1{\cdot}4_5$	8
	10[b]	400	20	−80	$9{\cdot}4_5$	$2{\cdot}3_7$	6
	15[b]	400	20	−80	$12{\cdot}_0$	3·0	6
	20[b]	420	20	−80	$13{\cdot}_3$	$3{\cdot}1_6$	6
	25[b]	435	20	−80	$14{\cdot}_4$	$3{\cdot}3_3$	6
	30[b]	440	20	−80	$15{\cdot}_4$	$3{\cdot}5_0$	6
	35[b]	445	20	−80	$15{\cdot}_4$	$3{\cdot}4_6$	6
	5·5[i]	380	50	RT	$9{\cdot}1_4$	$2{\cdot}4_1$	5
	14·0[i]	380	50	RT	$9{\cdot}9_0$	$2{\cdot}6_1$	5
	22·5[i]	380	50	RT	$9{\cdot}5_2$	$2{\cdot}5_1$	5
	31·0[i]	380	50	RT	$10{\cdot}_0$	$2{\cdot}6_3$	5
	39·5[i]	380	50	RT	$9{\cdot}7_2$	$2{\cdot}5_6$	5
	48·0[i]	380	50	RT	$9{\cdot}5_2$	$2{\cdot}5_1$	5
Ni .	4[a]	460	20[a]	−80[a]	$7{\cdot}0_5$	$1{\cdot}5_4$	8
Cu .	30[j]	360[k, u]	1 to 3	20	$19{\cdot}_1$	$5{\cdot}3_1$	7
	45[j]	360[k, u]	1 to 3	20	$18{\cdot}_5$	$5{\cdot}1_4$	7
	60[j]	360[k, u]	1 to 3	20	18·5	$5{\cdot}1_4$	7
	75[j]	360[k, u]	1 to 3	20	$18{\cdot}_5$	$5{\cdot}1_4$	7
	90[j]	360[k, u]	1 to 3	20	$18{\cdot}_5$	$5{\cdot}1_4$	7
Zn .	1·4[l] to 6·5	400	1 to 3	RT	7·6 ± 1·2[n]	1·9 ± 0·3[m]	1
	1·2[n] to 9·3	400	<5	RT	7·64 ± 0·5[o]	$1{\cdot}9_1$ ± 0·1[o]	2
	0·6[p] to 9·3	400	2·75	RT	7·50 ± 0·4[q]	$1{\cdot}7_5$ ± 0·1[q]	3
	4[a]	460	20[a]	−80[a]	6·4	1·4	8
Ag .	0·98[n] to 7·6	400	5	RT	$7{\cdot}4_4$[r]	$1{\cdot}8_6$ ± 0·1[r]	2
	30[j]	350[k]	1·8 to 2·55	20	$11{\cdot}_9$	$3{\cdot}4_0$	9
	60[j]	350[k]	1·8 to 2·55	20	$12{\cdot}_4$	$3{\cdot}5_4$	9
	90[j]	350[k]	1·8 to 2·55	20	$12{\cdot}_8$	$3{\cdot}6_6$	9

TABLE I—*continued.*

M	p	V_N	I	T	β	$\eta \times 10^{2}$	Ref.
Cd .	4^a	460	20^a	-80^a	$6{\cdot}4_5$	$1{\cdot}4_6$	8
Sn .	4^a	560	20^a	-80^a	$8{\cdot}2_0$	$1{\cdot}4_6$	8
Sb .	4^a	520	20^a	-80^a	$7{\cdot}7_5$	$1{\cdot}4_6$	8
Ta .	30^j	345^k	1·8 to 2·55	20	$12{\cdot}_4$	$3{\cdot}6_0$	9
	60^j	345^k	1·8 to 2·55	20	12·8	$3{\cdot}7_2$	9
	90^j	345^k	1·8 to 2·55	20	$13{\cdot}_3$	$3{\cdot}8_6$	9
W .	4^a	530	20^a	-80^a	$8{\cdot}1_0$	$1{\cdot}5_3$	8
W .	30^j	345^k	1·8 to 2·55	20	17·1	$4{\cdot}4_6$	9
	60^j	345^k	1·8 to 2·55	20	$17{\cdot}_6$	$5{\cdot}1_0$	9
	90^j	345^k	1·8 to 2·55	20	$18{\cdot}_1$	$5{\cdot}2_5$	9
Pt .	30^j	$350^{k,\,u}$	1 to 3	20	$27{\cdot}_6$	$7{\cdot}8_5$	7
	45^j	$350^{k,\,u}$	1 to 3	20	$27{\cdot}_6$	$7{\cdot}8_8$	7
	60^j	$350^{k,\,u}$	1 to 3	20	$28{\cdot}_0$	$8{\cdot}0_0$	7
	75^j	$350^{k,\,u}$	1 to 3	20	$27{\cdot}_6$	$7{\cdot}8_8$	7
	90^j	$350^{k,\,u}$	1 to 3	20	$28{\cdot}_0$	$8{\cdot}0_0$	7
Pt-Ir alloy	20^s	375^t	0·2 to 1·9	RT	$24{\cdot}_3$	$6{\cdot}4_5$	10
Au .	$0{\cdot}2$ to $2{\cdot}0^p$	400	0·1 to 0·5	RT	$8{\cdot}3_6$	$2{\cdot}0_9$	4
	30^j	340^k	1·8 to 2·55	20	$10{\cdot}_9$	$3{\cdot}2_1$	9
	60^j	340^k	1·8 to 2·55	20	$11{\cdot}_4$	$3{\cdot}3_5$	9
	90^j	340^k	1·8 to 2·55	20	$11{\cdot}_9$	$3{\cdot}5_0$	9
Pb .	4^a	540	20^a	-80^a	$8{\cdot}1_2$	$1{\cdot}5_1$	8

LEGEND TO TABLE I.

[a] No experimental details given, but these were stated to be the same as in earlier experiments, that is, probably the experimental arrangements detailed in note [b] below, and $\phi = 4$, $I = 20$.

[b] Plane cathode facing anode in a cylindrical glass tube 5 cm. diameter immersed in a bath at −80° C.

[c] Solid cylindrical cathode and anode mounted parallel in a glass tube 5 cm. diameter immersed in a bath at −80° C.

[d] For higher currents it was stated that a temperature effect on β was just detectable, but no data were given.

[e] Plane cathode facing plane anode in a cylindrical glass tube 4 cm. diameter and immersed in a bath at −80° C.

[f] Mean of 2 experiments.

[g] Mean of 4 experiments.

[h] Mean of 3 experiments.

[i] Plane cathode facing anode in a tube 20 cm. diameter in free air at room temperature; spacing continuously adjusted to maintain normal cathode fall.

[j] Small point electrodes in a bulb of 100 cm.³, immersed in a bath at 20° C.

[k] Finch, *private communication.*

[l] Plane cathode facing plane anode in glass tube about 10 cm. diameter in free air at room temperature.

[m] Mean of 35 experiments.

[n] Plane cathode facing plane anode in glass tube 10 cm. diameter in free air at room temperature.

[o] Mean of 27 experiments.

[p] Plane cathode facing anode in a tube 2·2 cm. diameter in free air at room temperature.

[q] Mean of 15 experiments.

[r] Mean of 27 experiments.

[s] Water cooled needle shaped electrodes 6·8 mm. apart situated at centre of glass bulb of 550 cm.³, in free air at room temperature.

[t] This value assumed by original authors (Wheeler, *private communication*).

[u] The present authors, however, find the following values of V_N from a consideration of the original authors' data for the electrode potential as a function of the electrode spacing: Cu, 420 volts; Pt, 400 volts.

Other Aspects of the Experimental Data.

(i) The Effect of Temperature.—When considering the effect of temperature on a discharge reaction, it must be remembered that precise information about the gas temperature is difficult to obtain ; the indications of thermometers or thermo-junctions probes are liable to uncertain errors arising from the heat evolved on surfaces where, for example, atomic and ionic recombination processes occur. For the type of experimental conditions with which we are now concerned, the available data [14] indicate that the gas temperature is not more than about 100° above that of the discharge tube surroundings. The thermal conductivity of a gas increases with temperature, and hence an increase of 100° in the surroundings probably corresponds with a rise of not more than 80° in the gas itself. The gas temperatures corresponding with the three temperatures cited in Table I may, therefore, be taken to be approximately 300°, 380°, and 620° K. Since there is no evidence of a temperature effect in any of the experiments reported in Table I, we conclude that no stage of any of the reaction mechanisms involved has an appreciable temperature coefficient.

(ii) The Effect of the Current.—Numerous cases are to be found in Table I.[1, 2, 3, 4, 5, 7, 9, 10, 11] in which β is almost constant over a considerable range of current. In some of these precise data for V_N, the potential difference between the electrodes are lacking, but the authors appear to have been of the opinion that this quantity was sensibly constant, and in many other cases it certainly was so. When V_N is independent of I, the current, the regime is that of the normal cathode fall (*cf.* Part I), and Z, the volume of the N.G. is then approximately proportional to I in a given apparatus at a given pressure.[14] For electrodes of Fe and Al in the regime of abnormal cathode fall [6] β increases with I.

(iii) The Effect of Pressure.—Whilst the influence of pressure on the N.G. reaction is incomparably smaller than that observed for the thermal reaction in the same system, a careful scrutiny of the data reveals certain definite and systematic effects. For an Fe cathode (— 80°) * β is constant from 0·3 to 7 mm., but V_N falls rapidly and becomes constant above about 3 mm. in the same range ; [6] above 7 mm. β rises at first rapidly and then more slowly, becoming constant in the range 30-35 mm.[6].† Further confirmatory evidence is afforded by the data for a cathode of Fe-Cr alloy,[12] and for one of Al in the range 4-16 mm.[6] For cathodes of Ag and Au in the ranges 1-7·6 mm.[2], and 0·2-2 mm.[4] respectively, β is practically constant ; but in the range 30-90 mm. β for each of these metals is again nearly constant but about half as large again ; and a similar difference occurs between β for a W cathode at 4 mm.[11] and in the range 30-90 mm.[9] For electrodes of Ta, Cu, and Pt, β is again nearly constant from 30-90 mm., but there are no data for the low pressure range. On the other hand, for a cathode of Fe in the range 6-48 mm. β is roughly constant : [5] this apparently contradictory result is shown later to be probably explicable in the special conditions (walls of the reaction vessel very much more remote from the discharge zone than in all other experiments) to which the data relate.

(iv) The Effect of the Cathode Metal—In the low pressure range (but *cf.* note *a*, Table I) the data for β lie close to their mean, but are approximately proportional to V_N ; this is emphasised by the greater constancy of the corresponding values of η (*cf.* Table I). In this range

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[14] Darrow, *Electrical Phenomena in Gases*, London, 1932.

* This temperature is that of the surroundings.

† Incidentally, the cessation of this increase in β at the upper end of this pressure range, and its constancy over a wide range in other experiments,[7, 9] excludes the possibility that it is attributable to the use of a constant electrode spacing and the consequent gradual increase in the total activity of the discharge arising from a corresponding growth of a P.C.

there is no indication that β depends on the ease with which the cathode sputters. In the high pressure range Finch and Mahler [9, 13] claim to have found a dependence of β on the extent of the cathode sputtering, basing their conclusions in part on data relating to mixtures other than electrolytic gas. But the fact these authors report that electrodes of Ta and W do not sputter, whilst β increases along the series Au, Ag, Ta, W, Cu, Pt, as determined in practically identical experiments shows that although sputtering is clearly not the factor controlling the magnitude of β, there is some factor associated with the metal of the cathode. Since the differences between the values of β for cathodes of Au, Ag, and Ta, are small, it is apparent that this effect associated with the cathode metal is of considerable magnitude only for cathodes of W, Cu, and Pt.*

(v) The Effect of varying the Hydrogen-Oxygen Ratio.—For a cathode of Al at 4 mm. (− 80°) and a constant current, β rises slowly from a very small value as the hydrogen content of the gas is progressively increased, reaching a broad maximum at about 90 % hydrogen; with further increase in the hydrogen content β falls rapidly towards zero.[6] A closely similar dependence of β on the gas composition, nearly independent of the pressure, is found for cathodes of Au and Ag in the high pressure range; [9] and a similar effect is reported for an Fe cathode at an unspecified pressure, probably between 6 and 48 mm.[5] On the other hand, in the high pressure range and in the same apparatus in which cathodes of Ag and Au were investigated,[9] for a Ta cathode β follows much the same course until the hydrogen content is raised to about 70 %; with further increase in the hydrogen content β increases rapidly, attaining the astonishing value of about 42 for the richest mixture investigated, 99·5 % hydrogen; this dependence of β for a cathode of Ta is independent of the pressure and current in the "high" range, and is stated to be paralleled by that of a W cathode.[9, 13]

There is little data available for the corresponding variation in the cathode fall, V_N. For an Al cathode at 4 mm. V_N is practically independent of the composition; for the Fe cathode mentioned above V_N passes through a slight maximum in the neighbourhood of that of β. In the experiments in the high pressure range with cathodes of Au, Ag, Ta, and W,[9] V_N (*cf.* Table I) remained practically constant until the hydrogen content becomes very large when it falls slightly.[15]

(vi) The Effect of the Addition of Water Vapour, Helium, and Argon to Electrolytic Gas.—The addition of small amounts of water vapour in the high pressure range slightly increases β for a cathode of Ta, but is without effect on one of Au.[9] For a cathode of Al at 18 mm. β remains constant until more than 40 % water vapour is added, larger amounts producing a rapid fall in β.[11] For a cathode of Al at 4 mm., the addition of helium has little effect until the helium content is large, more helium then diminishing β; under similar conditions the addition of argon diminishes β roughly in proportion to the amount added.[6]

2. The Interpretation of the Negative Glow Reaction.

The data for the reaction in the low pressure range, 0·3 to about 10 mm., show that the oxidation of hydrogen is caused mainly by a homogeneous process which does not involve branching chains; in particular β is practically independent of the pressure and temperature, the geometry of the apparatus, and the metal of the cathode. In most of the experiments V_N lies close to 400 volts. The slight variations of β with the cathode metal are found for the most part to correspond with variations in the same sense of V_N; and when β varies with the current

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* Probably a cathode of Pt-Ir alloy (*cf.* Table I) at 20 mm. also belongs to this group.

