No. 228.

Transactions of the Faraday Society.

FOUNDED 1903.

TO PROMOTE THE STUDY OF ELECTROCHEMISTRY, ELECTROMETALLURGY, CHEMICAL PHYSICS, METALLOGRAPHY, AND KINDRED SUBJECTS.

Vol. XXXVI. Part 4. APRIL, 1940. 5s.

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STUDIES IN MEMBRANE PERMEABILITY. II. THE ADSORPTION OF SUCROSE AND TWO SALTS ON CUPRIC FERROCYANIDE.

By B. C. McMahon, E. J. Hartung and W. J. Walbran.

Received 13th November, 1939.

The adsorption of solutes by cupric ferrocyanide is of interest in regard to the composition of the precipitated material and to its properties as an osmotic membrane, but relatively little work with any claim to accuracy has been devoted to the question. The investigations of Tinker in 1916 [1] merely showed that dried cupric ferrocyanide removed water preferentially to sugar from an aqueous sucrose solution. One of the present authors in 1919 [2] gave careful measurements on the adsorption of KCl and K_2SO_4 from aqueous solution by the precipitated gel which showed that K_2SO_4 was definitely adsorbed to a greater extent than KCl, and this result was correlated with the greater diffusibility of the chloride through the cupric ferrocyanide membrane. These otherwise very consistent measurements are unreliable at low concentrations, owing to the presence of residual salt in the washed gel. H. B. Weiser in 1930 [3] published analyses of solutions in which cupric ferrocyanide had been precipitated from aqueous $CuCl_2$ by $K_4Fe(CN)_6$, $Na_4Fe(CN)_6$ and $H_4Fe(CN)_6$ from which the extent of adsorption of the precipitant was inferred. As a typical case, free $K_4Fe(CN)_6$ did not appear in solution until the molar ratio of excess $K_4Fe(CN)_6$ to $Cu_2Fe(CN)_6$ in the precipitate was about 0·4, which Weiser regarded as irreversible adsorption of the precipitant on pure $Cu_2Fe(CN)_6$, while subsequent molar ratios up to 0·8 in solutions containing excess soluble $K_4Fe(CN)_6$ were classed as due to reversible adsorption. These ratios were lower for $Na_4Fe(CN)_6$ and for $H_4Fe(CN)_6$ but were still large. Experiments with K_2SO_4 and $CuCl_2$ on material precipitated by $H_4Fe(CN)_6$ indicated small positive adsorptions in each case. A similar point of view is shown in a later paper [4] using cupric ferricyanide an adsorbent.

It is, however, unusual to class composition changes of such magnitude, other than those due to hydration of gels, as demonstrating adsorption. Much work has been done on the composition of precipitated cupric and other ferrocyanides [5] from which it seems clear that these substances form solid solutions very readily with soluble ferrocyanides, and the composition of these solid solutions varies, as one would expect, with the composition of the liquid phase from which they separate. Moreover, the work of Messner [6] and of Reihlen and Zimmermann [7] makes it clear that part of the copper in $Cu_2Fe(CN)_6$ is in the anionic

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[1] F. Tinker, *Proc. Roy. Soc., A*, 1916, **92**, 357 ; 1917, **93**, 266.

[2] E. J. Hartung, *Trans. Faraday Soc.*, 1920, **15**, 160.

[3] H. B. Weiser, *Coll. Symp. Ann.*, **7**, 275 ; *J. physic. Chem.*, 1930, **34**, 335.

[4] H. B. Weiser, *ibid.*, 1826.

[5] E. Müller, Wegelin and Kellerhoff, *J. prak. Ch.*, 1912, (2), **86**, 82.

[6] Messner, *Z. anorg. Chem.*, 1895, **8**, 368 ; **9**, 126.

[7] H. Reihlen and W. Zimmermann, *Annalen*, 1927, **451**, 75.

form, so that the salt should be formulated $Cu[CuFe(CN)_6]$. This is borne out by the X-ray analysis of Keggin and Miles [8] which indicates that the structure is probably akin to Prussian blue, with alternate bivalent copper and iron atoms occupying the corners of a cubic lattice and cyanogen groups along the edges. The position of the bivalent copper cations is doubtful. One might suppose them to occupy the centres of alternate cubical cells, but Fordham and Tyson,[9] whose electron diffraction studies confirm completely the cubical lattice with 5 A. spacing, were not able to find them at all. They believe, however, that they cannot lie in these positions without giving rise to diffractions of an intensity too great to be overlooked. Nevertheless, these cations must be somewhere in the lattice, and it is possible that they may be distributed statistically to give a pseudo-cubic symmetry, in conformity with other known cases. Definite crystalline compounds of the type $M^{\cdot\cdot}[CuFe(CN)_6]''$ are known in which M is an alkaline earth metal and where one may reasonably assume complete replacement of cationic copper. Complete replacement by Na or K would involve filling the centres of all cells as in the Prussian blues, and this appears also here to have been attained.[6] One may therefore regard precipitated cupric ferrocyanide as exhibiting partial replacement of this kind, and not adsorption of one ferrocyanide in very large amount on another. The X-ray evidence adduced by Weiser, Milligan and Bates [10] in support of adsorption does not conflict with the view given above. These authors assume that either adsorption or double-salt formation takes place; they do not consider the possibility of solid solution, and rule out double-salt formation on the ground that their X-ray photographs show no special structure to be developed in gels containing much alkali ferrocyanide. But their diffraction patterns of gels precipitated by $K_4Fe(CN)_6$ at different excess concentrations, and by $H_4Fe(CN)_6$, are identical, thus showing that their method is unable to distinguish between cationic copper, potassium and hydrogen.

Precipitation of cupric ferrocyanide in the continuous presence of excess cupric ions excludes adsorption of ferrocyanide ions, yet the gel so prepared may contain much firmly bound alkali ferrocyanide. On washing it peptises ultimately due to cationic loss to the solution, forming the usual negative sol; this is promoted by addition of soluble ferrocyanide, due to true adsorption. We have found that the gel prepared from excess $CuAc_2$ and the acid itself cannot be peptised by washing, although it contains some excess of ferrocyanic acid over the stoichiometric ratio, yet a slight concentration of the acid or a soluble ferrocyanide peptises the washed gel at once as the anions are adsorbed. It is evident therefore that soluble ferrocyanides are unsuitable solutes for adsorption work with cupric ferrocyanide because of their solid-solution forming propensity. The present work was undertaken to afford accurate data for sucrose and two salts for which reliable diffusion data through a cupric ferro-cyanide membrane are also available.[11] Great pains were taken in regard to analytical procedure and purity of reagents, and distilled water was prepared in silica.

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[8] J. F. Keggin and F. D. Miles, *Nature*, 1936, **137**, 577.
[9] S. Fordham and J. T. Tyson, *J. Chem. Soc.*, 1937, 483.
[10] H. B. Weiser, W. O. Milligan and J. B. Bates, *J. physic. Chem.*, 1938, **42**, 945.
[11] E. J. Hartung, F. H. Kelly and J. Wertheim, *Trans. Faraday Soc.*, 1937, **33**, 398.

