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# THE HYDROGENATION AND EXCHANGE REACTIONS OF METHYL OLEATE. 

By J. H. Baxendale and E. Warhurst.<br>Received 7 th $\mathfrak{f u n e}, 1940$, and as amended on 14 th October, 1940.

The attempts to interpret the results of experiments on the catalysed reactions of hydrogen with unsaturated hydrocarbons have led to the formulation of two alternative mechanisms. These mechanisms are now referred to as the dissociative and the associative mechanisms. The former was first proposed by Farkas, Farkas and Rideal ${ }^{1}$ and has been developed in a series of papers by Farkas and Farkas. ${ }^{2,3,4,3}$ The latter was formulated by Horiuti and Polanyi. ${ }^{6}$ The mechanisms have been discussed fully by Greenhalgh and Polanyi ${ }^{7}$ in the light of the experimental evidence available up to the beginning of 1939. They are as follows :-

The dissociative mechanism-
A (I) exchange

$$
\mathrm{RH}_{2} \xrightarrow[+\mathrm{K},-\mathrm{H}]{ } \mathrm{RH}-\mathrm{K} \xrightarrow[+\mathrm{D},-\mathrm{K}]{ } \mathrm{RHD}
$$

A (2) hydrogenation

$$
\mathrm{RH}_{2}+\mathrm{H}_{2}-\mathrm{K} \xrightarrow[-\mathrm{K}]{ } \mathrm{RH}_{4}
$$

where $\mathrm{RH}_{2}$ represents an unsaturated hydrocarbon and K a catalyst atom. The hydrogenation and exchange reactions are considered to be entirely independent. The associative mechanism, on the other hand, postulates an intimate connection between the two reactions.

B The associative mechanism-


[^0]More recently, Twigg and Rideal, ${ }^{8}$ from a study of the exchange and hydrogenation reactions between deuterium and ethylene on a nickel catalyst, have concluded that the exchange reaction proceeds by an associative mechanism similar to the one formulated above, but they suggest that the hydrogenation reaction involves an independent mechanism consisting of the direct addition of a deuterium molecule to an ethylenc molecule (cf. mechanism A(2) above). Further work by Conn and Twigg ${ }^{9}$ has shown that no measurable exchange takes place between $\mathrm{C}_{2} \mathrm{D}_{4}$ and $\mathrm{C}_{2} \mathrm{H}_{4}$ on a nickel catalyst, thus adding further support to the theory that exchange between ethylene and deuterium proceeds by an associative and not by a dissociative mechanism.

One of the pieces of evidence adduced by Horiuti and Polanyi ${ }^{6}$ in favour of the associative mechanism was the fact that wandering of the double bond and cis-trans interconversion occurred during the hydrogenation of certain unsaturated compounds (e.g. oleic esters). Hilditch and Vidyarthi ${ }^{10}$ have shown that on partial hydrogenation of oleic esters (in which the double bond is situated between the 9:10 carbon atoms) unsaturated compounds with the double bond in (8:9) and (IO:II) positions were formed. The double bond wandering has also been established by Twigg ${ }^{11}$ for the case of I-butene on a catalyst in presence of hydrogen. This question was discussed more fully by Grecnhalgh and Polanyi ${ }^{7}$ who pointed out that, according to the associative mechanism, certain quantitative relationships should hold between the amounts of the various isomers produced.

For the case of the reaction between an oleic ester and a deuterium atom a complete scheme of the unsaturated products is shown in Fig. I. The esters produced by the wandering of the double bond from ( $9: 10$ ) to $(8: 9)$ and ( $10: 11$ ) positions we shall refer to as "shifted "compounds. The ratio of the amounts of oleic and elaidic acid in an equilibrium mixture has been shown to be I $: 2$ by Griffiths and Hilditch, ${ }^{12}$ who also found that this ratio holds approximately for the cis and trans forms of petroselenic ( $6: 7$ ) and erucic ( $13: 14$ ) acids. Noller and Bannerot's synthesis ${ }^{13}$ of oleic acid also produced an equilibrium mixture of oleic and claidic acids in approximately the same ratio. The relative amounts of the unsaturated products are given in Fig. I by the number immediately following the name of each particular ester (total product $=24$ ). These amounts have been calculated by assuming that there is an equal probability for the loss of hydrogen and deuterium atoms from the two half-hydrogenated states, and that the loss of any particular atom, followed by the closing of the double bond, leads to the equilibrium mixture of the corresponding cis and trans isomers for which the same equilibrium ratio ( $\mathrm{I}: 2$ ) holds for all pairs. The amounts correspond to the following relationship :-

Amount of light oleic ester $=$ amount of heavy oleic ester $=1 / 12$ total product.
Amount of light elaidic ester $=$ amount of heavy elaidic ester $=1 / 6$ total product.
Amount of cis shifted esters $=1 / 6$ total product.
Amount of trans shifted esters $=1 / 3$ total product.

[^1]

The mechanisms suggested by Farkas and Farkas ${ }^{4}, 14$ for the cistrans conversion and wandering of the double bond are as follows:-
(a) Cis-trans conversion

(b) Wandering of the double bond


On the basis of these mechanisms a relationship between the isomers such as the one given above is not to be expected.

Thus, the experimental work described below, which consists of an attempt to determine the amounts of these isomers produced in the partial hydrogenation of oleic ester, is in the nature of a critical experiment with regard to the two theories.

## Experimental.

## Materials.

Methyl Oleate.*-Oleic acid was prepared by hydrolysing olive oil. The acid was washed thoroughly with water and was then subjected to the lead salt process of Cox, Christian and Hardy. ${ }^{15}$ This process is used to remove elaidic and stearic acids as solid acids, which have sparingly soluble lead salts. The oleic acid was further purified from linoleic and palmitic acids by three recrystallisations of the lithium salts of the acids. This method is described by Keffler and MacLean, ${ }^{18}$ who showed that for a complete removal of these impurities as many as ten recrystallisations were required. From their data, however, we estimate that our product contained about 4 per cent. linoleic acid and $2-3$ per cent. palmitic acid. The purified acid was esterified by refluxing with methyl alcohol and dilute sulphuric acid in an atmosphere of nitrogen. The ester was then dried and distilled twice under reduced pressure to effect a further purification. The $F$-values of the ester were determined by quantitative hydrogenation and also by the bromine absorption method of Kauffmann and Hartweg; ${ }^{17}$ the two methods gave concordant results. Typical values were $F=1.02,1.02, \mathrm{I} \cdot 00$ for three different batches of the ester.

Platinum black catalyst was prepared according to Houben-Weyl 2-te Aufl., Vol. II, p. 496. About o•r gram of the catalyst was used for each experiment.

Deuterium Gas.-The gas evolved on electrolysis of pure $\mathrm{D}_{2} \mathrm{O}$ which contained a little KOH was purified by passing through a heated palladium thimble. The deuterium content was taken to be 100 per cent.

## Experimental Technique.

The hydrogenation and exchange experiments were carried out in an apparatus which enabled the deuterium to be bubbled through about

[^2]Io grams of methyl oleate containing the catalyst. The initial pressure of the gas was about 250 mm , and the circulation was effected by a glass piston which was operated electrically. The temperature of the ester was $170 \pm 2^{\circ} \mathrm{C}$. The decrease in deuterium percentage in the gas phase varied from $10 \%-26 \%$ in different experiments and the percentage hydrogenation of the ester varied from $30 \%-45 \%$. Large decreases in the percentage deuterium of the gas were avoided in order to minimise exchange reactions between the ester and hydrogen atoms, and to ensure, as far as possible, that all exchanged (i.e. heavy) unsaturated products contained only one deuterium atom per molecule. A thermal conductivity gauge of the Bonhoeffer and Harteck type ${ }^{18}$ was used for the analyses of the deuterium content of the gas phase. The process of deuterogenation was found to be first order with respect to deuterium pressure.

On the basis of the associative mechanism it is seen (Fig. I) that in the case of the formation of a shifted acid the deuterium atom appears on a carbon atom which is situated in $\beta$ position to the double bond, whereas all other exchange reactions lead to products containing the deuterium atom on an $\alpha$ carbon atom. It should be possible, therefore, to distinguish between these two types of unsaturated compounds by their behaviour on oxidation. In the first case, a mixture of mono- and dicarboxylic acids will be obtained which will still contain deuterium; in the second case, the deuterium on the $\alpha$ carbon atom will be converted to water and the resulting mono- and dicarboxylic acids will be light. We have employed this quantitatively in our experimental treatment of the ester after partial hydrogenation.

The partially hydrogenated ester was hydrolysed and the free acids subjected to the lead salt separation of Cox, Christian and Hardy. ${ }^{13}$ This process was applied twice in order to ensure an effective separation into the liquid acid fraction (olcic, and cis forms of shifted acids) and the solid acid fraction (elaidic, stearic and trans forms of shifted acids). The two fractions were weighed and the $F$-values of each determined by the bromine absorption method ${ }^{17}$ (in the liquid acids the amount of stearic acid was always found to be small, $\sim 5 \%$ which gives some idea of the effectiveness of the lead salt separation). Samples of the two fractions were then burned in a suitable combustion apparatus and the density of the resulting water was measured by the micropyknometer method of Gilfillan and Polanyi. ${ }^{19}$ Both fractions were then oxidised by potassium permanganate in boiling acetone (Hilditch and Vidyarthi ${ }^{10}$ ), the products extracted and combusted, and the density of the water measured. By determining the bromine absorption after oxidation it was found that this process was about $85 \%$ completed in one oxidation. In some cases complete oxidation was ensured by repeating the process; in other cases a correction for this was applied in the calculations. The deuterium content of the stearic acid was assumed to be two deuterium atoms per molecule. This is not strictly correct since the exchange reactions lead to the appearance of hydrogen in the gas phase. However, since the fall in deuterium content of the gas was never very large, the application of corrections, based on the assumption that the hydrogen and deuterium form stearic ester at rates proportional to their partial pressures, or even that hydrogenation proceeds at twice the rate of deuterogenation, does not affect the general features of our results.

The above data enable the quantities of the various products to be calculated. The bromine absorptions of the solid and liquid acid fractions give the amounts of stearic acid in each. The combustion results give the total deuterium contents of each fraction, from which, using the assumption of the deuterium content of the stearic acid, the amounts of heavy unsaturated products are obtained. The difference between the combustion

[^3]results before and after oxidation gives the amounts of heavy unsaturated material which contain deutcrium attached to an $\alpha$ carbon atom. In the case of the liquid acids on the basis of the associative mechanism, this product should be heavy oleic acid; in the case of the solid acids it should be heavy elaidic acid. The combustion results after oxidation give the amounts of heavy unsaturated material which contain deuterium attached to carbon atoms other than $\alpha$ carbon atoms. The associative mechanism implies that this deuterium should be attached to $\beta$ carbon atoms and in the case of the liquid acids the product should be the heavy cis isomers of shifted acids, and for the solid acids the heavy trans isomers of shifted acids. The residual product should be light oleic acid in the case of the liquid acids, and light elaidic acid in the case of the solid acids.

Two points of special importance were also investigated. Firstly, on account of the large number of hydrogen atoms attached to saturated carbon atoms, it was essential to know whether, in our experiments, any appreciable amount of exchange could take place by means of these hydrogen atoms. Secondly, it was desirable to ascertain whether cistrans conversion of oleic to elaidic ester could take place on platinum black at $170^{\circ} \mathrm{C}$. in the absence of hydrogen. Such a process would involve a different mechanism from the one outlined above.

With regard to the first point, experiments on the exchange of deuterium and methyl stearate were carried out. Stearic acid was esterified and the ester recrystallised three times from alcohol-water mixtures. The conditions for the exchange were identical with those of the methyl oleate experiments. It was found that in the initial stages of these experiments with methyl stearate the fall in deuterium concentration ( $\sim 4 \%$ ) proceeded rapidly. After this the rate of exchange altered sharply and became extremely slow, a further decrease of I $\%$ in deuterium concentration per 150 minutes. The initial stage was also accompanied by a slight decrease in pressure, indicating the presence of unsaturated material in the stearate. This may explain the initial rapid exchange, which we do not consider to be due to exchange with hydrogen atoms of saturated carbon atoms. At the end of each experiment the activity of the catalyst was checked by the addition of methyl oleate which was always hydrogenated rapidly. The rate of the slow exchange, which extended over a long period of time, was very much less than the rate of exchange of methyl oleate under the same conditions ( $\sim I_{5} \%$ in 90 minutes). This difference in the rates of exchange of saturated and unsaturated compounds has been established in many other instances. ${ }^{6,7,20}$ We have concluded, therefore, that our experiments with methyl oleate are not likely to be complicated appreciably by exchange reactions involving the hydrogen atoms of saturated carbon atoms.

In the experiments on the oleic-elaidic ester conversion, conditions identical with those used in the experiments with methyl oleate and deuterium were employed, except for the fact that nitrogen gas was bubbled through the ester. The nitrogen had been purified by passing it over molten sodium. It was found that small quantities of elaidic acid were formed ( $0 \cdot 2-0.4 \mathrm{~g}$. from 10 g . ester), but that, after an initial stage, the amount did not increase with time. The formation of this small quantity may be due to impurities such as hydrogen or water which could produce hydrogen atoms on the surface of the catalyst. In any case the quantities produced were very much smaller than those produced in the presence of deutcrium for the same time interval (see Table 1). This observation is in accordance with the work of Moore ${ }^{21}$ who also found no oleic-elaidic conversion on a nickel catalyst in the absence of hydrogen at about the same temperature as we have used. The results of the experiments with deuterium and methyl oleate are shown in Table I.

[^4]
## Discussion of the Results.

It can be seen that the composition of the products of the partial hydrogenation of methyl oleate which has been predicted on the basis of the associative mechanism does not completely accord with the results given in Table I, and these results cannot be regarded as furnishing positive evidence for the associative mechanism. They have, however,

Table I.-io g. Ester and ofr g. Pt. Initial concentration of Deuterium $100 \%$. Temperature $170^{\circ} \mathrm{C}$.

| Expt. No. | Time. | Hydrogenation of Ester. <br> \% | Final $D_{2}$ Conen. <br> \% | Solid Acids. |  |  | Liquid Acids. |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  |  | Wt. of Leght Elaidic Acid. | Wt. of Heavy Elaidic Acid. g. | Wt. of Heavy Trans Shifted Acids. g. g. | Wh. of Light Oleic Acid. g. | Wt. of Heavy Olelc Acid. g. g. | Wt. of Heavy Trans Shifted Acids. g. |
| I5 | 135 | $45^{\circ} 0$ | $73 \cdot 5$ | $2 \cdot 3$ | 0.6 | I•O | - | - | - |
| 17 | 70 | 32.5 | 89.0 | $3 \cdot 3$ | $0 \cdot 1$ | 0.2 |  | - |  |
| 18 | 50 | $36 \cdot 0$ | $90 \cdot 5$ | $3 \cdot 2$ | $\sim 0$ | $\sim 0$ | $0 \cdot 7$ | 0.4 | $0 \cdot 6$ |
| 22 | 170 | $0 \sim 40$ | $79^{\circ}$ | $2 \cdot 5$ | $0 \cdot 9$ | $0 \cdot 1$ | $0 \cdot 3$ | 0.4 | $0 \cdot 6$ |

some points of interest. The most striking feature is the relatively large amount of the product we have designated as light elaidic ester, which is formed rapidly at the beginning of the reaction. Actually this product need not be elaidic ester, but could be a mixture of the trans isomers of various esters which, in the lead salt separation, would all appear in the solid acid fraction. The production of large amounts of light elaidic acid even when the percentage deuterium in the gas phase is always greater than $90 \%$ (experiments 17 and 18 ) could be accounted for on the following lines. The first stage in the process leading to the half-hydrogenated state consists in the attack of carbon atom 9 or Io of an adsorbed oleic ester molecule by a deuterium atom in a manner similar to the mechanism for the optical inversion of aliphatic halides by negative ions. The deuterium atom approaches along
 the line of centres of the carbon and catalyst atoms, from the side furthest removed from the catalyst atom. The reaction path between the initial state and the half-hydrogenated state passes through a transition state which may be depicted as (I), the three remaining carbon valencies occupying a planar configuration. This transition state can be considered as a resonance between the states (II) and (III).


A
(II)

(III)

A closer approach of the deuterium atom leads to the production of the true half-hydrogenated state. If, however, a frequent mode of "decomposition " of this transition state consists, not in the formation of the true half-hydrogenated state, but in a simultancous release of the deuterium atom and the closing of the double bond between carbon atoms 9 and io, then the resulting products will be an equilibrium mixture of light elaidic and oleic esters. The production of both cis and trans geometrical configurations arises from the fact that the carbon atom can either retain its initial configuration (i.e. the one before the deuterium atom approaches) or become inverted, corresponding to the two alternative modes of relapse of the three carbon valencies from their planar configuration of the transition state. It is clear that our predictions in the introduction concerning the relative amounts of the isomers only apply to the true half-hydrogenated state and not to the above transition state.

On the basis of the mechanisms suggested by Farkas and Farkas ${ }^{4}, 14$ for the cis-trans conversion and wandering of the double bond, we cannot conceive how the formation of large amounts of light trans isomers in the presence of $90 \%$ deuterium can be explained. If it is assumed that the esters almost completely displace the deuterium from the catalyst surface and that the two processes take place chiefly by means of the hydrogen produced by the dissociation of the esters, then the reaction should occur in the complete absence of hydrogen gas. Our experiments with oleic ester in the absence of deuterium indicate that at least one of these reactions, viz. cis-trans conversion, does not occur appreciably. Furthermore, the latter mechanism involves the dissociation of a hydrogen atom attached to a saturated carbon atom, and our experiments with methyl stearate indicate that such a reaction does not take place to any appreciable extent under the experimental conditions which we have used. While at the moment, the explanation we have suggested for the formation of "light elaidic ester" may seem to be insufficiently supported by experimental evidence, nevertheless, we feel that some such type of associative mechanism must be correct. We cannot see how the above difficulties, which arise by postulating dissociative mechanisms for the various reactions, can be overcome.

The products other than light elaidic ester (heavy oleic, heavy elaidic, and heavy cis and trans shifted esters) are all formed in small quantities and the amounts could not be estimated with any high degree of accuracy ( $\pm 0.2 \mathrm{~g}$.). Considering the results as a whole it appears that these esters are all formed at rates which are of the same order of magnitude, which is roughly in accordance with our predictions. These esters might possibly, then, be regarded as arising from the true halfhydrogenated state in which case our previous considerations should be applicable.

In conclusion, the authors wish to thank Professor Polanyi for suggesting the problem and for very helpful advice during the work, and the D.S.I.R. for a grant to one of us (J. H. B.).

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Manchester.

# THE SUSPENSION OF SOLIDS IN MIXED LIQUIDS. 

By E. W. J. Mardies.

Received 7th October, 1940.
Occasionally in the literature of the subject of suspensions of finely divided solids in liquids there is reference to a change in the property of the suspension when a part of the dispersion medium is replaced by another liquid; thus, for example, it has been pointed out that the viscosity and thixotropic character of suspensions of zinc oxide or titanium oxide in hydrocarbons are considerably diminished by the addition of oleic acid, ${ }^{1,2,3}$ and this effect is offset by the presence of water. ${ }^{3}$

Colloidal substances usually show marked changes of behaviour in mixed liquids from that in the single liquids and often the maximum change occurs in mixtures of composition coinciding closely with that of a simple molecular mixture.

In this paper are given data on viscosity and settling properties of several suspensions in mixed liquids and the results obtained indicate that some of the interesting phenomena observed with dyes, proteins, cellulose derivatives and other colloidal substances in mixed liquids can also be observed with suspensions of finely divided solids.

The viscosity measurements were made using a simple form of plastometer at constant shear, avoiding low rates of shear and tubes of bore less than I mm.; conditions were chosen under which minimum viscosities were just obtainable and the results repeatable using different bore tubes.-

The settling tests were carried out, usually at room temperature and with a concentration of 15 grams per roo c.c. of medium, in tubes of 12 mm . diameter. The percentage volume occupied by the settled finely divided solid was measured from time to time, there being with most suspensions a sharp separation from the dispersion medium.

## Suspension of a Finely Divided Solid in Different Liquids.

When the dispersion medium is varied the ratio $\eta / \eta_{0}$, where $\eta$ is the viscosity of the suspension and $\eta_{0}$ that of the dispersion medium, varies considerably both with the viscosity of the dispersion medium and with its specific character. In liquids of low viscosity the particles during flow orientate relatively quickly and in this way by lying less across the stream cause less eddying and so lower viscosity ratios are obtained than in more viscous liquids where the particle movement is more sluggish. This effect in comparing the behaviour of a solid dispersed in different liquids can be eliminated by choosing conditions of temperature when the viscosities of the liquids are the same. ${ }^{2}$

In Fig. 1 are shown two families of curves relating the viscosity ratio and concentration for kaolin in several organic liquids under conditions

[^5]of equal viscosity and it will be scen that the viscosity ratios are highest with the non-polar hydrocarbons and least with oleic acid and linseed oil, while hydroxyl compounds, esters and aniline gave intermediate valucs.

At concentrations below I \% the viscosity ratios of kaolin in hydrocarbons and other liquids appear to be a linear function of volume concentration but the viscosity values obtained with kaolin in hydrocarbons were approximately four times those in accord with the theoretical equation proposed by Einstein, namely $\eta=\eta_{0}(1+2.5 \mathrm{~V})$, where $V$ is the volume occupied by the solid in I c.c. of the suspension. In polar liquids such as oleic acid there was a closer approach to the theoretical values.

The percentage volumes occupied by the dispersed kaolin, concentration $15 \mathrm{~g} . / 100 \mathrm{ml}$. in the various liquids after settling for several weeks were as follows: light mineral oil $70 \cdot 2$, benzyl alcohol $35 \%$, meta cresol $3 \mathrm{I} \cdot 5$, diamyl phthalate $49 \cdot 3$, aniline $33^{\circ} 3$, oleic acid $36 \cdot 5$, olive oil (washed)

57.4 , castor oil $66 \cdot 8$, glycerol 69 , boiled linseed oil 19.3 (dispersion partially stabilised, the supernatant liquid being turbid).

The viscosity and settling differences observed must be ascribed in the main to the aggregation of the dispersed solid particles. Kaolin similarly to zinc oxide gives relatively high viscosity readings when dispersed in hydrocarbons and shows evidence of thixotropy, the sedimented volume of kaolin in mincral oil being over $70 \%$ of the whole. The three dimensional scaffolding structure due to aggregates, simple or in clots, prevents much settling. On the other hand, in boiled linseed oil or in aniline where there is a high degree of dispersion the viscosities and the sedimented volume of the kaolin were very much lower; in boiled linseed oil a part of the dispersed solid had become stabilised for the supernatant liquid remained turbid and the coarser particles alone appeared to have settled into a hard precipitate. A completely dispersed system yields a hard coherent settlement of high solid content
whereas a thixotropic system yields a soft settlement of much lower solid content. ${ }^{1}$

Thixotropy occurs especially in organic liquids of low polar character: Winkler ${ }^{4}$ has shown that quartz, felspar and even glass of $\mathrm{r} \cdot 6 \mu$ diameter show thixotropy in benzenc but not in water. Ryan, Harkins and Gans ${ }^{5}$ found that in numerous non-polar organic media suspensions were highly flocculated and gave bulky sediments. When the particles adhere to form flocks then anomalous and high viscosity results are obtained, some of the shearing force being expended in breaking up the structure. It has been pointed out by Lawrence ${ }^{6}$ and Goodeve ${ }^{7}$ that when aggregated particles or clots are broken there occur impulses across the lines of flow with consequent raising of the viscosity.

Wo. Ostwald and Haller ${ }^{8}$ also have found in a study of the volume of sedimented bentonite in organic liquids that where aggregation occurs the amount of sedimentation is less than when the particles are finely dispersed. They concluded that, assuming the forces involved in lyo-


FIG. 2.-Effect of additions of oleic acid, etc., on the viscosity of a suspension of kaolin in petroleum spirit.
(a) Effect on viscosity ratios at different concentrations.
(b) Effect of different amounts of additions on the viscosity ratio of kaolin II $5 \%$ vol. concentration.
sorption have an electronic origin, then the strength of the field of force in the liquid is inversely proportional to the dielectric constant. They found a definite relation existing between lyosorption and the dielectric strength of the liquid media with tale and graphite in fifty different liquids.

## Effect of Additions.

It was found in the course of this work that the viscosity and settling of solids in olive, castor and mineral oils were considerably affected by the acidity of the materials; after alkali wash the viscosity values were greatly raised and the amount of settling was correspondingly lowered.

In Fig. 2 are shown data for viscosity ratios determined 10 minutes from the time of addition for differing amounts to a suspension of kaolin,

[^6]II. $5 \%$ vol, concentration in petroleum spirit of b.p. up to $120^{\circ} \mathrm{C}$. It will be seen that the first small additions have an important effect, whether of oleic acid, boiled linseed oil, wool fat or crêpe rubber. The viscosity ratios are also correspondingly lowered for different concentrations. In general, the character of the suspensions appears to have been completely

TABLE I.-Effect of Water on the Viscosity Ratio of a Suspension of Kaolin in Petroleum Spirit containing i \% Oleic Acid.

| $0.17 \%$ | vol. addition | $-19.8 \%$ | increase. |
| :---: | :---: | :---: | :---: |
| $0.33 \%$ | $"$ | $-41.2 \%$ | $"$ |
| $0.76 \%$ | $"$ | $-100.3 \%$ | $"$ | altered by the small additions and in the cases of oleic acid and boiled linseed oil resembles that of suspensions in these substances taken alone.

If water be added to the suspensions there is a big increase in viscosity, the effect increasing with time; in Table I are given some data obtained by adding water to a suspension of kaolin, II. $5 \%$ vol. concentration, in petroleum spirit containing I \% oleic acid.