[15] Finch, *private communication.*

V_N varies also and in the same sense. All these characteristics of β are provided for in the formal theory of Part I for the case of homogeneous negative glow reaction; and from the point of view of the theory of Part III the invariance of β strongly suggests that in the whole range of conditions concerned there is an active species formed by the discharge the utilisation of which in water formation is practically complete.

The data for the high pressure range, 30-90 mm., show again pressure and current invariance of β but this quantity is now about 50 % larger in the cases in which comparisons can be made (cathodes of Ag, Au, W), and V_N still lies close to 400 v. This would be explicable if, in addition, a second active species effects the oxidation of hydrogen, also under conditions of sensibly complete utilisation; but in this case the utilisation of this second active species must be insignificant in the low pressure range, and its gradual development must occur in the intervening range with a corresponding progressive increase in β. Such a change in β is clearly shown by one group of experiments, and partially by two others.[11, 12]

On extending these considerations relating to the main body of data for β in electrolytic gas to other mixtures, it is clear that if each reactant provides one active species which must then react with the other reactant, the total activity of the discharge for the oxidation of hydrogen will tend to diminish as the fractional concentration of either reactant is indefinitely increased. In both the low and high pressure ranges there are examples of a dependence of β on the gas composition which accords with this expectation.

There are, however, a few data relating to rather narrow ranges of conditions which do not appear to be completely explicable in terms of two reaction mechanisms initiated by these two active species, the second being completely developed only in the high pressure range. In electrolytic gas in the high pressure range β for cathodes of W, Cu, and Pt, although still pressure and current invariant, is abnormally large; it is also abnormally large in the same pressure range but only in hydrogen-rich mixtures for cathodes of Ta and W. These abnormal values are attributed to the effect of an additional reaction connected with the cathode surface; this matter is discussed in detail in the next paper of this series. Lastly, in one apparatus markedly different from all the others concerned, β is constant in electrolytic gas at a value intermediate between those characteristic of the low and high pressure ranges in a range which extends slightly into both these ranges.

The character of the explanation for the pressure and current invariance of the current efficiency, β, for any product of homogeneous negative glow reaction which is provided by theory in Part I, and elaborated in Part III, may be summarised as follows. In the simplest case, collisions of some specified type in the negative glow between electrons and a reactant species engender the formation of an active species which leads ultimately to the synthesis of the observed product. The rate of such electron-reactant collisions is then a factor controlling the rate at which the observed product is formed. But the active species may react other than by forming the observed product. The chance that the active species reacts to form the observed product is termed the fractional utilisation of this species, and is clearly another factor of prime importance in controlling the rate at which the observed product is formed. The theory of Part I shows that, when the cathode fall V_N is sensibly constant, the rate of the specified electron-reactant collisions, and hence of the production of the active species, is likely to be proportional to the current and independent of the pressure; that is, the current efficiencies for both these processes are likely to be current and pressure invariant. The theory of Part III shows that, in general, the fractional utilisation of the active species in the formation of the observed (or any specified) product is likely to depend on the pressure and the current in the following way. For any given value of the current, the fractional utilisation tends to approach unity asymptotically as the pressure is increased; thus at all pressures above some lower limit the fractional utilisation is practically unity, this limiting pressure increasing with the current. The range of pressure in which the fractional utilisation is practically constant is then a range in which the rate of synthesis of the observed product is governed by the rate of the specified electron-reactant collisions; and the existence of such a pressure range then offers an explanation for those cases in which it is observed that above some limiting pressure the current efficiency for the observed product is practically independent of the pressure and current. This explanation is acceptable, however, only when the number of product molecules formed per active species *reacting in that way* is also independent of the pressure, this case arising when branching chain mechanisms are not operative. And when the active species is identified together with the mechanism by which it reacts to give the observed product, the only quantity unknown in accounting for the magnitude of the current efficiency for the formation of the observed product, β, in this limiting case of practically complete utilisation of the active species is β_f, the current efficiency, or rate constant, for the occurrence of the particular electron-reactant collisions that generate the active species. This quantity is not usually known from experiment, but its magnitude must obviously conform to the condition that the rate at which electron energy is absorbed in effecting these collisions in the negative glow is less than the total rate at which energy is supplied to this zone; for there are, of course, many other types of collisions involving energy losses occurring simultaneously.

Detailed consideration of the fractional utilisation clearly requires not merely the identification of the active species and a knowledge of all the processes by which it can react or be destroyed in the given reactant gas, but it also requires a knowledge of the absolute rates at which it is consumed in the various possible ways including the formation of the observed product. This in turn demands a knowledge of the extent of the region in which it is produced and of that in which it reacts. The physical data for the negative glow show that the production of the active species must occur almost entirely within this zone, but that it is not uniform: it is therefore necessary to deal with the *volume average* rate of the formation of the active species, and hence if Z cm.^{3} is the volume of the zone, $\overline{R}_{er}$, the average rate of a specified type of electron-reactant collisions cm.$^{-3}$ sec.$^{-1}$ is, by the definition of the quantity β_f (*cf.* Part I), given by

$$\overline{R_{er}} = \beta_f I'_e/Z, \quad . \quad . \quad . \quad . \quad (1)$$

where I'_e is the current carried by the discharge in electronic charges sec.$^{-1}$. The corresponding rate of formation of the active species is then

$\phi_1 \overline{R}_{er}$ where ϕ_1 is the number of active species produced per electron-reactant collision of the specified kind. For the identification of the region in which the active species reacts in the experiments under consideration we rely on the observation of Brewer and Westhaver [6] that, in a cylindrical discharge tube of diameter little greater than that of the cathode, water is frozen out only on that part of the wall surrounding the negative glow; that is, the regions of generation and reaction are identical. It then follows that $\overline{R}_p$, the *volume average* rate of water formation in molecules cm.$^{-3}$ sec.$^{-1}$ is given by an expression similar to (1) or

$$\overline{R}_p = \beta I'_e/Z, \quad . \quad . \quad . \quad . \quad (2)$$

where $\beta I'_e$ is the time rate of water production found directly by experiment. In any given apparatus it is known from experiments with other discharges that, when the current and V_N are constant, the volume of the negative glow varies approximately inversely as the pressure: we therefore introduce for convenience the approximate relation

$$Z = Z_o/p, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where p is the pressure in mm., and Z_o cm.^{3} is the equivalent volume of the zone at unit pressure.

When the reaction is proceeding steadily the rate of production of the active species throughout the zone equals the rate at which it is lost in all possible ways; hence when the discharge and reaction zones are co-extensive

$$Z \,.\, \phi_1 \overline{R}_{er} = Z \,.\, (\overline{R}_{ac} + \overline{R}_{L}), \quad . \quad . \quad . \quad (4)$$

where $\overline{R}_{ac}$ and $\overline{R}_L$ denote, respectively, the *volume average* time rate at which the active species is lost in forming the observed product, and the corresponding combined rate at which it is lost by all other processes. From (1) this may be written

$$\overline{R}_{ac} + \overline{R}_L = \phi_1 \beta_f I'_e/Z, \quad . \quad . \quad . \quad (4.1)$$

or, when (3) is applicable,

$$\overline{R}_{ac} + \overline{R}_L = p\, \phi_1 \beta_f I'_e/Z_o. \quad . \quad . \quad . \quad (4.2)$$

When the reaction mechanism together with the processes otherwise destroying the active species are completely specified, $\overline{R}_{ac}$ and $\overline{R}_L$ can be expressed as functions of $\overline{\lambda}_a$, the volume average fractional concentration of the active species, and of the particular conditions in any given experiment; consequently when β_f is also known $\overline{\lambda}_a$ is the only unknown in (4.1) and (4.2) and hence may be evaluated for any given experimental conditions. When $\overline{\lambda}_a$ is known the numerical values of $\overline{R}_{ac}$ and $\overline{R}_L$ can be computed; and it is then possible to compute $\overline{f}_a$, the average fractional utilisation of the active species in forming the observed product, which (*cf.* Part III) is given by

$$\overline{f}_a = \overline{R}_{ac}/(\overline{R}_{ac} + \overline{R}_L). \quad . \quad . \quad . \quad . \quad (5)$$

From (4) it then follows that

$$\overline{R}_{ac} = \overline{f}_a \phi_1 \overline{R}_{er}; \quad . \quad . \quad . \quad . \quad (5.1)$$

and if each particle of the active species yields ϕ_2 molecules of the observed product *when it reacts in that way*, it follows that $\overline{R}_{a,p}$, the calculated volume average time rate of the formation of the observed product in molecules cm.$^{-3}$ sec.$^{-1}$ is

$$\overline{R}_{a,p} = \phi_2 \overline{R}_{ac},$$

or

$$\overline{R}_{a,p} = \overline{f}_a \phi_1 \phi_2 \overline{R}_{er}, \qquad . \quad . \quad . \quad . \quad (6)$$

which, from (1) may be written

$$\overline{R}_{a,p} = \overline{f}_a \phi_1 \phi_2 \beta_f I'_e/Z, \qquad . \quad . \quad . \quad (6.1)$$

or, when (3) is applicable

$$\overline{R}_{a,p} = p\overline{f}_a \phi_1 \phi_2 \beta_f I'_e/Z_0 . \qquad . \quad . \quad . \quad (6.2)$$

A comparison between $\overline{R}_{a,p}$, the calculated rate of production of the observed product as given by (6.1), with $\overline{R}_p$, the rate found from experiment by (2), shows that the quantity

$$\beta_a = \overline{f}_a \phi_1 \phi_2 \beta_f = \Phi_a \beta_f . \qquad . \quad . \quad . \quad . \quad (7)$$

is the theoretically computed current efficiency for the reaction corresponding with the specified type of electron-reactant collisions and resulting active species reacting and being otherwise destroyed by the specified mechanism. The validity of any hypothetical reaction mechanism in any given experimental conditions in which β is measured may thus be examined by comparing β with β_a as computed from (7) for the same conditions. When β_f is not known from experiment, the balance between the energy gained and lost by the electrons in the negative glow (*cf.* p. 1095 *supra*, and Part I) introduces the additional requirement that

$$V_e \beta_f < 0{\cdot}17\, V_N, \qquad . \quad . \quad . \quad . \quad (7.1)$$

where V_e ev. is the energy absorbed per elctron-reactant collision of the specified kind.

The theory of Part I does not lead to the identification of the active species concerned in any particular case, but only indicates the one or more types of electron-reaction collisions that are likely to be the main sources of any given active species. For this identification we turn to the data for reaction in hydrogen-oxygen mixtures initiated by light absorption, partly because any excitation process involved in the photo-reaction is likely also to be effected by electron impact in the negative glow. In the unsensitised photo-reaction oxygen atoms are the active species, and in the mercury sensitised case hydrogen atoms; the corresponding excitation process in oxygen is likely to be important in the negative glow (*cf.* Part I) but the generation of hydrogen atoms in this zone is quite different from the process operative in the mercury sensitised photo-reaction. In this paper we therefore explore the possibility that the same two active species initiate the oxidation of hydrogen in hydrogen-oxygen mixtures in the negative glow reaction: for oxygen atoms we invoke a reaction mechanism " A " based mainly on the data for unsensitised photo-reaction, and for hydrogen atoms another mechanism based on the kinetics of the mercury sensitised photo-reaction. A further mechanism " B " which is purely hypothetical is considered as an alternative to " A," but is, however, ultimately rejected. These mechanisms are specified in detail later.

We state next the particular forms of the expressions developed earlier which are appropriate to these particular mechanisms. For the collisions generating oxygen atoms we replace β_f by $\Sigma\beta_{f,0}$ because more than one type of such collision is likely to be involved ; and from (1) the gain and loss of this species from (4) is given by

$$\phi_{1,O}\, \Sigma\beta_{f,O}\, I'_e = (\overline{R}_{ac,O} + \overline{R}_{L,O}) \,.\, Z \qquad . \qquad . \qquad . \quad (8\cdot1)$$

or, when (3) is applicable, and after re-arranging

$$\overline{R}_{ac,O} + \overline{R}_{L,O} = p\phi_{1,O}\, \Sigma\beta_{f,O}\, I'_e/Z_0 \qquad . \qquad . \qquad . \quad (8\cdot2)$$

This expression is to be solved for $\overline{\lambda}_O$ the fractional concentration of oxygen atoms, for the particular values of p, I'_e, Z_0 and $\Sigma\beta_{f,O}$ corresponding with the particular experimental conditions in which the validity of mechanism " A " is investigated, the $\overline{R}$'s being then computable in terms of $\overline{\lambda}_O$, and the composition and pressure of the reactant gas. For the same range of conditions $\overline{f}_O$ is computed from (5) ; and finally β_A, the contribution to β by this mechanism, follows from (7) as

$$\beta_A = \overline{f}_O\, \phi_{1,O}\, \phi_{2,A}\, \Sigma\beta_{f,O} = \Phi_A\, \Sigma\beta_{f,O} \qquad . \qquad . \qquad . \quad (8\cdot3)$$

$\phi_{2,A}$ being a characteristic of the mechanism. A similar procedure is applicable in the case of mechanism " B " but $\phi_{2,B}$ has a different value. Similarly, for the collisions generating hydrogen atoms β_f is to be replaced by $\Sigma\beta_{f,H}$, and then for mechanism " C " we find expressions analogous to (8·1) and (8·2), namely

$$\phi_{1,H}\, \Sigma\beta_{f,H}\, I'_e = (\overline{R}_{ac,H} + \overline{R}_{L,H}) \,.\, Z \qquad . \qquad . \qquad . \quad (8\cdot4)$$

and

$$\overline{R}_{ac,H} + \overline{R}_{L,H} = p\, \phi_{1,H}\, \Sigma\beta_{f,H}\, I'_e/Z_0 \qquad . \qquad . \qquad . \quad (8\cdot5)$$

these have to be solved similarly for $\overline{\lambda}_H$, the average fractional concentration of hydrogen atoms, for the same range of experimental conditions. Similarly, $\overline{f}_H$ is then found from (5), and β_C, the contribution to β by this mechanism follows as *

$$\beta_C = \overline{f}_H\, \phi_{1,H}\, \phi_{2,C}\, \Sigma\beta_{f,H} = \Phi_C\, \Sigma\beta_{f,H} \qquad . \qquad . \qquad . \quad (8\cdot6)$$

The validity of the mechanisms " A" and " C " is then demonstrated by a comparison between β and $\beta_A + \beta_C$ for the particular experimental conditions under consideration. The alternative combination " B " and " C " is tested similarly by comparing β with $\beta_B + \beta_{B,C}$.* In either case the energy restriction stated in (7·1) now requires that

$$\Sigma(V_{e,O}\, \beta_{f,O}) + \Sigma(V_{e,H}\, \beta_{f,H}) < 0{\cdot}17 V_N \qquad . \qquad . \qquad . \quad (8\cdot7)$$

where the V_e's relate to the particular electron-reactant collisions concerned.