Experimental.

Cupric ferrocyanide was prepared by precipitating excess of $CuAc_2$ solution with aqueous $H_4Fe(CN)_6$, the acid being made by the method of Cumming.[12] As the gel so made could not be peptised by washing, all soluble matter was conveniently removed from it by centrifuging. This behaviour rendered subsequent separation from sucrose solutions relatively easy, whereas the gel prepared from alkali ferrocyanide peptises before soluble electrolytes are completely removed and then cannot be separated from sucrose solutions without altering the composition of the latter. After much preliminary work we selected the gel made from ferrocyanic acid and at least 10 % excess of copper acetate, and have used it exclusively. It was stored in distilled water at room temperature and appears then to keep indefinitely. After vigorous shaking, the turbid suspension could be sampled with a wide-mouthed pipette with less than 0·1 % variation. Analysis proved difficult, the method adopted finally being to determine the Cu/Fe ratio gravimetrically. Different batches of gel agreed closely in giving this ratio as 2·20 ($Cu_2Fe(CN)_6$ requires 2·28) indicating that the material contained 3·6 moles $H_4Fe(CN)_6$ per 100 moles of $Cu_2Fe(CN)_6$. For comparison, the gel made from alkali ferrocyanide and 25 % excess copper salt gave after complete washing a Cu/Fe ratio of 2·06, indicating 10·4 moles of $K_4Fe(CN)_6$ per 100 moles of $Cu_2Fe(CN)_6$.

Adsorption of Sucrose.

Measurements were performed in the usual way in stoppered capped 100 c.c. glass tubes rotated for two days (an ample time) in a thermostat at 25°. After centrifuging, the clear liquid was in part removed and the pipette washed back into the tube. The sucrose was determined with the Zeiss interferometer, and then more sucrose and water added to the tube for a new experiment, the synthetic composition of the tube contents being controlled entirely by weight. Ascending and descending concentration series were performed on the same tubes, and each experimental point was determined in quadruplicate with four different tubes and often different batches of gel. This method of working is convenient, but may introduce cumulative errors. However, the ascending and descending series agreed very well, particularly at the lower concentrations, thus indicating the practical reversibility of the phenomena and the dependability of the experimental results. The ratio of gel (estimated as dry material) to water was always maintained constant at 4·6 % ; it is difficult to work with higher ratios than this owing to the pasty nature of the systems.

Adsorption of NaCl and Na_2SO_4.

The general procedure for each salt followed closely that for sucrose, and the same gel-water ratio was always maintained. In spite of all care, however, the results are definitely less concordant. Moreover, a slight amount of cationic displacement of Cu from the gel by Na was observed, the maximum concentration of $Cu^{\cdot\cdot}$ ever appearing in solution being about 40 mg. per litre but usually very much less was present. As appreciable errors might have been introduced, the Cu was determined in the withdrawn sample colorimetrically, and a compensating amount added to the tube for the next determination to avoid cumulative loss of Cu, the interferometer readings being also corrected. Numerous experiments with variation of procedure indicated that only a very small amount of copper may be displaced in this way, and that the exchange takes place largely at the start of a series of measurements with the same material. Individual

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[12] Cumming, *J. Soc. Chem. Ind.*, 47, 84.

experiments on tubes of fresh gel instead of series with the same tubes were performed, but this method, besides being very wasteful of time and material, afforded no greater concordance in results. It is possible that cationic exchange may affect the adsorptive powers of the gel for anions but prolonged investigation has failed to afford any positive evidence for this. This applies also to those cases where a second form of cupric ferrocyanide appeared in some of the tubes (as described later). Very early changes in adsorptive power may take place after addition of salt to the gel, but we have not been able to devise any method for proving this with cupric ferrocyanide systems where adsorption equilibrium is rapidly attained. In no case was anionic exchange noted.

Adsorption of NaCl and Na_2SO_4 in Presence of Sucrose.

These experiments were undertaken in the hope of using sucrose as a reference substance to determine the hydration of the gel. A special form of weight pipette enabled samples to be taken from the tubes so that the total sample could be accurately weighed. Chloride was estimated volumetrically and sulphate gravimetrically after due investigation of the errors involved. Sucrose was determined with the interferometer by matching in each case with comparison solutions in which the concentrations of the other solutes were maintained at the predetermined analytical values. The sucrose-water ratio was always 5 %.

Discussion of Results.

The results of the experiments with sucrose alone are shown in Fig. 1, where increase in concentration of the solution over the synthetic sugar—total water ratio (in mg. per 100 g. water) is plotted against the equilibrium concentration of sucrose (in g. per 100 g. water). Each point on the graph represents the mean of 4 determinations on different tubes, which were usually so closely concordant that they could not be shown apart on the scale of the curve, and three different batches of gel are represented. It will be seen that adsorption is always negative, that the curve shows excellent linearity and passes through the origin. Without making artificial and unlikely assumptions as to the way in which sucrose adsorption may vary with concentration, the only interpretation of these results is that the bound water of the gel (*i.e.*, water unavailable to sucrose) is constant and that there is no sucrose adsorption at all. It is at first sight remarkable that the bound water should not vary with sucrose concentration, *i.e.*, with change in the activity of the water in solution. So far as we are aware, such behaviour is quite exceptional (see the review by Briggs [13]). The difficulty is removed if we consider the bound water to consist of two parts—a small amount of truly adsorbed or polarised water on the surface or even in the structure of the gel crystallites, and a larger amount of imbibed water between them. If all of this bound water is out of reach of the sucrose, which is likely since even very thin membranes of cupric ferrocyanide are impermeable to sucrose, calculation from the curve shows that 10·6 moles of water are bound by one mole of $Cu_2Fe(CN)_6$. Such a degree of hydration is more characteristic of hydrophilic than of electrocratic sols of this type. Moreover, it is impossible to find room for such a large amount of water in the $Cu_2Fe(CN)_6$ lattice, or even on its surface by polarised adsorption, and it is likely that most of it is merely imbibed by the gel, being thereby excluded from the large sugar molecules in the same way that water in

[13] D. R. Briggs, *J. physic. Chem.*, 1932, 36, 367.

swollen gelatine may be excluded to colloidal particles of suitable size. It is then understandable that the polarised water in the gel may vary with sucrose concentration as one would expect, although the total polarised and imbibed water remains independent of it because this bound water is in effect determined in the gel by spatial considerations.