The changes observed are due to the adsorption of the additions on the surface of the kaolin particles altering their degree of adhesion. Harkins and Dahlstrom ${ }^{9}$ have studied the wetting energy of the immersion of titanium oxide in various liquids and the data indicate that nearly all the energy is liberated in the adsorption of a monomolecular film from the liquid on the surface of the powder. They found, for example, the total energy of immersion and energy of adsorption for titanium oxide on a basis of an assumed area to be IIO ergs for benzene, but 210 in benzene 99.15 parts, boiled linseed oil 0.85 , and 175 in benzene 99.94 parts, raw linseed oil o.o6. The presence of a polar group greatly increases the energy of immersion.

The important influence on the settling and other behaviour of suspensions of small additions which are adsorbed by the dispersed particles is demonstrated in the following data, with additions of cellulose nitrate, proteins, rubber, linseed oil, oleic acid, etc., the character of the suspensions being sometimes profoundly altered.

Differences in the behaviour of a suspension can be observed also when a liquid such as ether is added to an alcohol suspension. In the following sections are presented data for solids dispersed in various binary mixtures.

## Ethyl Ether and Ethyl Alcohol Mixtures.

Ether-alcohol mixtures are well known solvents for cellulose nitrate, Kauri copal and other colloidal substances, although the pure liquids may be non-solvents. It appears that the ether in the mixture not only disturbs the equilibrium $(\mathrm{R} . \mathrm{OH})_{n} \leftrightharpoons n \mathrm{R} . \mathrm{OH}$, but adsorption of both kinds of molecules occurs on the surface of the solid to form a complex, the architecture of which is decided by spacial arrangements and interlocking of the molecules and by their polar character, Mardles. ${ }^{10}$

The suspensions of kaolin and other solids in their viscosity and settling behaviour in the ether-alcohol mixtures, although less pronounced differences were found, resemble cellulose nitrate and other colloidal substances, there being in the mixed liquids greater dispersion, as shown by the greater degree of settling.

In Fig. 3 are shown settling data for kaolin, silica and mica in etheralcohol mixtures with and without the addition of a small addition of

[^7]oleic acid, cellulose nitrate, etc. It will be seen that $(a)$ the sediment volume after settling overnight for kaolin and mica is slightly greater in ethyl ether than in ethyl alcohol; with silica the sediment volume is slightly greater in the alcohol and greater than that with kaolin or mica; (b) the settling-composition curves sag, indicating increased dispersion in the mixed liquids, and (c) cellulose nitrate has an important effect in decreasing the sediment volume with the kaolin and mica suspensions; oleic acid and resins were found to exert a relatively small effect while the silica suspension was considerably less sensitive to additions than either kaolin or the mica suspensions.

An interesting property of colloidal substances is their capacity to enhance any feature of the viscos-ity-composition curve for mixed liquids in which they are dispersed, any peak or minimum being usually magnified : finely divided powders also have this property as shown with solids in mixtures of alcohol and water and in


Fig. 3.-The settling of solids in ether-alcohol mixtures: (a) kaolin, (b) mica, and (c) silica (right: corresponding curves with additions of cellulose, nitrate, etc.). other mixed liquids described later. A possible explanation of this is that with increase in viscosity of the dispersion medium there is a corresponding increase in the viscosity ratio of the dispersion, ${ }^{2}$ while with molecular disaggregation and fall in viscosity of the medium there is a decrease in aggregation of the dispersed phase.

## Water-Ethyl Alcohol Mixtures.

This combination of liquids has received attention by numerous workers from the standpoint of the peptising action for various colloidal substances and it is known that the mixed liquids usually show a greater solvent action than the mean value: thus, for example, water at $10^{\circ} \mathrm{C}$. dissolved 30 mg . of a sample of gelatin per $100 \mathrm{c} . \mathrm{c}$. while a mixture containing $30 \%$ alcohol dissolved 35 mg . although with further additions of alcohol there was a rapid decrease in solubility. ${ }^{11}$ Zein has an optimum dispersion in close proximity to the mixture 1 mol, alcohol, 2 mols. water ${ }^{12}$ and potassium or sodium oleate in a $50 / 50$ mixture. ${ }^{13}$

In Fig. 4 are shown the effect on the viscosity of adding kaolin and other solids of concentration 15 gm ./ $100 \mathrm{c} . \mathrm{c}$. and various colloidal substances to alcohol-water mixtures; Fig. $4 b$ shows the relationship $\eta / \eta_{0}$ and it will be seen that the relationship is complex, there being a maximum

[^8]

Fig. 4.-Effect of solids on the viscosity of water-alcohol mixtures.
(a) Viscosity in poises. (b) Viscosity ratios, $\eta / \eta_{0}$.

Composition. Weight $\%$.
Tannic acid, Mardles, J. Chem. Soc., 1924, 125, 2244.
Potasium oleate, Bircumshaw, ibid., 1923, 123, 91.
Liquids (chain line), Dunstan, ibid., 1904, 85, 817.


Fig. 5.-The settling of solids in wateralcohol mixtures. (a) zinc oxide, (b) mica, (c) silica acid, and (d) kaolin.
and two minima. The position of the maximum is different for each substance and appears to be fixed by the degree of dispersion of the solids in the single liquids, thus, for example, zinc oxide in water is aggregated and has a high viscosity; mica behaves similarly but to a less extent and the addition of about $30 \%$ alcohol to both suspensions increases the degree of dispersion considerably. Kaolin, on the other hand, appears to be well dispersed and stable in water, more so than in alcohol, and the addition of alcohol causes only a small increase in dispersion.

Some additional information is revealed from the settling behaviour as shown in Fig. 5. Increased dispersion in the mixed liquids is shown by the presence of minima, and in the case of mica by the
formation of a minimum by the addition of $1 \%$ ammonium oleate. The sediment volume of kaolin in water is low, being $36 \%$ compared with $50 \%$ for alcohol; on the other hand, zinc oxicle is thixotropic in water and the sediment volume is little decreased by the addition of the soap. Silica and mica have similar sediment volumes in both liquids, in the neigh- bourhood of $60 \%$.

## Water and the Propyl Alcohols.

Results similar to those obtained with the water-ethyl alcohol mixtures were found with kaolin in mixtures of water and the propyl alcohols, there being an increase in the maximum of the viscosity-composition curve and increased dispersion as shown by the settling curves.

Some viscosity and settling data are shown in Fig. 6.
The accompaniment of increased dispersion with the formation of molecular hydrates and complexes in mixtures of water with alcohol and acetic acid and in ether-alcohol mixtures has given rise to the belief that the molecular complex is responsible for the increased solvent action. ${ }^{14,}{ }^{15}$ This conclusion, however, is contrary to the findings, described later, that in aniline mixtures with oleic or acetic acid there is a marked decrease in dispersion corresponding to the formation of molecular complexes; in some mixtures at least the anomaly appears to be explicable by the molecular disaggregation of the medium although complexes may have been formed, maxima and minima often occurring in the propertycomposition curves.

In the mixtures of acetic acid with methyl alcohol the molecular complex indicated


Fig. 6.-(a) Viscosity ratios, and (b) settling of kaolin in water-propyl alcohol mixtures. by the maximum to the viscosity-composition curve is again accompanied by increased dispersion of kaolin as indicated by the final sediment volumes (Fig. 7).

The apparent higher sediment volumes obtained after short periods of time are presumably due to the higher viscosities of the medium and it will be seen from the figure that the kaolin in common with cellulose acetate, gelatin, shellac and tannic acid enhances the maximum to the viscosity-composition curve of the pure liquids. The colloidal substances mentioned have a decidedly increased dispersion in the acetic acid-methyl alcohol mixtures than in the single liquids. ${ }^{13}$

The solvent and dispersing action of a mixture of liquids is not necessarily wholly attributable to one kind of molecule, simple or associated, but rather to the sum of the forces exerted on the colloidal particle by all the various molecules and molecular complexes. No theory is complete which does not take into consideration the important fact that dispersion is accompanied by adsorption of molecules from the medium on the surface of the dispersed particle.

[^9]In the mixture of aniline with acetic acid, two compounds are known definitely to exist, namely, $\mathrm{C}_{6} \mathrm{H}_{6} \mathrm{NH}_{2}, 2 \mathrm{C}_{2} \mathrm{H}_{4} \mathrm{O}_{2}$, m.p. $16.7^{\circ}$, and $2 \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{NH}_{2}, \mathrm{C}_{2} \mathrm{H}_{4} \mathrm{O}_{2}$, m.p. $-19.4^{\circ},{ }^{16}$ the latter being metastable under


Fig. 7.-The viscosity and settling of kaolin in acetic acid-methyl alcohol mixtures: (I) viscosity, and (II) settling after various times.
Tannic acid, etc., Mardles, J. Chem. Soc., 1924, 125, 2244.
all conditions. The complex $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{NH}_{2}, \mathrm{C}_{2} \mathrm{H}_{4} \mathrm{O}_{2}$ apparently does not exist. ${ }^{17}$ The results of viscosity and settling of kaolin in the aniline mixtures with acetic and oleic acids (Fig. 8) indicate considerable de-


Fig. 8.-Viscosity and settling of kaolin in aniline mixtures: $(a)$ and (b) viscosity and settling in aniline-acetic acid, (c) settling in aniline-oleic acid.
creases in the degree of dispersion, a finding in keeping with the rule that the presence of a complex of the components of the dispersion medium is associated with a fall in the degree of dispersion.

[^10]
## Benzyl Alcohol and Cyclohexanone Mixtures.

A study of suspensions of kaolin in this mixture has yielded interesting results; the resemblance of the behaviour of kaolin to that of


Fig. 9.-The viscosity and settling of kaolin in mixtures of benzyl alcohol and cyclohexanone: (a) viscosity, (b) sediment volumes, (c) ditto $+0.2 \%$ cellulose acetate.
cellulose acetate is again clear, as there not only is this increased dispersion in the neighbourhood of $80 \%$ cyclohexanone but the shape of the settling curve is similar to that for the solubility of cellulose acetate.

There is also the interesting finding that with increasing concentration the dispersion, whether of cellulose acetate or kaolin, becomes more sensitive to the change in composition of the solvents as indicated in Fig. 10 ; with higher concentrations there is greater aggregation of the particles allowing of a greater response to the higher dispersive activity of some of the mixture compositions.

## Summary.

A study has been made of the viscosity and settling of kaolin and other finely divided solids dispersed in several mixed liquids. It has been found that in viscosity and dispersion behaviour the suspensions resemble solutions of cellulose esters, proteins, soaps and other colloidal substances in mixed liquids.

Thixotropy and the high viscosity due to aggregation observed with solids in non-polar liquids such as


CYCLOHEXANONE WGT. \%
Fig. ro. - The sediment volumes of different concentrations (grams per roo c.c.) of kaolin in benzyl alcoholcyclohexanone mixtures; comparison with precipitation curve for cellulose acetate. hydrocarbons, were considerably reduced by the addition of polar-molecules such as oleic acid or linseed oil and by the addition of colloidal substances adsorbed by the dispersed solid.

Suspensions of higher concentration and those in non-polar liquids when aggregation is pronounced are more sensitive to changes in the

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composition of the dispersing medium and corresponding changes in its polar character. The formation of hydrates and molecular complexes in mixed liquids is accompanied by a fall in the dispersive action, but with some mixtures, although complexes are present, yet molecular disaggregation of the mixed liquids also occurs and maxima and minima were found with some of the property-composition curves for the suspensions in mixed liquids.

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# THE SURFACE TENSIONS OF AMINO-ACID SOLUTIONS AS A FUNCTION OF $p \mathrm{p}$ 

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The surface tensions of solutions containing amino-acids and proteins vary in an interesting manner with the hydrogen-ion concentration. Data for amino-acid solutions, which should help to explain the behaviour of proteins, are, however, scanty. Jones and Lewis ${ }^{1}$ found that the surface tension of $5 \%$ and of $10 \%$ glycine solutions showed a maximum in the region of the isoelectric point; and Pappenheimer, Lepie and Wyman ${ }^{2}$ measured the surface tensions of solutions containing $\epsilon$-aminocaproic acid and varying amounts of acid and alkali and obtained a welldefined maximum at the isoclectric point and a slight minimum on the acid side.

Protein solutions have received more attention, but the results recorded are not consistent. Davis, Salisbury and Harvey ${ }^{3}$ found that gelatin solutions gave a minimum surface tension not far from the isoelectric point, and this was confirmed by de Caro, ${ }^{4}$ who also found two maxima, one at $\mathrm{pH}_{3}$, the other at pH 9 . Johlin, ${ }^{5}$ however, found that although I \% gelatin showed a minimum surface tension at the isoelectric point, the curve changed with time, and that after twenty-four hours the irregularities had disappeared. Johnston and Peard ${ }^{6}$ obtained very different results; they obtained a maximum at the isoelectric point and another at $p \mathrm{H} 2 \cdot 8-3 \cdot 0$, and minima at $\mathrm{pH} 3 \cdot 9$ and pH 9 . On the other hand, Jermolenko ${ }^{7}$ records a minimum surface tension at the isoelectric point. The data for other protein solutions are similarly confused. Bottazzi ${ }^{8}$ and Errera and Millau ${ }^{9}$ conclude that proteins show a minimum surface tension at the isoelectric point. Johnston ${ }^{10}$ obtained a surface tension $-p \mathrm{H}$ curve for egg albumin which showed a maximum at the isoelectric point; and Lewis and Price ${ }^{11}$ have shown that $0.5 \%$

[^11]and $0.1 \%$ lecithin solutions give a very well-defined maximum at the isoelectric point $(2 \cdot 6)$ with minima at $\mathrm{pH} \mathrm{I} \cdot 7$ and $\mathrm{pH} 4^{\circ} 2$.

The experiments described below show that both maxima and minima may be obtained for amino-acid solutions, but that they do not necessarily occur at the isoelectric point. Further, the form of the surface tensionpH curve may be interpreted in terms of the adsorption of the various components at the surface.

## Experimental.

The surface tensions were measured by the bubble pressure methad as previously described by one of us. ${ }^{12}$ Two jets were used, one of radius 0.0128 cm . for the acid-glycine solutions, the other of radius $0.01 I_{4} \mathrm{~cm}$. for the other solutions; these radii were checked by standardisation with pure water and with pure benzene. The solutions investigated were ternary systems containing amino-acid-hydrochloric acid-water or amino-acid-sodium hydroxide water; they were made up by weight from the solid amino-acid and hydrochloric acid or sodium hydroxide of appropriate strength from a stock solution. The concentration of acid or alkali in these solutions was known except in the neighbourhood of the isoelectric point, where a mere trace of acid or alkali serves to change the $p$ н appreciably, and where, in order to obtain a desired $p \mathrm{H}$, solutions had to be made up by trial and error. The chemicals used were of Analar grade or had been recrystallised; the water was distilled from quartz and gave a surface tension of 72.01 dynes $/ \mathrm{cm}$. at $25^{\circ} \mathrm{C}$. at which temperature all the measurements were made. As soon as the surface tension of a solution had been measured, it was immediately transferred to another cell and its pн obtained by means of a hydrogen electrode, precautions being taken to avoid contamination between the two measurements.

## Binary Solutions.

The surface tensions of the binary solutions involved were measured, and are given in Table I. It should be noted that that of hydrochloric acid falls slightly with increasing acid concentration, indicating a positive absorption of the acid ; that of sodium hydroxide, however, increases with alkali concentration, water being adsorbed.

TABLE 1.

| Solution. | m. | $\gamma$. | Solution. | $m$. | $\gamma$. |
| :---: | :---: | :---: | :---: | :---: | :---: |
| HCl | 1.0 | 71.87 | Glycine | 0.5 | $72 \cdot 54$ |
| NaOH | 3.0 | $7 \mathrm{~T} \cdot 64$ |  | 1.0 | $73 \cdot \mathrm{II}$ |
|  |  |  |  | 2.0 | $74 \cdot 18$ |
|  | - 98 | 74.60 | Alanine | $0 \cdot 5$ | $72 \cdot 54$ |
|  | $1 \cdot 47$ | 75.73 |  | 10 | 72.90 |
|  | I. 95 | 76.59 | Valine Hippuric acid | ¢ $\begin{gathered}\text { O.I } \\ \text { Saturated. }\end{gathered}$ | $71 \cdot 92$ 71.04 |

## Ternary Solutions.

Measurements were made with glycine, alanine, valine, cystine and hippuric acid; the results are shown graphically in Figs. r, 2, and 3, in which the surface tension has been plotted against the pri. Three series
of measurements were made with the systems glycine-hydrochloric acidwater and glycine-sodium hydroxide-water, in which the glycine concentra-


Fig. 1.-Plot of surface tension- pH for glycine solutions at $25^{\circ} \mathrm{C}$.
tion was kept conant at $0.5 \mathrm{M}, \mathrm{I} \cdot \mathrm{M}$, and 2.0 M respectively while the pH varied between o and II. In the case of the other amino-acids only one series at constant amino-acid content has been examined. Curves with marked maxima and minima are observed only when an amino-acid of reasonable solubility is used, and in the case of glycine the fluctuations in surface tension are more marked the greater the concentration of the solution.

## General Thermodynamic Theory.

We shall now consider the general thermodynamic equations which are applicable to the surfaces of solutions containing amino-acids, and


Fig. 2.-Plot of surface tension- pH for analine and valine solutions at $25^{\circ} \mathrm{C}$.
will see how these lead to an interpretation of the form of the $\gamma-p H$ curve in terms of the adsorptions of the various components.

## Binary Systems.

For the binary system amino-acid water the Gibbs equation is
$\mathrm{d} \gamma=-\Gamma_{1} \mathrm{~d} \mu_{1}-\Gamma_{3} \mathrm{~d} \mu_{3}$ (I) where $\Gamma$ is the surface excess, $\mu$ is the chemical potential and the subscripts I and 3 refer to amino-acid and water respectively. For acids which raise the surface
tension of water (glycine and alanine), the dividing surface may be drawn so that $\Gamma_{1}=0$. The Duhem-Margules equation gives

$$
\begin{gather*}
n_{1} \mathrm{~d} \mu_{1}+n_{3} \mathrm{~d} \mu_{3}=0  \tag{2}\\
\mathrm{~d} \gamma=\Gamma_{3} \frac{m_{1}}{55^{\circ} 5} R T \mathrm{~d} \ln f_{1} m_{1} \tag{3}
\end{gather*}
$$

and hence
where $m_{1}$ is the molality of the amino-acid and $f_{1}$ is its activity coefficient. This equation may also be applied to the aqueous solution of the hydrochloride or the sodium salt of the glycine, as these both raise the surface tension of water.

For amino-acids the addition of which to water lowers the surface tension, it is more convenient to put $\Gamma_{3}=0$, when

$$
\begin{equation*}
\mathrm{d} \gamma=-\Gamma_{1} R T \mathrm{~d} \ln f_{1} m_{1} \tag{4}
\end{equation*}
$$

## Ternary Solutions.

For ternary solutions of amino-acid, acid or alkali water the Gibbs equation is

$$
\begin{equation*}
\mathrm{d} \gamma=-\Gamma_{1} \mathrm{~d} \mu_{1}-\Gamma_{2} \mathrm{~d} \mu_{2}-\Gamma_{3} \mathrm{~d} \mu_{3} \tag{5}
\end{equation*}
$$

where the subscript 2 refers to acid or alkali. Combining this with the Duhem-Margules equation

$$
\begin{gather*}
n_{1} \mathrm{~d} \mu_{1}+n_{2} \mathrm{~d} \mu_{2}+n_{3} \mathrm{~d} \mu_{3}=0  \tag{6}\\
\mathrm{~d} \gamma=-\Gamma_{1} \mathrm{~d} \mu_{1}-\Gamma_{2} \mathrm{~d} \mu_{3}+\Gamma_{3}\left(\frac{n_{1}}{n_{3}} \mathrm{~d} \mu_{1}+\frac{n_{2}}{n_{3}} \mathrm{~d} \mu_{2}\right)  \tag{7}\\
=\left(\Gamma_{3} \frac{n_{1}}{n_{3}}-\Gamma_{1}\right) \mathrm{d} \mu_{1}+\left(\Gamma_{3} \frac{n_{2}}{n_{3}}-\Gamma_{2}\right) \mathrm{d} \mu_{2}  \tag{8}\\
\left(\partial \gamma / \partial \mu_{2}\right) \mu_{4}=\Gamma_{3} \frac{n_{2}}{n_{3}}-\Gamma_{2}  \tag{9}\\
\left(\partial \gamma / \partial \mu_{1}\right) \mu_{2}=\Gamma_{3} \frac{n_{1}}{n_{3}}-\Gamma_{1} \tag{IO}
\end{gather*}
$$

we obtain

Hence
and
For a maximum or a minimum in the $\gamma-\mu_{2}$ curve $\left(\partial \gamma / \partial \mu_{2}\right)_{\mu_{2}}=0$ and

$$
\begin{equation*}
\Gamma_{2}=\Gamma_{3} \frac{n_{2}}{n_{3}} \tag{II}
\end{equation*}
$$

while for a maximum or minimum in the $\gamma-\mu_{1}$ curve $\left(\partial \gamma / \partial \mu_{1}\right)_{\mu_{2}}=0$ and

$$
\begin{equation*}
\Gamma_{1}=\Gamma_{3} \frac{n_{1}}{n_{3}} \tag{12}
\end{equation*}
$$

The position of a maximum or minimum on the $\gamma-\mu_{2}$ curve at constant $\mu_{1}$ may vary with $\mu_{1}$, and also that on the $\gamma-\mu_{1}$ curve at constant $\mu_{2}$ with $\mu_{2}$. From (8)

$$
\begin{equation*}
\frac{\mathrm{d} \gamma}{\mathrm{~d} \mu_{1}}=\left(\Gamma_{3} \frac{n_{1}}{n_{3}}-\Gamma_{1}\right)+\left(\Gamma_{3} \frac{n_{2}}{n_{3}}-\Gamma_{2}\right) \frac{\mathrm{d} \mu_{2}}{\mathrm{~d} \mu_{1}} \tag{13}
\end{equation*}
$$

which leads either to a relation between $\mu_{1}$ and $\mu_{2}$ corresponding to the maximum or the minimum, or to the slope $\mathrm{d} \gamma_{0} / \mathrm{d} \mu_{1}$ of the locus of the maximum or minimum on curves of $\gamma-\mu_{2}$ at constant $\mu_{1}$, or to the slope $\mathrm{d} \gamma_{0} / \mathrm{d} \mu_{2}$ of the locus of the maximum or minimum on curves of
$\gamma-\mu_{1}$ at constant $\mu_{2}$. For example, at such a maximum or minimum where the surface tension is $\gamma_{0}$,

$$
\begin{equation*}
\left(\partial \gamma_{0} / \partial \mu_{2}\right)_{\mu_{1}}=\Gamma_{3} \frac{n_{2}}{n_{3}}-\Gamma_{2}=0 \tag{14}
\end{equation*}
$$

Hence from (I3)

$$
\begin{equation*}
\frac{\mathrm{d} \gamma_{0}}{\mathrm{~d} \mu_{1}}=\Gamma_{3} \frac{n_{1}}{n_{3}}-\Gamma_{1} \tag{15}
\end{equation*}
$$

Thus $\mathrm{d} \gamma_{0} / \mathrm{d} \mu_{1}$ is positive or negative according as $\Gamma_{3} \frac{n_{1}}{n_{3}}$ is greater or less than $\Gamma_{1}$. If there is no change in $\gamma_{0}$ with $\mu_{1}$ then the relations

$$
\begin{equation*}
\frac{\Gamma_{1}}{n_{1}}=\frac{\Gamma_{2}}{n_{2}}=\frac{\Gamma_{3}}{n_{3}} \tag{I6}
\end{equation*}
$$

hold. Similar relations may be deduced for the $\gamma-\mu_{1}$ curves at constant $\mu_{2}$.

An interesting special case is when $n_{1}=n_{2}$, that is when equimolar quantities of amino-acid and acid alkali are present, thus corresponding to the hydrochloride or the sodium salt. If a maximum in the $\gamma-\mu_{2}$ curve at constant $\mu_{1}$ occurs at this point ( $c f$. glycine, below) then

$$
\begin{equation*}
\partial \gamma / \partial \mu_{1}=\Gamma_{3} \frac{n_{1}}{n_{3}}-\Gamma_{1}=\Gamma_{2}-\Gamma_{1} \tag{17}
\end{equation*}
$$

If the maximum is independent of $\mu_{1}$, then the surface excess of aminoacid is the same as that for acid or alkali. All these relations are quite general, and are independent of the position of the dividing surface.

The variation of the surface tension with pH at constant amino-acid content may be obtained from equation (9). Substituting

$$
\begin{align*}
\mathrm{d} \mu_{1} & =R T \mathrm{~d} \ln f_{1} m_{1}  \tag{I8}\\
\mathrm{~d} \mu_{2} & =2 R T \mathrm{~d} \ln f_{ \pm} n_{2}  \tag{I9}\\
p \mathrm{H} & =-\log f_{ \pm} m_{2} \tag{20}
\end{align*}
$$

we obtain

$$
\begin{equation*}
0.43(\partial \gamma / \partial \rho \mathrm{H})_{\mu_{1}}=2 R T \Gamma_{2}-2 R T \frac{n_{1}}{n_{3}} \Gamma_{3} \tag{2I}
\end{equation*}
$$

for the addition of acid. For the addition of alkali

$$
\begin{array}{cr} 
& p \mathrm{H}=-\log K_{10}+\log f_{ \pm} m_{2}  \tag{22}\\
\text { and then } & 0.43(\partial \gamma / \partial \mathrm{pH})_{\mu_{1}}=-2 R T \Gamma_{2}+2 R T \frac{n_{2}}{n_{3}} \Gamma_{3}
\end{array}
$$

If the activity coefficients in the three component system are not known, then an approximate relation may be obtained by putting them equal to unity. Hence
and

$$
\begin{gather*}
0.43(\partial \gamma / \partial \rho H)_{m_{1}}=2 R T \Gamma_{2}-2 R T \frac{n_{2}}{n_{3}} \Gamma_{3}  \tag{24}\\
0.43(\partial \gamma / \partial \rho \mathrm{H})_{m_{1}}=-2 R T \Gamma_{2}+2 R T \frac{n_{2}}{n_{3}} \Gamma_{3} \tag{25}
\end{gather*}
$$

for the addition of acid and alkali respectively. These equations are also independent of the position of the dividing surface.