Manifestly, it would be extremely laborious to examine the validity of expressions (8) to (8.9) for all experiments to which Table I relates we have therefore investigated their validity for the mechanisms " A," " B," and " C," to be specified in detail later, only for particular groups of experiments, noted later, which typify the principal characteristics of β, especially those associated with the three pressure ranges.

3. The Reaction Mechanisms " A," " B," and " C."

Mechanism " A."—The unsensitised photo-reaction in hydrogen-oxygen mixtures leads to the oxidation of the hydrogen partly as peroxide and partly as water ; because the devices used in the discharge experiments do not distinguish between these substances but relate to the equivalent water formed, it is convenient now to discuss the

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* When mechanism " B " replaces " A," as is shown later, there is a further term to be added to $\beta_{f,H}$ in (8·4), (8·5), and (8·6) ; and the corresponding contribution by mechanism " C " to β is then denoted by $\beta_{C,B}$.

oxidation in terms of the equivalent water formation. For the range λ 1719-1725, corresponding with the excitation of the $^3\Sigma_u^-$ level of oxygen, at ordinary temperature and in the pressure range 0·25-1 atm., the results of Kistiakowsky and Smith [22] indicate a yield of from 0·75 to 1·75 equivalent water molecules per quantum absorbed. In the range λ 1350-1750 (— 180°, and *ca.* 0·1 mm.) the data of Neujmin and Popoff lead to 0·1 water molecules as a very rough estimate, but the uncertainties in their determinations do not by any means exclude a value ten times higher.[20] We adopt here the maximum value of the quantum yield of Kistiakowsky and Smith, and since two oxygen atoms are formed per oxygen molecule excited, this is equivalent to writing $\phi_{2,A} = 0{\cdot}88$. The mechanism proposed by these latter authors assumes that there is no difference between the chemical activities of the two kinds of O atoms produced, and that the initial and rate determining step involves the ternary collisions $O + H_2 + M$ where M is either an oxygen or hydrogen molecules: the rate of such collisions is therefore to be identified with $R_{ac,O}$; * and for purposes of computation it is assumed that the collisional efficiency with respect to the somewhat arbitrary collisions numbers adopted in Part III is 10, a value that is not excluded, we believe, by any of the data for the kinetics of the photo-reaction.

We assume that the only other significant processes removing the active species are homogeneous recombination and diffusion to the wall, the total rate being identified with $\overline{R}_{L,O}$. The rate of loss by recombination is given by twice the rate of the ternary collisions $O + O + M$ where M has its previous significance; * and the collisional efficiency is taken to be 0·1 to allow for the fact that in most of these collisions at least one atom will be in the ^3P state and thus be characterised by assymetry in the electron cloud which introduces a steric effect. The equivalent average volume rate † of loss of the active species by diffusion to the walls for the special case in which (3) is applicable follows from expression (18·2) of Part III for the particular case of a cylindrical reaction vessel of radius r as

$$\overline{R}_{D,O} = 0{\cdot}5\, k_{w,O}\, \overline{\lambda_O}\, pNc_O/r. \qquad (9{\cdot}1)$$

where λ_O is the average fractional concentration of oxygen atoms,

$$N = 3{\cdot}55 \,.\, 10^{16}$$

is the number of particles in a gas per cm.^{3} at 1 mm. and the standard temperature,† c_O is the velocity of thermal agitation of oxygen atoms and is taken to be about 6 . 10^4 cms. sec.$^{-1}$ at the standard temperature, and $k_{w,O}$ is the probability of destruction at the wall. For hydrogen atoms at a glass surface saturated with water Poole [17] finds the corresponding quantity $k_{w,H}$ to be 1·6 . 10^{-4}, and since it is known that oxygen atoms are not less readily destroyed at a surface, we adopt the conservative estimate $k_{w,O} = 10^{-4}$.

A complete identification of all the electron-reactant collisions leading to the formation of oxygen atoms is not possible, but the data for the photo-reaction together with the considerations advanced in Part I indicate that the excitation of the $^3\Sigma_u^-$ and $^3\Sigma^+$ levels of oxygen are those likely to be of principal importance; the corresponding values of V_e are about 8 and 5·5 ev., respectively. For these levels $\phi_1 = 2$; and for reasons stated later (*cf.* pp. 31, 32) $\Sigma\beta_{f,O}$ is estimated to be about 4·3 when V_N is about 400 volts.

* The particular expressions found for these and similar rates in electrolytic gas and other mixtures are given in the appendix.

† If the temperature is not the standard, the appropriate correction must be made.

Mechanism "B."—The following sequence of reactions in which oxygen atoms are again the active species, and for which ϕ_2 has a maximum value of unity is the basis of mechanism "B"

$$O + H_{2,v} = OH^* + H \qquad . \quad . \quad . \quad (b1)$$

followed by

$$OH^* + H_2 = H_2O + H, \qquad . \quad . \quad . \quad (b2)$$

where $H_{2,v}$ denotes a molecule in the first vibrational level, and OH^* also denotes a vibrationally excited molecule; but it is to be noted that reaction (b1) requires that $\beta_{f,v}$, the current efficiency for the electron-reactant collisions generating $H_{2,v}$ molecules shall amount to at least $2\Sigma\beta_{f,O}$, a process for which V_e is 0·53 ev. * On account of the large internal energies of the molecules involved in these reactions it is to be anticipated that the collisional efficiencies are likely to be high; † on the other hand their occurrence is not known from experiment. An important aspect of this mechanism, which later leads in part to its rejection, is that it provides for the generation of two hydrogen atoms, the active species of mechanism "C," per water molecule formed: this is equivalent to a generation of hydrogen atoms numerically equal to $2\beta_B$, where β_B is the contribution to β by this mechanism.

Mechanism "C."—The quantum yield for the oxidation of hydrogen in the mercury sensitised photo-reaction in hydrogen-oxygen mixtures in equivalent water molecules[16] is about 2·5, and since each quantum absorbed leads ultimately to the generation of two hydrogen atoms, it follows that $\phi_{2,C} = 1{\cdot}25$ referred to these atoms as the active species. The initial and rate determining step is generally accepted to involve the ternary collisions $H + O_2 + H_2$, and hence the rate of these collisions is to be identified with $\overline{R}_{ac,H}$; ‡ for the collisional efficiency we adopt Bodenstein's[28] value 0·17 which is based on a review of all the relevant data.

We assume that the only other significant processes removing the active species are again homogeneous recombination and diffusion to the wall, the total average rate of these being identified with $\overline{R}_{L,H}$; § for the collisional efficiency of the recombination process we adopt the value 10 given by Farkas and Sachse.[27] The equivalent average volume rate of loss of the species by diffusion to the wall for the special case in which (3) is applicable and for the case of a cylindrical reaction vessel then follows by analogy with (9·1) as ‡

$$\overline{R}_{D,H} = 0{\cdot}5 k_{w,H} \overline{\lambda}_H pNc_H/r \qquad . \quad . \quad . \quad . \quad (9{\cdot}2)$$

where $\overline{\lambda}_H$ is the average fractional concentration of hydrogen atoms, c_H is the velocity of thermal agitation of hydrogen atoms, and is taken to be $2{\cdot}5 \,.\, 10^5$ cm. sec.$^{-1}$, and $k_{w,H}$ is the probability of destruction at the wall for which we adopt Poole's[17] value for a water saturated glass surface, $1{\cdot}5 \,.\, 10^{-4}$.

Again, the identification of the electron-reactant collisions leading to the formation of hydrogen atoms (apart from the processes considered in mechanism "B") is incomplete, but the considerations advanced in

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* Although this additional loss still fulfils (8·7), the margin of energy then available for other processes is then too small to be acceptable; in addition, such a high value for $\beta_{f,v}$ is improbable.[18]

† For absolute rates, see Appendix.

[16] Bonhoeffer and Harteck, *Photochemie*, Leipzig, 1933.

‡ For the corresponding numerical expression see Appendix.

[17] Poole, *Proc. Roy. Soc.*, *A*, 1937, **163**, 446.

[18] Massey, *Trans. Faraday Soc.*, 1934, **31**, 556.

Part I, and the data for other discharges,[14] indicate that those leading to the excitation of the $^3\Sigma_u^+$, $^3\Sigma_g^+$, and possibly $^1\Pi_u$ levels are likely to be of principal importance ; * for these, the corresponding values of V_e are, respectively, 9·5, 12, and 12 ev. For all these levels $\phi_1 = 2$; and for reasons stated below $\Sigma\beta_{f,\mathrm{H}}$ is estimated to be about 1·6 when V_{N} is about 400 volts.

4. The Experiments selected for and the Detailed Examination of the Validity of Mechanisms " A," " B," and " C."

Before stating these experiments and investigating the validity of the mechanisms, it is convenient to refer firstly to the conclusion that in the low pressure range β has value about 8 and that this is likely to correspond with the full development of one mechanism ; this is identified as " A " so that the maximum possible value of $\Phi_{\mathrm{A}}\,\Sigma\beta_{f,\mathrm{O}}$ is to be identified as about 8, and hence the maximum value of $\Sigma\beta_{f,\mathrm{O}}$ must be about 4. Secondly, there is also the conclusion that in the high pressure range β is about 12 for cathodes of Ag, Au, Ta, and W, and that this is likely to correspond with the full development of another mechanism in addition : this is identified as " C " so that the maximum possible value of $\Phi_{\mathrm{C}}\,\Sigma\beta_{f,\mathrm{H}}$ is about 4, and hence the maximum value of $\Sigma\beta_{f,\mathrm{H}}$ must be about 1·6. The alternative possibility is that mechanism " B " replaces " A." It transpires that, in investigating the validity of the various mechanisms, in the particular experimental conditions it is not for the most part necessary to consider the implications of the simultaneous operation of the mechanisms, and this, of course, involves a somewhat complicated procedure.

4.1. Low and Intermediate Pressure Range.

The experiments selected are those of Brewer and Westhaver [6] relating to a cylindrical vessel immersed in a bath at − 80°, a constant current of 20 milliamps., and the pressure range 0·3 to 35 mm. of electrolytic gas ; V_{N} is, however, constant in the middle of this range only, whilst β is constant at 8·4 from 0·3 to 7 mm. No data are given for Z : for the range of constant $V_{\mathrm{N}} = 400$ volts, we estimate from the dimensions of the apparatus and experience with other discharges that Z_0 is about 10 cm.^{3}, but admit a range of uncertainty from about 5 to 20 cm.^{3} ; † and for larger values of V_{N} we make the plausible assumption based on experience with other discharges that Z_0 varies directly as V_{N}. For the reasons stated on page 1092 we take the temperature of the gas as about 300° K.

For reasons already stated, we begin by considering the validity of mechanism " A " at the upper end of the low pressure range in which β is constant at $8{\cdot}3_8$, $p = 7$, by supposing that Φ_{A} has its maximum value of $2 \times 0{\cdot}88 = 1{\cdot}76$. But, although the constancy of β in this range at first

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* For a discussion of the cross-sections for the excitations of these levels see Lunt and Meek.[21] Dr. Teller has pointed out that there is some likelihood that molecule in the $^1\Pi_u$ level may decompose on collision ; [19] imprisonment of the resonance radiation from such excited molecules is a factor tending to enhance this process of atom production.

† It will be appreciated that Z_0 enters into the calculations in a subsidiary way only, that is, for the estimation of the relative rates of competing reactions. The basic factor for the calculation of the absolute reaction rate in the negative glow is the rate of electron-reactant collisions of specified kinds which involves primarily only the current and the potential fall maintaining the discharge.

[19] Teller, *private communication.*

[20] Neujmin and Popoff, *Z. physik. Chem., B*, 1934, **27**, 15.

[21] Lunt and Meek, *Proc. Roy. Soc., A*, 1936, **157**, 146.

[22] Kistiakowsky and Smith, *J.A.C.S.*, 1936, **57**, 835.

TABLE II.