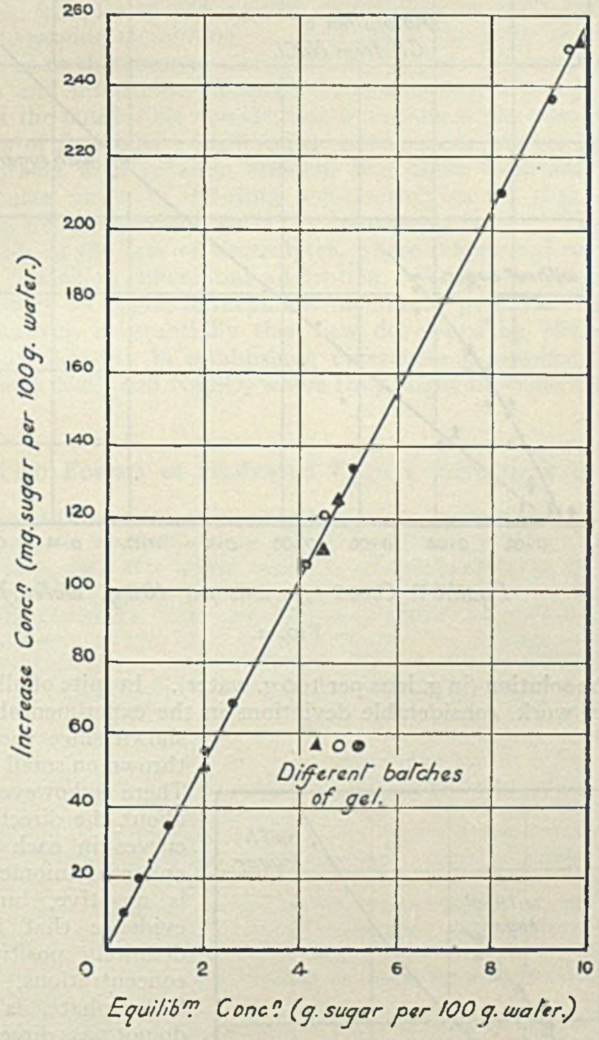

FIG. 1.

If this argument be correct however, sucrose cannot be used with security to measure the amount of bound water in the gel in relation to other solutes. For if these solutes are able to penetrate the cupric ferrocyanide membrane, it is likely that the imbibed water may be available to them although not to sucrose. Indeed the results for NaCl and Na_2SO_4 with and without sucrose in solution give some indication that this is the case.

In Figs. 2 and 3 respectively are plotted for NaCl and Na_2SO_4 increase in concentration of the solution over the synthetic concentration (in mg. ions per 100 g. water) with and without sucrose present in fixed concentration of 5 g. per 100 g. water against the equilibrium concentration of the solution (in g. ions per 100 g. water). In spite of all care in the analytical work, considerable deviations in the experimental points are shown since the errors are thrown on small differences. There is, however, no doubt about the directions of the curves in each case. The apparent anionic adsorption is negative, but there is evidence that it becomes definitely positive at low concentrations, especially for sulphate, as the curves do not pass directly through the origin. It is also evident that the presence of sucrose diminishes the negative anionic adsorption in each case, but it is possible to account for this by supposing that sucrose diminishes the polarised water on the gel owing to the lowered activity of the water in the solution while the imbibed water is available to the ions

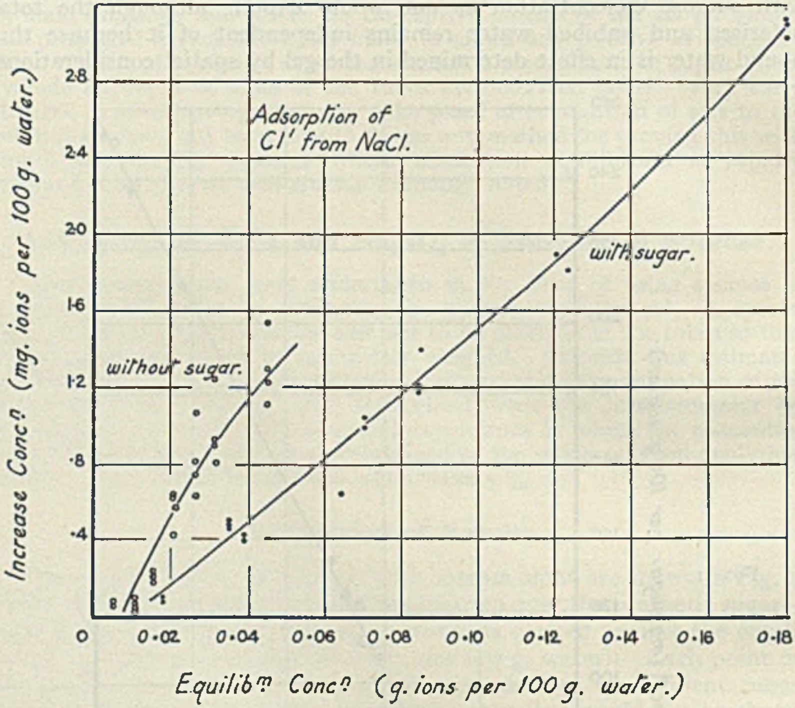

FIG. 2.

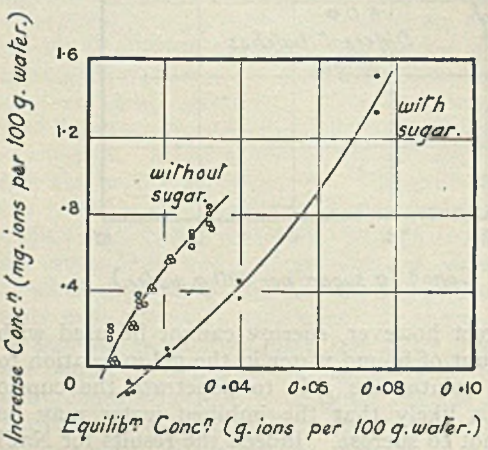

FIG. 3.

of the salts, which one would expect owing to their ready penetration of the gel membrane.

The negative adsorption of NaCl and Na_2SO_4 is in marked contrast with the results obtained by one of us[2] for KCl and K_2SO_4 on the gel prepared from $K_4Fe(CN)_6$ which showed pronounced positive adsorption. No significant differences in adsorption between NaCl and Na_2SO_4 have been found, in spite of the greater diffusibility of NaCl through the cupric ferrocyanide membrane, in one case in the ratio of 4·5 to 1.[11] Our results show therefore no connection in the case of these salts between adsorption and diffusibility through the membrane, although they indicate that the indiffusible non-electrolyte sucrose is not adsorbed at all. The results of Collander[14] with cupric ferrocyanide and of Michaelis[15] and co-workers with celloidin indicate that these membranes behave like molecular sieves to diffusing non-electrolytes, so that molecular diameter in relation to pore size is the dominating factor. The problem is less simple in the case of electrolytes, where differential permeability to ions is related to differential adsorption. Work now in progress in this laboratory on cupric ferrocyanide membrane potentials in presence of salts confirms substantially this view developed by Michaelis,[16] in spite of our difficulty in establishing differences in adsorption experimentally with NaCl and Na_2SO_4 where they might be expected on other grounds.

Two Forms of Hydrated Cupric Ferrocyanide.