If the $p \mathrm{H}$ is kept constant and the amino-acid content varied, then equation (Io) may be used. For the additions of acid or alkali
which

$$
\begin{align*}
\left(\partial \gamma / \partial m_{1}\right)_{p \mathrm{~B}} & =\left(\Gamma_{3} \frac{n_{1}}{n_{3}}-\Gamma_{\mathrm{L}}\right) R T\left(\frac{\partial \ln f_{1} m_{1}}{\partial m_{1}}\right)_{p \mathrm{H}}  \tag{26}\\
& \simeq\left(\frac{\Gamma_{3}}{m_{3}} \cdot-\frac{\Gamma_{1}}{m_{1}}\right) R T \tag{27}
\end{align*}
$$

when the activity coefficient is ignored.
In order to calculate numerical values of surface adsorptions, however, the position of the dividing surface must be defined. If the surface tension of the solution increases with amino-acid concentration, then it is convenient to place the surface so that $\Gamma_{1}=0$. Then

$$
\begin{equation*}
\left(\partial y / \partial m_{1}\right)_{p \mathrm{H}} \bumpeq \frac{\Gamma_{3} R T}{m_{3}} \tag{28}
\end{equation*}
$$

and knowing $\Gamma_{3}, \Gamma_{2}$ may then be calculated from (23). If the surface tension of the amino-acid solution decreases with concentration, then it is more convenient to draw the surface so that $\Gamma_{3}=0$. We then obtain
and

$$
\begin{align*}
& 0.43(\partial \gamma / \partial p \mathrm{H})_{m_{1}}=2 R T \Gamma_{2}  \tag{29}\\
& 0.43(\partial \gamma / \partial \rho \mathrm{H})_{m_{1}}=-2 R T \Gamma_{2}
\end{align*}
$$

for the addition of alkali and acid respectively; and also

$$
\begin{equation*}
\left(\partial \gamma / \partial m_{1}\right)_{p H} \bumpeq-\frac{\Gamma_{1} R T}{m_{1}} \tag{3I}
\end{equation*}
$$

There is an interesting difference between ternary systems in which the amino-acid is negatively adsorbed at the surface, e.g. glycine and alanine, and those in which it is positively adsorbed as are most of the higher amino-acids and proteins. For both systems equation (II) holds, and for maxima and minima in the $\gamma-$ pH curve at constant amino-acid concentration we have approximately from (23)

$$
\Gamma_{2}=\Gamma_{3 n_{3}}
$$

When the amino-acid is negativcly adsorbed and the dividing surface can be drawn so that $\Gamma_{1}$ is zero, then $\Gamma_{2}$ and $\Gamma_{3}$ will be both positive; but when the adsorption of the amino-acid is positive, then we may draw the surface so that $\Gamma_{3}$ is zero, when $\Gamma_{2}$ is also zero. Now at the $p \mathrm{H}$ of the pure aqueous ampholyte either amino-acid or water is positively. adsorbed, depending on the sign of $\mathrm{d} \gamma / \mathrm{d} m_{1}$; hence this $p \mathrm{H}$ can only correspond to a maximum or a minimum on the $\gamma-p H$ curve for those amino-acids the surface tension of whose solutions decrease with increasing concentration of amino-acid. This result is borne out by experiment; the pH of aqueous glycine and of alanine lie between maxima and minima, while those of higher acids and of proteins lic very close to either a maximum or a minimum.

## Glycine Solutions.

Three series of measurements were made with the ternary systems glycine-acid-water and glycine-alkali-water, in which the glycine content was kept constant at $0.5 \mathrm{M}, 1.0 \mathrm{M}$ and 2.0 m , while the pH varied between

0 and II. The results are given in Fig. I, in which the surface tension is plotted against the pr. Each curve shows two maxima and one minimum on the acid side and one minimum on the alkaline side; the two maxima are nearly independent of glycine content and occur at $\mathrm{pH} \mathrm{I} \cdot 4$ and pH 5.3 . The minimum on the alkaline side appears at a greater pH as the glycine content decreases; the curve then rises stecply, flattens, and then increases its slope as the amount of alkali is increased. The whole curve presents a more flattened appearance as the glycine content is reduced. The plot of the surface tension against $p H$ is convenient for the whole range of hydrogen-ion concentration, but it obscures an interesting result on the acid side. When the surface tension is plotted against the acid concentration the curves become straight lines which intersect exactly at equivalent amounts of glycine and acid. This seems to indicate that the effect of glycine hydrochloride on the surface tension is greater than that of glycine itself, the maximum corresponding to the binary system glycine hydrochloride-water; when excess acid is added the surface tension falls because of the depressing action of the acid. On the alkaline side there is no such maximum ; the effect of the sodium salt is greater than that of glycine, and excess alkali produces a still further increase in the surface tension.

The central minimum does not occur exactly at the isoelectric point, but a little towards the alkaline side; the addition of hydrochloric acid to aqueous glycine thus produces an increase in surface tension, the addition of alkali a decrease. In the case of glycine the p H of the pure aqueous ampholyte is almost the same as that of the isoelectric point, but this is not generally true for amino-acids, the two only coinciding when $K_{a}$ is equal to $K_{b}$. The isoelectric solution may therefore be a three-component system. From the point of view of surface tension and surface adsorption it is therefore better to consider the pH of the pure ampholyte solution as the central point rather than the isoelectric point. We may now discuss the application of the general thermodynamic theory to glycine solutions.

## (1) The Binary System Glycine-Water.

It may be noted that the $p$ of a 1.0 m glycine solution is only 0.00 I pH units different from that of the isoelectric point at infinite dilution. As the surface tension increases with glycine concentration, water is positively adsorbed at the surface. Values of $\Gamma_{3}$ in moles $/ \mathrm{sq} . \mathrm{cm}$. calculated from equation (3) are given in Table II. The activity coefficients of glycine solutions have been taken from the data of Smith and Smith. ${ }^{13}$

TABLE II.

| $\mu_{1}$. | 0.1 | 0.3 | 0.5 | 0.7 | $I \cdot 0$ | $I \cdot 2$ | $I .5$ | $I \cdot 7$ | 2.0 |
| :--- | ---: | ---: | ---: | ---: | ---: | ---: | ---: | ---: | ---: |

The amount of water adsorbed, which varies very little with the glycine concentration, corresponds approximately to a unimolecular layer.

## (2) The System Glycine-Hydrochloric Acid-Water.

(a) When acid is first added to aqueous glycine, the surface tension increases until a maximum at $p \mathrm{H} 5 \cdot 2 \cdot 5 \cdot 4$ is reached. The adsorption of water and of hydrochloric acid may be calculated approximately from equations (24) and (28), the second term on the right side of (24) being negligible for low acid concentrations. At $p \mathrm{H} 6.0$ the water adsorbed is thus $22 \times 10^{-10}$ moles $/ \mathrm{sq} . \mathrm{cm}$., and is independent of the glycine content This value is about the same as that for an aqueous glycine solution. Hydrochloric acid is negatively adsorbed, the amount becoming less as the acid concentration increases; the values for pH 6.0 are :-

$$
\begin{array}{cccc}
m_{1} & 0.5 & 1.0 & 2.0 \\
\Gamma_{2} & -3.1 & -7.5 & -26.4 \times 10^{-12} \text { moles } / \mathrm{sq} . \mathrm{cm} .
\end{array}
$$

The surface is thus covered with a layer of water molecules into which more acid molecules penetrate as their concentration increases.
(b) At $p \mathrm{H} 5.2 .5 \cdot 4$ equation (II) may be applied. Here both water and hydrochloric acid are adsorbed; assuming that that of water is the same as at $p \mathrm{H} 6 \cdot 0$, that of hydrochloric acid is $2 \times 10^{-16} \mathrm{moles} / \mathrm{sq} . \mathrm{cm}$.
(c) The curve next falls to a minimum at $\mathrm{pH} 3 \cdot 6-4^{\circ} \mathrm{O}$. For a pH of 4.3 (about the middle of this portion) the adsorption of water calculated from equation (28) is $24 \times 10^{-10} \mathrm{moles} / \mathrm{sq}$. cm ., about the same value as before, but with a tendency to fall with decreasing glycine concentration. Hydrochloric acid is also positively adsorbed in increasing amount with increasing glycine content:-

$$
\begin{array}{llll}
m_{1} & 0.5 & 1.0 & 2.0 \\
\Gamma_{2} & 3.1 & 3.5 & 3.9 \times 10^{-12} \text { moles } / \mathrm{sq} . \mathrm{cm} .
\end{array}
$$

The value of $(\partial \gamma / \partial \rho H)_{m_{1}}$ in this portion at first increases and then falls until the minimum is reached; the adsorption of acid therefore increases to the value given above and then falls.
(d) At the minimum at $p$ Hi $3 \cdot 6 \cdot 4 \cdot 0$ equation (1 i) may again be applied. If the adsorption of water has remained constant that of hydrochloric acid is $7.5 \times 10^{-15} \mathrm{moles} / \mathrm{sq} . \mathrm{cm}$.
(e) The curve now rises to a maximum at $\mathrm{pH}^{2} 14 . \quad(\partial y / \partial \mathrm{pH})_{m_{1}}$ is negative, but hydrochloric acid is positively adsorbed as the second term on the right side of equation (14) is now greater than the first. If the water adsorption is assumed constant at its previous value, that of the acid is given by $0.4 \times 10^{-10} m_{2}$.
(f) At the next maximum there are equimolar quantities of glycine and hydrochloric acid present, and the system may be treated as a twocomponent system containing glycine hydrochloride and water. For concentrations between I M and 2 m the amount of water adsorbed as calculated from the approximate form of the Gibbs equation (3) is $25 \times 10^{-10} \mathrm{moles} / \mathrm{sq} . \mathrm{cm}$., that is about what it is at the surface of a glycine solution. There is an apparent paradox here, for equation (II) applies to this maximum and indicates that both water and acid are adsorbed, the amount of the latter being given by equation (17). The dividing surface for the glycine hydrochloride solution is drawn, however, so that the surface excess of glycine hydrochloride is zero, while the surface for which equation (II) applies is drawn so that the surface excess of glycine is zero.
(g) At $p H$ values less than $I \cdot 4\left(\partial \gamma / \partial p_{H}\right)_{m_{1}}$ is positive, there is excess acid in the solution, and both water and acid are adsorbed. The amount
of water adsorbed as calculated from equation (28) is $24 \times 10^{-10}$ moles/ sq. cm . for pH 0 and the corresponding amount of acid $5 \times 10^{-11}$ and $10^{-11}$ moles/sq. cm. for I m and 2 m glycine respectively.

## (3) The System Glycine-Sodium Hydroxide-Water.

For this system equations (25), (28) and (II) are applicable.
(a) When sodium hydroxide is added to the pure ampholyte solution the surface tension is decreased and $(\partial \gamma / \partial \mathrm{pH})_{m_{1}}$ is negative. The values of $\left(\partial \gamma / \partial m_{1}\right)_{p \mathrm{H}}$ are not constant, but an approximate calculation using equation (28) gives $\Gamma_{3}$ as $13 \times 10^{-10}$ moles $/ \mathrm{sq}$. cm . for 0.75 m glycine and $8 \times 10^{-10}$ for 1.5 M . The water adsorption thus seems to have fallen. Sodium hydroxide is positively adsorbed; from equation (25) we obtain:-

| $n_{1}$ | 0.5 | $\mathrm{I} \cdot \mathrm{o}$ | 2.0 |
| :--- | :--- | :--- | :--- |
| $\Gamma_{2}$ | 3 | 7 | $26 \times 10^{-12}$ moles $/ \mathrm{sq} . \mathrm{cm}$. |

It should be noted that at the surface of sodium hydroxide solutions the solute is negatively adsorbed.
(b) The $p H$ corresponding to the minimum point varies between $6 \cdot 3$ and 7 according to the glycine concentration, whereas the maxima and minima for the system glycine-hydrochloric acid-water are independent of the glycine concentration. From equation (15), when the dividing surface is drawn so that $\Gamma_{1}=0$, the adsorption of water is positive, and may be calculated from $\mathrm{d} \gamma_{0} / \mathrm{d} \mu_{1} ; 17 \times 10^{-10}$ moles $/ \mathrm{sq} . \mathrm{cm}$. is the value corresponding to $m_{1}=\mathrm{I} \cdot 5$, but it is less for lower glycine concentrations. The adsorption of sodium hydroxide is also positive at the minimum, but it is very small as the alkali concentration is very low (equation (II)).
(c) The remainder of the curve may be divided into three parts, first a steep rise, then a flattened portion, and finally another steep rise; $(\partial \gamma / \partial \mathrm{pH})_{m_{1}}$ is positive throughout. The shift of the minimum to the alkaline side as the concentration of glycine is reduced causes some difficulty in calculating the adsorptions in this region. For the steep portion the second term in equation (25) may be neglected; sodium hydroxide is therefore negatively adsorbed. This also applies to the flattened portion; when, however, it is horizontal, according to equation (II) there will be a slight positive adsorption of alkali. The adsorption of water varies with the glycine content and is apparently rather greater than that on the acid side. Thus
$\left.\begin{array}{lcc}p_{\mathrm{H}} & 8 & 10 \\ m_{1} & \Gamma_{3} & \Gamma_{3} \\ 1 \cdot 5 & 32 & 36 \\ 0.75 & 22 & 29\end{array}\right\} \times 10^{-10}$ moles/sq. cm.

As the alkali concentration increases the second term on the right side of equation (25) increases, and at some point the adsorption of alkali will become positive.

## The Effect of Salt.

The surface tensions of the systems I m glycine-hydrochloric acid-water-I $M \mathrm{NaCl}$ and I m glycine-sodium hydroxide-water-I M NaCl were measured. The plot of $\gamma$ against $p_{H}$ is given in Fig. I. The curve has the same general shape as in the absence of salt; there is a minimum at pH 6 very near the isoelectric point, there is a distinct minimum on the
alkaline side instead of the flattened portion, and the maximum on the acid side is displaced to a power $p \mathrm{H}$. For the three-component system glycine-sodium chloride-water it has been shown that water is adsorbed at the surface. ${ }^{14}$ If we put, then, the surface excess of salt also equal to zero, the equations previously deduced will have the same form and the curve might have essentially the same shape.

## Other Amino-Acids.

The surface tension- pH curves for other amino-acids have been obtained; these are given in Figs. 2, 3 and 4. The interpretation of their form in terms of the adsorption of the various components is analogous to that given for glycine.

Alanine. The curve obtained for im alanine shows a minimum at about pH 8 and a maximum at pH 3.7 . A few measurements with 0.5 alanine indicated that that curve was more flattened. Alanine increases the surface tension of water, but not so much as does glycine; the equations already used for systems containing the latter should therefore apply. Water is adsorbed at the surface of the pure ampholyte solutions. On the addition of small quantities of hydrochloric acid the latter is at first negatively adsorbed, but before pH 3.7 is reached this adsorption becomes positive, for there equation (II) must hold; further addition of acid corresponds to positive adsorption. When sodium hydroxide is added to the pure ampholyte solution alkali is at first adsorbed as well as water, but beyond the minimum at $p \mathrm{H} 8$ negative adsorption of the alkali occurs. There is no maximum in this curve corresponding to equimolecular quantities of ampholyte and hydrochloric acid; the replacement of alanine by its hydrochloride produces no increase in the surface tension as it does in the case of glycine.

The effect of sodium chloride is interesting; the addition of Im gives a curve with a maximum instead of a minimum in the isoelectric region, while in the case of glycine a curve of the same form was obtained. It is significant, however, that the effect of sodium chloride on the surface layer of alanine solutions is to change the sign of the adsorption of amino-acid from negative to positive. ${ }^{14}$

Valine.-Valine is not as soluble as the two former amino-acids, and consequently experiments had to be done with much lower ampholyte concentrations. The curve shows a minimum at about pH 8 , from which it rises steadily on the alkaline side, but on the acid side shows a flat maximum. The surface tension of valine decreases with increasing valine concentration; the Gibbs equation may be applied by drawing the dividing surface such that the surface excess of water is zero, when equations (29) and (30) hold. As the $p$ H of the pure ampholyte solution is 6 , there is no adsorption of hydrochloric acid until the curve begins to descend when the adsorption is positive. On the addition of alkali its adsorption is first positive, is zero at the minimum and negative beyond. Valine is presumably positively adsorbed throughout.

Gystine.-Only a very dilute solution may be obtained. The curve was therefore very flat, but it showed indications of a slight maximum on the acid side and a minimum on the alkaline, thus corresponding with that for valine.

Hippuric Acid.-This acid depresses the surface tension of water and so the equations applicable are as for valine. Measurements were
made between $p_{H} 2.66$ and $p_{1} 2.95$, and the curve obtained shows a maximum at about $p \mathrm{H} 2.77$, a minimum at $\mathrm{p} \% 2 \cdot 8$, a maximum at 2.84 , and another minimum about $p \mathrm{H} 2.87$. The pH of pure ampholyte solution is 2.8 I . On the addition of hydrochloric acid the acid is therefore first negatively adsorbed until the maximum is reached, where its adsorption is zero; at lower pH values it is positively adsorbed. On the addition of sodium hydroxide alkali is negatively adsorbed; the maximum at pH 2.84 is difficult to explain, as it would appear that the adsorption became positive and then again negative within a very small pH range.

The position of the surface tension of the pure aqueous ampholyte on the $\gamma-p H$ curves for all these amino-acids is in agreement with the remarks made earlier in the thermodynamic treatment. The $p H$ for glycine-water and for alanine-water systems, for both of which the aminoacid is negatively adsorbed, corresponds to a point about midway between a maximum and a minimum (Figs. I and 2) ; that for valine (Fig. 2), which is positively adsorbed lies at a maximum, and that for hippuric acid (Fig. 3) lies at a minimum. Further, the surface tensions of isoelectric gelatin, albumin and lecithin solutions, all of which show positive adsorption of protein, correspond to a maximum or a minimum on the $\gamma$ - pH curve.

## Summary.

The surface tensions of aqueous solutions of glycine, alanine, valine, cystine and hippuric acid to which either hydrochloric acid or sodium hydroxide had been added have been measured; the results are given in the form of the surface tension-pH curve at constant amino-acid concentration. The curves for glycine show two maxima and two minima, one near but not at the isoelectric point; the curves are flatter as the concentration of the amino-acid is reduced. The thermodynamic theory of such systems is given and the form of the curves interpreted in terms of the adsorption of the various components at the surface ; it has been found possible to calculate the surface excess for various portions of the curves. Those acids which lower the surface tension of water show a minimum or a maximum surface tension at the $p \mathrm{H}$ corresponding to pure aqueous ampholyte, while for those which increase the surface tension of water this $p \mathrm{H}$ corresponds to a point between a maximum and a minimum; investigations on protein solutions also agree with this conclusion, which is shown to be in agreement with theory. The influence of sodium chloride has also been investigated.

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# THE ELECTRON DIFFRACTION INVESTIGATION OF THE MOLECULAR STRUCTURE OF DI-LEAD-HEXAMETHYL. 

By H. A. Skinner and L. E. Sutton.

Received 27th September, 1940.
Relativcly few compounds of lead have been investigated by the electron diffraction method, and no accurate measurement of the covalent radius of Pb has been made. Brockway and Jenkins ${ }^{1}$ investigated the molecular structure of $\mathrm{Pb}(\mathrm{Me})_{4}$ by the electron diffraction method, but could not obtain good diffraction photographs. They showed only three measurable rings, and of these, the first gave very uncertain measurements of its diameter, so that the value obtained for the $\mathrm{Pb}-\mathrm{C}$ distance was based upon relatively few measurements. The final value given by these authors was $\mathrm{Pb}-\mathrm{C}=2.29 \pm 0.05 \mathrm{~A}$, which corresponds to the value of $1.52 \pm 0.05 \mathrm{~A}$ for the Pb radius.

In the table of normal covalent radii of the elements given by Pauling and Huggins, ${ }^{2}$ the value $\mathrm{I} \cdot 46 \mathrm{~A}$ is given for the Pb radius. This value was obtained by extrapolation from the normal radii of $\mathrm{C}, \mathrm{Si}, \mathrm{Ge}$ and Sn . The difference of 0.06 a between the two values for the Pb radius is sufficiently large to render desirable some more accurate determination of this value.

The recent preparation by Calingaert and Soroos ${ }^{3}$ of dilead-hexamethyl ( $\mathrm{Pb}_{2} \mathrm{Me}_{6}$ ) offered a very suitable compound for investigation by the electron diffraction method, from which an accurate measurement of the normal covalent radius of Pb could be made. We have now prepared this compound and studied its structure, using the diffraction method. Good photographs showing six measurable rings were obtained, from which the $\mathrm{Pb}-\mathrm{Pb}$ distance was determined within small limits of error, and found to be $2.88 \pm 0.03 \mathrm{~A}$. This gives a value for the lead radius of $1.44 \pm 0.02 \mathrm{~A}$.

Preparation.-The sample of dilead-hexamethyl was prepared by the method of Calingaert and Soroos, ${ }^{3}$ from the interaction of magnesium methyl bromide and lead dichloride at $-5^{\circ} \mathrm{C}$. The observed meltingpoint of the compound was $3^{\circ} \mathrm{C}$., in agreement with the value given by Calingaert.

Experimental.-The technique used in obtaining the electron diffraction photographs has been described." The effective wave-lengths of the electron beam were approximately 0.06 A.U., and the distance from the point of diffraction to the photographic plate was 28.05 cms . The sampel of dilead-hexamethyl was contained in a Pyrex tube and heated to $70^{\circ}-80^{\circ}$ C., inside a small copper oven. The photographs were measured visually on a comparator.

[^12]
## Electron Diffraction Photographs from Dilead-hexamethyl.

Six plates were measured, each showing six rings. The maxima appeared to be symmetrical, and decreased in intensity with increasing diameter. The second, third, and fourth maxima were roughly of equal intensity.

TABIE I.

| Max. | Min. | sobs. | I. | c. |
| :---: | :---: | :---: | :---: | :---: |
| I |  | (3.30) | 10 | 10 |
|  | I | (4.13) |  |  |
| 2 |  | 4.98 | 8 | 13 |
|  | 2 | $5 \cdot 85$ |  |  |
| 3 |  | $6 \cdot 98$ | 7 | 13 |
|  | 3 | $8 \cdot 26$ | , | , |
| 4 |  | $9 \cdot 21$ | 7 | 10 |
|  | 4 | $10 \cdot 37$ |  |  |
| 5 |  | 11.34 | 5 | 4 |
|  | 5 | 12.61 |  |  |
| 6 |  | 13.52 | 3 | I |



Fig. 1.

The measured $s$ values, the visually estimated intensities of the maxima, and the calculated $C$ values, ${ }^{5}$ are given in Table I.

The radial distribution curve is reproduced in Fig. r. This curve shows three peaks corresponding to the internuclear separations:

$$
\mathrm{Pb}-\mathrm{Pb}=2.85 \mathrm{~A}, \text { and } \mathrm{Pb}-\mathrm{C}=2.15 \mathrm{~A}, \text { and } 4.10 \mathrm{~A} .
$$

Four models were investigated by the correlation method. Each of the models was based on the skeleton structure (I).

(I) In this structure, the carbon atoms are arranged tetrahedrally about the lead atoms (so that the angles $\mid \mathrm{C}-\mathrm{Pb}-\mathrm{Pb}$ equal $109^{\circ}{ }^{2} 8^{\prime}$ ), and are presumed to remain fixed in the staggered position. The methyl groups were assumed to be rotating freely about the $\mathrm{Pb}-\mathrm{C}$ axes. The models investigated differed from one another in the assumed values of the $\left(\frac{\mathrm{Pb}-\mathrm{Pb}}{\mathrm{Pb}-\mathrm{C}}\right)$ ratios.
In the calculations of the theoretical scattering curves the $(\mathrm{C}-\mathrm{H})$ and (C-C) interaction terms were neglected, in view of their unimportance relative to the scattering terms involving lead atoms.

The assumed distances and the $\left(\frac{\mathrm{Pb}-\mathrm{Pb}}{\mathrm{Pb}-\mathrm{C}}\right)$ ratios in the models are given in Table II.

The theoretical scattering curves for the above models are reproduced in Fig. 2. Qualitatively there are only small differences between the four curves. The curve

TABLE II.

| Model. | $\binom{\mathrm{Pb}-\mathrm{Pb}}{\mathrm{Pb}-\mathrm{C}}$ <br> ratio. | $\mathrm{Pb}-\mathrm{Pb}$. | $\mathrm{Pb}-\mathrm{C}$, |
| :---: | :---: | :---: | :---: |
| 1 | I .24 | 2.88 A | 2.23 A |
| 2 | I .27 | 2.80 A | 2.20 A |
| 3 | I .32 | 2.90 A | 2.20 A |
| 4 | I .36 | 3.00 A | 2.20 A | for model 4 is the least satisfactory of the four curves, since it fails to

[^13]reproduce the fifth minimum. The curves for the first three models are very similar to one another, and do not enable any choice to be made from qualitative comparison alone.