THE CALCULATED CONTRIBUTION TO β FOR MECHANISMS "A" AND "C" TOGETHER, $\beta_A + \beta_C$, AND THE CALCULATED CONTRIBUTION FOR MECHANISMS "B" AND "C" TOGETHER, $\beta_B + \beta_{C,B}$, FOR THE EXPERIMENTAL CONDITIONS OF BREWER AND WESTHAUER[6] (ELECTROLYTIC GAS).

p	V_N	Mechanisms "A" and "C".								β (exptl.)	Mechanisms "B" and "C".									
		$\overline{\lambda}_P$	$\overline{\lambda}_O$	$\overline{f}_O$	β_A	$\overline{\lambda}_H$	$\overline{f}_H$	β_C	$\beta_A+\beta_C$		$\beta_B+\beta_{C,B}$	$\overline{\lambda}_P$	$\overline{\lambda}_O$	$\overline{f}_O$	β_B	$\overline{\lambda}_V$	$\overline{f}_V$	$\overline{\lambda}_H$	$\overline{f}_H$	$\beta_{C,B}$
0·3	800	0·3	0·54	0·53	2·4	0·09	$0{\cdot}0_31$	$0{\cdot}0_23$	2·4	8·4	10·4	0·6	0·003	0·99	10·3	$0{\cdot}0_46$	0·95	0·36	0·003	0·09
0·6	600	0·75	0·12	0·95	8·1	0·10	$0{\cdot}0_27$	0·032	8·1	8·4	9·2	0·7	0·002	0·99	9·0	$0{\cdot}0_33$	0·95	0·25	0·007	0·19
1·0	450	0·9	0·04	0·99	8·3	0·06	0·024	0·11	8·4	8·4	8·5	0·85	0·002	1	8·3	$0{\cdot}0_32$	0·95	0·14	0·009	0·22
2·0	420	1	0·01	$0{\cdot}99_7$	7·9	0·03	0·056	0·24	8·1	8·4	9·2	0·95	0·002	1	8·6	$0{\cdot}0_48$	0·95	0·076	0·023	0·62
3·5	400	1	$0{\cdot}0_24$	1	7·6	0·02	0·11	0·46	8·1	8·4	9·6	1	0·002	1	8·6	$0{\cdot}0_45$	0·95	0·056	0·040	1·02
5·0	400	1	$0{\cdot}0_21$	1	7·6	0·01	0·13	0·54	8·1	8·4	10·0	1	0·002	1	8·6	$0{\cdot}0_43$	0·95	0·031	0·087	1·45
7·0	400	1	$0{\cdot}0_32$	1	7·6	$0{\cdot}0_28$	0·19	0·75	8·3	8·4	10·5	1	0·002	1	8·6	$0{\cdot}0_42$	0·95	0·022	0·077	1·91
10·0	400	1	$0{\cdot}0_31$	1	7·6	$0{\cdot}0_26$	0·25	1·01	8·6	9·4	11·4	1	0·002	1	8·6	$0{\cdot}0_42$	0·95	0·015	0·11	2·83
15·0	400	1	$<0{\cdot}0_31$	1	7·6	$0{\cdot}0_23$	0·46	1·85	9·4	12·0	13·0	1	0·002	1	8·6	$0{\cdot}0_41$	0·95	0·009	0·17	4·40
20·0	420	1	do.	1	8·0	$0{\cdot}0_22$	0·57	2·40	10·4	13·3	14·6	1	0·002	1	9·0	$0{\cdot}0_58$	0·95	0·007	0·21	5·59
30·0	440	1	do.	1	8·4	$0{\cdot}0_21$	0·68	3·00	11·4	15·4	18·3	1	0·002	1	9·5	$0{\cdot}0_56$	0·95	0·004	0·31	8·89
35·0	445	1	do.	1	8·5	$0{\cdot}0_21$	0·73	3·29	11·8	15·4	19·3	1	0·002	1	9·6	$0{\cdot}0_65$	0·95	0·003	0·34	9·76

sight suggests that this is the only mechanism operative, the examination of mechanism "C" reveals that its contribution, β_C, for $p = 7$ is about $0{\cdot}7_5$ when $\Sigma\beta_{f,\mathrm{H}}$ is taken to be 1·6 as indicated above. We therefore identify the full development of mechanism "A" with the balance so that $\beta_A = 7{\cdot}6_3$, and find for $\Sigma\beta_{f,\mathrm{O}}$ the value $7{\cdot}6_3/1{\cdot}76 = 4{\cdot}3$. This result and the value 1·6 adopted for $\Sigma\beta_{f,\mathrm{H}}$ refer to $V_N = ca.$ 400 volts. Since the corresponding quantity for ionisation in electron beam experiments (the $P_i(V)$ of Part I) varies approximately linearly with the electron energy,[33] it is a reasonable expectation that a similar relationship is valid for the dependence of $\Sigma\beta_{f,\mathrm{O}}$ and $\Sigma\beta_{f,\mathrm{H}}$ on V_N, which is the view now adopted. It is then to be seen that $\Sigma(V_{e,\mathrm{O}}\,\beta_{f,\mathrm{O}}) + \Sigma(V_{e,\mathrm{H}}\,\beta_{f,\mathrm{H}})$ complies with (8·7) for all values of V_N, and leaves a reasonable margin of energy for the other processes occurring. The next step is to solve (8·2) for $\overline{\lambda_O}$ and (8·5) for $\overline{\lambda_H}$ for the particular values of p and I'_e in the experiments. For $p = 1$ mm. or less, it is found that $1 - (\overline{\lambda_O} + \overline{\lambda_H}) = \overline{\lambda_P}$, the total average fractional concentration of the reactants, begins to depart appreciably from unity. Under these conditions the values derived for the β_f's are no longer applicable because they relate to electrolytic gas. We make a rough allowance in such cases by supposing that the effective values of these quantities are given by their values in electrolytic gas multiplied by $\bar{\lambda}_P$: in this case it is necessary to solve for $\bar{\lambda}_O$ and $\bar{\lambda}_H$ by successive approximation. From the values thus found for $\bar{\lambda}_O$ and $\bar{\lambda}_H$, the corresponding values of $\bar{f}_O$ and $\bar{f}_H$ are found from (5), the appropriate substitutions being made for each mechanism. Finally, β_A and β_C are computed from (8·3) and (8·6) ; these, and the other data relating to the calculations are reported in Table II.

We consider next the possibility that mechanism " B " is operative in place of " A." Again the constancy of β in the low pressure range suggests that full utilisation occurs for $p = 7$ mm. Now it has already been seen that at full utilisation this mechanism requires that $\beta_{f,v} = 2\Sigma\beta_{f,O}$, but some allowance must be made for other destructive processes ; we therefore suppose that for $V_X = 400$, $\beta_{f,v}$ is about 9, that is, 0·4 units in excess of $2\Sigma\beta_{f,O}$.* For the destructive processes we make the generous assumption that the probabilities per collision for homogeneous destruction (degradation of internal energy) and at the wall are, respectively, about 10^{-4} and 10^{-2}. If, as has been supposed, reactions (*b*1) and (*b*2) have collisional efficiencies close to unity, we may write an expression for the generation and destruction of vibrationally excited hydrogen molecules analogous to (8·2) which is simultaneous to (8·2) itself ; the solution of these simultaneous expressions yields values for $\bar{\lambda}_O$ and $\bar{\lambda}_v$, the average fractional concentration of vibrationally excited hydrogen molecules. Then $\bar{f}_O$ and $\bar{f}_v$ may be found after making the appropriate substitutions in (5) ; and finally β_B, the contribution to β by mechanism B is found from (8·3) when these new values of $\bar{f}_O$ are inserted and $\phi_{2,A}$ is replaced by $\phi_{2,B} = 1$. This mechanism has been seen to generate hydrogen atoms equivalent in amount to an addition to $\Sigma\beta_{f,H}$ of $2\beta_B$. On solving (8·5) after this correction to $\Sigma\beta_{f,H}$ has been made, new values are found for $\bar{\lambda}_H$; these in turn yield new values for $\bar{f}_H$ from (5) ; and finally (8·6) after again introducing the corrected value for $\Sigma\beta_{f,H}$ yields $\beta_{C,B}$, the contribution to β by this modification of mechanism " C ". The relevant data are given in Table II.

Discussion of Table II.—An inspection of Table II shows that the combination of mechanisms " A + C " provides a detailed explanation for the constancy of β in the low pressure range, and for the observation that as the pressure is diminished below this range β diminishes rapidly.[6] In the intermediate range the initial increase and the tendency towards a constant value of β at the upper end of this range is predicted ; $\beta_A + \beta_C$ is, however, a little smaller than β.

On the other hand the combination " B + C " does not provide so good an explanation for the constancy of β in the low pressure range ; $\beta_B + \beta_{C,B}$ tends to rise as the pressure is diminished at the lower end of this range, and the calculations indicate that this sum does not begin to diminish until pressures much lower than 0·3 mm. are reached. In the intermediate range $\beta_B + \beta_{C,B}$ parallels the trend of β more closely than does $\beta_A + \beta_C$ except at the upper end of the range where it shows little tendency to become constant.

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* (8·7) is still fulfilled, but the margin for other processes is rather small to be acceptable.

[23] Emeléus and Lunt, *Trans. Faraday Soc.*, 1936, **32**, 1504.

[24] Lunt, *Trans. Faraday Soc.*, 1936, **32**, 1691.

[25] Lunt and Swindell, *Trans. Faraday Soc.*, previous paper.

[26] Lunt, Meek, and Swindell, *shortly to be communicated.*

[27] Farkas and Sachse, *Z. physik. Chem.*, *B*, 1934, **27**, 111.

[28] Bodenstein, *private communication.*

We conclude that the balance of evidence is in favour of the combination " A + C " ; and it is pertinent to recall that mechanism " B " is purely hypothetical, and that it does not leave an acceptably large margin of energy for the other processes that must occur simultaneously (*cf.* footnotes *, † to p. 1100).

It is now convenient to consider some other aspects of the data for the low pressure range. For the dependence of β on the current we consider the experiments at 4 mm. relating to the same apparatus to which Table II relates;[6] and since the data show that the conditions relate to the regime of abnormal cathode fall,[14] in order to take account of the increase of Z with V_N which is to be anticipated from experience with other discharges,[14] we suppose for simplicity that Z varies linearly with V_N. For the combination " A " + " C " we then find the data given in Table III. From this it is seen that the mechanisms account roughly for the variation in β; and it can be shown that a closer parallelism is attained if it is supposed that Z varies as V_N^m where m is less than unity, which is not excluded by the physical data for other discharges. Next, there is the slight dependence of β on the metal of the cathode accompanied, however, by a similar variation in V_N (*cf.* Table I). In one series of experiments, the cathode metal is the only factor changed:[8] for these we deduce from the considerations of Part I that $\Sigma\beta_{f,O}$ and $\Sigma\beta_{f,H}$ vary directly as V_N; and if, in addition Z does not change much, which is likely, it is readily shown that $\beta_A + \beta_C$ is proportional to V_N, that is, that $(\beta_A + \beta_C)/V_N$ is constant. But from the definitions in Part I, this latter quantity is the theoretical counterpart to the energy efficiency of equivalent water formation η: thus the constancy of $(\beta_A + \beta_C)/V_N$ provides in this way an explanation for the constancy of η evidenced for these experiments[8] in Table I. The influence of the gas composition is difficult to discuss because there is no evidence for the corresponding variation of the β_f's. If, however, we make the plausible assumption that, when I'_e, p, and V_N are constant, which is the case for one group of experiments,[6] the β_f's each vary with the fractional concentration of the reactant to which they relate, then it is easily shown that $\beta_A + \beta_C$ parallels the behaviour of β in the sense that this sum passes through a maximum, but the composition corresponding with the maximum cannot be predicted.

TABLE III.

THE DEPENDENCE OF β ON THE CURRENT.

Current, ma.	10	20	40
V_N	345	397	470
β	5·4	8·4	11·5
$\beta_A + \beta_C$	6·8	8·1	9·4

It remains to consider $\overline{\lambda}_W$, the fractional concentration of water vapour in the experiments, and the corresponding quantities other species than the reactants likely to be present. Because the wall of the reaction vessel is refrigerated to − 80° practically no water molecules are reflected on reaching the wall; in this case expression (19·4) of Part III is applicable to this species, and yields for $\lambda_{W,max.}$, the maximum fractional concentration of the species

$$\lambda_{W,max.} = \beta I'_e/(\pi r N D_W), \quad . \quad . \quad . \quad . \quad (10)$$

where D_W is the diffusion constant for water vapour in the reacting gas at 1 mm., and is now estimated to be about 10^3. On substituting the experimental values for p, β, and I'_e, we find $\lambda_{W,max.}$ to be less than 0·01 over the whole range of conditions; and the average value, $\overline{\lambda_W}$, must be considerably smaller than this. The fact that the addition of water vapour to electrolytic gas has no effect on β for values of λ_W less than 0·4 [11] leads to the expectation that in any case the small amount of water present is likely to have exerted little net effect. Ideally, the fractional concentration of all other species should be considered similarly; but in view of the uncertainty concerning the detailed steps of the photo-reaction,[22] we have not felt justified in attempting this. It is, however, a reasonable inference that since the λ's for the active species and the observed product are thus found to be acceptably small, the same is likely to be true for all intermediate species.

4.2. High Pressure Range.

We consider in detail most of the experiments relating to this range. The first group (Finch and Mahler [9]) relates to hydrogen-oxygen mixtures in which x, the fractional concentration of oxygen, varies from 0·005 to about 0·95; the gas is *circulated* through a discharge tube immersed in a bath at 20°; the pressure range is 30-90 mm., and the current range 1·5-2·5 ma. The only factor varied in these experiments is the metal of the cathode; the corresponding variations in V_N are very small, 340-350 volts (*cf.* Table I). From the little data available,[6, 15] we estimate Z_0 to be about 10 cm.^{3}, but admit a range of uncertainty from about 5 to 20 cm.^{3} (*cf.*, footnote †, p. 1101). The second group relates to electrolytic gas in the same pressure and practically the same current ranges in a closely similar apparatus, but there is no circulation of the gas.[6] The electrodes are Cu and Pt, and V_N is about 400 volts; and the above estimate for Z_0 is applicable. In all these experiments β is independent of the current and, in electrolytic gas, increases very slightly with the pressure. It is convenient to deal firstly with the data relating to electrolytic gas, and then with those for other mixtures.

We examine firstly the validity of the same combination of mechanisms as before, but, on account of the high pressure, it is at once apparent that the f's for mechanisms " A " and " B " must be sensibly unity so that it is necessary to consider in detail the chemical activity attributable to hydrogen atoms only. The results of the calculations for electrolytic gas and for a current of 2·5 ma. are given in Table IV below, the reaction zone being assumed to be co-extensive with the discharge zone.

TABLE IV.