As some of the experiments with the salt solutions in contact with the gel progressed, it was noted that the gel showed a tendency to separate on centrifuging into two layers which in certain cases were very distinct and striking. The upper layer was light reddish-brown and the lower the original deep chocolate. The pale form appeared to be more finely divided than the other; it was more easily dispersed on shaking and peptised readily on washing but did not change colour again on coagulation with $CuSO_4$. Separation of the two layers for analysis was fairly easily accomplished and the Cu/Fe ratio was determined for each. The average value for the pale material was 2·18 and for the dark 2·17 while that of the original was 2·20 to 2·21. Both show therefore loss of Cu which, as before stated, was found in solution but the analytical differences are trifling in view of the great alteration in appearance. We were also unable to detect any certain differences in adsorptive power between the two forms and have not yet succeeded in discovering their nature. Ionic exchange cannot be responsible for the formation of the pale variety for we have sometimes found it in sucrose solutions in the absence of electrolytes. Little difference in hydration of the two forms can be detected; both become lighter in colour on drying, the pale form being then yellow, but the original appearance returns in each case on hydration in moist air and the differences in colour persist.

If the dry yellow form be exposed to benzene or ether vapour, or wetted with the liquids, it rapidly becomes deep indigo, the colour being roughly complementary to that of the dry material. This change is reversible and can be induced repeatedly. Preliminary experiments give some indication that the indigo material is a new phase, as judged from benzene vapour pressure measurements in contact with it, and the matter is now being further investigated.

[14] R. Collander, *Kolloidchem. Beihefte*, 1924, **19**, 72.

[15] L. Michaelis, *Coll. Sym. Monog.*, 1928, **5**, 135.

[16] Ibid., *J. gen. Physiol.*,. 1925, **8**, 33.

Summary.

1. Careful measurements of the adsorption of hydrated cupric ferrocyanide for sucrose and for NaCl and Na_2SO_4, alone and in presence of sucrose, have been performed.

2. The apparent adsorption of sucrose is negative and results indicate that no sucrose is adsorbed by the gel, the hydration of which remains constant, independent of sucrose concentration.

3. This bound water is regarded as being partly polarised on the gel surface and partly imbibed between the crystallites. Only the former depends on the activity of the water in the solution.

4. NaCl and Na_2SO_4 are also negatively adsorbed, but at low concentration there is evidence of positive adsorption. Slight cationic exchange occurs between the gel and the salts, but no anionic exchange has been detected.

5. In presence of sucrose, the negative adsorption of the salts is diminished, indicating that the imbibed water may be available to the ions though not to sucrose. Hence sucrose cannot be used to measure the hydration of the gel in presence of the salts.

6. A new form of cupric ferrocyanide is recorded.

We wish to record our thanks to Dr. E. Heymann and Dr. J. S. Anderson for very helpful discussion.

Chemistry Department,
University of Melbourne.

THE CATALYTIC EXCHANGE OF HYDROGEN ATOMS BETWEEN MOLECULAR DEUTERIUM AND PROPANE AND BUTANE.

By A. Farkas.

Received 30*th November*, 1939.

Examples of the catalytic exchange of hydrogen atoms between molecular hydrogen and saturated hydrocarbons were first given by Taylor and his collaborators.[1, 2] According to these authors, methane, ethane and propane will exchange on a nickel-kieselguhr catalyst at temperatures above 180°, 110° and 65° C. respectively at pressures around half an atmosphere, within some hours. Later it was shown by Farkas and Farkas [3] that both cyclohexane and *n*-hexane will undergo exchange reactions on a platinum catalyst at temperatures slightly above room temperature. The present paper refers to experiments on the exchange of propane and butane on the same type of catalyst.

Experimental Method.

The experimental arrangement was the same as used in previous investigations.[4] It consisted of a reaction vessel containing a platinised platinum foil catalyst (10 × 18 mm.), a U-tube cooled to − 40° to − 80° C.

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[1] Morikawa, Benedict and Taylor, *J. Am. Chem. Soc.*, 1936, **58**, 1445, 1795.

[2] Morikawa, Trenner and Taylor, *ibid.*, 1936, **59**, 1103.

[3] Farkas and Farkas, *Trans. Faraday Soc.*, 1939, **35**, 917.

[4] Farkas and Farkas, *J. Am. Chem. Soc.*, 1938, **60**, 22.

and a mercury manometer. The butane used was prepared by hydrogenating *n*-butene, which in turn was prepared from *n*-butyl alcohol. The propane was obtained by hydrogenating acetone.[5] In one experiment ethane was used. It was produced from ethylene by hydrogenation.

Exchange of Butane.

A typical exchange experiment (No. 11) between 16 mm. butane and 30 mm. deuterium at 67° is shown in Fig. 1, curve 11. In the first 40 minutes of the experiment the butane was condensed in a side tube. The absence of any decrease in the D-content indicated clearly that the catalyst did not contain appreciable amounts of light hydrogen. As soon as the butane was evaporated, a rapid exchange set in, and the D-content of the heavy hydrogen fell in 33 minutes from 96 % to 18 %.

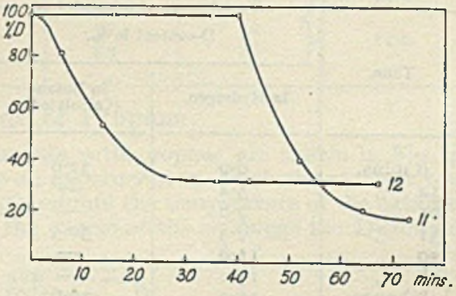

Fig. 1.

Expt. 11 : 16 mm. Butane + 30 mm. D_2 at 67° C.
Expt. 12 : 14 mm. Butane (29% D) + 20 mm. D_2 at 66° C.

Allowing for the relative amounts of hydrogen and butane in the reaction mixture and assuming that all ten hydrogen atoms of the butane molecule participate in the exchange, a D-content of 29·4 % in the butane can be calculated from the decrease of the D-content in the heavy hydrogen. This figure corresponds to a distribution ratio of

$$(H/D)_{\text{hydrogen}} \cdot (D/H)_{\text{butane}} = \frac{82}{18} \cdot \frac{29{\cdot}4}{70{\cdot}6} = 1{\cdot}89$$

which agrees with that derived from theoretical considerations[6] and from exchange experiments with other hydrocarbons.[2, 3] This proves that in fact all hydrogen atoms of the butane molecule participate equally in the exchange.

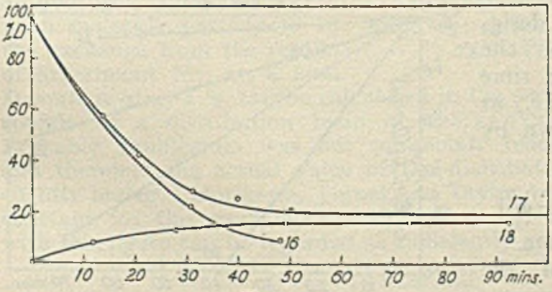

Fig. 2.

Expt. 16 : 28 mm. Butane + 28 mm. D_2 at 26° C.
Expt. 17 : 27 mm. Butane (18% D) + 27 mm. D_2 at 26° C.
Expt. 18 : 27 mm. Butane (34% D) + 19 mm. H_2 at 26° C.