The $s$ values at the maxima and minima of the calculated curves and the ratios scale./ sobs. are given in Table III.

The quantitative comparison shows that there is little to choose between the curves for models 1,2 and 3; the best agreement is given by curves 1 and 2, which give slightly smaller average deviations than curve 3 . The general similarity in the curves arises from the fact that the total scattering is largely composed of the $\mathrm{Pb}-\mathrm{Pb}$ interaction terms, the contribution of the Pb - C scattering terms being relatively small, so that large changes in the assumed $\mathrm{Pb}-\mathrm{C}$ distance make only small changes in


Fig. 2.

TABLE III.

| sobs. | $s_{1}$. | $s_{2}$. | $s_{3}$. | $s_{4}$. | $s_{1} / s_{\text {obs }}$. | $s_{2} / s_{0}$ obs. | $s_{3} / s_{\text {obs }}$. | $s_{1} / s_{\text {obs }}$. |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| (3.30) |  | - | - | - | - | - | - | - |
| (4.13) | 4.00 | 4.10 | 4.00 | $3 \cdot 83$ | (0.969) | (0.993) | (0.969) | (0.927) |
| 4.98 | 4.88 | 5.08 | $4 \cdot 88$ | 4.73 | 0.980 | 1.020 | 0.980 | 0.950 |
| $5 \cdot 85$ | $5 \cdot 79$ | 6.02 | $5 \cdot 82$ | $5 \cdot 66$ | 0.990 | I.029 | 0.995 | 0.968 |
| $6 \cdot 98$ | $6 \cdot 82$ |  | 6.69 | 6.62 | 0.977 | 1.003 | 0.958 | 0.948 |
| $8 \cdot 26$ | $8 \cdot 28$ | $8 \cdot 46$ | $8 \cdot 20$ | 8.00 | 1.002 | 1.024 | $0 \cdot 993$ | - 0.969 |
| 9.21 | $9 \cdot 29$ | 9.50 | $9 \cdot 33$ | 9.10 | 1.009 | 1.031 | 1.013 | 0.988 |
| $10 \cdot 37$ | 10.37 | 10. 58 | 10.30 | 10.06 |  | 1.020 | 0.993 | 0.970 |
| 11.34 | 11.60 | $\pm \mathrm{x} \cdot 92$ | 11.62 | 10.97 | 1.023 | 1.051 | 1.025 | 0.967 |
| 12.61 | 12.88 | $13 \cdot 10$ | 12.82 | 11.73 | 1.021 | 1.039 | 1.016 | 0.930 |
| 13.52 | 13.80 | 14.20 | 13.68 | 12.92 | 1.021 | 1.050 | 1.01 1 | 0.956 |
| Mean Value |  |  |  |  | I.003 | 1.030 | $0 \cdot 998$ | 0.961 |
| Average Deviation |  |  |  |  | 0.014 | 0.012 | 0.016 | 0.013 |

the total scattering. In consequence, it is not possible to estimate the $\mathrm{Pb}-\mathrm{C}$ distance accurately, but the $\mathrm{Pb}-\mathrm{Pb}$ distance can be obtained within small limits of error. When the average $s / s_{\text {obs. }}$. values are multiplied by the assumed distances, the four models give the values 2.88 A or 2.89 A for the $\mathrm{Pb}-\mathrm{Pb}$ distance. The best value for the $\mathrm{Pb}-\mathrm{Pb}$ distance is taken as:

$$
\mathrm{Pb}-\mathrm{Pb}=2.88 \pm 0.03 \mathrm{~A}
$$

The closest fit with the experimental results is given by the curves for models I and 2 , and if the $\mathrm{Pb}-\mathrm{Pb}$ distance is taken as 2.88 A in these models, the corresponding $\mathrm{Pb}-\mathrm{C}$ distances are 2.23 A and 2.27 A . The value taken for the $\mathrm{Pb}-\mathrm{C}$ distance is 2.25 A , with a limit of error of 0.06 A , corresponding to a lead radius of $1 \cdot 4^{8} \mathrm{~A}$. The present investigation, therefore, gives results consistent with a constant lead radius of 1.44 A , within the limits of experimental error.

This value is in close agreement with the value 1.46 A given by Pauling and Huggins, and indicates that the Brockway and Jenkins value of 1.52 A is too large.

Although the third peak on the radial distribution curve at 4 .Io $A$ agrees with a $\mathrm{C}-\mathrm{Pb}-\mathrm{Pb}$ angle of about $109 \cdot 5^{\circ}$, no satisfactory independent determination of angle can be made within $\pm 10^{\circ}$.

## Summary.

The molecular structure of $\mathrm{Pb}_{2} \mathrm{Me}_{8}$ has been determined using the electron diffraction method. The main bond distances in the molecule were found to be: $\mathrm{Pb}-\mathrm{Pb}=2.88 \pm 0.03 \mathrm{~A}$, and $\mathrm{Pb}-\mathrm{C}=2.25 \pm 0.06 \mathrm{~A}$. From the measurement of the $\mathrm{Pb}-\mathrm{Pb}$ distance it follows that the normal covalent radius of singly-linked Pb is $\mathrm{I} .44 \pm 0.02 \mathrm{~A}$.

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> The Dyson Perrins Laboratory, Oxford.

## THE ELECTRON DIFFRACTION INVESTIGATION OF THE MOLECULAR STRUCTURE OF ALUMINIUM TRIMETHYL IN THE VAPOUR PHASE.

By N. R. Davidson, J. A. C. Hugill, H. A. Skinner, and L. E. Sutton.

Received 27th September, 1940.
The preparation of the sample of aluminium trimethyl was carried out in this laboratory by N. R. Davidson. A report on this, and of some properties of the compound, will be given elsewhere. The electron diffraction photographs by aluminium trimethyl were taken by N. R. Davidson and J. A. C. Hugill. The outbreak of war prevented either of the above from making any analysis of the photographs. The analysis has therefore been completed by the other authors (H. A. S. and L. E. S.).

## Experimental.

The diffraction photographs were obtained, using the apparatus of de Laszlo, previously described. ${ }^{1}$

## Qualitative Description of Plates.

Six plates, each showing five rings, were measured visually on a comparator. The maxima and minima appeared to be sym. metrical, with the exception of the second maximum, which was steeper on the inside. The second maximum appeared to be stronger than the first, and the third more intense than the fourth. The fourth minimum was very clearly defined.

The visually estimated intensities of the maxima, and the observed

$$
s\left(=4 \pi \frac{\sin \theta / 2}{\lambda}\right)
$$

values at the maxima and minima are given in Table I.
A radial distribution curve was calculated, using the observed intensity values, and is reproduced in Fig. r. The curve showed strong peaks at distances corresponding to: $2.07 \mathrm{~A}, 3.42 \mathrm{~A}, 5.30 \mathrm{~A}$; and gave inflexions at 2.60 A and 3.93 A . A simple correlation between these distances and the internuclear separations in the aluminium trimethyl molecule is not possible at this stage. If the molecule is assumed to be monomeric-

$\mathrm{AlMe}_{3}$-some of the pcaks cannot be related to distances in the molecule at all, and the only reasonable assumption is that the peak at 2.07 A represents the $\mathrm{Al}-\mathrm{C}$ distance. If, on the other hand, the molecule is dimeric- $\mathrm{Al}_{2} \mathrm{Me}$-reasonable correlations can be made. The peak at 2.07 A represents the unresolved $\mathrm{Al}-\mathrm{C}$ and $\mathrm{Al}-\mathrm{Al}$ distances, and the peak at 3.42 A the longer Al-C distance: the peak at 5.30 A is due to

$$
{ }^{1} \text { de Laszlo, Proc. Roy. Soc., A, 1934, 146, } 672 .
$$

unresolved non-bonded carbon-carbon and carbon-hydrogen distances: the inflexion at $2 \cdot 60 \mathrm{~A}$ gives the $\mathrm{Al}-\mathrm{H}$ distance.

The large number of overlapping distances in the dimeric molecule renders the radial distribution curve of little real value, but the curve is better interpreted by the dimeric than by the monomeric molecule.

Vapour density measurements indicate that aluminium trimethyl is dimeric in the vapour phase at pressures corresponding to those used in the diffraction chamber. ${ }^{2}$ As will be shown, the electron diffraction experiments bear out these conclusions.

Fig. 2 reproduces the scattering curve for a monomeric model. In this model the Al and C atoms were assumed to be coplanar, with the $\mathrm{C}-\mathrm{Al}-\mathrm{C}$ angles $=120^{\circ}$.


Fig. 2. (This model compares with $\mathrm{BMe}_{3}{ }^{3}$ Al-C was assumed to be $2 \cdot 10 \mathrm{~A}$, as required by the radial distribution curve.)

The scattering curve for this monomeric model does not reproduce the features of the photographic plates. Its first maximum is wrongly placed, and it fails to reproduce the observed intensity relations of the actual third and fourth maxima, showing the latter as stronger than the former. The quantitative agreement of this curve with the plates is correspondingly poor. Any change in the assumed Al-C distance would only alter the scale but not the form of the scattering curve, so that it can be stated that the monomeric $\mathrm{AlNe}_{3}$ model, assumed to have a similar structure to $\mathrm{BMe}_{3}$, cannot fit in with the electron diffraction results. A large number of models of the climeric aluminium trimethyl molecule have been investigated by the correlation method. In order to simplify the problem of attack on this complicated molecule, it was treated as one involving only three parameters, in which first of all the correct $\mathrm{C}-\mathrm{Al}-\mathrm{Al}$ angle and Al-Al/Al-C ratio have to be evaluated by qualitative comparison, and then the scale factor for giving absolute bond lengths has to be obtained by quantitative comparison. This is only an approximate treatment, since the carbon-hydrogen bond distance remains constant, at an assumed value of $x .09 \mathrm{~A}$; but in actuality it is quite good because the chief terms involving hydrogen, i.e. the aluminium-hydrogen ones, depend much more upon the Al-Al and Al-C distances than upon the C-H distance. Experience soon showed, in fact, that this ratio and angle were the important factors determining the qualitative character of the curve.

A description of the various models, and the results, follows.

## Type A Models.

The Type A models were based upon the ethane-like skeleton (I) and ( $I_{A}$ ). The A models have the $C$ atoms fixed in the " staggered" position, and the

[^14]methyl groups are assumed to be rotating freely about the Al-C axes.
The C-Al-Al angles are $109 \frac{1}{2}^{\circ}$. The A models differ from one another in the values of the ratio $\frac{(\mathrm{Al}-\mathrm{Al})}{(\mathrm{Al}-\mathrm{C})}$.

Eight models of Type A were studied, having the $\frac{(\mathrm{A} 1-\mathrm{Al})}{(\mathrm{Al}-\mathrm{C})}$ ratio values $\mathrm{I} \cdot 22, \mathrm{I} \cdot \mathrm{I}_{5}$, x.10, $1 \cdot 05, \mathrm{I} \cdot 025$, 1.00, 0.90, o. 85 .

The scattering curves for these models are reproduced in Figs. $3(a)$ and $3(b)$. In the calculations of these curves, all the interaction terms, with the exception of the hy. drogen,-hydrogen terms, were taken into account. Each curve was in effect a mean of those for separate models having each methyl group fixed in the extreme positions taken up during free rotation, relative to the particular atom from which the distance is being measured. By comparing the description of the plates (p. 1213) with the theoretical scattering curves shown in Figs. $3 a$ and $3 b$, it is readily seen that some of these curves agree well, while others agree


Fig. $3 a$.
TABLE II.-Qualitative Comparisons of the A Curves with the Plates.

| Curve. | $\frac{(\mathrm{Al}-\mathrm{Al})}{(\mathrm{Al}-\mathrm{C})}$ ratio. | $\begin{aligned} & \text { Assumed } \\ & \text { Al-A1 } \\ & (\text { in A). } \end{aligned}$ | $\begin{aligned} & \text { Assumed } \\ & \text { Al-C } \\ & \text { (in A). } \end{aligned}$ | Class. |
| :---: | :---: | :---: | :---: | :---: |
| A. I | 1. 22 | $2 \cdot 25$ | I.85 | $\gamma$ |
| A. 2 | $1 \cdot 15$ | $2 \cdot 25$ | 1.95 | $\beta$ |
| A. 3 | I. 10 | $2 \cdot 25$ | 2.05 | $\alpha \beta$ |
| A. 4 | I. 05 | $2 \cdot 15$ | 2.05 | $\alpha$ |
| A. 5 | 1.025 | 2.05 | $2 \cdot 00$ | $\alpha$ |
| A. 6 | 1.00 | 2.00 | $2 \cdot 00$ | $\alpha$ |
| A. 7 | $0 \cdot 90$ | I. 85 | $2 \cdot 05$ | $\alpha \beta$ |
| A. 8 | 0.85 | 1.75 | 2.05 | $\beta$ |

poorly. A full qualitative classification is given in tabular form in Table II, wherein the letters $\alpha, \beta$, and $\gamma$ signify good, fair, or poor agreement.


Fig. $3 b$.

The best qualitative agreement is given by curves A. 4, A. 5, and A. 6 , so that the most satisfactory A models have the

$$
\frac{(\mathrm{Al}-\mathrm{Al})}{(\mathrm{Al}-\mathrm{C})}
$$

ratio values between $1 \cdot 00$ and I. 05.

The quantitative agreement of the various A curves with the plates is summarised in the Table III, which gives the values of the scalc. $/$ sobs, $^{\text {ratios. }}$

The smallest average deviations from the mean $s_{\text {calc. }} / s_{\text {obs., }}$ and correspondingly the best quantitative agreements, are given by the curves A. 3, A. 4, A. 5 , A. 6 ; the qualitative comparison with the plates has already shown that the curves A. 4 . A. 5, and A. 6 are

TABLE III.

| $\frac{s_{A .1}}{s_{\text {obs. }}}$ | $\frac{s_{\text {A }-2}}{s_{\text {obs }}}$ | $\frac{s_{\text {A. }} 3}{s_{\text {obs. }}}$ | $\frac{s_{\text {A. }} /}{s_{\text {obs }}}$ | $\frac{s_{\text {A. } 5}}{s_{\text {obs }}}$ | $\frac{s_{\text {A. }} \mathrm{E}}{s_{\text {abs }}}$ | $\frac{s_{\text {A }} \cdot}{} s_{\text {obs }}$ | $\frac{s_{\text {A } / 8}}{s_{\text {Obs }}}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| ( 1.032 ) | (0.986) | (0.991) | - (I.04I) | (1.050) | (1.050) | ( 1.087 ) | (1.123) |
| (1.045) | (1.017) | (0.986) | (1.028) | ( $1 \cdot 045$ ) | (1.052) | ( $\mathrm{I} \cdot 080$ ) | ( $1 \cdot 108$ ) |
| I. 050 | 1.018 | 0.990 | 1.000 | I.037 | I. 044 | I. 060 | 1.076 |
| 0.991 | - 960 | $0 \cdot 938$ | 0.938 | 0.989 | 0.998 | I.008 | 1.011 |
| $1 \cdot 0.55$ | 1. 027 | 0.998 | 1.006 | 1.047 | I. 052 | 1.063 | 1.087 |
| 1.014 | 0994 | 0.968 | 0.989 | I'OI5 | 1.020 | I'040 | 1.069 |
| I-O19 | 0994 | $0 \cdot 966$ | - $\cdot 975$ | 1.006 | 1.010 | 1.016 | $1 \cdot 019$ |
| I.069 | 1.001 | $0 \cdot 967$ | $0 \cdot 974$ | I.008 | I. 012 | I.02I | 1.037 |
| I-162 | 1.024 | 0.979 | 0.987 | 1.021 | I-028 | 1.034 | I $\cdot 047$ |
| Mean Values I. 05 I | 1.003 | 0.972 | 0.981 | 1.018 | I.023 | 1.032 | I-049 |
| Average Deviation 0.038 | 0.018 | 0.014 | 0.016 | 0.015 | $0 \cdot 015$ | 0.017 | 0.024 |

the most satisfactory. The average value of the $s_{\text {calc. }} / s_{\text {obs. }}$ ratios for the three best models is multiplied by the assumed distances in these models, with the results given in Table IV. In this way an approximate cstimate of the distances which the models A. 4, A. 5, and A. 6 would require to give $s_{\text {calc. }} / s_{\text {obs. }}$ ratios of I•000 can be made.

The best type A model is therefore taken as

TABLE IV.-Calculated Distances in the Best A models.

| Model. | scalc./sobs. | (Al-Al) <br> derived. | $(\mathrm{Al}-\mathrm{C})$ <br> derived. |
| :--- | :---: | :---: | :---: |
| A. 4 0.081 <br> A. 5 1.018 <br> A. 6 2.11 A <br>  2.09 A | 2.01 A |  |  |

$$
\left\{\begin{array}{l}
\mathrm{Al}-\mathrm{Al}=2.10 \pm 0.05 \mathrm{~A} . \\
\mathrm{Al}-\mathrm{C}=2.03 \pm 0.05 \mathrm{~A} .
\end{array}\right.
$$

## Type B Models.

The B models investigated were of similar structural form to the A models, except that all the

$$
\mathrm{C}-\mathrm{Al}-\mathrm{Al}
$$

angles were $90^{\circ}$. Three B models, differing from one another only in their

$$
\frac{(\mathrm{Al}-\mathrm{Al})}{(\mathrm{Al}-\mathrm{C})}
$$

ratios, were investigated by the correlation method.

The scattering curves for these models are reproduced in Fig. 4. The qualitative classification of the agreement with the curves is given in Table V.

The quantita. tive comparison of the B curves with the plates is given in Table VI, which shows the $s_{\text {calc. }} / s_{\text {obs. }}$ ratios.

The quantitative comparison of the $B$ curves is poor compared with the A curves, and corresponds to the less satisfactory qualitative agreement of these
Fig. 4.

The curve B. 2 is the most satisfactory of the B type. If this ratioi.e. $1 \cdot 25$-is taken as the best for a B model, one would have the best quantitative agreement with the distances:

$$
\begin{aligned}
& \mathrm{Al-Al}=2.57 \pm 0.07 \mathrm{~A} . \\
& \mathrm{Al}-\mathrm{C}=2.05 \pm 0.05 \mathrm{~A} .
\end{aligned}
$$

Although such a model cannot be completely ruled out, it must be em-

TABLE V.

| Curve. | Ratio. | Assumed <br> (Al-Al). | Assumed <br> (Al-C). | Class. |
| :---: | :---: | :---: | :---: | :---: |
|  |  |  |  |  |
| B. I | 1.12 | 2.30 A | 2.05 A | $\gamma$ |
| B. 2.25 | 1.50 A | 2.00 A | $\beta$ |  |
| B. 3 | 1.39 | 2.50 A | 1.80 A | $\gamma$ | phasised that the curve for it is less satisfactory, both qualitatively and quantitatively, than the best $A$ curve.

## Type D Curves.

The type D curves were similar to the A models, except that the $\mathrm{C}-\mathrm{Al}-\mathrm{Al}$ angles were $\mathrm{I} 20^{\circ}$. Two D models were investigated (D. I, ratio 0.90 , and $D .2$, ratio 1.05 ) the scattering curves for which are reproduced in Fig. 4. In the calculation

TABLE VI.

| sobs. | $\frac{s_{\text {B. }} 1}{s_{\text {obs }}}$ | $\frac{5^{5} .8}{\text { sobs. }}$ | $\frac{s_{\text {B. } 3}}{s_{\text {obs. }}}$ |
| :---: | :---: | :---: | :---: |
| 2-19 | ( $1 \cdot 260$ ) | (I•164) | (I.187) |
| 2.87 | (1.254) | (I.160) | (1.052) |
| $3 \cdot 83$ | I.091 | I.089 | 1.196 |
| $5 \cdot 28$ | 0.998 | $0 \cdot 981$ | 1.06I |
| $6 \cdot 21$ | 1.082 | 1.018 | I.058 |
| 7-II | I-101 | 1.003 | I.034 |
| $7 \cdot 85$ | I-090 | 1.019 | 1.070 |
| 8.89 | 1.064 | I-016 | 1.082 |
| 9.86 | 1.075 | 1.053 | I.097 |
| Mean | I.07I | 1.026 | I.068 |
| Average Deviation | 0.023 | 0.026 | 0.034 |

TABLE VII.

| ${ }^{5} \mathrm{D} .1 / \mathrm{sobs}$. | ${ }^{5}$ D. ${ }^{3} / s_{0}$ bs. |
| :---: | :---: |
| (I.142) | (x.187) |
| (0.983) | (0.997) |
| I.089 | I-000 |
| I. 042 | 0.985 |
| I. 058 | $0 \cdot 998$ |
| I-OOI | - |
| $0 \cdot 994$ | 0.927 |
| I 010 | $0 \cdot 937$ |
| I.045 | 1.085 |
| Mean |  |
| 1.034 | 0.989 |
| Average |  |
| Deviation 0.028 | 0.039 |

of these curves the non-bonded carbon-hydrogen scattering terms were not included. The curves are therefore only an approximation to the complete scattering curves for these models, but experience with the $A$ and $B$ curves had shown that this approximation lies very near to the truth, since the omitted terms largely cancel one another in effect.

The D curves obviously do not give a close qualita-

| Curve. | Ratio. | Assumed <br> Al-A1. | Assumed <br> Al-C. | Class. |
| :---: | :---: | :---: | :---: | :---: |
| 1). I | 0.90 | 1.80 A | 2.00 A | $\beta$ |
| 1.2 | 1.05 | 2.10 A | 2.00 A | $\gamma$ | tive comparison with the plates (see description, p. I2r3 and Fig. 4). The quantitative features of the curves are given in Tables VII. and VIII.

The quantitative agreement of the $D$ curves is just as poor as the qualitative agreement. D. I is considerably better than D .2 , but compares very unfavourably with the A curves. These results indicate that the


Fig. 5.
C-Al-Al angle is not as large as $120^{\circ}$. This was emphasised further by the calculation of two curves for models in which C-Al-Al was $135^{\circ}$. The curves for these models (C-curves, ratios 0.95 and 1.05 ) are not reproduced here, but we can report that they compared less favourably with the plates than the D curves.

Type E Models.
The type E models were similar

| Curve. | Ratio. | Assumed <br> A1-A1. | Assumed <br> Al-C. | Class. |
| :--- | :---: | :---: | :---: | :---: |
|  |  |  |  |  |
| E. I | 1.00 | 2.00 A | 2.00 A | $\beta$ |
| E. 2 | $I \cdot 10$ | 2.20 A | 2.00 A | $\alpha$ |
| E. 3 | 1.25 | 2.50 A | 2.00 A | $\beta$ | to previous models, except that the C-Al-Al angle was $100^{\circ}$. The curves for the $E$ models are approximate, the non-bonded carbon-hydrogen terms being neglected.

Three E models were studied-E. 1, ratio I•00, E. 2, ratio I•Io, and E. 3, ratio $1 \cdot 25$. The scattering curves for these models are shown in Fig. 5.

The qualitative agreements of the E curves are summarised in Table IX. The quantitative features of the curves are summarised in Table X.
The best quantitative and qualitative agreement with the plates for the E curves is given by E. 2.

TABLE X .

| $s_{\text {E. } 1 / 1 /} /{ }_{\text {obs }}$ | ${ }^{3} \mathrm{E} .2{ }^{1 / 5} \mathrm{~s}$ bs. | $s_{\mathrm{E}} .3^{1 / 5} \mathrm{obs}$. |
| :---: | :---: | :---: |
| (I-196) | (I.I42) | (1.050) |
| (I.143) | (I•IOI) | (1.045) |
| I.097 | 1.057 | 1.018 |
| I'00,4 | $0 \cdot 977$ | 0.932 |
| I.076 | $1 \cdot 031$ | $0 \cdot 958$ |
| - | I-OI 5 | 0.942 |
|  | 0.994 | $0 \cdot 971$ |
| I. 007 | I.OOI | $0 \cdot 988$ |
| $1 \cdot 10.1$ | I-OI4 | 1.032 |
| $\begin{gathered} \text { Mean } \\ \text { 1.039 } \end{gathered}$ | I•OI3 | $0 \cdot 978$ |
| Average Deviation |  |  |
| 0.045 | 0.019 | 0.030 | The agreement for this curve compares with that of the best A curves. If the ratio I-10 is taken as the best for E type models, the derived distances in the best E model are :

$$
\begin{aligned}
\mathrm{Al}-\mathrm{Al} & =2.23 \mathrm{~A}, \\
\text { and } \quad \mathrm{Al}-\mathrm{C} & =2.03 \mathrm{~A} .
\end{aligned}
$$

The comparison of the various curves studied with the plates is sum-marised in Table XI. In this $\alpha, \beta, \gamma$ refer to the qualitative comparison, and the numerals I, 2,3 to the quantitative comparison (I-good, 2-fair, and 3-poor).

The C-Al-Al angle cannot be estimated exactly: the theoretical scattering curves are not sufficiently sensitive to small variations in this angle to allow small limits of error. The results show that the C-Al-Al angle is certainly not larger than $120^{\circ}$, and is greater than

TABLE XI.

$90^{\circ}$. The most probable angle lies between $100^{\circ}$ and $110^{\circ}$. We take the best value for the angle to be

$$
\mathrm{C}-\mathrm{Al}-\mathrm{Al}=105 \pm 10^{\circ} .
$$

Accordingly, the values for the $\mathrm{Al}-\mathrm{Al}$ and $\mathrm{Al}-\mathrm{C}$ distances are :

$$
\mathrm{Al}-\mathrm{Al}=2.20 \pm 0.15 \mathrm{~A}, \quad \text { and } \quad \mathrm{Al}-\mathrm{C}=2.05 \pm 0.10 \mathrm{~A} .
$$

The large limits of error in the $\mathrm{Al}-\mathrm{Al}$ and $\mathrm{Al}-\mathrm{C}$ values depend upon the uncertainty in the $\mathrm{C}-\mathrm{Al}-\mathrm{Al}$ angle. If this angle is assumed to be ro9 $\frac{1}{2}^{\circ}$, the distances are: $\mathrm{Al}-\mathrm{Al}=2.10 \pm 0.06 \mathrm{~A}$, and $\mathrm{Al}-\mathrm{C}=2.03 \pm 0.05 \mathrm{~A}$.