THE CALCULATED CONTRIBUTION TO THE CURRENT EFFICIENCY OF EQUIVALENT WATER PRODUCTION IN THE HIGH PRESSURE RANGE FOR THE MECHANISMS " A + C " AND " B + C " IN ELECTROLYTIC GAS, β DENOTING THE MEAN VALUE FOUND BY EXPERIMENT FOR CATHODES OF SILVER AND GOLD.[9]

p	A + C; $B_A = 7.6$				β	B + C; $\beta_B = 8.6$			
	$\overline{\lambda}_H$	$\overline{f}_H$	β_C	$\beta_A + \beta_C$		$\beta_B + \beta_{C,B}$	$\overline{\lambda}_H$	$\overline{f}_H$	$\beta_{C,B}$
30	$0\cdot0_32$	0·93	$3\cdot7_1$	11·3	11·4	16·5	0·004	0·31	7·9
60	$0\cdot0_46$	0·98	$3\cdot9_2$	11·5	11·9	21·5	0·002	0·51	12·9
90	$0\cdot0_43$	0·99	$3\cdot9_6$	11·5	12·2	29·1	$0\cdot0_47$	0·73	18·5

Discussion of Table IV.—There is insufficient data about the streaming of the gas to attempt any detailed allowance for the effect of streaming. Qualitatively, the effect is to increase the effective volume of the reaction zone; and since the time rate of production of the active species is still proportional to the sum of the $I\beta_f$'s it is easily seen that streaming must tend to reduce the λ's below the values as computed in the above Table, and hence to increase the $\bar{f}$'s. In the case of the combination " A + C " this can have little effect of the calculated values $\beta_A + \beta_C$ because, without allowing for any effect of streaming, the f's for mechanism " A " have been taken to be unity because of the high pressure concerned, and those for mechanism " C " are already very close to unity. On the other hand, for the combination " B + C," whilst again the f's for mechanism " B " are taken to be unity on account of the pressure, the effect of streaming must tend to increase the f's associated with mechanism " C," and hence $\beta_B + \beta_{C,B}$ must tend to approach the maximum value of 32·1. The combination " A + C " thus provides a satisfactory explanation for the absolute values of β found for cathodes of Ag, Au, and Ta; but in this case it must be supposed that an additional mechanism is operative to account for the much larger values of β found for cathodes of W, Cu, and Pt. On the other hand, the combination " B + C " leads to large values for $\beta_B + \beta_{C,B}$ which, although just adequate to account for the value of β found for Pt cathodes (no streaming) at the highest pressure, fail to account for the absence of any pressure effect. In addition, to account for absence of any pressure effect on β for cathodes of W (streaming gas) and Cu (no streaming), it must be supposed that an additional *destructive* mechanism is operative at the higher pressures only; and to account for the same effect in the case of cathodes of Ag, Au, and Ta (all streaming gas) the destructive mechanism must be considerable even at the lowest pressure and increase rapidly as the pressure is increased. Finch [9, 13] proposed a destructive mechanism which makes no attempt to account for the pressure invariance of β and which assumes that the metal sputtered from the cathode (or the resulting oxide) is the destructive agent; since he reports that W and Ta do not sputter whilst the other four metals sputter freely, there is clearly no connection between the extent of sputtering and the values of β, and hence this suggestion is to be rejected. We have been unable to find any destructive mechanism having the required properties. The fact that in all these experiments the principal factor changed is only the metal of the cathode, V_N changing but slightly, strongly suggests that the excess in β over the minimum value of about 12 for cathodes of Ag, Au, and Ta, is attributable to an additional mechanism associated with the cathode surface, a conclusion that is elaborated in Part V. We now adopt this conclusion, and reject the combination " B + C " because of the defects just mentioned and those cited in discussing the data of Table II, and in view of the evidence discussed below concerning the reaction in hydrogen-rich mixtures in this pressure range. That is, we conclude that the combination " A + C " is operative and affords a satisfactory explanation of the characteristics of β when allowance is made for the possible existence of a reaction associated with the cathode surface. In this case it is easily shown that in the narrow range of current concerned $\beta_A + \beta_C$ is practically independent of the current in accordance with experiment.

The fractional concentration of water vapour in these experiments is difficult to estimate because the conditions do not correspond closely with those which are considered in Part III. Neglecting any effect of streaming, expression (10) yields $\lambda_W < 10^{-3}$ which is satisfactorily small; and so are the values of λ's for the active species in Table IV. These latter indicate the λ's for all intermediate species are probably very small too.

We consider next the data for the effect of the gas composition on β as found from the experiments on streaming gas.[9] As in the discussion of the low pressure data, the mechanisms lead to the expectation that $\beta_A + \beta_C$ passes through a maximum and tends to zero towards each end of the composition range: this provides a qualitative explanation for the values of β for cathodes of Ag and Au over the whole range, and for those of Ta and W in mixtures less rich in hydrogen than electrolytic gas. To discuss the abnormally large values of β found for these latter metals in mixtures richer in hydrogen than electrolytic gas we consider the value $\beta = 42$ found for the most extreme composition investigated, 0·005 % oxygen. The oxygen content is then so low that the excitation of oxygen must be extremely small and most of the electron energy absorbed by hydrogen molecules. Mechanisms " A " or " B " contribute insignificantly to β; and the restriction expressed in (8.7) then leads to an estimate of about 6 for the maximum possible value of $\Sigma\beta_{f,H}$ If the discharge and reaction zones are co-extensive β_C amounts to about 0·15 at 30 mm. In discussing Table IV it has been seen that the effect of streaming for a comparable value of $\Sigma\beta_{f,H}$ cannot be large; thus the true value of β_C is likely to be a little greater than 0·15, and probably ten times this value is a reasonable estimate for its upper limit. These values agree satisfactorily with the extrapolated values of β for cathodes of Ag and Au. Mechanism " C " is thus quite inadequate to account for the large values of β found in hydrogen-rich mixtures for cathodes of Ta and W. Since the metal of the cathode is the only factor changed, and since V_N tends to fall slightly as the hydrogen content is progressively increased,[15] we conclude that some additional mechanism connected with the cathode surface is operative; this conclusion is elaborated in Part V.

It remains to mention the one group of data in which β is constant at about 9·6 from 6 to 48 mm.[6] and which thus stand in opposition to all the others exhibiting the transition from one value of β in the low pressure range to a higher one above 30 mm. Whilst the maximum values of β_A or $\beta_A + \beta_C$ account roughly for the observed value of β, no explanation appears to be available for the absence of the pressure effect in the intermediate range. We suspect, however, that this explanation is probably to be found in the unusual conditions in the experiments; the reaction vessel wall is very much more remote from the discharge zone than in all the other experiments, and the current is very large, 50 ma., although V_N is constant at 380 volts.

Summarising Statement.—Apart from the above exception, mechanisms " A " and " C " provide a detailed explanation for the characteristics of β deduced from the selected typical experiments extending over the whole pressure range after allowing in a few cases for the effect of a cathode surface reaction. The coherence of the data as a whole indicates that this explanation is likely to be general.

5. The Effect of Water Vapour and other Diluents.

Water Vapour.—Before attempting to interpret the data for β when water vapour is added to electrolytic gas,[11] it is pertinent to consider the data for β_W, the number of water molecules decomposed per electron by the N.G. in water vapour. Linder's data [30] relate to a discharge tube 6 cm. diameter and lead to a value of about 5·5; but since his data demonstrate that some reformation of water occurred, the true value is somewhat larger. The collisions of lowest energy in water vapour that lead to decomposition almost certainly correspond with excitation to a repulsive level, the products being H and OH [32]; since neither of these fragments can react with water to cause further decomposition, the value of β_{W}, after correction for the re-formation of water in the experiments, is to be identified with $\beta_{f,\mathrm{W}}$, the number of water molecules decomposed per fast electron reaching the N.G. from the C.D.S. (*cf.* Part I). On the other hand, the data of Guntherschulze and Schnitger [31] relating to a vessel 25 cm. diameter lead to $\beta_{\mathrm{W}} = ca.\ 0{\cdot}2$. An obvious explanation for this apparent discrepancy is that the re-formation of water is much more extensive in the latter experiments, for it is known that the reaction $H + OH = H_2O$ occurs readily in the gas phase.[29]

Since experiment shows that $\beta_{f,\mathrm{W}}$ for pure water vapour is at least 5·5, and is thus comparable in magnitude with our estimates $\Sigma\beta_{f,\mathrm{O}} = 4{\cdot}3$ and $\Sigma\beta_{f,\mathrm{H}} = 1{\cdot}6$ in electrolytic gas, we deduce that when water vapour is added to electrolytic gas in comparable amount to its oxygen content, the water vapour competes with the oxygen and hydrogen for the available electron energy. The part of this energy that is diverted to the excitation of water produces two active species, H and OH; the H atoms can react by mechanism "C"; the OH molecules can react by $OH + OH = H_2O + O$, and the O atom can then react by mechanism "A," but there is the additional possibility of the reaction $OH + H_{2,v} = H_2O + H$, since there must be some direct production of vibrationally excited hydrogen by electron impact. Neglecting the reaction between two OH molecules, these possibilities give a maximum yield of 3 water molecules synthesised per molecule of water decomposed, or a nett yield of 2; and this must compensate for the diminution in $\beta_{\mathrm{A}} + \beta_{\mathrm{C}}$. At 18 mm., however, $\bar{f}_{\mathrm{H}}$ will certainly be less than unity (*cf.* Table II), and the nett yield will be correspondingly less. Thus, although the data are inadequate to predict quantitatively the effect of adding water vapour to electrolytic gas at 18 mm.,[11] the foregoing considerations provide a possible explanation for the observation that β is unchanged by the addition of water vapour up to 40 %; [11] the diminution in β with further increase in the amount of water vapour present finds an explanation in the decreasing availability of hydrogen and oxygen for mechanisms "A" and "C."

Helium and Argon.—Since the lowest critical potential of helium is 19·8 volts, it is to be expected that no significant fraction of the electron energy in the negative glow is absorbed by this gas when mixed with electrolytic gas, and hence that β remains unchanged, until the fractional concentration of helium is large; this is the result of experiment.[6] On the other hand, since the lowest critical potential of argon lies but little above those of electrolytic gas, it is to be expected that the addition of argon to electrolytic gas results in a reduction of the energy absorbed by electrolytic gas, and hence also in β; this again is the result found by experiment.[6]

6. Other Possible Mechanisms.

We state here a number of alternative possibilities to mechanisms "A" and "C" which we have considered in detail; we find that none of them can contribute significantly to the observed large formation of water, and for brevity, merely outline the principal considerations which lead to this conclusion.

(i) Molecular Positive Ions of the Reactants.—We deduce that

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[29] Rodebush and Campbell, *J. Chem. Physics*, 1936, **4**, 293.

[30] Linder, *Physic. Rev.*, 1931, **38**, 679.

[31] Guntherschulze and Schnitger, *Z. Physik*, 1936, **103**, 627.

[32] Oldenberg, *J. Chem. Physics*, 1933, **3**, 266.

$\beta_{f,i}$, the number of ions produced per fast electron reaching the N.G. does not exceed about 0·5 for each reactant because in hydrogen and in nitrogen the total number of ions formed by an electron of about 70 ev. is about unity.[33] To account for the observed value of β then requires that Φ should be at least about 8; branching chain mechanisms being excluded, there appears to be no possible reactions which would yield so large a value for Φ; and there is the additional likelihood that the activation energy of bimolecular reactions between molecular ions and the reactants is not inconsiderable.[34]

(ii) Recombination between O_2^- and H_2^+ Ions.—Whilst no data are available for the production of O_2^- ions in electrolytic gas, an upper limit to the extent of this process is set by the value of $\beta_{f,i}$ for H_2^+ which (*cf. supra*) is estimated to be about 0·5. Even if every recombination yields two OH molecules, these would lead to a maximum production of one water molecule in the low pressure range; that is, the maximum contribution to β in this way could not exceed about 0·5. Furthermore, since the ion concentrations are likely to be roughly proportional to the current, it is to be expected that water formation by this process would be proportional to a power of the current higher than unity. Similar considerations exclude the recombination between O^- and H_2^+.

(iii) O^+ Ions.—Since the four lowest states of O_2^+ are attractive, we estimate that $\beta_{f,i}$ for the lowest repulsive state, dissociating into $O + O^+$, does not exceed about 1/20th of $\beta_{f,i}$ for direct production of O_2^+ in its lowest state from the uncharged ground state molecule; that is, for the production of O^+ ions $\beta_{f,i}$ does not exceed about 0·03. Even if reaction with molecular hydrogen occurs yielding $OH + H$, in the low pressure range the maximum contribution to β from the reaction

$$OH + OH = H_2O + O$$

is 0·03 (0·5 + 0·88), assuming that the O atom reacts by mechanism " A." The O atom produced in the initial dissociation can react by mechanism " A," but the contribution to β in this way does not exceed 0·03 × 0·88.

(iv) H^+ Ions.—Since the lowest excited state of H_2^+ is repulsive, we estimate $\beta_{f,i}$ for the production of ions in this level to be about 1/4 of that for the direct production of H_2^+ ions; that is, $\beta_{f,i}$ for the production of H^+ ions is about 0·1. Nothing is known about the reaction between such ions and molecular oxygen; but the bimolecular reaction would be endothermic unless the energy of dissociation of OH^+ is greater than that of O_2. In any case, the maximum contribution to β by such a reaction in the low pressure range could not amount to more than about twice $\beta_{f,i}$, or about 0·2.

(v) The Direct Formation of Hydroxyl.—Although the formation of hydroxyl must occur to some extent by ternary collisions involving an atom from each reactant, the rate of this process cannot exceed about $3\bar{\lambda}_0$ times that of the first step in mechanism " C "; the low values found for $\bar{\lambda}_0$ in the low pressure range show that the reaction is therefore insignificant in this range, and the same is true in the high pressure range because the values of $\bar{\lambda}_0$ are then very much smaller.

Summary.

The quantitative data for the oxidation of hydrogen in the negative glow reaction in hydrogen-oxygen mixtures have been collected, recalculated to facilitate comparisons, co-ordinated, and critically reviewed.

It is shown that the main features of the reaction find a detailed explanation in terms of the general theory of Part I and of particular reaction mechanisms involving oxygen and hydrogen atoms as the active species based mainly on the kinetics of the non-sensitised and mercury sensitised photo-reactions in hydrogen-oxygen mixtures.

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[33] Langmuir and Jones, *Physic. Rev.*, 1928, 31, 402.

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APPENDIX.