In experiment No. 12, 14 mm. butane containing 29 % D obtained in the above experiment was brought into contact with 20 mm. fresh D at 66° C. As shown by curve 12 in Fig. 1, the exchange proceeded at a similar speed as in the previous experiment. These experiments proved definitely that the observed exchange involved actually butane and not butene, which might be said to have been contained in it as impurity, as any such butene would have been hydrogenated in the previous experiment. The final D-

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[5] Farkas and Farkas, *J. Am. Chem. Soc.*, 1939, 61, 1336.

[6] Wirtz, *Z. Elektrochemie*, 1937, 43, 662.

content of 31 % in the heavy hydrogen corresponds to a D-content of 48 % in the butane and to a distribution ratio of 69/31 . 48/52 = 2·05, which is very close to the value given above.

On a freshly platinised catalyst (Expt. No. 16) a rapid exchange occurs at room temperature, as is shown by Fig. 2. Curve 16 represents the interaction of 28 mm. of butane and 28 mm. of deuterium (96 % D) and curve 17, that of 27 mm. deuterium (97 %) and 27 mm. of butane containing 18 % D obtained in the previous experiment. In experiment No. 17, the D-content in the heavy hydrogen fell to 17·5 % after 19 hours, at which time the equilibrium must have been reached. As in the course of this exchange the D-content of the butane rose to 34 %, the equilibrium corresponds to a distribution ratio of

82·5/17·5 . 34/66 = 2·43.

TABLE I.

TABLE I.—Expt. 19, 21 mm. H_2 + 26 mm. Butane Containing 32 % D. Temperature 26° C.

Time.	D-content in %.	
	In Hydrogen.	In Butane (Calculated).
0 mins.	0·0	32·0
14 ,,	5·4	—
21 ,,	7·8	—
31 ,,	9·3	30·5
50 ,,	11·8	—
78 ,,	13·0	—
48 hours	15·0	29·6

In experiment No. 18, 27 mm. butane containing 34 % D were brought into contact with 19 mm. H_2. In the first 35 minutes the butane was condensed in a side tube and during this time no increase in the D-content appeared in the hydrogen. The progress of the exchange reaction after the evaporation of the butane is shown by curve 18, Fig. 2.

The progress of experiment No. 19 is shown in Table I. The equilibrium corresponds to a distribution ratio of 85/15 . 29·6/40·4 = 2·38.

The progress of the exchange reaction with time can be satisfactorily represented by the formula

$$D_t - D_\infty = (D_0 - D_\infty)\, e^{-kt} \quad . \quad . \quad . \quad (1)$$

where D_0, D_t and D_∞ designate the D-content of the heavy hydrogen at the time $t = 0$, t and $t = \infty$ (*i.e.*, at equilibrium), as is shown by Fig. 3, in which

$$\log [D_t - D_\infty]/(D_0 - D_\infty)]$$

is plotted against the time.

The dependence of the rate of exchange on temperature is shown in Table II for three series of experiments. The half periods of exchange listed in this table were determined on the basis of formula (1). The apparent energy of activation of the exchange reaction as calculated from its dependence on temperature is 26·3 k.cal. in the temperature region 26°-41° C. and falls to 11·0 k.cal. at 77°-95° C.

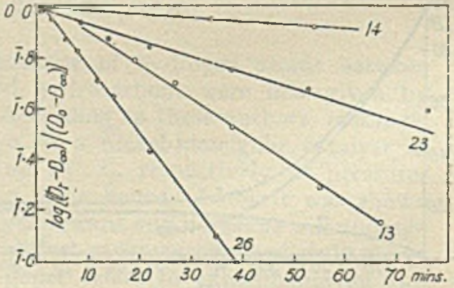

FIG. 3.

Expt. 13: 28 mm. Butane + 29 mm. D_2 at 41° C.

Expt. 14: 22 mm. Butane + 25 mm. D_2 at 26° C.

Expt. 23: 17 mm. Propane (27% D) + 29 mm. D_2 at 51° C.

Expt. 26: 32 mm. Butane + 33 mm. D_2 at 72° C.

TABLE II.

No.	Deuterium (mm.).	Butane (mm.).	Temp. (°C.).	Half Period (mins.).	Energy of Activation (k.cal.).
13	29	28	41	25	26·3
14	25	22	26	210	
14*a*	25	22	59	10·5	17·9
28	26	26·5	27	120	15·7
27	26	26	52	16	
40	22	21	77	32	11·0
39	20	21	95	16	

Exchange of Propane.

Two typical exchange experiments with propane are shown in Fig. 4. Curve 21 (Expt. No. 21) refers to an experiment in which the catalyst was in a very active state. In the 64th minute the temperature of the catalyst was raised from 26° to 53°. In the course of the exchange the D-content of the hydrogen fell from 98 % to 15·2 %. Curve 25 represents an experiment (No. 25) carried out at 73° on the same catalyst in a somewhat less active state. It will be seen that while the decrease in the D-content was very slight in the course of the first 37 minutes, during which the propane was kept condensed in a side tube, a rapid exchange set in as soon as the propane was admitted to the deuterium in the reaction vessel.

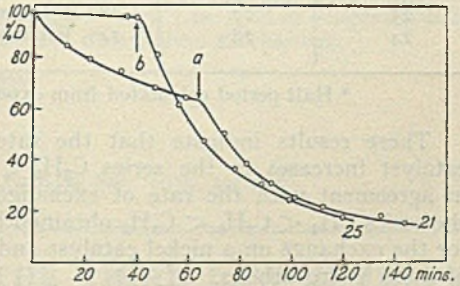

Fig. 4.

Expt. 21: 17·5 mm. Propane + 23 mm. D_2. At *a* the temperature was raised from 26 to 53° C.

Expt. 25: 28 mm. Propane + 27 mm. D_2 at 73° C. Propane added at *b*.

If it is assumed again that all hydrogen atoms in the propane molecule participate in the exchange from the results of experiment No. 21, a final D-content of 27·2 % can be calculated in the propane. This figure corresponds to a distribution ratio of $84{\cdot}8/15{\cdot}2 \cdot 27{\cdot}2/72{\cdot}8 = 2{\cdot}08$ at 53°. Probably equilibrium was not completely reached in this experiment and therefore the actual value of the distribution coefficient should be slightly higher. Morikawa, Turner and Taylor [2] found for the equilibrium constant for this exchange reaction $K = 2{\cdot}57$ at 80°. The agreement with this figure can be regarded as sufficiently good.

TABLE III.

No.	Deuterium (mm.).	Propane (mm.).	Temp. (°C.).	Half Period (mins.).	Energy of Activation (k.cal.).
21	23	21·5	26	90	11·6
21*a*	23	21·5	53	18	
31	22	19	40	160	10·2
31*a*	22	19	73	33	
38	22	24	97	67	8·8
37	21	20	126	28	

The dependence of the rate of exchange on temperature is given in Table III, together with the energies of activation. It is possible that in experiment 21, some deactivation of the catalyst occurred by heating it to 53°, so the obtained energy of activation appears smaller than it actually is.