The $\mathrm{Al}_{2} \mathrm{Me}_{6}$ models studied above were assumed to have the carbon atoms fixed in the " staggered" position relative to one another. A model with the same assumed distances, and ratio, as the model $A$. 4, but having the carbon atoms fixed in the "opposite" or "eclipsed" position, was investigated, and the curve for it is shown in Fig. 5. This curve is in all essentials similar to the curve A. 4, and is equally as good both quantitatively and qualitatively as the " staggered " model. It is therefore not possible to choose between the "staggered" or " eclipsed" forms.

Two models, again with the same dimensions as the model A. 4, in which the methyl groups were fixed, were also studied. The curves for these models were in all essentials similar to one another and to the curve A. 4. We are not able, therefore, to conclude whether or not the methyl groups are free to rotate.

It is useful to note that the model A. 4 is in excellent agree-

## TABLE XII.

| Peak. | Distances in A. $4^{*}$ |
| :---: | :---: |
| 2.07 A. | $\left\{\begin{array}{l} \mathrm{Al}-\mathrm{Al}=2.15 \mathrm{~A} . \\ \mathrm{Al}-\mathrm{C}=2.05 \mathrm{~A} . \\ \text { (39) } \end{array}\right.$ |
| 3.42 A. | $\left\{\begin{array}{l}\mathrm{Al}-\mathrm{C}_{4}=3.43 \mathrm{~A} . \\ \mathrm{C}_{2}-\mathrm{C}_{2}=3.34 \mathrm{~A} . \\ \text { (18) }\end{array}\right.$ |
| $5 \cdot 30 \mathrm{~A}$ $2 \cdot 60 \mathrm{~A}$ | $\mathrm{C}_{1}-\mathrm{C}_{6}=5.22 \mathrm{~A}$. (9) and some non-bonded carbon-hydrogen distances. $\mathrm{Al}-\mathrm{H}=2.61 \mathrm{~A}$. (20) |
| 3.93 A . | $\mathrm{C}_{1}-\mathrm{C}_{4}=3.89 \mathrm{~A}$. (18) |

* The figures in brackets give the relative importance of the various scattering terms. ment with the radial distribution curve. The observed peaks can be correlated with the internuclear distances in this model, as shown in Table XII.


## Discussion.

At first sight aluminium trimethyl, $\mathrm{Al}_{2} \mathrm{Me}_{6}$, presents a similar structural problem to diborane, $\mathrm{B}_{2} \mathrm{H}_{6}$. In both cases, there are twelve valence electrons from which to construct seven (at least) valence bonds. The structure of $\mathrm{B}_{2} \mathrm{H}_{6}$ is now considered to be a resonance form, among the seven structures of the Lewis type :- ${ }^{4}$

|  | $H$ | $\stackrel{+}{H}$ |  |
| :--- | :--- | :--- | :--- |
| $H: \ddot{B}$ | $\ddot{B}$ | $H$ | $H: B$ |
| $\ddot{H}$ | $\ddot{B}$ | $H$ | etc. |
|  | $\ddot{H}$ | $\ddot{H}$ | $\ddot{H}$ |

and numerous one-electron bonded forms:- $\dagger$

| $H$ | $H$ | $H$ |
| :---: | :---: | :---: |
| $H$ | $\ddot{B} \cdot \ddot{B} \cdot H$, | $H \cdot \ddot{B} \cdot \ddot{B} \cdot H$ |
| $\ddot{H} \ddot{H}$ | $\ddot{H} \ddot{H}$ |  |

It is doubtful whether such explanations can be accepted unconditionally in the case of $\mathrm{Al}_{2} \mathrm{Me}_{6}$.

[^15]It is necessary, in the first place, to consider reasons for the polymerisation of $\mathrm{AlMe}_{3}$ to the dimer. The most obvious reason is that $\mathrm{AlMe}_{3}$ would have a shared sextet of electrons, which has a strong tendency to increase to the more stable octet. The existence of diborane may be correlated with the unsaturated character which the sextet in $\mathrm{BH}_{3}$ would impose upon this unknown hydride. The unsaturation in $\mathrm{BH}_{3}$ is relieved by polymerisation to $\mathrm{B}_{2} \mathrm{H}_{6}$ which is able to occur since one-electron links between B and H atoms are stable. On the other hand, $\mathrm{BMe}_{3}$ exists, and shows no tendency to polymerise. Since back-co-ordination from a methyl group is presumably impossible, the shared sextet in $\mathrm{BMe}_{3}$ must be real in $\mathrm{BMe}_{3}$, which is indicated by the length of the B-C links, since these are 0.09 A shorter than would be expected. ${ }^{3}$ It is reasonable to assume that polymerisation in $\mathrm{BMe}_{3}$ would occur if it were possible: since there is no polymerisation, we may state that single electron-links cannot be formed between B and C atoms. Theoretically, one-electron links can only be formed between like atoms, or between unlike atoms which are closely similar-e.g. close similarity in electronegativity. ${ }^{5}$

The electronegativity values given by Pauling, ${ }^{6}$ for the atoms $\mathrm{H}, \mathrm{B}, \mathrm{C}$, and Al are :

$$
\mathrm{H}=2 \cdot \mathrm{I}, \quad \mathrm{~B}=2 \cdot 0, \quad \mathrm{C}=2 \cdot 5, \quad \text { and } \quad \mathrm{Al}=1 \cdot 5 .
$$

The electronegativity difference between $B$ and $H$ is very small, sufficiently so to render one-electron links between these elements stable. The greater difference between B and C $(=0.5)$ would appear to be too great to allow one-electron link formation, which would account for the non-existence of $\mathrm{B}_{2} \mathrm{Me}_{6}$. There is even greater disparity between the values for Al and $\mathrm{C}(=\mathrm{I} \cdot \mathrm{O})$, and on these considerations, one-electron links between Al and C are not possible.* There is, therefore, no close analogy between $\mathrm{Al}_{2} \mathrm{Me}_{8}$ and $\mathrm{B}_{2} \mathrm{H}_{8}$, and this is emphasised further in that the compounds do not show a close similarity in chemical behaviour. $\mathrm{Al}_{2} \mathrm{Me}_{6}$ should be compared rather with the polymerised methyl derivatives of $\mathrm{Ga}, \mathrm{In}$, and Li and Be . In all these compounds the mechanism of polymerisation is at present extremely obscure.

The normal covalent radius of single-bonded Al is given by Pauling ${ }^{7}$ as $\mathrm{I} \cdot 26 \mathrm{~A}$. This value is the same as the tetrahedral radius of Al, which is obtained from crystal measurements, and also by extrapolation from the values for $\mathrm{Cl}, \mathrm{S}, \mathrm{P}$, and Si . The recent measurements of the dis-
${ }^{5}$ Pauling, loc. cit., p. $19 . \quad{ }^{-1}$ Ibid., p. 64.

* In a recent communication, Davidson makes the suggestion that it may be incorrect to use the electronegativity table of Pauling. Thus in the case of $\mathrm{B}_{2} \mathrm{H}_{8}$, we are considering resonance between (II) and (III). In (II) and (III) the left hand B atom has three of its orbitals filled, and in (II) there is an electron

| $H$ | $H$ | $H+H$ |
| :--- | :--- | :--- |
| $H: \ddot{B}$ | $\ddot{B}$ | $H$ |
| $\ddot{H}$ | $\ddot{H}$ | $H: B: \ddot{B}: H$ |
|  | $\ddot{H} \quad \ddot{H}$ |  | in an $H$ orbital, which occurs in a $B$ orbital in (III). Therefore we must compare the electron attracting power of $\mathrm{H}^{+}$and B with 3 orbitals filled, or the ionisation potential of H - and B with four orbitals filled. Whereas B with 3 orbitals filled has almost the same electronegativity as H with one orbital filled, B with 4 orbitals filled should have a much smaller electronegativity. Davidson suggests this contradiction is best resolved by rejecting the application of Pauling's electronegativity values in determining electronegativity differences. In this case, the electronegativity difference as given by Pauling's table between Al and C may be unreal. Even if this is true, the objection against the one-electron formulation, based upon the link distances, remains unaltered.

${ }^{7}$ Pauling and Huggins, Z. Krist., 1934, 87, 205.
tances ${ }^{8}$ in $\mathrm{Al}_{2}(\mathrm{Hal})_{6}$ agree with the Pauling value, since some of the $\mathrm{Al}-\mathrm{Hal}$ links in the halides are normal and have the calculated lengths.

Taking the value I-26 A for the Al radius, the lengths to be expected for $\mathrm{Al}-\mathrm{Al}$ and $\mathrm{Al}-\mathrm{C}$ bonds are : $\mathrm{Al}-\mathrm{Al}=2.52 \mathrm{~A}$, and $\mathrm{Al}-\mathrm{C}=2.03 \mathrm{~A}$. Comparing these values with the obscrved values in $\mathrm{Al}_{2} \mathrm{Me}_{8}$ ( $\mathrm{Al}-\mathrm{Al}=2.20 \pm 0.15 \mathrm{~A} ; \mathrm{Al}-\mathrm{C}=2.05 \pm 0.10 \mathrm{~A}$ ), we see that $\mathrm{Al}-\mathrm{C}$ bonds are normal, but the Al-Al bond is about 0.32 A short.

We shall now consider various structures for $\mathrm{Al}_{2} \mathrm{Me}_{6}$, bearing in mind these observed internuclear distances.

## One-electron Link Structures.

We have already outlined theoretical reasons against the postulate that one-electron links can be formed between Al and C atoms. There are further cogent arguments against the one-electron link hypothesis in this molecule. The link distances in $\mathrm{B}_{2} \mathrm{H}_{6}$ have been measured by the electron diffraction method, ${ }^{9}$ and both the $\mathrm{B}-\mathrm{B}$ and $\mathrm{B}-\mathrm{H}$ links are longer than for normal single bonds, as would be expected for links with less than unit covalent character. This feature is not observed in the $\mathrm{Al}-\mathrm{Al}$ and $\mathrm{Al}-\mathrm{C}$ links in $\mathrm{Al}_{2} \mathrm{Me}_{\mathrm{B}}$ : on the contrary, the $\mathrm{Al}-\mathrm{Al}$ link is short.

## Lewis Structures.

The molecule may resonate among 7 structures of the type shown at (IV). From Davidson's argument (see footnote $\dagger$ ) the resulting structure is seen to be identical with the one-electron structure discussed

(IV)-Type $a$.

(V)-Type b.
above. The $\mathrm{Al}-\mathrm{Al}$ and $\mathrm{Al}-\mathrm{C}$ links should be longer than normal for single bonds, since they have only $6 / 7$ unit covalent character.

We may introduce a factor to shorten the Al-Al bond by postulating Lewis structures of the type shown at (V). Such structures are unlikely for two reasons: (I) the Al-C links have only $\frac{1}{2}$ unit covalent character, and should be considerably longer than observed, and (2) there is evidence that doublebonds are unstable in the second Period (e.g. P shows great reluctance to form bonds of the type $\mathrm{P}=\mathrm{P}$ ).

The most promising Lewis type is shown at (VI). In this, both Al atoms have only
 the sextet of electrons, so that the Al radius is no longer $1 \cdot 26 \mathrm{~A}$. The radius of Al with a sextet is not known from direct observation. An estimate of its probable value can be made from analogy with the $B$ radius in $\mathrm{BMe}_{3}$, which is 0.09 less than the normal

[^16]value of 0.88 A . If we take the same percentage shortening for the Al radius, the value of 1.12 A is obtained. This would give the values $\mathrm{Al}-\mathrm{Al}=2.24 \mathrm{~A}$ and $\mathrm{Al}-\mathrm{C}=\mathrm{I} .89 \mathrm{~A}$, in $\mathrm{Al}_{2} \mathrm{Me}_{6}$. The $\mathrm{Al}-\mathrm{Al}$ value is still longer than observed, but the difference is within the uncertainty of the measurement. The $\mathrm{Al}-\mathrm{C}$ value is about $0 \cdot \mathrm{IO} \mathrm{A}$ shorter than the observed value; but since the A1-C bonds in (VI) have only $2 / 3$ unit covalent character, we would expect the observed value to be longer than the calculated value of I .89 A , as in fact it is.

Although seven structures of type (VI) can be drawn, it is by no means certain that the hybrid would be more stable than two monomeric $\mathrm{AlMe}_{3}$ molecules, for while the aluminium atoms are in the sextet state in either case the charges on the methyl radicals scem likely to make the component structures quite unstable. Furthermore, if such structures as (VI) are important in $\mathrm{Al}_{2} \mathrm{Me}_{6}$, it is difficult to see why a similar type of polymerisation does not occur with $\mathrm{BMe}_{3}$. The answer may lic in the relative strengths of the M-C bonds concerned, but at present no information is available on this point.

## Structures Involving the "Inner" Electrons.

There is a possibility that the $\mathrm{AlMe}_{3}$ molecules may be held together by a bond involving the "non-valence" electrons-i.e. the $2 p$ clectrons of the Al core. The radius of the Al atom using "inner" electrons is not known, but it may well be smaller than the normal radius. Furthermore, the type of bond postulated may explain the existence of similar compounds to $\mathrm{Al}_{2} \mathrm{Me}$. The disadvantages of the proposed type of bonding are:
(1) The molecule would be unsaturated-i.e. the $2 p$ core of electrons would contain only 5 electrons. Against this, there is the possibility that the unsaturated cores may reach saturation by formation of a further bond, giving in effect a double bond between the Al atoms.
(2) The energy to promote an electron from the inner shell to the valence shell is enormous. In the case of Al , we are specifically concerned with transitions of the type:

$$
(I s)^{2}(2 s)^{2}(2 p)^{8}(3 s)^{2}(3 p) \rightarrow(I s)^{2}(2 s)^{2}(2 p)^{5}(3 s)^{2}(3 p)^{2} .
$$

Such transitions have not been actually observed in the Al ${ }^{1}$ spectrum. An estimate of the energy required for such transitions can be made however, from the X-ray spectrum of Al, involving transitions of the outer electrons to the $L$ shell. For Al, $L$ transitions require 72 e.v. ${ }^{10}$ For Ga the corresponding transitions involve the $M$ shell, and require 43 e.v., and for In we are concerned with the transitions to the $N$ shell, which require ca. i8 e.v. All these

TABLE NiII.

|  <br> Cd. $\left(4^{d}\right)^{10}(5 s)^{2}$ |
| :---: |
|  |  |
|  |  |
|  |  | energies (even in the case of In) are considerably greater than the energy that would be gained by subsequent polymerisation, through the formation of tetrahedral $s p^{3}$ bonds.

Furthermore, in the case of Zn , Cd , and Hg , transitions of the type under consideration have actually been observed by Beutler. ${ }^{11}$ The energies concerned are listed in Table XIII. The values for the corre-

[^17]sponding transitions in the X -ray spectra of Zn and Cd are about 12 c.v., comparing well with the correct Beutler values: this lends support to the approximate values for A1, Ga, and In, obtained from the X-ray spectra. The hypothesis of the promotion of "inner" electrons to the valence core may be worthy of more detailed examination, but it does appear unlikely at present that the energies required could be met by any normal bond formation.

In conclusion, we may summarise our considerations thus: The shortening of the $\mathrm{Al}-\mathrm{Al}$ bond, together with certain theoretical considerations, suggests that the simple assumption of one-electron bonding is not applicable in the case of $\mathrm{Al}_{2} \mathrm{Me}_{6}$. The Lewis structures can be moulded to explain the results, by the postulate that the Lewis type (c) is the main resonance type in $\mathrm{Al}_{2} \mathrm{Me}_{6}$. We are unable to give any theoretical justification for the importance of the (c) resonance type, and until this can be proved or disproved, the explanation based upon the resonance among the Lewis structures of type (c) can only be taken as a tentative suggestion. We have considered the possibility that "inner" electrons may be used in valence bond formation in $\mathrm{Al}_{2} \mathrm{Me}_{6}$, and similar types of compound. An estimate has been made of the energies required for the initial promotion of electrons from the "inner" to the valence cores, and the energies concerned are in all cases far greater than the energies met with in normal bond formation. Unless, therefore, there is some energy source we have not foreseen, it seems impossible that the inner electrons could be used in the way suggested. In short, there seems to be no convincing explanation.

## Summary.

The molecular structure of aluminium trimethyl in the vapour phase has been studied by the method of electron diffraction. The molecule is dimeric, having an "ethane-like" structure. The distances are :-

$$
\begin{aligned}
\mathrm{C}-\mathrm{Al}-\mathrm{Al} & =105^{\circ} \pm 10^{\circ} \\
\mathrm{Al-Al} & =2.02 \pm 0.06 \mathrm{~A} . \\
\mathrm{Al}-\mathrm{C} & =2.05 \pm 0.05 \mathrm{~A} .
\end{aligned}
$$

It is not possible to determine whether the carbon atoms are fixed in the "staggered" or "eclipsed" positions, nor whether the methyl groups are free to rotate, or are fixed.

The nature of the bonding in the molecule has been considered, and some tentative proposals have been put forward.

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## STUDIES IN HYDROGEN OVERVOLTAGE AT HIGH CURRENT DENSITIES: PART I-THE INFLUENCE OF ELECTRODE MATERIAL, CURRENT DENSITY, AND TIME, IN AQUEOUS SOLUTION.

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In recent years a number of careful studies have been made ${ }^{1}$ of hydrogen overvoltage phenomena in aqueous solutions at very low current densities, usually less than $10^{-3}$ amp./sq. cm., but reliable results for higher current density ranges are almost entirely lacking. This is mainly due to the fact that in the measurement of the hydrogen evolution potential against a standard electrode by the direct method, an indeterminate resistance error, equal to the product of the current strength and the surface resistance at the working electrode, is included: at minute currents this error is negligible, but it may become very large at moderate currents. The results of attempts to climinate this error by the use of mechanical commutators, which enabled the potential to be measured after the polarising current had been interrupted, have not been generally accepted in view of the rapid rate of decay of overvoltage, and the marked difference in the nature of the results obtained ${ }^{2}$ from those yielded by the direct method. One of the present authors recently described ${ }^{3}$ a new method of measuring polarisation potentials by means of which accurate results may be obtained free from resistance error. The method involves the interruption of the polarising current electrically for very brief periods, much shorter than can be obtained by any mechanical commutator, and the measurement of the potentials at the ends of these periods by a special method; extrapolation of the potential decay graph to zero time can then be made with considerable accuracy, and the true potential thus obtained. A comprehensive investigation of hydrogen overvoltage phenomena in both aqueous and non-aqueous solutions, in the current density range $10^{-3}$ to 1 amp ./sq. cm ., is now being carried out by this method, and the present paper deals with the values obtained for hydrogen overvoltage in aqueous solution at a wide variety of electrodes in this range, and the dependence of these values upon current density and time.

## Experimental.

N-hydrochloric acid was used as electrolyte throughout the present experiments": gaseous hydrogen chloride was generated from "pure"

[^18]hydrochloric acid and concentrated sulphuric acid, dissolved in distilled water, and diluted to the requisite strength. The form of the electrolytic cell is shown in Fig. I. It consisted of a water-jacketed vessel of about 250 c.c. capacity, with rubber stopper carrying a thermometer, platinised platinum electrode, cathode, and anode compartment. The latter was a tube as shown, the lower end of which was stopped by a tight filter paper plug; the anode was of platinum foil. Cylinder hydrogen was passed through a sintered glass bubbler into alkaline pyrogallol solution, washed with $\mathrm{N}-\mathrm{HCl}$, and then bubbled into the cell via the platinised platinum electrode which served as a hydrogen reference electrode; the passage of the hydrogen caused a considerable measure of stirring in the electrolyte. All exit tubes from the cell were protected from the air by gas bubblers (not shown). In use, about $200 \mathrm{c} . \mathrm{c}$. of catholyte were taken, boiled for a few minutes to remove dissolved air, introduced into the cell, saturated with hydrogen for 30 minutes before commencing the electrolysis, and then hydrogen passed throughout the experiment; no elaborate attempts were made to eliminate the last traces of air, since direct experiment showed that at the currents used in the present work introduction of air had only a very slight effect upon the cathode potentials. The level of the acid in the anode compartment was kept well below that of the catholyte, and under these conditions diffusion of chlorine into the catholyte was negligible; even in long continued electrolyses, the chlorine in the catholyte could not be detected by starch-iodide paper, i.e. its concentration was less than $10^{-3} \%$.

The cathodes used were wires or thin rods of the solid materials, or in some cases the metals were electrolytically deposited, usually on copper wire, and they were sealed into glass tubes with sealing wax. The apparent area exposed was O.I sq. cm. except where otherwise stated. It was found that comparatively gentle cleaning of the smooth metals gave


Fig. I.-Electrolytic cell. the most reproducible results, and in general the cathodes were merely rubbed with filter paper and washed with water. In some cases the electrodes became covered with deposits during use which could not be removed by the above treatment, and then cleaning with warm dilute hydrochloric acid, or very occasionally light scraping ${ }^{5}$ of the metal, were employed. Where electrodeposited metals were used, these were formed under such conditions that smooth, bright coatings were obtained (except for platinised platinum), and were inspected microscopically before and after use ; at the first sign of any discoloration or flaw in the coating the metal was replated.

Overvoltage measurements were carried out at $16 \pm I^{\circ} \mathrm{C}$. with C.D.'s of $10^{-3}, 10^{-2}, 10^{-1}$, and I amp./sq. cm . ; additional C.D.'s were used where necessary to define the shape of the overvoltage - log C.D. graph. The procedure finally adopted was to carry out an electrolysis at the lowest current first, making frequent measurements of the cathode potential relative to the hydrogen reference electrode (i.e. the overvoltage) by the
${ }^{5}$ This is sometimes useful with soft metals ; cf. Grant, Trans. Faraday Soc., 1928, 24, 226.
special method (vide infra), until the potential was substantially constant. The current was then switched off and the potential of the cathode allowed to decay to its usual static value, and observations then carried out at the next current, and so on. After this the initial measurements were repeated, and the set of results accepted only if the original observations were reproducible within $1-2$ centivolts. The potential measurements were carried out with the interrupter operating at a frequency of about 25 cycles and set to give periods of approximately $5,7.5,10,15$, and $20 \times 10^{-5} \mathrm{sec}$. severally, and the decay curves then extrapolated to zero time." Between measurements the interrupter was left in action, set for the shortest time interval; the difference between the current readings with and without the interrupter running was inappreciable. At the lowest C.D., the potential obtained by extrapolation was usually identical with that given by the direct method, but at the higher currents the direct method gave markedly higher values, indicating the presence of considerable resistance errors. Typical decay curves for iron and rhodium cathodes are shown in

Fig. 2. It may be


Fig. 2.-Potential decay curves. noted that over the period studied the decay is insignificant at the lowest C.D. but becomes appreciable as the C.D. is raised. This phenomenon-a rapid increase in the rate of potential decay as the C.D. is raised above $10^{-3} \mathrm{amp} . / \mathrm{sq}$. cm. - was observed with nearly all the electrodes studied. ${ }^{7}$ In all cases, however, extrapolation could be carried out fairly accurately; the probable error even at the highest C.D. is less than 2 centivolts.

The reproducibility of overvoltage measurements in the present work at different times and with different samples of the same metal was investigated carefully, and it was found that by the methods here adopted a reproducibility of $2-3$ centivolts could usually be expected. Occasionally bigger shifts of overvoltage were found, but it was noteworthy that these only resulted in changes of the absolute values, and did not in general change the shape or the slope of the overvoltage-log C.D. graphs.

## Results.

The following cathode materials have been studied: in the form of solid rods or wires-Pt, $\mathrm{Au}, \mathrm{Cu}, \mathrm{Pb}, \mathrm{Ag}, \mathrm{Al}, \mathrm{W}, \mathrm{Fe}, \mathrm{Sn}, \mathrm{C}$ (graphite, arc carbon, filament carbon) ; as thin films produced by electrodeposition (on copper except where otherwise stated)- Pt , platinised Pt (on platinum), $\mathrm{Au}, \mathrm{Cu}$ (on silver), $\mathrm{Pb}, \mathrm{Rh}, \mathrm{Ni}, \mathrm{Cr}, \mathrm{Bi}, \mathrm{Cd}$, and Hg (formed by direct amalgamation).

[^19]Influence of Time.- Of the materials used in the massive form, only tungsten gave an overvoltage which after the first few minutes showed no further change with time. The majority of the materials required electrolysis for $\mathrm{I}-2$ hours at each C.D. before the overvoltage became substantially constant (drift less than oor volt in 30 minutes). In general, the potential rose at a diminishing rate towards the constant value, although in a few odd cases, notably that of aluminium, the initial overvoltage was higher than the ultimate value to which it gradually changed. Usually the time taken to reach a constant value was greatest at the lowest C.D., but this was not invariably the case. With platinum and gold at all C.D.'s the overvoltage continued to rise (in the case of gold very irregularly) even after several hours electrolysis, and there was little sign of any constancy being attained.

With the metals formed in thin films, the variation of overvoltage with time was very markedly reduced. In most cases the overvoltage attained a constant value within a few minutes from the start of electrolysis, and even with smooth platinum satisfactory constancy was reached after $g 0$ minutes. The marked difference between the behaviour of the massive and electro deposited metals is illustrated in Fig. 3 by the overvoltagetime curves for platinum and gold at a C.D. of $10^{-2}$ amp./sq. cm.