The Absolute Values of the Collision Rates used in the detailed application of Mechanisms "A," "B," and "C".—The approximate collision numbers introduced in Part III and used here are based on the estimate that at atmospheric pressure the rate of binary collisions suffered by a single particle of species (a) in gas consisting of species (b) is about 10^{10} cm.$^{-3}$ sec.$^{-1}$, and that the fraction of binary collisions which are ternary is 10^{-3}. If k_2 denotes the collisional efficiency for some particular consequence of a binary collision process, it follows that R_2, the rate of such fruitful collisions is given approximately by

$$R_2 = 4{\cdot}6 \times 10^{23} k_2 \lambda_a \lambda_b p^2 \quad . \quad . \quad . \quad . \quad (11)$$

where p is the total pressure in mm. Hg, and λ_a, λ_b, denote, respectively, the fractional concentrations of the species (a) and (b). Similarly, if k_3 denotes the collisional efficiency for some particular consequence of a ternary process involving a third species (c) at the fractional concentration λ_c, it follows that R_3, the rate of such fruitful collisions is given approximately by

$$R_3 = 6 \,.\, 10^{17} k_3 \lambda_a \lambda_b \lambda_c p^3 \quad . \quad . \quad . \quad . \quad (11{\cdot}1)$$

For mechanism "A" in electrolytic gas it is thus found that

$$\overline{R}_{ac,O} = 3{\cdot}8 \,.\, 10^{18} \overline{\lambda}_O p^3 \quad . \quad . \quad . \quad (11{\cdot}2)$$

and

$$\overline{R}_{d,O} = 11{\cdot}4 \,.\, 10^{16} \overline{\lambda}_O^2 p^3 \quad . \quad . \quad . \quad (11{\cdot}3)$$

where $\overline{R}_{d,O}$ is the volume average rate of loss of the active species by homogeneous recombination, and allowance is made for the fact that two particles are thus lost per ternary collision. For mechanism "B" in electrolyic gas it follows from (11) that the rate of the reaction (b1) (*cf* p. 1100) when the collisional efficiency is unity is given by

$$\overline{R}_{ac,O,B} = 4{\cdot}6 \times 10^{23} \overline{\lambda}_O \overline{\lambda}_V p^2 \quad . \quad . \quad . \quad (11{\cdot}4)$$

but $\overline{R}_{d,O}$ remains unchanged. Similarly, for mechanism "C" in electrolytic gas it follows that

$$\overline{R}_{ac,H} = 2{\cdot}1 \times 10^{17} \overline{\lambda}_H p^3 \quad . \quad . \quad . \quad (11{\cdot}5)$$

and

$$\overline{R}_{d,H} = 1{\cdot}1_4 \times 10^{18} \overline{\lambda}_H^2 p^3 \quad . \quad . \quad . \quad (11{\cdot}6)$$

where $\overline{R}_{d,H}$ is the volume average rate of loss of the active species by homogeneous recombination, and allowance is made for two particles being lost per collision. For mechanism "C" in a mixture containing 99·5 % of hydrogen (*cf.* p. 1107) it is found similarly that

$$R_{ac,H} = 4{\cdot}7 \times 10^{14} \overline{\lambda}_H p^3 \quad . \quad . \quad . \quad . \quad (11{\cdot}7)$$

but $\overline{R}_{d,H}$ remains unchanged. Finally, the total consumption of the active species is given by

$$\overline{R}_{L,O} = \overline{R}_{d,O} + \overline{R}_{D,O} \quad . \quad . \quad . \quad . \quad (11{\cdot}8)$$

and

$$\overline{R}_{L,H} = \overline{R}_{d,H} + \overline{R}_{D,H} \quad . \quad . \quad . \quad . \quad (11{\cdot}9)$$

where $\overline{R}_{D,O}$ and $\overline{R}_{D,H}$ are given by (9·1) and (9·2), respectively.

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NOTE ON AN EXCHANGE REACTION BETWEEN HYDROGEN AND HYDROGEN IODIDE.

By H. Steiner.

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Some years ago Rosenbaum and Hogness[1] investigated the conversion of *para*-hydrogen into *ortho*-hydrogen in equilibrium mixtures of hydrogen, iodine and hydrogen iodide. They attributed the conversion to the reaction sequence

$$H_{2p} + I_2 = 2HI$$
$$2HI = H_{2o} + I_2$$

but the rate was much too fast to be accounted for by this mechanism alone, and it was obvious that an additional reaction was taking part. Rosenbaum and Hogness believed this additional conversion to be due to paramagnetic iodine atoms, present in thermal equilibrium concentration. The kinetics observed were in agreement with this assumption, in addition the absolute value for the rate as calculated from the experiments was in rough agreement with that calculated according to Wigner's theory of the *ortho-para*-hydrogen conversion catalysed by paramagnetic gases.[2] The only point of divergence was the considerable temperature coefficient observed. After allowance is made for the temperature dependence of the iodine dissociation equilibrium ($I_2 \rightleftharpoons 2I$) there still remains an activation energy of 24 kcal. to be accounted for. An activation energy of this magnitude has never been observed in a reaction of this kind, and is also in complete disagreement with Wigner's theory, which in general reproduces the experimental facts fairly well.

Note added in proof.—It was thought that, by reason of the great sensitivity of the paramagnetic conversion on the distance of nearest approach of the colliding partners (inverse sixth power), an interpenetration of the van der Waals fields of H_2 molecule and I atom might cause an appreciable temperature coefficient. However an estimation of this effect, using an inverse power function for the van der Waals field and plausible values for the constanta, led to a temperature coefficient corresponding to an activation energy of only about 2-4 kcal.

In this note an alternative mechanism is put forward. This mechanism is in agreement with the experimental facts available, and likewise accounts for the large temperature coefficient. It has an additional interest in that it makes the occurrence of an exchange reaction of hydrogen and hydrogen iodide likely. Similar exchange reactions of hydrogen chloride and hydrogen bromide have been studied recently, and it is now possible to make a comparison of all three reactions.[3]

Instead of introducing the reaction $H_{2p} + I = H_{2o} + I$, it is proposed to attribute the additional conversion to the exchange reaction

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[1] E. J. Rosenbaum and T. R. Hogness, *J. Chem. Physics*, 1934, **2**, 267.

[2] E. Wigner, *Z. physik. Chem.*, *B*, 1933, **23**, 28.

[3] Ph. Gross and H. Steiner, *J. Chem. Physics*, 1936, 4, 163; H. Steiner and E. K. Rideal, *Proc. Roy. Soc.*, *A*, 1939, **173**, 503; H. Steiner, *ibid.*, 531.

$H_{2p} + HI = H_{2o} + HI$. It will now be shown that under the experimental conditions used by Rosenbaum and Hogness this change is fully compatible with the kinetics observed. Rosenbaum and Hogness assumed the following simultaneous reactions to occur :—

$$\begin{aligned} H_{2p} + I_2 &= 2HI,\ k_1 \\ 2HI &= H_{2o} + I_2 \quad . \quad . \quad . \quad . \quad (I) \\ H_{2p} + I &= H_{2o} + I,\ k_2 \quad . \quad . \quad . \quad (II) \\ H_{2p} + H &= H_{2o} + H,\ k_3 \quad . \quad . \quad . \quad (III) \end{aligned}$$

Reactions I and II have been dealt with, reaction III represents the well-known *ortho-para*-hydrogen conversion initiated by hydrogen atoms, which at the temperature of the experiments occurs only to a minor extent. Using this scheme, the following expression is derived for the rate of reaction :—

$$\ln \frac{x_0 - \frac{1}{4}}{x_t - \frac{1}{4}} = \left(\frac{k_1}{2}[I_2] + 4k_2[I] + k_3[H]\right)t \quad . \quad . \quad (1)$$

In formula (1) x_0 and x_t stand for the *para*-hydrogen content at times 0 and t respectively, and the k's are the rate constants of the reactions as indicated above. On introduction of the equilibria

$$\frac{[I]^2}{[I_2]} = K_2 \text{ and } \frac{[H]^2}{[H_2]} = K_3$$

one obtains

$$\ln \frac{x_0 - \frac{1}{4}}{x_t - \frac{1}{4}} = \left(\frac{k_1}{2}[I_2] + 4k_2\sqrt{K_2}\sqrt{[I_2]} + k_3\sqrt{K_3}\sqrt{[H_2]}\right)t \quad (2)$$

Formula (2) was shown to be in good agreement with the experimental results. Introduction of reaction IV

$$H_{2p} + HI = H_{2o} + HI,\ k'_4 \quad . \quad . \quad . \quad . \quad (IV)$$

in place of reaction II, but otherwise leaving the previous scheme unchanged, leads to the following expression for the rate :—

$$\ln \frac{x_0 - \frac{1}{4}}{x_t - \frac{1}{4}} = \left(\frac{k_1}{2}[I_2] + \frac{k_4}{\sqrt{K_4}}\sqrt{[H_2][I_2]} + k_3\sqrt{K_3}\sqrt{[H_2]}\right)t \quad (3)$$

In this expression k_4 counts all the exchanges, whether leading to an inversion of nuclear spins or not. The equilibrium constant K_4 is given by

$$K_4 = \frac{[H_2]\,[I_2]}{[HI]^2}$$

Formula (3) is identical in form with (2), with the exception of the second term, which contains the square root of the hydrogen concentration. However, in all experiments of Rosenbaum and Hogness the hydrogen concentration was the same,* it can therefore be treated as a constant, and there is then no difference in the variables of formulas (2) and (3). Consequently, it is impossible on the basis of their data to distinguish on kinetic grounds between the two mechanism. It would not be difficult, of course, to come to a decision by further experiments in which the hydrogen concentration is varied, or by experiments with deuterium.

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* The author is much indebted to Professor Hogness for this additional information not contained in the original paper. The hydrogen concentration in all experiments was $1{\cdot}17 \times 10^{-5}$ mol./c.c.

In Table I are given the values for the rate constant of the reaction $H_{2p} + HI = H_{2o} + HI$ as calculated from equation (3) and from the data of Rosenbaum and Hogness. The average values only are given, since the percentage deviations of the single constants from the mean are the same as those given in Rosenbaum and Hogness paper. The activation energy calculated from the data of Table I is 44 ± 3 kcal. Using the usual formula of the collision theory, this leads to a collision diameter of 1×10^{-8} cm. In view of the approximate nature of the collision theory and of the large uncertainty in the value for the activation energy, this seems quite reasonable. In general, it seems justifiable to conclude that the exchange reaction $H_{2p} + HI = HI + H_{2o}$ accounts for the experimental data concerning the additional *ortho-para*-hydrogen conversion, including the large temperature coefficient observed.

TABLE I.

$T°$ abs.	k_1 (mol./c.c.$^{-1}$ sec.$^{-1}$)
693	1·09
716	2·11
753	10·6

As indicated, the exchange reaction of hydrogen and hydrogen iodide can be compared with the similar one of hydrogen chloride and hydrogen bromide. In these cases the exchange is due partially to atomic reactions, but in the hydrogen chloride reaction a bimolecular reaction analogous to the hydrogen iodide one could be observed and measured with some accuracy. Activation energies calculated by the Eyring-Polanyi method[4] were in agreement with the experiments in that they gave a reasonable value for the activation energy of the hydrogen chloride reaction, and also showed that in the hydrogen bromide case the bimolecular reaction was too slow to compete with the atomic one. The activation energy for the hydrogen iodide reaction has now been calculated. Seventeen per cent. additive binding was adopted, which was shown to be appropriate in all cases of bimolecular four-atom reactions studied so far. The results are given in Table II, and are compared with those obtained for hydrogen chloride and hydrogen bromide. The latter values have been recalculated, and differ slightly from those given previously.

TABLE II.

Reaction.	Activation energy (kcal.).	
	Calculated.	Observed.
$H_2 + HCl$	57	57 ± 4
$H_2 + HBr$	50	> 51
$H_2 + HI$	41	44 ± 3

The agreement seems good, but it must be noted that in all these calculations no correction for the zero point energy of the initial and the transition state has been applied, since this would necessitate the laborious calculation of the vibration frequencies of the transition state. The inclusion of this correction would not alter the agreement, but it may very well cause small shifts in the individual values.

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[4] H. Eyring and M. Polanyi, *Z. physik. Chem.*, *B*, 1932, **12**, 279.

THE INFRA-RED ABSORPTIONS OF SOME POLY-HYDROXYLIC COMPOUNDS.

By M. M. Davies.

Received 19*th August*, 1940.

A considerable interest attaches to those compounds in which more than one hydroxyl group appears to be joined to a single carbon atom. A recent infra-red study of chloral hydrate has indicated a considerable interaction between the OH groups and the adjacent CCl_3 radical.[1] This interaction is of the type of that in *o*-chlorphenol, and seems to be largely electrostatic in nature. Some further observations on chloral hydrate, more particularly in its relation to trichloracetic acid ($CCl_3 . COOH$) and its monohydrate ($CCl_3COOH . H_2O$) are presented here, together with an examination of the monohydrate of diphenyltriketone

$$(C_6H_5 . CO . C(OH)_2 . CO . C_6H_5)$$

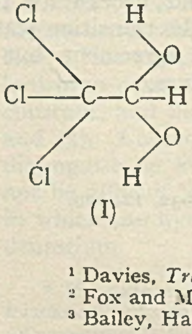
and related compounds.

Experimental.

Quartz and fluorite prisms in the Hilger D. 83 instrument have been used in the present work. The setting of the prisms, done in the visible with a small Hg-arc, was checked by plotting the 2·764 μ benzyl alcohol band in CCl_4,[2] and the absorption centred at 5·991 μ in liquid benzene.[3] Cells with fluorite windows have been used throughout for solutions, whilst solid films have been prepared by melting a little of the substance to be examined between two thin rock-salt plates pressed together. Corrections for cell and solvent absorptions have been applied in all cases. Trichloracetic acid solutions were made from the middle third distilling in an all-glass apparatus, from a sample freshly recrystallised from benzene. The hydrate was prepared by adding the calculated quantity of water to a few grams of the anhydrous acid. Solvent chloroform has been prepared from B.P. grade by repeated shaking with water, then standing over $CaCl_2$ and twice distilling from P_2O_5.