The rate of exchange of propane has been compared with that of butane at 26° and 95°, and with that of ethane at 72°. The results obtained are listed in Table IV. It will be noted that while exchange of butane proceeds about 4 times faster in the temperature region 26° to 97° than that of propane, that of ethane is 36 times smaller.

TABLE IV.

No.	Pressure (mm.).			Temperature (°C.).	Half Period (mins.).
	Deuterium.	Hydrocarbon.			
20	19	25	Butane	26	25
21	23	21·5	Propane	26	90
38	22	24	Propane	97	67
39*	21	20	Butane	97	14·5
25	27	28	Propane	72	20
24	28	24	Ethane	72	720

* Half period calculated from experiment No. 39 at 95°.

These results indicate that the rate of exchange on a platinum catalyst increases in the series $C_2H_6 < C_3H_8 < C_4H_{10}$. This series is in agreement with the rate of exchange observed with hexane,[3] with the series $CH_4 < C_2H_6 < C_3H_8$ obtained by Taylor and his collaborators for the exchange on a nickel catalyst and also with the general stability of these hydrocarbons.

The nature of the hydrocarbon excludes the possibility of associative mechanism and the simplest mechanism for this type of exchange reaction is the dissociative mechanism

$$\begin{gathered} D_2 = 2D \\ C_nH_{2n+2} = C_nH_{2n+1} + H \\ D + C_nH_{2n+1} = C_nH_{2n+1}D, \text{ etc.} \end{gathered}$$

This mechanism was originally suggested for the exchange reaction for ethylene [4, 7] and later applied to the reaction of a number of other unsaturated and saturated hydrocarbons.[1, 2, 3, 8, 9]

In the light of the present experiments, two recent papers deserve reconsideration. The first [5] refers to the catalytic interaction of acetone and heavy hydrogen. In this reaction an exchange was observed which was attributed to a reaction involving acetone. As in the interaction of acetone and hydrogen propane is formed, one would think that in the exchange reaction actually the propane might have been involved also. A comparison of the present results with the previous experiments shows, however, that a reasonably fast exchange of propane can be found at low temperature only on a very active freshly prepared catalyst. Since the catalyst used in the experiments with acetone was only an ordinary catalyst, it would not be expected to be sufficiently active to cause an exchange with propane.

[7] Farkas, Farkas and Rideal, *Proc. Roy. Soc. A.*, 1934, 146, 630.

[8] Farkas and Farkas, *Trans. Faraday Soc.*, 1937, 33, 827.

[9] Farkas, *ibid.*, 1939, 35, 906.

In the second paper,[10] the hydrogenation and exchange of propylene and butene on a nickel catalyst is described by Twigg. He thought that the participation of all hydrogen atoms of the hydrocarbons molecules in the exchange is inconsistent with the dissociative mechanism and can be explained only by the associative mechanism. The present experiments, however, definitely establish the exchange of all hydrogen atoms in hydrocarbons of such a type that the associative mechanism cannot be operative at all.

Summary.

The exchange of hydrogen atoms between molecular hydrogen and propane and butane on a Pt catalyst has been investigated at pressures around 40 to 50 mm. at 26 to 126° C. These hydrocarbons exchange all their hydrogen atoms in a reversible manner. On a very active catalyst the exchange takes place readily at room temperature. The exchange of propane is 4 to 5 times slower than that of butane but 36 times faster than that of ethane.

The energy of activation for the exchange of butane is 26 k.cal. in the region 26°-41° C. and falls to 11 k.cal. at 77°-95° C. The energy of activation for the exchange of propane is 12·9 k.cal. It is suggested that the exchange reaction proceeds by the dissociative mechanism.

Department of Physical Chemistry,
The Hebrew University,
Jerusalem.

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[10] Twigg, *Trans. Faraday Soc.*, 1939, 35, 934.

CALCULATION OF THE THIRD LAW ENTROPY OF ETHYL CHLORIDE.

By J. W. Linnett.

Received 20th December, 1939.

A comparison of the observed values for the thermodynamic quantities, entropy and heat capacity, with those obtained by theoretical calculations has been used in attempts to determine whether or not, in certain molecules, there is free internal rotation of one part of the molecule with respect to another part. In some cases, such as that of ethane, a quite definite decision has been reached. If the entropy of ethyl chloride could be obtained and if the necessary calculations could be made, it should be possible to determine whether free rotation of the methyl group occurs in this molecule.

The third law entropy of ethyl chloride has not been determined directly, but a value should be obtainable from data on the equilibrium in the system $C_2H_5Cl = C_2H_4 + HCl$, since the entropies of ethylene and of hydrogen chloride are known with considerable certainty. Data on this system have been obtained by Rudkovskii, Trifel and Frost,[1] who studied the equilibrium over the range 170° to 230° C. The standard entropy change for this reaction may, therefore, be estimated and from it the third law entropy of ethyl chloride at 200° C. obtained.

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[1] Rudkovskii, Trifel and Frost, *Ukrain. Khem. Zhem.*, 1935, 10, 277.

For the theoretical calculation of the entropy it is necessary to know (*a*) the three principal moments of inertia of the ethyl chloride molecule, and (*b*) the fundamental vibration frequencies of the molecule. The only serious uncertainty in the dimensions of this molecule is in the carbon-chlorine distance, so that in the present paper the moments of inertia have been calculated for several values of this bond length. From the observed Raman and infra-red spectra of ethyl chloride, and by comparison with the frequencies of related molecules, it has been possible to obtain a set of fundamental vibration frequencies which are sufficiently accurate for the present purpose.

The calculation of the vibrational contribution to the entropy was made with the aid of tables compiled by Cross and Crawford, the vibrations being assumed to be of a simple harmonic character. The translational and rotational contributions were calculated using the usual formulæ, assuming the rotational levels to be fully excited. All the entropies calculated refer to the standard state.

Entropy of Hydrogen Chloride.

The third law entropy of hydrogen chloride has been determined experimentally by Giauque and Overstreet,[2] who give 44·5 cal./degree C. as the value for this quantity at 298° K. Since the internuclear distance, vibration frequency and isotopic constitution of this molecule are known very accurately the entropy may be calculated with a certainty that is greater than that of the experimental results. Taking the inter-nuclear distance as 1·272 A. and the vibration frequency as 2989 cm.$^{-1}$, the entropy is calculated to have the values listed in Table I. The figure, 44·62, for the entropy at 298° K. agrees closely with the experimentally determined value.

Entropy of Ethylene.

Smith and Vaughan [3] have calculated the entropy of ethylene, giving the value at 298° K. as 52·55 cal./degree C. In this paper the entropy has been calculated using rather different values for the constants. The moments of inertia of the ethylene molecule have been determined recently by Thompson [4] who gives the values: $33{\cdot}197 \times 10^{-40}$, $27{\cdot}48 \times 10^{-40}$, and $5{\cdot}714 \times 10^{-40}$ g./cm.^{2}. These results agree closely with the earlier values of Badger [5] determined by a quite independent method.