It is apparent that unless the influence of time is allowed for in recording overvoltage measurements, the results will in many cases be valueless (sce Discussion). The


Fig. 3.-Overvoltage-time curves. practice in the present work, therefore, has been to accept the constant, reproducible values which are ultimately attained.

Influence of C.D.-The results of the overvoltage measurements are summarised in Table I. Where a metal was used in both the massive and electrodeposited forms, the latter is indicated by an asterisk.

The general order of the results is similar to that observed by other workers for the lower C.D. ranges, the easily fusible metals showing high overvoltáges, while the high melting-point metals have relatively low values; the low overvoltage of arc carbon as compared with graphite and filament carbon is of interest. The variation of overvoltage with C.D., however, brings out a number of novel features which are most readily seen from the overvoltage-log C.D. graphs in Fig. 4. Bi, Fe, Ni, W, $\mathrm{Au}^{*}$ and platinised Pt give straight line graphs (A). $\mathrm{Hg}, \mathrm{Cu}, \mathrm{Cu*}$ and arc $C$ give graphs ( $B$ ) departing slightly from linearity, the overvoltages at the high C.D.'s being somewhat less than those to be expected from a linear relation; to define the Hg graph more definitely, an overvoltage
measurement was made with a C.D. of to amp./sq. cm., using an electrode of $0.01 \mathrm{sq} . \mathrm{cm}$. area, and, as may be seen, the point falls accurately on the curve. Cd, filament C, $\mathrm{Sn}, \mathrm{Al}, \mathrm{Pt}^{*}$ and Rh give graphs (C) which indicate that the overvoltage of each electrode tends to a specific constant value

TABLE $I$.

| Material. | Overvoltage. |  |  |  |
| :---: | :---: | :---: | :---: | :---: |
| c.D. | ${ }^{10}{ }^{-3}$. | $\mathrm{TO}^{-2}$. | $\mathrm{so}^{-1}$. | $1 \mathrm{amp} . / \mathrm{sq} . \mathrm{cm}$. |
| $\mathrm{Hg}^{\text {g }}$ | 1.04 | I. 15 | I-21 | 1.24 |
| $\mathrm{Cd}^{\mathrm{Cd}}$ | $0 \cdot 99$ | 1.20 | I. 25 | 1.23 |
| $\mathrm{Pb}^{\text {Sn }}$ | 0.91 | 1.24 | I. 26 | 1.22 |
| $\stackrel{\mathrm{Sn}}{\mathrm{Bi}}$ | 0.85 0.69 | 0.98 | $\bigcirc 09$ | $0 \cdot 98$ |
| Pb | 0.67 | 0.83 0.97 | - 0.9 I |  |
| Cu | $0 \cdot 60$ | 0.75 | 0.82 | $0 \cdot 84$ |
| Al | 0. 58 | 0.71 | 0.74 | 0.78 |
| $\mathrm{Cu}^{*}$ | 0.50 | 0.62 | 0.74 | - 0 - |
| ${ }^{\text {Ag }}$ | 0.46 | 0.66 | 0.76 | †- |
| Cr | $\ddagger-$ | - | 0.67 | 0.77 |
| Fe | 0.40 | 0.53 | 0.64 | $0 \cdot 77$ |
| Ni | - 33 | 0.42 | 0.51 | - 59 |
| W | 0.27 | $0 \cdot 35$ | 0.47 | - 54 |
| $\mathrm{Pt}^{*}{ }^{\text {a }}$ | 0.25 | $0 \cdot 35$ | 0.40 | 0.40 |
|  | $0 \cdot 17$ | 0.25 | $0 \cdot 32$ | $0 \cdot 42$ |
| ${ }_{\text {§ }}^{\text {R }}$ Pt | 0.09 | 0.39 | 0.50 | $0 \cdot 44$ |
| $\mathrm{Rl}_{1}$ - | 0.08 | 0.22 | - 33 | - 34 |
| Platinised Pt | 0.01 | 0.03 | 0.05 | $0 \cdot 07$ |
| $c\left\{\begin{array}{l}\text { Filament C } \\ \text { Graphite }\end{array}\right.$ | -0.95 | I. 13 | 1.18 | $1 \cdot 17$ |
| c\{ $\begin{aligned} & \text { Graphite } \\ & \text { Arc C }\end{aligned}$ | 0.47 | $\bigcirc \cdot 76$ | $\bigcirc \cdot 99$ | 1.03 |
| Arc . | $0 \cdot 27$ | $0 \cdot 34$ | 0.4 r | 0.41 |

$\dagger$ At a C.D. of I amp./sq. cm. the silver cathode became covered with a black deposit and reproducible potential measurements could not be obtained.
$\ddagger$ At low C.D.'s the chromium deposit dissolved away in the acid electrolyte.
§ The values recorded for massive platinum were those obtained after 120 minutes electrolysis when the rate of increase of overvoltage at the different C.D.'s had become fairly uniform.

II Values for massive gold are not recorded, since they could not be accurately reproduced.
when the C.D. becomes sufficiently high. $\mathrm{Pb} *, \mathrm{~Pb}$, graphite and Pt give graphs (D) of the same general type as those shown in (C) but characterised by marked steepness of the initial portion, and in all cases but graphite

TABLE II.

| Arca of electrode (sq. cm.) | . | 0.01 | 0.1 | $I \cdot 0$ | 10 |
| :--- | :---: | :---: | :---: | :---: | :---: |
| Overvoltage (volts). | . | $I \cdot I 5$ | $I .15$ | $I . I G$ | $I \cdot I 3$ |

the overvoltage measured at a C.D. of I amp./sq. cm. is slightly less than at $0 \cdot \mathrm{x} \mathrm{amp} . / \mathrm{sq}$. cm.

Influence of Electrode Area. -It was recorded by Baars ${ }^{8}$ that with different sized electrodes of mercury at the same C.D. different over-
voltages were obtained ; the larger the area of the electrode, the higher was the overvoltage rccorded. No such phenomenon has been observed in the present work. Using amalgamated copper electrodes of areas $0 \cdot 01, \mathbf{O} \cdot \mathbf{I}, \mathrm{I} \cdot \mathrm{O}$,


Fig. 4.-Overvoltage-log C.D. graphs.
and 10 sq. cm. with a constant C.D. of oor amp./sq. cm., the results shown in Table II were obtained. It is apparent that, within the limits of experimental error, area of electrode has no direct effect on overvoltage.

## Discussion.

The fact that the overvoltage of most cathodes tends to rise with time was noted by Tafel ${ }^{9}$ who found that of the metals examined by him, only platinised platinum and mercury gave constant potentials; lead, cadmium, tin, and bismuth reached polarisation maxima in a short time (up to 30 minutes), while with copper, nickel, gold and smooth platinum the potential went on increasing for hours, and with platinum no maximum could be reached at all. Subsequent workers provided general confirmation of these results, ${ }^{10}$ and Baars, ${ }^{8}$ working under extremely rigorous experimental conditions at low current densities, found that in many cases the potentials continued to change even after several days' electrolysis. The results of the present work show that, cven at high current densities, appreciable time is required for overvoltage equilibrium to be set up except with mercury, platinised platinum and tungsten cathodes, although with electrodeposited metals this time is markedly reduced. It would appear, therefore, that the variation of overvoltage with time is a fundamental feature of overvoltage phenomena at certain cathodes, and is not due to inadequate experimental control, as has sometimes been suggested; it is, moreover, a feature for which any general theory of overvoltage must account. Explanations hitherto put forward have been of a specific nature, and mainly concerned with the case of platinum, which shows the phenomenon very clearly. It has been variously suggested that the rise of overvoltage with time is due to a progressive inactivation of active centres on the metal, ${ }^{11}$ and to the slow rate of attainment of adsorption saturation, ${ }^{12}$ but in the absence of any generally acceptable view of the mechanism of hydrogen overvoltage such hypotheses would appear premature.

The importance of the time factor in determining the conditions of overvoltage measurement seems to have been singularly neglected, and this may be largely responsible for the widely discordant values obtained by different workers. Thus, in the method of measurement which appears to have been generally adopted, the electrode is polarised at some arbitrary high current density for a given time and then observations are rapidly made at a series of decreasing, followed by a series of increasing, current densities; agreement between the two sets of values is considered to constitute a satisfactory check of reproducibility. This practice is unsatisfactory because, except with electrodes which attain equilibrium quickly, such as mercury, platinised platinum and tungsten, the overvoltage does not have an opportunity to reach its equilibrium value. Furthermore, the polarisation set up at any one current density often takes a considerable time to decay, and may affect the next measurement. Using this procedure at the beginning of the present work, it was found that the overvoltage results so obtained could be varied widely by changing the time of initial polarisation, the value of the initial polarising current, and the period taken over the separate observations. It cannot be too strongly emphasised, therefore, that results of fundamental significance cannot be obtained by this method.

[^20]On the other hand, the procedure finally adopted in the present investigation, in which the potential is allowed to decay after each polarisation, so that equilibrium with the solution is reached and the electrode is then polarised at a steady current until the potential is constant, has given uniformly satisfactory results, although it is very laborious and time consuming: while the potentials in the early stages of electrolysis sometimes differ in supposedly identical experiments, the final potential attained is usually reproducible, as stated, within $2-3$ centivolts.

It appears to be generally accepted ${ }^{13}$ that for moderate current densities the overvoltage ( $\eta$ ) of a given cathode is related to the current density ( $I$ ) by Tafel's equation ${ }^{14} \eta=a+b \log I$, where $a$ and $b$ are constants, and it has been suggested that this relation holds up to very high current densities. ${ }^{15}$ The results (Fig. 4) of the present investigation show that while Tafel's equation is accurately obeyed by $\mathrm{Bi}, \mathrm{Fe}, \mathrm{Ni}, \mathrm{W}$, Au , and platinised Pt over the current density range explored, all the other cathodes show a tendency, slight in the case of $\mathrm{Hg}, \mathrm{Cu}$, and $\operatorname{arc} \mathrm{C}$, but marked with Cd , filament $\mathrm{C}, \mathrm{Sn}, \mathrm{Al}, \mathrm{Pt}, \mathrm{Rh}, \mathrm{Pb}$, and graphite, to approach approximately constant values of overvoltage at high current densities. It might be suggested that these deviations from linearity ${ }^{16}$ are due to some error in the experimental method, but careful consideration would seem to render this view quite untenable. Thus, at the high currents used, it is possible that some measure of concentration polarisation is set up, but this would have the effect of making the measured overvoltage greater, not less, than that expected from Tafel's equation. Again, considerable energy is dissipated at the high currents, and might conceivably cause a local increase of temperature at the cathode leading to a diminution of overvoltage ; if this is so, however, it might pertinently be asked why the effect is not also present with the cathodes to which the logarithmic relation does apply. A further criticism which might be made is that with the cathodes which depart from Tafel's equation, the rate of decay of overvoltage may be very high, and hence the extrapolations may be uncertain : against this view it should be pointed out that the rates of decay of overvoltage are not in general very different for the cathodes which give the straight line graphs (Fig. 4A), and those which give the curves (Figs. 4B and C), as may readily be seen from the potential decay curves for Fe and Rh (Fig. 2) ; furthermore, it should be noted that the error involved would have to be several tenths of a volt in many cases, and this is completely out of the question. Hence we must conclude that in many cases the hydrogen overvoltage of a cathode tends towards a specific constant value at high current densities, and it seems not improbable that this would apply to all

[^21]metals if sufficiently high current densities could be used. ${ }^{17}$ The slight lowering of overvoltage at the highest current in the case of Pb and solid Pt (Fig. 4D) may or may not be genuine; the rates of decay of overvoltage in these cases are very high, and the Pt results are not very satisfactory, since the potentials do not become constant with time.

Some considerable interest is attached to the value of the constant $b$ in Tafel's equation, since according to the modern view, which attributes overvoltage to the slowness of the reaction $\mathrm{H}^{\cdot}+\epsilon \rightarrow \mathrm{H}$, this should be equal ${ }^{18}$ to $2.302 \times 2 R T / F$, i.e. 0.116 at $17^{\circ} \mathrm{C}$. For the metals which give straight line $\eta-\log I$ graphs, the values of $b$ obtained from the slopes are as follows:

Bi 0.10, Fe 0.12, Ni 0.09, W 0.09, Au* 0.08, platinised Pt 0.02.
For the cathodes which give curved $\eta-\log I$ graphs, approximate values of $b$ may be obtained from the slopes of the tangents to the curves at the lowest current density, and utilising this method the following additional figures are obtained :
$\mathrm{Hg} 0.12, \mathrm{Cu} 0.16, \mathrm{Cu}^{*} 0.12$, arc $\mathrm{C} 0.08, \mathrm{Cd} 0.25$, filament $\mathrm{C} 0.2, \mathrm{Sn} 0.2$, $\mathrm{Al} 0.12, \mathrm{Pt}^{*} 0.1 \mathrm{If}, \mathrm{Pt} 0.3, \mathrm{Rh} 0.14, \mathrm{~Pb}^{*}>0.3, \mathrm{~Pb} 0.3$, graphite 0.3 .

It is to be noted that while $b$ has in many cases a value in the vicinity of O.I, there is in general no precise agreement with the theoretical figure, and markedly higher results are often obtained. No extensive set of comparable values for $b$ at low current densities in acid solutions is available, as there has been a tendency for isolated investigations of single metals, particularly mercury, to be made, and it is often very difficult in view of the sparsity of experimental detail given to determine the relative reliability of these results. Baars, ${ }^{8}$ however, for a series of metals obtained the values $\mathrm{Hg} 0.147, \mathrm{Ag} 0.120, \mathrm{Cu} 0.105, \mathrm{Au} 0.123$, Pt 0.085 , and Pb 0.200 , while Bowden and co-workers ${ }^{20}$ recorded Hg $0 \cdot 120, \mathrm{Ag} 0.120, \mathrm{Pt} 0.077-0.19$ (depending upon time of polarisation), Ni 0.095 , electroplated Ni 0.110 , arc C 0.84 , Pd 0.116 , Bi 0.116 .0 .145 , Co 0.116 , and Sb 0.29 . Isolated values of $0.048 \cdot 0 \cdot 116$ for $\mathrm{Pd}^{20} 0.21$ for

[^22]$\mathrm{Ta}_{1}{ }^{21} 0.073-0.116$ for $\mathrm{Cu},{ }^{22} 0.19$ for $\mathrm{Pb},{ }^{23}$ and 0.116 for $\mathrm{C}^{23}$ have been reported. It is apparent that, as in the results of the present work, no general agreement with the theoretical value of 0.116 is to be found. There has been a marked tendency in recent years to suggest that $b$ has always the theoretical value for pure metals, ${ }^{24}$ and that discrepancies are due to contamination of the surfaces studied; ${ }^{25}$ this would only account, however, for values of $b$ greater ${ }^{26}$ than 0.116 , and it is very doubtful how far the contention can be successfully maintained.

## Summary.

I. Hydrogen overvoltage measurements have been made in the current density range $10^{-3}$ to $1 \mathrm{amp} . / \mathrm{sq}$. cm . for a wide variety of cathode materials in aqueous solution, using a method of potential measurement which eliminates resistance error.
2. With most cathodes in the massive form, appreciable time is required for overvoltage equilibrium to be set up, and the importance of this factor in determining the conditions of overvoltage measurement is emphasised. With electrodeposited metals the period is markedly reduced.
3. Of the cathodes studied, $\mathrm{Bi}, \mathrm{Fe}, \mathrm{Ni}, \mathrm{W}, \mathrm{Au}$, and platinised Pt give straight line overvoltage-log C.D. graphs as required by Tafel's equation. $\mathrm{Hg}, \mathrm{Cu}, \mathrm{C}, \mathrm{Cd}, \mathrm{Sn}, \mathrm{Al}, \mathrm{Pt}, \mathrm{Rh}$, and Pb all show deviations from this equation, there being a general tendency for the overvoltage to approach a constant value in each case at high current densities.
4. Values of the constant $b$ in Tafel's equation are obtained, and it is shown that there is no general agreement with the theoretical value required by one of the modern views of overvoltage.
5. Variation of the area of electrode has no effect on overvoltage at constant current density.

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${ }^{21}$ Frumkin, Act. sci. ind., 1936, 373, Paris.
${ }^{22}$ Wirtz, Z. physikal. Chem. B, 1937, 36, 435.
${ }^{23}$ Erdey-Gríz and Wick, ibid. A, 1932, 162, 53.
${ }^{24}$ Platinised platinum invariably gives a very low value for $b$ and is accepted as an exception.
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## STATIONARY AND NON-STATIONARY STATES OF FLOW OF HYDROGEN IN PALLADIUM AND IRON.

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The rate of flow of some gases through metals normally obeys two laws:

Rate $=k \sqrt{p}$ ( $p$ denotes pressure of diffusing gas).
Rate $=k_{1} \mathbf{c}^{\frac{-E}{\overline{R T}}}$ ( $E$ is a characteristic quantity having the dimensions of energy).

Attention has been directed to deviations from the $\sqrt{p}$ law which are of great significance ${ }^{1,2}$ when considering the mechanism of flow. These deviations are investigated in the following paper.

Another quantity of great theoretical significance is the diffusion constant $D$ weithin the metal substance. Various methods have been adopted for the measurement of $D$, nearly all of which suffer from objections because of the interference of phase boundary reactions. At least six phase boundary reactions have been proposed, ${ }^{3}$ any of which might conceivably be rate controlling and so tend to obscure transport of gas by pure diffusion. New lines of approach are required for the measurement of $D$. Two methods which may be employed are :-
(I) In the steady state of flow

$$
P=-D \frac{\partial C}{\partial x},
$$

where $P$ denotes the permeability, susceptible to direct measurement, and $\partial C / \partial x$ is the concentration gradient across the metal. If the gradient can be measured, $D$ may be calculated. The problem is successfully attacked in this paper for a special case.
(2) The rate of evolution of gas on the outgoing side of the metal membrane slowly builds up, until a linear pressure-time curve results. This line extrapolated back to zero time gives an intercept on the time axis which is related to the diffusion constant. When the concentrations are $C_{1}$ on the ingoing side, $C_{2}$ on the outgoing side, and $C_{0}$ initially in the membrane, the intercept ${ }^{4} L$ is

$$
L=\frac{l^{2}}{6 D} \frac{1}{\left(C_{1}-C_{2}\right)}\left[C_{1}+2 C_{2}-3 C_{0}\right]
$$

where $l$ denotes the thickness of the membrane. This solution neglects the possibility of rate controlling phase-boundary reactions. A treatment ${ }^{5}$ which considered two simultaneous phase boundary reactions has also been attempted.

The equation for the time lag $L$ in setting up the stationary state of flow through the walls of a tube has not formerly been obtained. Many membranes, e.g., of plastics or of metals, are most conveniently used in the form of tubes, and in order to interpret the present data the value of $L$ must be found for such systems. (See Appendix.)

## Permeability Constants for Tubes and Slabs.

The permeability constant, $P$, for a slab would be defined as the gas flowing in c.c. at N.T.P./second/unit area/unit thickness $/ \mathrm{cm}$. of mercury pressure difference. The permeability constant, $P$, for a hollow tube, becomes the gas flowing in c.c. at N.T.P./second/unit area of outgoing surface/unit difference of internal and external radii/cm. of mercury pressure difference, when the external radius of the tube has a standard value. This value of $P$ becomes identical with that through a slab

[^23]only when the radius of the tube becomes infinite. For example, in a tube of internal and external radii 0.39 and 0.67 mm . respectively
$$
P_{\text {Tube }}=-D\left(\frac{\partial v}{\partial r}\right)_{r=r_{2}}=D \frac{v_{1}-v_{2}}{r_{2}} \frac{\mathrm{I}}{\log \frac{r_{1}}{r_{2}}}=D \frac{v_{1}-v_{2}}{0.2 \mathrm{IO}}
$$
(In these expressions the $v$ 's denote concentrations, as defined in the Appendix.) In a standard tube, of wall thickness 1 mm . and with $r_{1} \rightarrow \infty$
$$
P_{\text {Std. Tube }}=-D\left(\frac{\partial v}{\partial r}\right)_{r=r_{2}}=D \frac{v_{1}-v_{2}}{I} .
$$

This "standard tube" is in fact a plate I mm. thick since $r_{1} \rightarrow \infty$, and so, by means of these relationships, from the measured permeability of this particular tube one may calculate the permeability of the metal as a plate 1 mm . thick by the relationship

$$
P_{\text {Tube }} \times 0.210=P_{\text {Plate }} .
$$

## Experimental.

As suitable metals palladium and iron were chosen, because of their high permeability both to hydrogen atoms supplied at low temperatures electrolytically and to hydrogen atoms supplied from molecular hydrogen at high temperatures.

Two forms of membrane were used. In the first, a palladium plug was soldered with platinum solder in the end of a thick-walled platinum tube. The palladium plug was in the form of a cylinder of I mm . diameter and I mm. thickness. The platinum tube was sealed into soda glass, and the assembly used to measure the permeability, diffusion constant, and concentration gradient at temperatures of $270^{\circ}$ to $400^{\circ} \mathrm{C}$. The palladium disc was guarded by liquid air traps from mercury vapour or tap grease. When the hydrogen atoms were supplied by electrolysis, palladium or iron tubes were made the cathode in a bath of caustic soda. The palladium cathode was soldered by gold solder to a platinum tube and the latter was sealed through soft glass. The iron tube was soldered to brass or steel by soft solder or, in later experiments, by silver solder. The anode in each case was of platinum wire or foil.

Hydrogen gas was generated electrolytically, passed over $\mathrm{Cu}-\mathrm{CuO}$ at $330^{\circ} \mathrm{C}$., through a liquid air trap and phosphoric oxide tubes, and was finally stored over phosphoric oxide.

## Preliminary Observations.

Both palladium and iron membranes underwent irreversible surface changes which made it difficult to get numerous measurements in a single sequence. A number of tubes were used, in all stages of surface activity, the extent of the activity being largely fortuitous. Partial recovery of palladium membranes could be effected by heating the membrane containing occluded hydrogen to a dull red heat. This treatment, however, eventually led to the disruption of the tube, probably because of the violent evolution of gas on heating.

## Tests of the Applicability of the Equation used in the Time Lag Method.

The expression used in computing $D$ (Appendix I) has not taken account of phase boundary reactions. It is important to know, therefore, whether the intercept $L$ of equation ( $I_{4}$ ) in the Appendix is sensitive to phase
boundary processes over the range of activities covered. In Table I are values of $P$ and $D$ obtained by diffusion of hydrogen through palladium and iron. To these may be added the measurements of Table VI. In Table VI the palladium was at first in an extremely active state; but during the last three measurements it was inactive. In all cases in Tables I and VI the variations in $P$ are reflected only to a much smaller extent in changes in $L$, and therefore in $D$. Qualitatively, therefore, one is in this case justified in calculating $D$ from $L$ by an equation which neglects phase boundary reaction processes.

On page 1239 it is shown how phase boundary processes reduce the concentration gradient $\left(C_{1}-C_{2}\right) / l$ across a plate. In an earlier paper ${ }^{5}$ it
table I.-Data on Diffusion of Hydrogen through Palladium and Iron Tubes at various Activities.

|  | $P$ for $r=\infty$ (c.c. at N.T.P. $/$ sec. $/ \mathrm{cm} .^{2} / \mathrm{mm}$. thick/I amp. per cm. ${ }^{2}$ ). |  | Temperature ( $\left.{ }^{\circ} \mathrm{C}.\right)$. |
| :---: | :---: | :---: | :---: |
| Palladium | $\begin{aligned} & 1.51 \times 10^{-4} \\ & 3.02 \times 10^{-5} \\ & 6.55 \times 10^{-6} \end{aligned}$ | $\begin{aligned} & 3.2 \times 10^{-7} \\ & 2.5 \times 10^{-7} \\ & 2.25 \times 10^{-7} \end{aligned}$ | $\begin{aligned} & 23 \cdot 5 \\ & 20 \cdot 5 \\ & 23 \cdot 5 \end{aligned}$ |
| Iron | $\begin{aligned} & 1.24 \times 10^{-8} \\ & 0.85 \times 10^{-8} \\ & 0.38 \times 10^{-8} \end{aligned}$ | $\begin{aligned} & 2.8 \times 10^{-8} \\ & 2.4 \times 10^{-8} \\ & 1.63 \times 10^{-8} \end{aligned}$ | $\begin{aligned} & 20 \cdot 5 \\ & 20 \cdot 5 \\ & 20 \cdot 5 \end{aligned}$ |

was shown that the concentration decrease due to this cause can be very large. The method of the time intercept gives experimentally the large decreases required by theory when phase boundary reactions predominate (e.g. Table IV). Once more the method behaves in a qualitatively satisfactory manner.

One may summarise the position as follows. The new method is in all cases quantitatively correct when phase boundary reactions are unimportant. The method remains qualitatively valid when these reactions govern the velocity of flow, since it still gives results following the requirements of theory and shows intercepts, $L$, which are not affected in order of magnitude by large changes in interface reaction velocities.