Results.

Owing to its greater solubility, chloral hydrate is better examined in $CHCl_3$ than in CCl_4 or in CS_2 where the previous results were obtained. The absorption corresponding to the OH valence fundamental gives the band at 2·825 ± 0·005 μ (Fig. 1). This is shifted to a very slightly longer wave-length ($\delta\lambda = 0·005\ \mu$) from its centre in CCl_4, as is generally the case for this change of solvent. Its displacement from the normal position, at 2·77 μ, of the absorption for simple alcohols and phenols is a measure of the intramolecular interaction which is apparently sufficient to tie the hydrogens towards the chlorines.



(I)

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[1] Davies, *Trans. Faraday Soc.*, 1940, **36**, 333.

[2] Fox and Martin, *Proc. Roy. Soc., A*, 1937, **162**, 419.

[3] Bailey, Hale, Ingold and Thompson, *J. Chem. Soc.*, 1936, 931.

From the absence of the characteristic water absorptions, of which the principal may be expected near 2·75 μ, it follows that chloral hydrate in these solutions is not decomposed to any great extent. This does not apply to trichloracetic acid hydrate for which observations in CCl_4 and $CHCl_3$ indicate the presence of a considerable proportion of water. Fig. 2 is typical of the results in $CHCl_3$. The peak at 2·75 μ is due to water. Whether the subsidiary peak at 2·84 μ arises from the hydrate

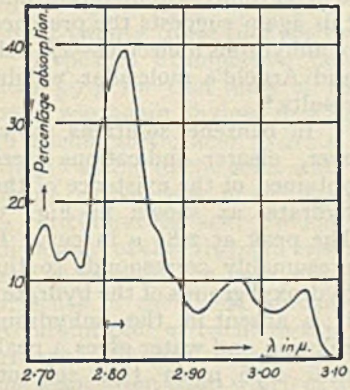

FIG. 1.—Saturated solution of chloral hydrate in $CHCl_3$, 0·35 mm. cell.

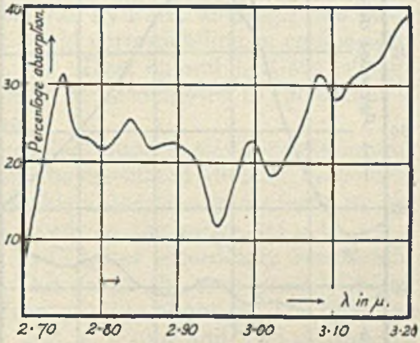

FIG. 2.—0·073 M. trichloracetic acid hydrate in $CHCl_3$, 0·35 mm. cell.

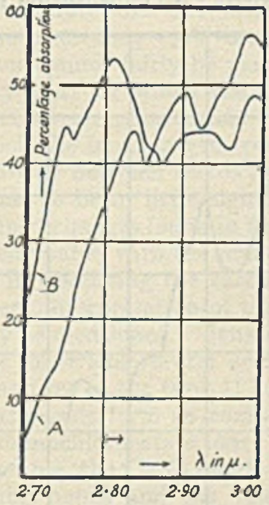

FIG. 3.—0·241 M. trichloracetic acid in benzene, 0·35 mm. cell.

A = anhydrous solution.

B = anhydrous solution after saturating with water.

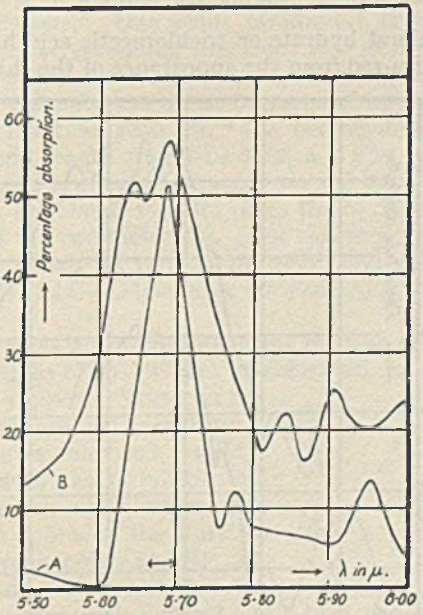

FIG. 4.

A = chloral hydrate (approx. 1·4 M.) in $CHCl_3$, 6·05 mm. cell.

B = 0·0405 M. trichloracetic acid hydrate in $CHCl_3$, 0·35 mm. cell.

is an open question: the monomeric anhydrous acid has its OH absorption at 2·86 μ. It is clear from Fig. 2 that the association band for the acid is quite pronounced and this again suggests the presence of anhydrous molecules—*cf.* Bell and Arnold's molecular weight results.[4]

In benzene solutions, however, clearer indications were obtained of the existence of the hydrate, as shown in Fig. 3. The peak at 2·81 μ in curve B presumably corresponds to the hydroxyl groups of the hydrate: it is absent in the anhydrous solution and water gives a peak near 2·76 μ in this solvent. After consideration of the other possible formulations,[4] this result favours the structure $CCl_3 . C(OH)_3$, analogous to that of chloral hydrate, for the acid derivative.

The loss of water from either chloral hydrate or trichloracetic acid hydrate should be detected in the infra-red from the appearance of the characteristic C=O absorption near 5·7 μ. Both these compounds show this absorption in $CHCl_3$ (Fig. 4).

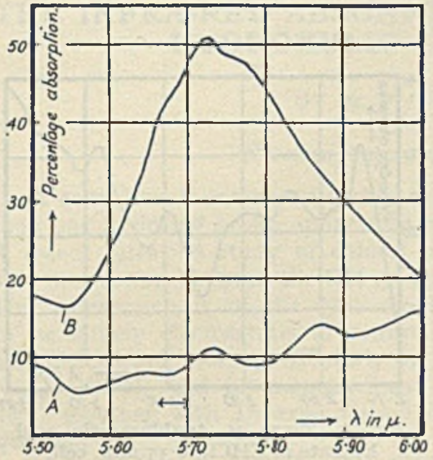

FIG. 5.—Absorption of thin films between rock-salt plates.
A = chloral hydrate.
B = trichloracetic acid hydrate.

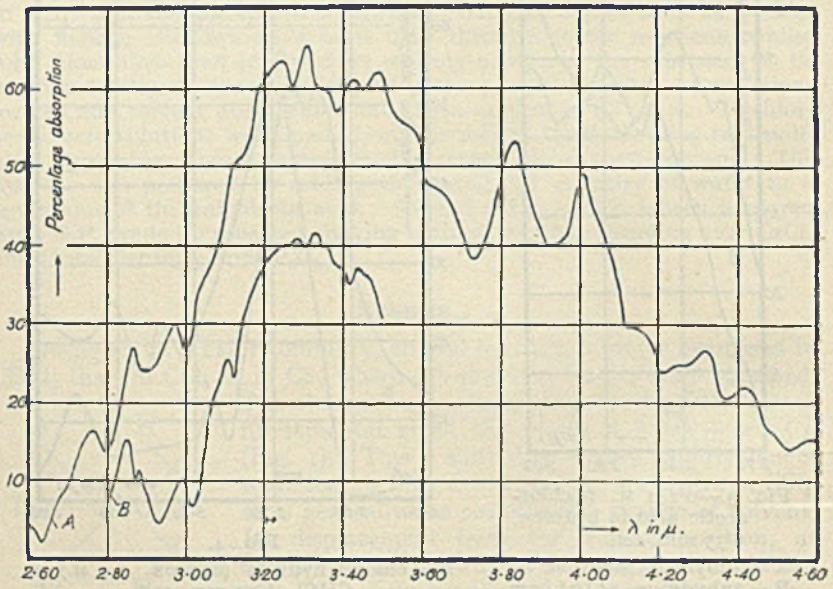

FIG. 6.
A = 0·072 M. trichloracetic acid in CCl_4, 0·35 mm. cell.
B = 0·024 M. trichloracetic acid.

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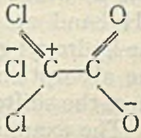
[4] Bell and Arnold, *J. Chem. Soc.*, 1935, 1432.

It is to be noted in the case of chloral hydrate that despite the strong absorption, probably only a very small fraction of the hydrate is decomposed in solution, as both the concentration and cell length were about twenty times that for the trichloracetic hydrate.

Repeated examination failed to show any appreciable absorption near 5·7 μ for thin films of solid chloral hydrate, although the C=O band was again obvious in a film of liquid corresponding in composition to trichloracetic acid hydrate (Fig. 5). Thus chloral hydrate is completely stable in the solid state but may be decomposed to the extent of about 0·1 per cent. in $CHCl_3$ solution.

Trichloracetic acid provides an excellent opportunity for determining the extent of the OH band arising from the associated (dimeric) carboxylic acid molecules. In most other cases this absorption is confused by the presence of the C—H fundamental bands in the range 3·2 μ to 3·5 μ. A careful plot of trichloracetic acid in CCl_4 has accordingly been made, using the fluorite prism (Fig. 6A). This shows the very great width of the association band which extends from 3·0 μ to about 4·2 μ. Although rather poorly defined, the peaks at 3·25 μ, 3·30 μ and 3·48 μ form the strongest elements in the band, whilst two maxima at 3·83 μ and 4·02 μ are also pronounced. In the curve shown, the monomeric hydroxyl absorption is only just noticeable as a weak peak about 2·86 μ : it is sharply defined in the more dilute solution examined with the quartz prism (Fig. 6B). Possible reasons for the extent of the band for the dimer have been discussed elsewhere.[5] One point of interest is the location of its centre, as from the corresponding frequency it is possible to estimate the OH distance in the dimer. Davies and Sutherland almost certainly took too high a value for the dimer frequency,[5] but the latter cannot fairly be placed at less than 2860 cm.$^{-1}$ (*i.e.* corresponding to 3·50 μ) for which the OH bond length would be $1{\cdot}12_2$ A. Fox and Martin have pointed out [6] that 4·20 μ gives a frequency on the basis of which the bond length would be calculated so as to place the hydrogen mid-way between the oxygens of the two molecules. But this structure seems to be of little significance if only in view of the small and well-defined changes found in the C=O and C—O bonds for the same structure as compared with the monomer.

In discussing the carboxylic acids an interesting point relating to a recent interpretation of the strengths of the di- and tri-chloracetic acids may be mentioned. Jenkins has suggested [7] that, in the case of trichloracetic acid, resonance between twelve structures of the type II contributes enhanced stability to the ionic form as compared with the unsubstituted or monochloracetate ions. Were this contribution considerable, the C—Cl bonds would approach the state of double bonds and the valence frequencies, at least, of the CCl_3 group would be considerably modified. According to Kohlrausch and Cabannes and Rousset,[8] the two valence vibrations of the CCl_3 group in chloroform (of which ν_{23} is doubly degenerate) are to be assigned as $\nu_1 = 668$ cm.$^{-1}$, $\nu_{23} = 760$ cm.$^{-1}$.



(II)

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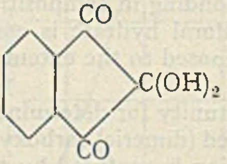
[5] Badger and Bauer, *J. Chem. Physics*, 1937, 5, 839 ; Davies and Sutherland, *ibid.*, 1938, 6, 755.

[6] Fox and Martin, *Faraday Society Discussion on the Hydrogen Bond*. This vol., p. 897.

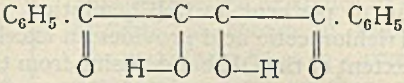
[7] Jenkins, *Nature*, 1940, 145, 625.

[8] Kohlrausch, *Z. physik. Chem.*, *B*, 1935, 28, 340 ; Cabannes and Rousset, *Ann. Physique*, 1933, 19, 229.

Both these frequencies occur almost undisturbed as principal lines in the Raman spectrum of sodium trichloracetate at 664 cm.$^{-1}$ and 742 cm.$^{-1}$.[9] They appear at very much the same positions in trichloracetic acid and chloral hydrate and their location has been confirmed by infra-red observations of these two compounds.[1] If, in addition, it is stated that the frequency corresponding to ν_1 of the CCl_3 group occurs at 654 cm.$^{-1}$ in ethyl chloride and has been further detected as an infra-red absorption at 15·0 μ (666 cm.$^{-1}$) for lead trichloracetate, it is obvious that the C—Cl valence force constant changes very little in these compounds. Accordingly, Jenkins' interpretation of the acid strengths does not receive any support from these data.



(III)



$$C_6H_5\,.\,\underset{\underset{O}{\|}}{C}\text{———}\underset{\underset{\text{H—O}}{|}}{C}—\underset{\underset{\text{O—H}}{|}}{C}\text{———}\underset{\underset{O}{\|}}{C}\,.\,C_6H_5$$

(IV)

It is well known that polyketonic compounds form hydrates whose stability suggests that the water is attached to the molecule forming a polyhydroxy derivative. Ketomalonic acid and its salts appear to be known only as hydrates, $(HO)_2C(COOM)_2$; the hydrate of triketohydrindene, used as a biochemical reagent, is formulated as III. Of these compounds we have examined the hydrate of diphenyltriketone,

$$C_6H_5\,.\,CO\,.\,C(OH)_2\,.\,CO\,.\,C_6H_5.$$

That this compound is best represented as IV appears from its absorption in the region of the OH fundamental (Fig. 7). The curve is somewhat complex, but the main absorption is certainly located at 2·92 μ, which is far ($\Delta\nu = 190$ cm.$^{-1}$) from the normal position of the OH band at 2·77 μ. The shift measures the degree of interaction of the hydroxyl groups with the adjacent carbonyls. A similar case, where the absorption is again broad, is benzoin V, there the shifted OH band is centred at 2·89 μ.