There is still some uncertainty regarding the vibration frequencies of ethylene. Smith and Vaughan employed the assignment suggested by Bonner.[6] In the present case the following frequencies have been used: Planar vibrations: Raman active: 3019, 1623 and 1342; 3076 and 1240; Infra-red active: 2988 and 1444; 3107 and 950; Non-planar vibrations: Raman active: 1110; Infra-red active: 940; Inactive: 740 cm.$^{-1}$. This assignment explains all the Raman and infra-red spectral data and has the advantage that it reproduces the observed heat capacities much more satisfactorily than does the assignment due to Bonner. For this reason, particularly, it has been used in the entropy

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[2] Giauque and Overstreet, *J.A.C.S.*, 1932, 54, 1742.

[3] Smith and Vaughan, *J. Chem. Physics*, 1935, **3**, 341.

[4] Thompson, *Trans. Faraday Soc.*, 1939, **35**, 697.

[5] Badger, *Physic. Rev.*, 1934, 45, 648.

[6] Bonner, *J.A.C.S.*, 1936, 58, 34.

calculations. The calculated values of the translational and rotational entropy, the vibrational entropy, and the total entropy are given in Table I. It will be noted that, in this table, the entropy at 298° K. is given as 52·41, which does not differ greatly from the value of Smith and Vaughan. In the last column of Table I are given the sums of the entropies of hydrogen chloride and ethylene at the various temperatures listed in the first column.

TABLE I.—THE CALCULATED ENTROPIES OF GASEOUS HYDROGEN CHLORIDE AND ETHYLENE.

T(°K).	S_{HCl}.	Ethylene.			$S_{HCl} + S_{C_2H_4}$.
		S_{t+r}.	S_{vib}.	S_{total}.	
273	44·01	51·08	0·47	51·55	95·56
298	44·62	51·77	0·64	52·41	97·03
323	45·18	52·51	0·86	53·37	98·55
373	46·18	53·56	1·37	54·93	101·11
423	47·06	54·56	1·97	56·53	103·59
473	47·84	55·44	2·63	58·07	105·91
523	48·54	56·24	3·33	59·57	108·11
573	49·18	56·97	4·05	61·02	110·20

Entropy of Ethyl Chloride.

The Moments of Inertia. As has been remarked previously, the difficulty that arises in the calculation of the principal moments of inertia of this molecule is the fixing of the carbon-chlorine interatomic distance. The value of this distance in methyl chloride is uncertain as has been indicated by Sutherland.[7] The distance in the ethyl compound has been determined by electron diffraction. An early determination by Brú [8] gave the internuclear distance as 1·81 ± 0·08 A., but, more recently, Beach and Stevenson [9] have re-examined the problem and give the result 1·76 ± 0·02 A. Because of this uncertainty, calculations have been made assuming the bond length to be (*a*) 1·70, (*b*) 1·75, and (*c*) 1·80 A. The carbon-carbon distance has been taken to be 1·54, and the carbon-hydrogen distance 1·093 A. All the angles have been assumed to be tetrahedral. These assumed dimensions cannot differ greatly from those existing. The results for the principal moments of inertia are: (*a*) Cl^{35} : 16·23, 95·41 and 85·60 ; Cl^{37} : 16·26, 97·24 and 87·40 ; (*b*) Cl^{35} : 16·44, 98·63 and 88·62 ; Cl^{37} : 16·46, 100·54 and 90·50 ; (*c*) Cl^{35} : 16·63, 101·93 and 91·72 ; Cl^{37} : 16·66, 103·92 and 93·68. All the above figures are given in atomic weight and Angstrom units.

The Vibration Frequencies. The infra-red absorption spectrum of ethyl chloride has been examined by Cross and Daniels.[10] At frequencies below 1500 cm.$^{-1}$ bands have been observed at ca. 750, 790, 975, ca. 1050, ca. 1090, ca. 1120, 1400 and 1455 cm.$^{-1}$. The early work on the Raman spectrum of ethyl chloride is summarised in Kohlrausch's *Smekal-Raman Effekt*. The spectrum has also been examined by Harkness and Haines.[11]

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[7] Sutherland, *Trans. Faraday Soc.*, 1938, 34, 325.

[8] Brú, *Anales soc. espan. fis quim.*, 1933, 31, 115.

[9] Beach and Stevenson, *J.A.C.S.*, 1939, 61, 2643.

[10] Cross and Daniels, *J. Chem. Physics*, 1933, 1, 52.

[11] Harkness and Haines, *J.A.C.S.*, 1932, 54, 3920.

The Raman frequencies are: 337, 438, 655, 966, 1071, 1276, 1448, 2875, 2930 and 2966 cm.$^{-1}$.

Ethyl chloride has seventeen distinct fundamental vibrations in addition to the possible torsional oscillation. Of these eighteen motions eleven may be regarded as symmetrical and seven as antisymmetrical From the available spectroscopic data it is quite impossible to make an unambiguous assignment of the fundamental frequencies. By analogy with similar molecules, however, it is possible to fix the probable magnitudes of the frequencies and then by comparison with the spectroscopic data to obtain a list of fundamental frequencies accurate enough for the present calculations.

TABLE II.

Group Vibrating.	Symmetry.	Description of Vibration.	Related Vibration of Simpler Molecules.	Approx. Frequency.
Framework	S	C—C valency	C—C valency	950
	S	C—Cl valency	C—Cl valency	700
	S	C—C—Cl deform.	C—C—Cl deform.	350
Methyl	S	C—H valency	C—H Symm. valency	2940
	S	C—H valency		
			C—H Degenerate valency	3050
	A	C—H valency		
	S	CH_3 Symm. deform.	CH_3 Symm. deform.	1350
	S	CH_3 deform.		
			CH_3 Degenerate deform.	1450
	S	CH_2 deform.		
			CH_3 Degenerate deform.	1000
	A	CH_3 deform.		
	A	CH_3 deform.		
Methylene	S	C—H valency	C—H valency (SS)*	2950
	A	C—H valency	C—H valency (SA)	3050
	S	CH_2 deform.	CH_2 deform. (SS)	1400
	S	CH_2 bending †	CH_2 bending (AS)	1100
	A	CH_2 rocking †	CH_2 rocking (SA)	1050
	A	CH_2 twisting †	CH_2 twisting (AA)	850

* The letters S and A indicate the symmetry of the vibration in the molecules of the type Y . CH_2 . Y with respect to the two planes of symmetry.

† For the significance of the terms bending, rocking and twisting, see *J. Chem. Physics*, 1938, 6, 695.