## Thermal Diffusion of Hydrogen through Palladium.

Hydrogen gas diffused through a Pd disc at high temperatures. The permeability constants $(P)$ are given in Table II, and conform to an $\frac{-10500}{R T}$ expression $P=3 \times 10^{-2} \mathrm{e}^{\frac{\boldsymbol{R T}}{}}$ (c.c. at N.T.P. $/ \mathrm{sec} . / \mathrm{cm} .2 / \mathrm{mm} . / \mathrm{cm} . \mathrm{Hg}$

TABLE II.-Permeability Constants through Inactive Palladium.

| Temperature ${ }^{\circ} \mathrm{C}$. | 35.4 | 350 | 343 | 335 | 334 | 334 | 311 | 3:1 | 311 | 310 | 302 | $298 \cdot 5$ | 272 | 271 | I 3 |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $10^{8}$ ): P (c.c. at N.T.P.jsec./cm. ${ }^{2} /$ men./cra./Hg pressure). | 0.56 | 0.53 | $0 \cdot 45$ | 0.51 | 0.48 | 0.44 | 0.33 | 0.34 | $0 \cdot 34$ | $0 \cdot 32$ | $0 \cdot 29$ | 0.27 |  | 0.15 | $0 \cdot 000055$ |

pressure). The time intercepts, $L$, and the values of $D$ calculated from them are given in Table III. Owing to the difficulty of ascertaining such small intercepts with accuracy, these data show some fluctuations. However,
the best curve through points on the $\log D$ vs. I/ $T$ curve conforms to the equation $D=0.3 \mathrm{e}^{\frac{-10300}{\boldsymbol{R} T}}$ (Fig. 5). Finally, using the equation

$$
P=-D \frac{\partial C}{\partial x}=D \frac{\left(C_{1}-C_{2}\right)}{l}
$$

and smoothed values of $P$ and $D$ one may calculate the value of $\left(C_{1}-C_{2}\right)$ across the membrane (Table IV). The pressure on the ingoing side was ~ I atmosphere, and on the outgoing side $<x$ atmosphere. Therefore in the steady state of flow and in the absence of slow phase boundary reactions one would have ( $C_{1}-C_{2}$ ) $\simeq C_{1}$, if $C_{1}$ and $C_{2}$ are now equilibrium concentrations appropriate to these pressures. At one atmosphere, the solubilities of $\mathrm{H}_{2}$ in Pd are: ${ }^{\text {: }}$

$$
\begin{array}{llll}
T^{\circ} \mathrm{C} . & =310 & 334 & 350 \\
C_{1} \text { (c.c. } \mathrm{H}_{2} / \text { 100 grms. Pd) } & =163 & 150 & 143
\end{array}
$$

so that Table IV shows how the phase boundary reactions have diminished the concentration gradient across the metal.

It may be pointed out that since the solubility of $\mathrm{H}_{3}$ in Pd at equilibrium is the same for all Pd samples, the ratio of the velocity constant of

TABLE IV.-The Concentration Difference between Ingoing and Outgoing Surfaces.

| Temperature ${ }^{\circ} \mathrm{C}$. | $\begin{gathered} P(\mathrm{smoothed}) \times 10^{3} \\ \text { c.c. } / \mathrm{sec} . / \mathrm{cm} .{ }^{2} / \mathrm{mm} . \text { thick } / \mathrm{cm} . \mathrm{Hg} . \end{gathered}$ | $D\left(\underset{\mathrm{~cm} . .^{2}}{(\text { sec. }-1} .\right.$ | $\begin{gathered} \left(C_{2}-C_{2}\right) \\ \text { c.c. } \mathrm{H}_{2} / \text { c.c. Pd. } \end{gathered}$ |
| :---: | :---: | :---: | :---: |
| 350 | 0.65 | $6 \cdot 8$ | 0.73 |
| 334 | 0.52 | $5 \cdot 4$ | $0 \cdot 73$ |
| 310 | 0.366 | $3 \cdot 7$ | $0 \cdot 75$ |
| 272 | - 193 | $2 \cdot 0$ | 0.74 |

the process of solution at the phase boundary to that of the converse process must be the same for all $\mathrm{H}_{2}-\mathrm{Pd}$ systems, whatever the absolute velocity constants of these processes.

## Diffusion of Hydrogen through Iron and Palladium Cathodes.

Diffusion of hydrogen occurred freely through iron and palladium cathodes in the temperature range $0^{\circ} \mathrm{C}$. to $100^{\circ} \mathrm{C}$. The susceptibility of the cathodes to poisoning prevented long sequences of measurements, and Table $V$ gives typical permeabilities for both metals. When a

[^24]Table V.-Permeability Constants at Low Temperatures.

| Metal. | Temperature ( ${ }^{\circ} \mathrm{C}$.). | $P$ (reduced to that through a plate in c.c. at N.T.P. $/ \mathrm{crn}{ }^{2} / \mathrm{scc}$. $/ \mathrm{mm}$. thick/r amp. per crn. ${ }^{2}$.). |
| :---: | :---: | :---: |
| Pd (inactive surface condition) | $\begin{aligned} & 23 \cdot 5 \\ & 31 \cdot 5 \\ & 40 \cdot 6 \\ & 59 \cdot 3 \\ & 75 \cdot 5 \end{aligned}$ | $\begin{aligned} & 6.79 \times 10^{-6} \\ & 9.33 \times 10^{-6} \\ & 1.86 \times 10^{-5} \\ & 3.62 \times 10^{-5} \\ & 5.80 \times 10^{-5} \end{aligned}$ |
| Pd (most active surface condition)* | $37 \cdot 5$ | $1.85 \times 10^{-3}$ |
| Fe (active surface condition) | 40 80 | $\begin{aligned} & 4.13 \times 10^{-6} \\ & 2.56 \times 10^{-5} \end{aligned}$ |
| Fe (active surface condition) | $\begin{aligned} & 18 \\ & 30.7 \\ & 36.1 \\ & 42.8 \\ & 53.5 \\ & \text { I } 9.5 \text { (check } \\ & \text { measurement) } \end{aligned}$ | $\begin{aligned} & 1.62 \times 10^{-6} \\ & 2.75 \times 10^{-6} \\ & 2.78 \times 10^{-8} \\ & 3.95 \times 10^{-6} \\ & 5.41 \times 10^{-6} \\ & 1.50 \times 10^{-6} \end{aligned}$ |
| Fe (inactive surface condition) | $\begin{aligned} & 23 \\ & 56 \end{aligned}$ | $\begin{aligned} & 3.20 \times 10^{-8} \\ & 3.71 \times 10^{-7} \end{aligned}$ |

reasonably long sequence of measurements was obtained they gave linear $\log P$ vs. i/T curves. Data for two samples of palladium followed the expressions

$$
\begin{aligned}
& P=13 \cdot \mathrm{re} \\
& \text { and } \quad P=7 \cdot 06 e^{\frac{-8500}{R T}}\left(\text { c.c. at N.T.P. } / \mathrm{sec} . / \mathrm{cm} .^{2} / \mathrm{mm} \text {. thick } / \mathrm{r} \text { amp. per } \mathrm{cm} .^{2}\right. \text { ) } \\
&\text { (c.c. at N.T.P. } \left./ \mathrm{sec} . / \mathrm{cm} .^{2} / \mathrm{mm} \text {. thick } / \mathrm{r} \mathrm{amp} . \text { per } \mathrm{cm} .{ }^{2}\right) .
\end{aligned}
$$



Fig. r.-Typical time-lags in setting up the stationary state of flow of hydrogen through palladium.

The set of data for active iron in Table $V$ conformed to the expression

$$
\left.P=1.67 \times 10^{-1} \mathrm{e}^{\frac{-6740}{R T}} \text { (c.c. at N.T.P./sec. } / \mathrm{cm} .^{2} / \mathrm{mm} . / \mathrm{r} \text { amp. per } \mathrm{cm} .{ }^{2}\right)
$$

In all inactive samples it is probable that the value of $E$ is nearly that for some rate controlling phase boundary reaction. To show how these reactions reduce the value of $\left(C_{1}-C_{2}\right)$ the equation

$$
P=-D \frac{\partial C}{\partial x}=-D \frac{\left(C_{1}-C_{2}\right)}{l}
$$

TABLE VI.-Data on Diffusion of Hydrogen in Palladium at
Low Temperatures.

|  | Temperature ${ }^{\circ} \mathrm{C}$. | $\underset{(\min .)}{\left(\mathrm{Lag}_{2}\right)}$ | $D\left(\mathrm{~cm} .{ }^{\text {a sec. }}{ }^{-1}\right.$ ) . | $P$ (c.c. $/ \mathrm{sec} . / \mathrm{cm} .{ }^{2} / \mathrm{mm}$. thick/r amp. per cm. ${ }^{2}$ ). |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Active Pd | 37.5 | $25 \cdot 5$ | $2.43 \times 10^{-7}$ | $\mathrm{I} .85 \times 10^{-3}$ <br> (independent of current density) | 750 |
| Inactive Pd | $\begin{aligned} & 24.2 \\ & 43.5 \\ & 65.0 \end{aligned}$ | $\begin{gathered} 22.5 \\ 6.5 \\ 2.75 \end{gathered}$ | $2.74 \times 10^{-7}$ $9.5 \times 10^{-7}$ $2.24 \times 10^{-6}$ | $\begin{aligned} & 1 \cdot 16 \times 10^{-8} \\ & 2.61 \times 10^{-8} \\ & 8.14 \times 10^{-8} \end{aligned}$ | $\begin{aligned} & 0.38 \\ & 0.25 \\ & 0.33 \end{aligned}$ |

has again been used in conjunction with values of $P$ and $D$ (computed from the time lags, $L$ (Fig. I), to give ( $C_{1}-C_{2}$ ) (Table VI). The set of data for " Active Pd" in Table VI is noteworthy because the value of $\left(C_{1}-C_{2}\right)$ is that for a system in which phase boundary reactions play


Fig. 2.-Time-lag in establishing steady state of flow through rolled Fe sheet. Hydrogen generated by action HCl (Edwards (7)).
no part. Palladium will sorb about 800 volumes of hydrogen in agreement with the figure given in Table VI. Such an active sample should have shown a permeability independent of current density since the ingoing surface was saturated. This was actually the case, as Fig. 4 in the next section shows.

Most of the phenomena noted with palladium are reproduced by iron or steel. Nascent hydrogen may be generated by the action of acids on the surface, or by electrolysis. For example, Fig. 2 shows the time lag
table vit.-Diffusion Constants.

| Termperature ${ }^{\circ} \mathrm{C}$. | $D\left(\mathrm{~cm} .^{2} \mathrm{sec} .^{-1}\right)$. | $D=D_{0} \mathrm{e}^{\overline{\bar{R}} T}\left(\mathrm{~cm}^{2} \mathrm{sec} .^{-1}\right)$. |
| :--- | :--- | :--- |

(A) Nascent Hydrogen in Steel $\left(\mathrm{H}_{2}\right.$ liberated by HCl .

| 0 | $0.52 \times 10^{-8}$ |  |
| ---: | ---: | ---: |
| 10 | $0.16 \times 10^{-8}$ |  |
| 20 | $0.26 \times 10^{-8}$ |  |
| 40 | $0.67 \times 10^{-8}$ |  |
| 50 | $1.15 \times 10^{-8}$ |  |
| 75 | $2.90 \times 10^{-8}$ |  |
| 100 | $1.26 \times 10^{-7}$ |  |

(B) Hydrogen in Iron ( $\mathrm{H}_{2}$ generated by electrolysis).

| 23 37 | $0.42 \times 10^{-8}$ $0.58 \times 10^{-8}$ |  |
| :---: | :---: | :---: |
| 40 | $0.73 \times 10^{-9}$ |  |
| 5 I 54.5 | $1.36 \times 10^{-8}$ $\mathrm{r} 73 \times 10^{-8}$ | $\mathrm{III} \times 10^{-2} \mathrm{e}^{-\frac{-8740}{18 T}}$ |
| 7 I | $3.12 \times 10^{-8}$ |  |
| 80 | $3.84 \times 10^{-8}$ |  | in setting up the stationary state of flow when the nascent hydrogen is generated chemically.* Table VII gives diffusion collstants for hydrogen generated by chemical action,* and by electro. lysis respectively. Two quite different samples of metal were employed in obtaining these data, but the diffusion constants agree over the whole range of temperatures. Comparison of Tables VII (A) and V shows that $D_{\mathrm{H}_{2}-\mathrm{Fe}}$ is ca. $1 \mathrm{o}^{-2} \times D_{\mathrm{H}_{2}-\mathrm{Pd}}$. Smoothed values of $P$ and $D$ for active iron, taken from Tables V and VII ( A ), lead to the following values of ( $C_{1}-C_{2}$ ), the concentration difference between ingoing and outgoing surfaces:-

$T\left({ }^{\circ} \mathrm{C}\right.$ ) - . . . $\quad 20 \quad 30 \quad 40 \quad 50$
$\begin{array}{llllll}C_{1}-C_{2} \text { (c.c. at N.T.P./c.c. of } \mathrm{Fe} / \mathrm{r} \text { amp. per } \mathrm{cm} .{ }^{2} \text { ) } & 45 & 40.4 & 30.6 & 32.8\end{array}$
These values are large, and therefore indicate that phase boundary reactions here play only a minor part. When the iron was in an inactive state the value of $\left(C_{1}-C_{2}\right)$ fell to less than I c.c./c.c. $\mathrm{Fe} / \mathrm{I}$ amp. per $\mathrm{cm} .^{2}$, so that phase boundary processes were then important.

This method, in which $P, D$ and the equation $P=D \frac{\left(C_{1}-C_{2}\right)}{l}$ are used to determine ( $C_{1}-C_{2}$ ), is a perfectly general way of finding whether phase boundary reactions govern the tempo of diffusion. Only when these reactions do not govern the diffusion rate does $\left(C_{1}-C_{2}\right)$ approach its equilibriurn value, controlled by the pressures at the ingoing and outgoing surfaces.

## Permeation Velocity as a Function of Current Density.

When palladium metal was in an inactive condition, the relation between the permeation velocity and the current density was that in Fig. 3. The curve had a " foot " at low current density, but as the current density $(I)$ increased the permeation velocity became a linear function of $\sqrt[V]{\bar{I}}$. This behaviour has been observed when hydrogen diffuses through a nickel cathode, ${ }^{8}$ or through metals at high temperatures. 9,10

[^25]A very active sample of palladium gave the permeation rate-current density relationships of Fig. 4 (curve I). The rate was independent of the current density, ${ }^{11}$ and therefore the metal just inside the ingoing surface was saturated with bydrogen. As the surface activity fell off, successive stages of deactivation gave the [curves II and III, in which the rate became more and more nearly proportional to $\sqrt{\text { Current Density }}$.

## Discussion.

Two attempts to explain the "foot" in the


Fig. 3.-The influence of increasing current density upon permeation velocity, showing "foot" to curve. L Temperature $78^{\circ} \mathrm{C}$. curve of Fig. 3 have previously been made. In the first it was supposed that at low current density (or gas pressure) the surface was not saturated with hydrogen. If the fraction of the surface covered was $\theta$, the permeation velocity was written as


Fig. 4.-Influence of current density upon permeation velocity of $\mathrm{H}_{2}$ through Pd of various degrees of activity.

$$
\text { Rate }=k \theta \sqrt{\bar{p}} .
$$

This formula should be valid at low pressures or high temperatures. At higher pressures or at low temperatures $\theta \rightarrow \mathrm{I}$, and so

$$
\text { Rate }=k \sqrt{p} .
$$

The experimental data, however, always show that the "foot" in the curve of Fig. 3 is more pronounced when the temperature is lowe, i.e., when $\theta$ should be unity. At high temperatures, $\theta \neq \mathrm{I}$, yet the "foot" has almost disap. peared. Thus the experiments indicate a behaviour which is the converse of that predicted by the theory.
A second attempt ${ }^{2}$ attributed all departures from the $\sqrt{p}$ or $\sqrt{1}$ law to impurities in the metal. It was found that the $\sqrt{p}$ law held
with less accuracy if impurity was present in the metal. It has not, however, been shown that the purest metals fail to show any "foot" such as indicated in Fig. 3 and it is probable that the two effects are due to different causes.

The "foot" may be explained in terms of slow phase boundary reactions. Suppose both reactions
(i) $\mathrm{H}_{2}$ (outside surface of metal) $\rightarrow \mathrm{H}_{2}$ (dissolved within surface) (ii) $\mathrm{H}_{2}$ (dissolved within surface of metal) $\rightarrow \mathrm{H}_{2}$ (outside surface)
have velocities comparable with that of diffusion within the solid. A slow transfer in process (i), and a more rapid diffusion away from the interface prevents the building up of the equilibrium concentration just inside the ingoing surface. At the outgoing surface, if (ii) is slow


Fic. 5.
compared with diffusion, the concentration at that surface builds up, and becomes greater than the equilibrium concentration. The actual concentration difference, $\left(C_{1}-C_{2}\right)$, can then become very small indeed, as the data of Tables IV and VI show. The form of the permeation velocity-pressure isotherm depends on $\left(C_{1}-C_{2}\right)$, and is not a simple function of the pressure.

Experiment shows, however, that the permeation velocity is without exception a linear function of $\sqrt{p}$ at higher pressures. Wang, ${ }^{3}$ who assumed six surface processes, showed that the $\sqrt{p}$ law was indeed theoretically valid for larger values of $p$. Implicit in Wang's treatment is the assumption that $C_{1}$ and $C_{2}$ are $C_{s}$, where $C_{s}$ denotes the saturation concentration of gas in the metal. ${ }^{*}$ Thus the form of the permeation rate-pressure isotherms can be adequately explained in terms of slow phase boundary reactions.

Attempts to measure the diffusion constants of hydrogen in palladium have now been made by a number of methods. These include :
(i) The velocity of desorption or absorption. ${ }^{12}$ This method is sensitive to phase boundary reactions.
(ii) Electrochemical method. ${ }^{13}$ The central part of a Pd wire was charged with hydrogen, and the electrochemical potential measured at various points along the wirc. The diffusion of hydrogen along the wire was then followed by noting changes of this potential with time.
(iii) Photographic method. ${ }^{14}$ The hydrogen charged part of the wire produces blackening of a photographic plate, but uncharged wire produces no blackening. The movement of the blackened zone due to diffusion of hydrogen along the wire served for measurements of the diffusion constant.
(iv) The method of the time intercept, developed in this paper.

Methods (ii) and (iii) are not capable of a high degree of experimental accuracy. Method (iv) is casy to apply, and the experimental observations may usually be made with accuracy. The intercept does not appear to be very sensitive to phase boundary reactions. A summary of all the published data is given in Fig. 5. The best straight line through all the data in Fig. 5 follows the equation

$$
D=1.5 \times 10^{-2} \mathrm{e}^{-\frac{6800}{R T}} \mathrm{~cm} .^{2} \mathrm{sec} .^{-1}
$$

although the slopes of individual $\log D-1 / T$ curves vary from $E=$ $20,100 \mathrm{cal}$. to $E=5740 \mathrm{cal}$.

## APPENDIX.

## Calculation of the Intercept $L$ for Hollow Tubes.

The present treatment neglects phase boundary reactions. Consider an infinite hollow cylinder of internal and external radii $r_{2}$ and $r_{1}$ and concentrations of solute $v_{2}$ and $v_{1}$ at $r=r_{2}$ and $r=r_{1}$ respectively. Within the wall of the tube the initial concentration is $v_{0}$. In order to solve the equation of flow the initial system of Fig. $6 a$ is divided into the two systems of Figs. $6 b$ and $6 c$,

(a)

(b)

(c)

Fig. 6. of which Fig. $6 b$ gives the steady state of flow eventually set up in the wall, and Fig. $6 a$ is such that

$$
\begin{equation*}
u+w=v_{0} \text { at } t=0 \tag{I}
\end{equation*}
$$

For the steady state system of Fig. 6b,

$$
\begin{equation*}
u=\frac{\left(v_{2}-v_{1}\right) \log r+v_{1} \log r_{2}-v_{2} \log r_{1}}{\log r_{2}-\log r_{1}} \tag{2}
\end{equation*}
$$

[^26]Thus

$$
\begin{equation*}
w=v_{0}-\left[\frac{\left(v_{2}-v_{2}\right) \log r+v_{1} \log r_{2}-v_{2} \log \gamma_{2}}{\log \gamma_{2}-\log r_{1}}\right] \tag{3}
\end{equation*}
$$

at $t=0$.
For all values of $t>0$,

$$
w=\frac{\pi^{2}}{2} \sum_{1}^{\infty} \alpha_{n}{ }^{2} \cdot \frac{\mathrm{~J}_{0}{ }^{2}\left(\alpha_{n} r_{2}\right)}{\mathrm{J}_{0}{ }^{2}\left(\alpha_{n} r_{1}\right)-\mathrm{J}_{0}{ }^{2}\left(\alpha_{n} r_{2}\right)} \mathrm{e}^{-D \alpha_{n} t} \cdot U_{0}\left(\alpha_{n} v\right) \int_{r_{2}}^{r_{1}} v w \cdot U_{0}\left(\alpha_{n} r\right) \mathrm{d} r
$$

In this expression $J_{0}$ denotes a Bessel function of the first kind and of zero order, and $U_{0}$ is defined by

$$
U_{0}(\alpha r)=\mathrm{J}_{0}(\alpha r) \mathrm{H}_{0}^{(1)}\left(\alpha r_{2}\right)-\mathrm{J}_{0}\left(\alpha r_{2}\right) \mathrm{H}_{0}^{(1)}(\alpha, r)
$$

where $H_{0}{ }^{(1)}$ denotes a Bessel function of the third kind, and $\alpha$ is a root of $\mathrm{J}_{0}\left(\alpha r_{1}\right) \mathrm{H}_{0}{ }^{(1)}\left(\alpha r_{2}\right)-\mathrm{J}_{0}\left(\alpha r_{2}\right) \mathrm{H}_{0}^{(1)}\left(\alpha r_{1}\right)=0$. Then $\mathrm{U}_{0}\left(\alpha r_{2}\right)=0=\mathrm{U}_{0}\left(\alpha r_{1}\right)$.

The complete solution is then $v=u+w$ and from it, by differentiation one finds

$$
\begin{align*}
\left(\frac{\partial v}{\partial r}\right)_{r=r_{2}}=\frac{v_{2}-v_{1}}{r_{2}} & \cdot \frac{I}{\log _{r_{2}}^{r_{2}}} \\
& +\frac{\pi^{2}}{2} \sum_{1}^{\infty} \frac{\alpha_{n}{ }^{2} \mathrm{~J}_{0}^{2}\left(\alpha_{n} \gamma\right)}{\mathrm{J}_{0}{ }^{2}\left(\alpha_{n} r_{1}\right)-\mathrm{J}_{0}^{2}\left(\alpha_{n} r_{2}\right)} \mathrm{e}^{-D \alpha_{n}{ }^{2} t} \cdot\left[U_{0}^{\prime}\left(\alpha_{n} \gamma\right)\right]_{r=r_{2}} I \tag{4}
\end{align*}
$$

where

$$
I=\int_{r_{1}}^{T_{1}} r \cdot w \cdot U_{0}\left(\alpha_{n} r\right) \mathrm{d} r
$$

and

$$
U_{0}^{\prime}=\frac{\partial}{\partial r}\left(U_{0}\right) .
$$

Suppose vg $=$ the increase in concentration in the gas phase (vg small, i.e. $v_{2}$ nearly constant), and let $V=$ the volume of the gas phase on the outgoing side.