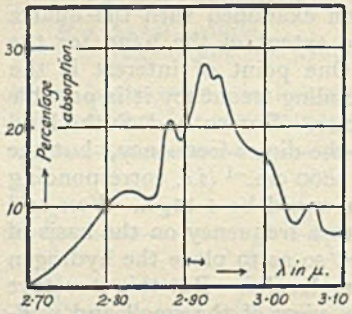
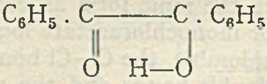


FIG. 7.—Dilute solution of diphenyltriketone hydrate in $CHCl_3$, 0·35 mm. cell.



$$C_6H_5\,.\,\underset{\underset{O}{\|}}{C}\text{———}\underset{\underset{\text{H—O}}{|}}{C}\,.\,C_6H_5$$

(V)

The examination of the effect of the interaction upon the frequency of the remaining carbonyl groups, as shown by a comparison of the triketone and its hydrate in the region of the C=O valence frequency, is represented in Fig. 8. The carbonyl frequency seems to be split into two components; the weaker, at 5·81 μ (1720 cm.$^{-1}$), remaining unchanged, whilst the other moves from 5·98 μ (1672 cm.$^{-1}$) in the triketone to 5·94 μ (1684 cm.$^{-1}$) in the hydrate. Although small, the direction of this displacement is unexpected, as the interaction with the hydroxyls would be anticipated to decrease the strength and hence the frequency, of the C=O bond. Presumably

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[9] Ghosh and Kar, *J. Physic. Chem.*, 1931, 35, 1735.

other factors, possibly arising from the adjacency of the three equivalent vibrators in the triketone, eliminate the expected effect. It appears desirable to emphasise the influence of the phenyl group on the frequency of an adjacent ketonic bond. In the ketones R . CO . CH_3 the carbonyl frequency is almost constant at 1710 cm.$^{-1}$, when R is an aliphatic group, decreasing only to 1702 cm.$^{-1}$, when R is a tertiary aliphatic radical; but in acetophenone it is found at 1677 cm.$^{-1}$ (5·96 μ), coincident with the main absorption in Fig. 8. This effect possibly results from the ability of the phenyl group to favour resonance with the structure VI. The results for *o*-hydroxybenzyl alcohol (saligenin) in the OH region are of importance in elucidating the factors controlling the appearance of two separate hydroxyl frequencies in compounds of this type. In his interpretation of two distinct hydroxyl frequencies Pauling suggested,[10] in the case of catechol, for instance, that the interaction was due to the preliminary fixture of the OH groups in the plane of the benzene ring through resonance with a structure VII. It now appears that the interaction is much greater in saligenin than in catechol, the frequency separation of the components being 157 cm.$^{-1}$ and 64 cm.$^{-1}$ respectively in the fundamental. As in the former, there is no possibility of an initial fixture of one of the hydroxyl groups in the benzene plane this factor is best omitted from the explanation. The greater extent of the interaction in saligenin is easily accounted for by the much closer approach possible for the hydroxyl

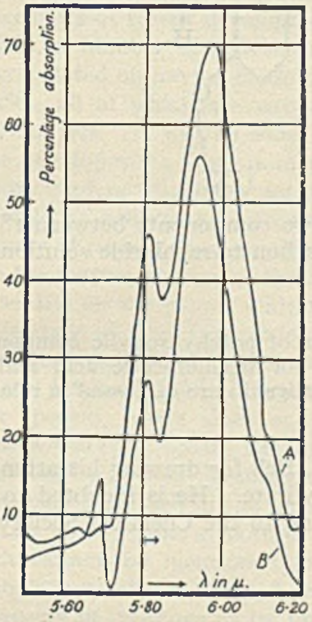


FIG. 8.

A = dilute solution diphenyl-triktone in CCl_4.
B = saturated solution diphenyl-triketone hydrate in CCl_4.
Cell = 0·35 mm.

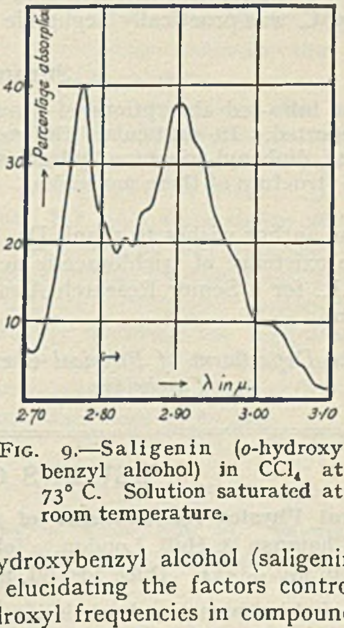
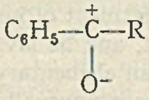


FIG. 9.—Saligenin (*o*-hydroxy benzyl alcohol) in CCl_4 at 73° C. Solution saturated at room temperature.



$$C_6H_5-\overset{+}{C}(-O^-)-R$$

(VI)

(VII)

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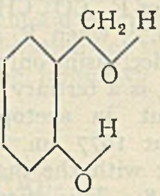
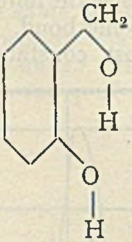
[10] Pauling, *J. Amer. Chem. Soc.*, 1936, 58, 94.

groups in this case, but whether the molecules assume form VIII or IX, or an equilibrium of both, cannot be decided. The temperature effect on the relative intensities of the two components between 18° C. and 73° C. was practically negligible in carbon tetrachloride solutions.



(VIII)



(IX)

Summary.

The infra-red absorptions of a number of polyhydroxylic compounds are reported. In particular, the results for trichloracetic acid and its hydrate, diphenyl-triketone hydrate and saligenin are discussed in relation to the structure of these molecules.

The author wishes to thank Dr. R. P. Bell for drawing his attention to the existence of trichloracetic acid hydrate. He is indebted to the D.S.I.R. for a Senior Research Award and to the Chemical Society for a grant.

The Department of Physical Chemistry,
Cambridge.

REVIEWS OF BOOKS.

General Physics for Students of Science. By Prof. R. B. LINDSAY. (Chapman & Hall, London. John Wiley & Sons, New York. 1940. Pp. xiv + 534. Price 22s. 6d. net.)

Prof. Lindsay's text-book is intended to provide a survey of physics for the use of students who have some acquaintance with quite elementary calculus. Its five sections—General Introduction, Mechanics, Heat, Electricity and Magnetism, Radiation—cover rather more than the course usually given to students of intermediate grade, but this statement must not be taken to imply that an intermediate student will find the book too much for him. On the contrary; the author's treatment of his subject is admirably calculated to hold the reader's interest, and he lays stress on many points which are apt to be hurried over in an elementary course. The discussion of fundamental mechanical principles is unusually full, and the treatment of the mass and force concepts much more satisfactory than is commonly the case. The student who has worked through this section of the book will be competent to attack, not only puzzles concerned with stones dropped into wells, but also simple and practical problems in two-dimensional rigid dynamics.

Each chapter is accompanied by a well-selected set of problems; the book may be unreservedly commended. A. F.

Reports on Progress in Physics. Vol. vi. Pp. v + 434. (London: The Physical Society, 1940.) 22s. 6d.

This volume appears in the usual form and size. The general scheme which has characterised these Reports from their inception has been continued with undoubted success; it consists in presenting, in addition to accounts of recent developments in the more common branches of the subject, a number of articles on special topics. A new editor is to be congratulated on having made an attractive and varied selection for these articles, all of which are written by men with first-hand knowledge of their subject. It will be some years before even the most important of these developments appears in the text-books and thus the present work enables readers who have not access to a large range of periodicals nor the time to collect the information, to have at hand carefully written accounts of recent progress. The mathematical work, which is inseparable from the matter of some of the reports, is generally confined to that which is essential for the proper understanding of the subject.

Readers of the *Transactions* will welcome particularly the articles on induced radioactivity and on the separation of isotopes and will find much of interest in the accounts of the Zeeman effect in atomic and molecular spectra, where some excellent photographs are given. As might be expected from recent developments, the solid state claims attention in several directions, luminescence, solid reactions and electrical breakdown being reviewed in the light of recent work, while in X-ray analysis, progress with organic structures and silicates is discussed. Other articles, which cannot be mentioned individually, maintain the high standard which is generally associated with these reports. The book is as comprehensive in its range as its forerunners and is to be thoroughly recommended to those who wish to keep their knowledge up to date.

R. H. H.

Conversion of Petroleum. Production of Motor Fuel by Thermal and Catalytic Processes. By A. N. Sachanen. (Chapman & Hall, London; 1940. Pp. 413. Price 36s. net.)

The author, in this book, relating to the fundamental principles and modern practices of converting petroleum into fuels, has included much information derived from recently published papers on the subject, including his own, and he has arranged in a concise and orderly manner the scattered information on hydrocarbon chemistry both in its academic and commercial aspects. There are at frequent intervals in the text useful summaries of facts and conclusions.

To the organic research chemist the book is of considerable value; nearly a half of the 413 pages is given to the chemistry of hydrocarbons, their thermal and catalytic hydrogenation and dehydrogenation, splitting decomposition, isomerisation, alkylation, aromatisation, polymerisation and other chemical changes which have recently been studied. To the fuel technologist and motor engineer the book can be of considerable service, as it contains a survey, up to 1940, of important commercial methods of manufacturing petroleum fuels and oils and of their engine behaviour. To the industrial chemist there is an abundance of data for devising methods of analysis, together with criticisms of existing tests, which, in the light of newly discovered facts, must become obsolescent. The book is also invaluable to students preparing for the Institute of Chemistry Examination in the fuel technology section.

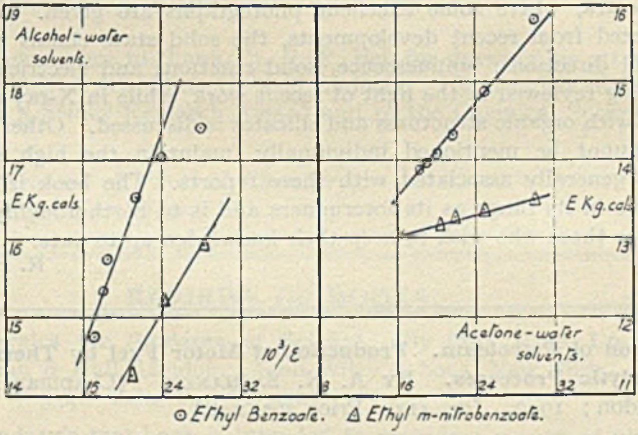
The experimental results are represented " molecularly " ; there are 204 tables and 56 figures, and there are few typographical errors. The book is carefully balanced in its treatment of the different sections of the subject. The descriptions are clear and adequate, and the refinery nomenclature, such as for example, " lubdistillate," " paraffinicity," " crack-per-pass," etc., becomes self-explanatory from the text.

Descriptions and methods of manufacture of the high knock-rating synthetic aviation spirits such as iso-octane and neo-hexane (2, 2-dimethyl butane) are given, together with recent data on the subject of knock-rating and " lead " response.

E. M.

ERRATUM.

Page 819. The figure to which reference is made is as follows:—



NOTICE

NOTICE IS HEREBY GIVEN that a Special General Meeting of the Society, followed by the Annual General Meeting of the Society, will be held at a date hereafter to be notified in December, 1940, or in January, 1941.

It is also intended that the Annual General Meeting shall be followed by a short GENERAL DISCUSSION on "THE OIL/WATER INTERFACE".

SPECIAL GENERAL MEETING: The business of this meeting will be to approve a temporary alteration in the Rules by the addition of a new rule 20* as follows:—

> "During the present war, those provisions of Rules 19 and 20 whereby the President, Vice-Presidents and ordinary Members of Council are not eligible to hold office for more than the periods in those Rules mentioned shall cease to have effect."

ANNUAL GENERAL MEETING: The business will be to consider the Report of Council and Statement of Accounts for the year 1939 and to re-elect the President, Vice-Presidents and Members of Council.

Transactions of the Faraday Society

INSTRUCTIONS TO AUTHORS

Authors submitting papers for publication are requested to note the following particulars:—

i. All communications made to the Society are the property of the Society. When papers have been accepted for publication, authors are not at liberty, save by permission of the Council, to publish them elsewhere. Such permission will not be unreasonably withheld. Communications which have appeared in any other Journal may not usually be published in the Transactions.

ii. (*a*) **Papers should be as brief as is compatible with clarity,** and no experimental details should be included which are not necessary for the understanding of the paper or for verifying any conclusions that may be drawn. Paragraphs should not be unnecessarily sub-divided.

(*b*) Tables should be reduced to a minimum and, where possible, results should be shown by means of curves rather than tables. Only in exceptional cases may tables be published as well as graphical representations of their contents.

(*c*) Each paper should include a brief summary indicating in general terms its purpose and conclusions.

iii. (*a*) Papers must be typewritten, with double spacing, on one side only of the paper, with a good margin on the left side.

(*b*) **References** should be typed in numerical order (and in the following sequence: journal; date; volume number; page) at the end of the paper; the necessary reference numbers only should appear in the text.

(*c*) Symbols, formulæ and equations should be written or typewritten with great care. The symbols recommended in the Report of the Joint committee of the Chemical Society, the Faraday Society and the Physical Society should be employed.

iv. (*a*) **Line drawings** may in the first instance be submitted in sketch form. For publication, however, they must be made with Indian ink on Bristol-board or preferably tracing *cloth.* Freehand must not be employed and all lines must be firmly and evenly drawn. Drawings should, generally, be capable of reduction to about one-half scale, depending on their nature and complexity; all drawings relating to one paper should be so made that they will all be reduced to the same extent. In the case of curves the ordinates and abscissæ must be drawn in ink and reliance must not be placed on the printed lines of scale paper.

(*b*) Where possible, lettering should be outside the diagram. Lettering should be put in lightly with lead pencil.

(v) **Rapidity of publication** is facilitated if papers are submitted in duplicate with duplicate photographs or tracings of diagrams, so that each paper with its drawings and photographs will go into a foolscap envelope.

(vi) Authors must retain copies of their communications.

Correction of Proofs.—The address to which proofs are to be sent should be written on every paper. Authors resident overseas may name agents in Britain to whom may be referred matters concerning their papers, including the correction of proofs, in order that delay in publication may be avoided.

Two galley proofs are provided, one of which duly corrected should be returned to the Editor. Authors are required to submit their communications in such form that corrections other than of printer's errors will be unnecessary. **Authors making other corrections will be required to bear the cost thereof.**

Reprints.—Twenty-five reprints (without covers) are presented to each author **who is a member of the Society.** Other reprints may be obtained by authors or co-authors at cost price.