Then

$$
V \cdot \frac{\partial v_{o}}{\partial t}=D\left(\frac{\partial v}{\partial r}\right)_{r=r_{1}}
$$

whence

$$
\begin{align*}
V . v_{0}= & \frac{v_{2}-v_{1}}{\gamma_{2}} \frac{I}{\log \frac{\gamma_{2}}{r_{1}}} D \cdot t \\
& +\frac{\pi^{2}}{2} \cdot \sum_{1}^{\infty} \frac{\mathrm{J}_{0}{ }^{2}\left(\alpha_{n} \gamma\right)}{\mathrm{J}_{0}{ }^{2}\left(\alpha_{n} \gamma_{1}\right)-\mathrm{J}_{0}{ }^{2}\left(\alpha_{n} r_{2}\right)} \cdot\left(\mathrm{I}-\mathrm{e}^{-D \alpha_{n}{ }^{2} t}\right)\left[U_{0}{ }^{\prime}\left(\alpha_{n} \gamma\right)\right]_{r=r_{2}} I \tag{5}
\end{align*}
$$

Thus as $t \rightarrow \infty$, the curve of $v g$ against $t$ approaches the asymptote given by the expression

$$
\begin{align*}
v_{0}=\frac{v_{2}-v_{1}}{r_{2}} \cdot \frac{D}{V \cdot \log \frac{r_{2}}{r_{1}}}\{ & t+\frac{\pi^{2}}{2 D} \cdot \frac{\log \left(\frac{r_{2}}{r_{1}}\right) \cdot r_{2}}{v_{2}-v_{1}} \\
& \left.\times \sum_{1}^{\infty} \frac{\mathrm{J}_{0}{ }^{2}\left(\alpha_{n} r_{2}\right)}{\mathrm{J}_{0}{ }^{2}\left(\alpha_{n} r_{1}\right)-J_{0}{ }^{2}\left(\alpha_{n} r_{2}\right)}\left[U_{0}^{\prime}\left(\alpha_{n} r\right)\right]_{r=r_{2}} I\right\} \tag{6}
\end{align*}
$$

Had there been no delay in establishing a steady state the expression would be

$$
\begin{equation*}
v_{0}=\frac{v_{2}-v_{1}}{r_{2}} \cdot \frac{D}{V \cdot \log \frac{r_{2}}{r_{1}}} t \tag{7}
\end{equation*}
$$

so that the intercept, $L$, on the axis of $t$ is

$$
\begin{equation*}
L=\frac{-\pi^{2}}{2 D} \cdot \frac{\left(\log \frac{r_{2}}{r_{1}}\right) r_{2}}{\left(v_{3}-v_{1}\right)} \sum_{1}^{\infty} \frac{\mathrm{J}_{0}{ }^{2}\left(\alpha_{n} \gamma_{2}\right)}{\mathrm{J}_{0}{ }^{2}\left(\alpha_{n} r_{2}\right)-\mathrm{J}_{0}{ }^{2}\left(\alpha_{n} r_{2}\right)} \cdot\left[U_{0}^{\prime}\left(\alpha_{n}{ }^{v}\right)\right]_{r=r_{2}} I \tag{8}
\end{equation*}
$$

The most important experimental case arises when
whence

$$
\begin{gather*}
v_{2}=0 \quad v_{0}=0 \\
w=\frac{v_{1} \cdot \log \frac{r}{r_{2}}}{\log \frac{r_{2}}{r_{1}}} . \tag{9}
\end{gather*}
$$

In this case, and since
one finds

$$
r_{2}\left[U_{0}^{\prime}\left(\alpha_{n} \gamma\right)\right]_{r=r_{2}}=-\frac{2 i}{\pi} \frac{J_{0}\left(\alpha_{n} r_{1}\right)}{J_{0}\left(\alpha_{n} r_{2}\right)}
$$

$$
\begin{equation*}
L=\frac{-\pi i}{D v_{1}} \sum_{1}^{\infty} \frac{\mathrm{J}_{0}\left(\alpha_{n} \gamma_{2}\right) \mathrm{J}_{0}\left(\alpha_{n} r_{1}\right)}{\mathrm{J}_{0}^{2}\left(\alpha_{n} \gamma_{1}\right)-\mathrm{J}_{0}{ }^{2}\left(\alpha_{n} r_{2}\right)} I \tag{I0}
\end{equation*}
$$

Let

$$
\begin{aligned}
I & =\int_{\tau_{1}}^{r_{1}} v_{1} r\left(\log r-\log \gamma_{\mathrm{E}}\right) U_{0}\left(\alpha_{n} \gamma\right) \mathrm{d} r \\
& =v_{1} \int_{\tau_{1}}^{r_{1}}-r \log r_{2} U_{0}\left(\alpha_{n} r\right) \mathrm{d} r+v_{1} \int_{T_{1}}^{r_{1}} r \log r U_{0}\left(\alpha_{n} r\right) \mathrm{d} \gamma \\
& =I_{1}+I_{2} .
\end{aligned}
$$

Since $\int r U_{0}\left(\alpha_{n} r\right) \mathrm{d} r=\frac{r}{\alpha_{n}} U_{1}\left(\alpha_{n} \gamma\right)$, one has

$$
\begin{equation*}
I_{1}=-v_{1} \log r_{2}\left[\frac{r_{1}}{\alpha_{n}} \cdot U_{2}\left(\alpha_{n} r_{1}\right)-\frac{r_{2}}{\alpha_{n}} U_{1}\left(\alpha_{n} r_{2}\right)\right] \tag{I2}
\end{equation*}
$$

Also $I_{2}$ reduces to

$$
\begin{equation*}
I_{2}=\frac{r_{1} v_{1}}{\alpha_{n}} U_{1}\left(\alpha_{n} \gamma_{1}\right) \log r_{1}-\frac{r_{2} v_{1}}{\alpha_{n}} U_{1}\left(\alpha_{n} \gamma_{2}\right) \log r_{2} \tag{I3}
\end{equation*}
$$

since $\left[\frac{U_{0}\left(\alpha_{n} \gamma\right)}{\alpha_{n}{ }^{2}}\right]_{r_{2}}^{r_{2}}=0$, from $U_{0}\left(\alpha \gamma_{2}\right)=U_{0}\left(\alpha \gamma_{1}\right)=0$.
Thus

$$
\begin{aligned}
I & =\frac{r_{1} v_{1}}{\alpha_{n}} U_{1}\left(\alpha_{n} \gamma_{1}\right) \cdot \log \frac{\gamma_{1}}{\gamma_{2}} \\
& =\frac{2 i v_{2}}{\pi \alpha_{n}^{2}} \cdot \log \frac{r_{1}}{r_{2}}, \text { since }\left[r \cdot \frac{\partial U_{0}}{\partial r}\right]_{r=r_{1}}=\frac{-2 i}{\pi}
\end{aligned}
$$

and

$$
U_{1}(\alpha r)=-\frac{\partial\left(U_{0}(\alpha r)\right)}{\partial(\alpha r)}
$$

Then one finally obtains

$$
\begin{equation*}
L=\frac{2}{D} \cdot \sum_{1}^{\infty} \frac{1}{c_{n}^{2}} \cdot \frac{J_{0}\left(\alpha_{n} \gamma_{2}\right) J_{0}\left(\alpha_{n} r_{1}\right)}{J_{0}^{2}\left(\alpha_{n} r_{2}\right)-J_{0}{ }^{2}\left(\alpha_{n} r_{2}\right)} \cdot \log \frac{r_{1}}{r_{2}} \tag{I4}
\end{equation*}
$$

where $\alpha_{n}$ is the $n$th positive root of

$$
U_{0}\left(\alpha r_{2}\right)=0 .
$$

These roots may be calculated in each case by the formula of Gray and Matthews. ${ }^{15}$ For one of the palladium tubes used in this paper, $r_{1}=0.67 \mathrm{~mm}$., $r_{2}=0.39 \mathrm{~mm}$. and thus

$$
D=\frac{2.7 \times 10^{-1}}{L}
$$

when $L$ is expressed in minutes.
${ }^{15}$ Gray, Mathews and MacRobert, Trealise on Bessel Functions (Macmillan and Co., 1922).

## Summary.

A new method has been applied to measure the diffusion constants of hydrogen in iron and palladium. The mathematical analysis required to use this method, previously given only for slabs, is here extended to hollow tubes.

Values of the permeability $(P)$ and the diffusion constant $(D)$ were determined for palladium from room temperature to several hundred degrees centigrade; and for iron over the interval $0^{\circ}$ to $80^{\circ} \mathrm{C}$. Expressions for $P_{0}, D_{0}, E$ and $E_{1}$ in the equations

$$
\begin{aligned}
& P=P_{0} \mathrm{e}^{\frac{-E}{\bar{R} \tilde{F}^{1}}} \\
& D=D_{0} \mathrm{e}^{\frac{-E}{\bar{R} \tilde{T}}}
\end{aligned}
$$

were given both for palladium and iron, and other experimental data were summarised.

When phase-boundary reactions are rate controlling the curve permeation rate against $\sqrt{\text { current density }}$ has a foot at low current density but becomes a straight line at high current density. This phenomenon, of general occurrence, was successfully analysed in terms of combined phase-boundary reactions and diffusion. It is not due to adsorption effects.

When phase-boundary reactions were eliminated by suitable activation the permeability of a Hydrogen-Palladium system increased $2.5 \times 10^{3}$-fold. The permeation velocity then became independent of current density.

The experimental work described in this paper was carried out in the Colloid Science Laboratory, Cambridge, during the tenure of a Research Fellowship at Clare College, Cambridge ; and in the Chemical Laboratories, the Technical College, Bradford. During the latter part of the work the author received a grant from the Chemical Society.

The Chemical Laboratories,
The Bradford Technical College.

## A NEW TECHNIQUE OF ELECTROCAPILLARY MEASUREMENTS.

By J. Jackson.

Received 25th October, 1940.
Ohmic Drop in the Electrocapillary Cell.-When a mercury surface is exposed to an aqueous solution containing air but not mercury ions, the potential of the metal as a rule rapidly becomes more positive, soon acquiring a more or less stationary value. The maintenance of the steady potential is most easily explained as arising from an equalisation of the rates of two electrochemical processes, the reduction of dissolved oxygen at cathodic areas and the discharge into solution of mercury ions at anodic areas, though there is reason to believe that this is an over-simplified conception of the reaction mechanism.

In electrocapillary investigations a range of negative potentials are applied to an interface of this nature (or, more rarely, of other types) and the variation in interfacial tension observed. The experimental method commonly adopted, essentially that described by Gouy, ${ }^{1}$ utilises an interface formed in a fine tapering capillary, polarisations being applied through a reversible electrode in the solution. Polarisation disturbs the equilibrium of electrical transfer across the interface, and gives rise to a balance of current in one direction. Except at the extremities of the electrocapillary curve, the current flowing is usually almost solely due to oxygen reduction, and the magnitude of the diffusion current is not greatly influenced by the nature or the concentration of the electrolyte present. Thus over a significant range of negative polarisations the ohmic drop in a given electrocapillary cell is roughly proportional to electrolyte dilution, and begins to become appreciable when this is of the order of oor n. It is of course essential to know its value if the polarisation of the small electrode is to be known. An approximate value is readily calculated by measuring the current and estimating the electrolytic resistance, but this procedure is inadequate where ohmic drop is at all large, and an accurate determination does not appear practicable with the means at present available.* Thus neither Gouy nor most subsequent workers using his technique have attempted determinations in electrolytes more dilute than 0.01 N . In other cases neglect of the ohmic drop factor has clearly given rise to erroneous results, e.g., in some curves for 0.001 N . solutions plotted by Kemula and Becr. ${ }^{2}$ At the higher dilution elimination of oxygen would normally remove the source of error, but in extremely dilute electrolytes, e.g., a good conductivity water, the small current density due to the onset of hydrion deposition further limits the range of potential over which ohmic drop is negligible; and, in any case, without a very specialised procedure, the removal of traces of oxygen or other cathodic depolariser in sufficient amount to affect the results proves exceedingly difficult. (Cf. Gatty and Spooner ${ }^{3}$ on a related subject.) These facts prompted the devising of an experimental technique affording a considerable reduction of ohmic drop in the electrocapillary cell for a given current density.

Normally the cell resistance resides mainly in the column of electrolyte between the meniscus and the mouth of the capillary. Its length, which is naturally kept small, cannot be reduced indefinitely because of the operation, found essential for the accuracy of the measurements, of oscillating the meniscus prior to taking a reading, ensuring thereby its having reached an equilibrium position. In Gouy's work this length ${ }^{4}$ was from $\mathrm{O} \cdot \mathrm{I}$ to 0.2 mm .

The New Technique.-In the present modification the meniscus is brought slowly to the open end of the capillary by gradually increasing the head of mercury above it until the mercury commences to drip. The

[^27]hydrostatic pressure difference across the interface at this instant, calculated from the heights of the mercury column and of the aqueous solution above the capillary tip, is assumed proportional to the interfacial tension. Assuming in both cases that the depolarisation current is uniformly distributed over a hemispherical interface, $\dagger$ the ohmic drop in the Gouy technique is approximately 2 pil volt, where $\rho$ is the specific resistance of the solution in ohms, $i$, the current density in amp. $\mathrm{cm} .^{-2}$, and $l$, the length of the electrolyte column in the capillary in cm ., or of the order of $0.02 i_{\rho}$ volt. Using the new method the value is pir volt, where $r$ is the radius of the capillary at its end, or of the order of $0.002 i \rho$ volt. The expression, pir, is equally valid when the interfacial tension is measured by drop-weight, as has been done in some electrocapillary investigations, $r$ being the diameter of the drop, but here depolarisation current is augmented by capacity current, and in any case it would be difficult to use a sufficiently fine dropping electrode to preserve the numerical advantage, which is dependent on the magnitude of $\gamma$.

Verification.-A test of the method was made by applying it to determine the curves for mercury against $0.5,0.05$ and 0.005 M . aq. sodium sulphate solutions, in air at room temperature ( $18-20^{\circ} \mathrm{C}$.) and comparing the results with known data. A simple form of apparatus was used. A long vertical tube containing mercury was connected through a low side arm, by means of sulphur-free pressure tubing, to a mercury reservoir capable of being smoothly raised and lowered. The capillary, which was attached to the bottom of the tube with pressure tubing, dipped into a beaker of the solution, connection to an N . calomel half-cell being made through a salt bridge of the ground-stopper type. ${ }^{5}$ The capillary is conveniently drawn from thick-walled tubing, 6 mm . ext., and 2 mm . int. bore. About 1.5 cm , is heated, a few cm. from one end, and allowed to thicken till almost on the point of sealing, when it is removed from the blowpipe flame and drawn out to a length of approximately 10 cm . If at a distance $3-4 \mathrm{~cm}$. from the unmelted portion the capillary has a suitable diameter, as measured roughly by microscope with eye-piece scale, it is considered satisfactory and the glass is scratched at this point with a glass knife and eventually snapped off. The capillary has a wall thickness of approximately rmm . at its end and so is not readily damaged. In these tests an internal bore of $0.035-0.04 \mathrm{~mm}$. was chosen, leading to somewhat smaller heads of mercury than are customarily used in electrocapillary apparatus. The use of capillary tubing of uniform bore, recently introduced into both electrocapillary ${ }^{6}$ and polarographic ${ }^{7}$ apparatus, in preference to drawn capillaries, does not seem suitable for the technique here described.

A given potential is applied to the cell and the mercury reservoir fairly rapidly raised to give a first approximate reading. The commencement of dripping is readily discerned when the well-illuminated beaker is furnished with a white background, even with the eye over a yard away. To avoid the possibility of polarising the calomel electrode, the applied potential is then switched off. When the potential is far from $\gamma_{\text {max. }}$ this measure also suffices to interrupt the mercury flow. The catheto-
$\dagger$ Hydrogen bubble formation along the side of the mercury thread has been taken to indicate that the current is distributed over an interfacial area much greater than that of the hemispherical meniscus. But the disengagement of hydrogen in this position seems more likely to arise from migration of electrolyte adjacent to the polarised meniscus and charged with the gas along to the vertical interface when this has a higher tension due to zero, or possibly feeble, polarisation. Such migration may of course also cause a break in the mercury thread by accumulation of electrolyte.
${ }^{5}$ G. W. Irving and N. R. Smith, Ind. Eng. Chem. Anal. Ed., 1934, 6, 480.
${ }^{6}$ L. A. Hansen and Williams, J. Physic. Chem., 1935, 39, 439.
${ }^{7}$ J. Heyrovsky in Böttger, Physik. Methoden der Anal. Chemie, Vol. III, Leipzig, 1939, p. 436.
meter is adjusted for a height reading, and if necessary, the mercury flow stopped by applying suction above the mercury column. Another determination is made, raising the mercury reservoir more cautiously when the level of the first reading is being approached. A further repetition usually gives a result within $O \cdot 1 \mathrm{~mm}$. of the previous value. It is, of course, essential to avoid errors due to vibration. The experiments described here were carried out in a basement laboratory with concrete floor, and the only disturbances due to this cause arose from the passage of vehicular traffic along an adjoining street.

The corrected heights were converted to the interfacial tension units employed by Gouy ( $\gamma_{\max .} \mathrm{Hg}_{\mathrm{g}}-\mathrm{H}_{\mathrm{i}} \mathrm{O}=1000 \cdot 0$ ) on the basis of the maximum of the curve for 0.5 M . solution, and the points plotted together with curves drawn from Gouy's data for the same solutions. ${ }^{8}$ Gouy worked at $18.0 \pm 0.2^{\circ} \mathrm{C}$. ; the error in making a comparison with results for the slightly higher and wider temperature range is less than o. per cent. The curves in the diagram are spaced along the $V$-axis, since the maxima for the three solutions are almost coincident; in each case a vertical line indicates the point obtained at zero potential to N . calomel.

Fig. 1. - Electrocapillary curves of mercury aqueous sodium sulphate.


The capillaries are kept immersed in distilled water when not in use. After three or four weeks the glass surface appears to become contaminated, the meniscus does not move along the capillary quite smoothly, and the results lose in consistency. As the drawing and calibration of a new capillary is quite a simple matter, no serious attempt was made to determine whether contaminated ones could be cleansed for re-use.

Apart from the special value of the new technique for dilute electrolytes, it has certain general advantages over the traditional method :-
(a) the visual observation by which the mercury head adjustment is made is of a type likely to involve less error than the one it replaces;
(b) the speed at which satisfactory measurements can be made is greatly enhanced;
(c) the measurements are much less fatiguing to the eyes.

On the other hand considerable care is needed in applying the technique to solutions, the composition of which indicates they may show electrocapillary viscosity.

It is of interest to note that when mercury commences to flow from the capillary at a given potential, the flow ceases when the mercury head
${ }^{8}$ G. Gouy, Physik Methoden der Anal. Chemie, Vol. III, Leipzig, 1939, p. 182.
is reduced to a value also sharply defined. In an experiment with 0.02 M. sodium sulphate, using a thin-walled capillary, a rough electrocapillary curve was plotted assuming the pressure difference across the interface at the cessation of mercury flow to be proportional to its tension. The curve obtained resembled the anomalous curves of IKuçera, ${ }^{0}$ who measured the tension by drop-weight. The degree of proportionality between the minimum pressure necessary to sustain flow and the value of the dropweight was not investigated. The question is no doubt complex, and influenced by the rate and possibly other conditions of dropping.

## Summary.

I. A modification of the Gouy technique of electrocapillary measurements is described by which ohmic drop error is minimised.
2. Certain general advantages of the new method are mentioned.

This work was carried out in the Graham Colloid Research Laboratory of the University of Manchester.

${ }^{9}$ B. Kuçera, Annalen, 1903, (4), 11, 529, 698.

## REVIEW OF BOOK.

Scattering of Light and the Raman Effect. By S. Bhagavantam. (Andhra University, Waltair, India. Pp. $\times \times 333$, with 2 plates and 4 I figures. Price 225 . or Rs. 15 net.)

This book comprises a series of lectures to advanced students, and will be welcomed as a consecutive account of the main results obtained in this field, and of the theory underlying them. Perhaps it will not suffice to satisfy all the critics, especially those who are concerned about the fundamental nature of the Raman Effect, and its exact significance in the philosophy of physics and chemistry. The discussion is reasonably detailed, yet easy to follow, and there are a number of valuable appendixes; the one dealing with group theory being particularly lucid.

A general reading of the book suggests how much has been accomplished on the basis of classical electromagnetism, a matter of great importance when a subject is being brought before graduate students about to begin a course of research. A fair proportion of space is reserved for experimental matters, though these tend to make less interesting reading than the rest.

Physical chemists will be glad to find a chapter devoted to their special needs, which includes an adequate description of the liquid state.

Even allowing for war-time conditions, the book is not very well produced : its price, however, is moderate enough to allow libraries to obtain a copy, even in these days.
F. I. G. R.


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    ${ }^{11}$ Lewis and Price, ibid., 1929, 26, 638.

[^12]:    ${ }^{1}$ Brockway and Jenkins, J.A.C.S., 1936, 58, 2036.
    ${ }^{2}$ Pauling and Huggins, Z. Krist., 1934, 87, 205.
    ${ }^{3}$ Calingaert and Soroos, J. Org. Chem., 1938, 2, 535.
    ${ }^{4}$ de Laszlo, Proc. Roy. Soc., A, 1934, 146, 672.

[^13]:    ${ }^{5}$ Schomaker and Degard, J.A.C.S., in press.

[^14]:    ${ }^{2}$ Quincke, Z. physikal. Chemn., 1889, 3, 164.
    ${ }^{3}$ Lévy and Rrackway, J. Amer. Chem. Soc., 1937, 59, 2055.

[^15]:    4 Pauling, The Nature of the Chemical Bond, Cornell, 1939, p. 240.
    $\dagger$ In reference to the resonance between the one-electron link forms and the Lewis structures, Davidson points out that from considerations of the appropriate valence bond wave-functions, the single-electron link structures are merely linear combinations of the Lewis structures and certain unstable "long-bond " structures, hence they are not independent structures and they do not really increase the stability of the molecule.

[^16]:    8 Palmer and Elliott, J. Amer. Chem. Soc., 1938, 60, 1852.
    ' Bauer, ibid. 1937, 59, 1096.

[^17]:    ${ }^{10}$ Siegbahn, "Spektroskopie der Rōntgenstrahlen," Berlin, 193x.
    ${ }^{11}$ Beutler, Z. Physik, 1933, 86, 710; Beutler and Guggenheimer, ibid., 1933. 87, 176.

[^18]:    ${ }^{1}$ For references, see Bowden and Agar, Ann. Reports, 1938, 35, 90. Out of the many individual papers on hydrogen overvoltage, the work of Baars, Sitzungsber. Ges. Beförd. Naturwiss. Marburg, 1928, 63, 213 , is particularly notewortly as constituting an extremely thorough experimental survey of the whole subject.
    ${ }^{2}$ See Newbery, J. Chem. Soc., I916, 109, 1051, Iro7, for a compilation of early commutator results. Ferguson, Trans. Amer. Electrochem. Soc., 1939, 76, preprint I4, gives a useful discussion of the difficulties inherent in the commutator method.
    ${ }^{3}$ Hickling, Trans. Faraday Soc., 1937, 33, 1540.
    ${ }^{4} \mathrm{HCl}$ was chosen as electrolyte since it is convenient for use in non-aqueous solutions in which it is hoped later to obtain comparable results.

[^19]:    - For further details, see Hickling. ${ }^{3}$
    ${ }^{7}$ A full study of the decay of hydrogen overvoltage is to be made later.

[^20]:    : Z. physikal. Chem., 1905, 50, 64 I .
    ${ }^{10}$ See, for example, Newbery, $J$. Chem. Soc., 1916, 109, 1052 ; Harkins and Adams, J. Physical Chem., 1925, 29, 205.
    ${ }^{11}$ Baars, loc. cit. ${ }^{1}$; Masing and Laue, Z. physikal. Chem., 1936, 178, x ; see also Knort and Schwartz, Z. Elektrochem., 1934, 40, 38; Z. physikal. Chem., 1936, 176, 161.
    ${ }^{12}$ St. von Náray-Szabó, ibid., 1937, 178, 355.

[^21]:    ${ }^{13}$ Glasstonc, Ann, Reports, 1937, 34, 107.
    ${ }^{14}$ See Bowden and Agar (loc. cit.) for a modified form of the equation.
    ${ }^{15}$ Kabanov, Acla Physicochim. U.R.S.S., 1936, 5, 193.
    ${ }^{16}$ Centnerszwer and Straumanis (Z. physikal. Chem., 1925, 18, 438) reported that the overvoltages of metals tended to constant values at current densities greater than $0.075 \mathrm{amp} . / \mathrm{sq} . \mathrm{cm}$. This conclusion, however, rested on the direct plotting of current density against overvoltage which normally, of course, gives a curve. Replotting their results against log current density reveals only slight curvature, and their range of current density is inadequate for any significance to be attached to this. The same criticisms apply to the work of Knobel, Caplan and Eiseman (Trans. Amer. Electrochem. Soc., 1923, 43, 55) who recorded that the overvoltages of metals tended towards a constant value of $1 \cdot 3$ volts at high current densities; these investigators, moreover, adopted the somewhat arbitrary procedure of electrolysing for I minute at each current density and then reading the potential.

[^22]:    ${ }^{17}$ Kabanov (loc. cit. ${ }^{15}$ ) claimed that Tafel's equation applied accurately to silver, amalgamated silver, and platinum up to current densities of the order of $100 \mathrm{amp} . / \mathrm{sq} . \mathrm{cm}$. ; a careful examination of his work, however, shows it to be open to very strong criticism. He used the direct method of potential measurement, and corrected for the resistance error by subtracting from the observed overvoltages amounts determined by calculations involving the current density, the specific resistance of the electrolyte, the distance between cathode and reference electrode, and the diameter of the cathode. At high current densities the magnitude of these corrections was sometimes of the same order as, or greater than, the overvoltage. This procedure totally ignores the fact that most of the resistance error arises in the diffusion layer on the cathode surface in which the resistance may be quite different from that in the body of the electrolyte. No mention was made of the period of polarisation which elapsed before individual measurements were taken.
    ${ }^{18}$ For a very pertinent criticism of the value of $b$ as a criterion of the truth of the modern theory of overvoltage, see Adam, The Physics and Chemistry of Surfaces, r938, pp. 325-333.
    ${ }^{10}$ Bowden and Rideal, Proc. Roy. Soc. A, 1928, 120, 59, 80 ; Bowden, ibid., 1929, 126, 107; Bowden and Stout, and Bowden and Price, quoted in Ann. Report, 1938. It is noteworthy that these workers do not comment on any complications due to the variation of overvoltage with time except in the case of smooth platinum.
    ${ }^{20}$ Knorr and Schwartz, loc. cit. ${ }^{11}$

[^23]:    ${ }^{1}$ C. Smithells and Ransley, Proc. Roy. Soc., A, 1935, 150, 172.
    ${ }^{2}$ C. Post and W. Ham, J. Chem. Physics, 1938, 6, 599.
    ${ }^{3}$ C. Wang, Proc. Camb. Phil. Soc., 1936, 32, 657.
    ${ }^{4}$ R. M. Barrer, Trans. Faraday Soc., 1939, 35, 628.
    ${ }^{3}$ R. M. Barrer, Phil. Mag., 1939, 28, 148.

[^24]:    ${ }^{6}$ A. Sieverts and W. Danz, Z. physik. Chem., 1936, 34B, 158.

[^25]:    * From data of Edwards?
    ${ }^{7}$ C. Edwards, J. Iron and Steel Inst., 1924, 15, 9.
    ${ }^{8}$ Borelius and Lindblom, Ann. Physih, 1927, 82, 201.
    ${ }^{\circ} \mathrm{C}$. Smithells, Gases and Metals (Chapman and Hall), 1937.
    ${ }^{10}$ R. Barrer, this paper; also Phil. Mag., 1939, 28, 353.

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    ${ }^{24}$ A. Coehn and Sperling, Z. Physik, 1933. 83, 291.

[^27]:    ${ }^{1}$ G. Gouy, Ann. Chim. Physique, 1903, (7), 29, 148.

    * For use with a different form of electrocapillary cell, a modification of the commutator method of determining polarisation, employing an intermittent thermionic shunt, has been developed in this laboratory. The use of thermionic valves in this type of potential measurement was introduced by Hickling, Trans. Faraday Soc., 1937, 33, 1540.
    ${ }^{2}$ V. Kemula and E. Beer, Roczniki Chem., 1936, 16, 259.
    ${ }^{3}$ O. Gatty and E. C. R. Spooner, The Electrode Potential Behaviour of Corroding Metals in Aqueous Solutions, 1938, p. I10.
    *G. Gouy, Ann. Chim. Physique, 1903. (7), 29, 155.