The vibrations of the ethyl chloride molecule may be divided into three sets: (1) Vibrations of the C—C—Cl framework, (2) Vibrations of the methyl group, (3) Vibrations of the methylene group. The torsional oscillation is not included in the present considerations. The vibrations of set (1) may be related to the vibrations of a non-linear triatomic molecule, those of set (2) to the vibrations of the methyl group in the methyl halides, CH_3X, and those of set (3) to the vibrations of the methylene group in the methylene halides, Y . CH_2 . Y. This correspondence between the vibrations of the ethyl chloride molecule and the vibrations of the more simple molecules is shown diagrammatically in Table II. The approximate magnitudes of the vibration frequencies for the simpler molecules are given in the last column. From the above correspondence a rough set of frequencies for the ethyl chloride molecule is deduced to be: Five of 3000, two of 1450, 1400, 1350, 1100, 1050, two of 1000, 950, 850, 700, and 350 cm.$^{-1}$. Combining these with the frequencies observed in the Raman and infra-red spectra we are led to the following list of frequencies: Five of 3000, two of 1450, 1400, 1290, 1120, 1070, 1050 and 1000, 970, 790, 655 and 337 cm.$^{-1}$. These frequencies have been used in calculating the vibrational contribution to the entropy. It is not suggested that the above assignment would be sufficiently accurate for general use, but it is certainly good enough for the present entropy calculations, and will lead to an error in the vibrational contribution at 200° C. of not more than 0·5 cal. per g./mol.°C.

Calculation of the Entropy of Ethyl Chloride. Using the above values for the moments of inertia and the vibration frequencies calculations of the entropy have been made for the two extreme conditions, namely (1) completely free rotation of the methyl group, and (2) completely restricted rotation of the methyl group, excluding even the contribution to the entropy arising from a torsional oscillation. Assumption of a torsional oscillation or a partially restricted rotation would give a value between these limits. For the calculation of the rotational entropy when free internal rotation of the methyl group is involved the treatment given by Kassel[12] has been employed. The values calculated for the entropy of ethyl chloride are given in Table III.

TABLE III.—CALCULATED VALUES OF THE ENTROPY OF ETHYL CHLORIDE.

T(°K).	Completely Restricted Rotation.			Completely Free Rotation.		
	r_{CCl} = 1·70.	1·75.	1·80.	1·70	1·75.	1·80 A.
273	62·94	63·02	63·10	66·29	66·37	66·45
298	64·07	64·15	64·23	67·51	67·59	67·67
303	65·18	65·26	65·33	68·69	68·77	68·85
373	67·35	67·43	67·50	71·00	71·08	71·16
423	69·47	69·55	69·62	73·25	73·33	73·41
473	71·53	71·61	71·69	75·42	75·50	75·58
523	73·54	73·62	73·70	77·53	77·61	77·69
573	75·51	75·59	75·67	79·59	79·67	79·75

The Observed Change in Entropy for $C_2H_4 + HCl = C_2H_5Cl$.

The equilibrium in the system ethyl chloride, ethylene and hydrogen chloride has been investigated by Rudkovskii, Trifel and Frost. They studied this system at 170°, 200° and 230°, the rate of attainment of the equilibrium being accelerated by the presence of bismuth chloride on silica. They obtained the following expression for K_p as a function of the absolute temperature:

$$\log K_p = 4{\cdot}96 - \frac{2935}{T}.$$

The above value of K_p is obtained from a process occurring at constant pressure, and so the entropy change of $-$ 22·7 cal. per °C. calculated from it represents the change in entropy on passing from a mixture of 1 g. molecule of ethylene and 1 g. molecule of hydrogen chloride at

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[12] Kassel, *J. Chem. Physics*, 1936, 4, 276.

atmospheric pressure and 200° C. to 1 g. molecule of ethyl chloride at atmospheric pressure and 200° C. To obtain the standard entropy change, $S_{C2H4} + S_{HCl} - S_{C2H5Cl}$, it is necessary to introduce a correction for the entropy change on mixing the ethylene and hydrogen chloride. This will make $S_{C2H4} + S_{HCl} - S_{C2H5Cl}$ equal to 19·9 cal. per °C.

Discussion.

If 19·9 is subtracted from the sum of the entropies of hydrogen chloride and ethylene at 200° C., the value obtained for the entropy of ethyl chloride at this temperature is 86. Comparing this value with those given in Table III, it will be seen to be considerably higher even than the value calculated assuming free rotation. In this case the discrepancy is about 10·4 entropy units, while for restricted rotation the discrepancy is 14·3 units. Both these errors are certainly outside that which could possibly arise in the theoretical calculations. It must be concluded, therefore, that the experimental value for the entropy change is unsatisfactory. In Table IV are given the calculated values for the entropy change.

TABLE IV.—CALCULATED VALUES OF THE STANDARD ENTROPY CHANGE FOR THE REACTION $C_2H_5Cl = C_2H_4 + HCl$.

T(°K).	Completely Restricted Rotation.			Completely Free Rotation.		
	r_{CCl} = 1·70.	1·75.	1·80.	1·70.	1·75.	1·80 A.
273	32·62	32·54	32·46	29·27	29·19	29·11
298	32·96	32·88	32·80	29·52	29·44	29·36
323	33·37	33·29	33·22	29·86	29·78	29·70
373	33·76	33·68	33·61	30·11	30·03	29·95
423	34·12	34·04	33·97	30·34	30·26	30·18
473	34·38	34·30	34·22	30·49	30·41	30·33
523	34·57	34·49	34·41	30·58	30·50	30·42
573	34·69	34·61	34·53	30·61	30·53	30·45

The error in the experimental value of the entropy change may arise because of small errors in the values of K_p at each of the temperatures studied causing a line with the incorrect slope to be drawn when log K_p is plotted against the reciprocal of the absolute temperature. Alternatively the equilibrium constants at the three temperatures may be badly in error because of some unnoticed effect, such as, for example, a side reaction. It would certainly seem that little effort was made to prove that the simple reversible reaction $C_2H_5Cl = C_2H_4 + HCl$ was all that was taking place in the system examined by Rudkovskii, Trifel and Frost. In favour of the first possibility it is to be observed that, though the individual results at 230° C. are quite consistent, those at the lower temperatures show considerable variation.

The difference between the entropy change calculated assuming free rotation and that calculated assuming completely restricted rotation is approximately 4 entropy units. This would mean a difference for the two extreme conditions in the temperature independent term of the expression for log K_p of about one unit. It must be concluded, therefore, that if accurate data were available on the equilibrium in this system it would be possible to obtain information regarding the motion of the methyl group in the ethyl chloride molecule.

Summary.

The entropy of ethyl chloride between 273° and 573° K. has been calculated both assuming restricted and assuming free rotation of the methyl group. By combining these results with the calculated entropies of ethylene and hydrogen chloride the entropy change for the reaction $C_2H_5Cl = C_2H_4 + HCl$ has been calculated for the same range of temperature. From data on the equilibrium in the above system it has been possible to obtain an experimental value for the entropy change at 200° C. It is found that the calculated and experimental values at this temperature are widely different, and it is concluded that the experimental result is in error. The practicability of using the entropy change for this reaction to obtain information regarding the problem of internal rotation in ethyl chloride is discussed.

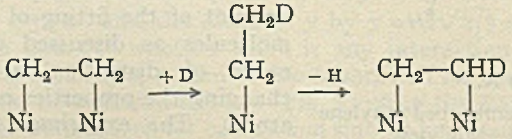
Balliol College,
Oxford.

THE CHEMISORPTION OF OLEFINES ON NICKEL.

BY G. H. TWIGG AND ERIC K. RIDEAL.

Received 17th January, 1940.

Recent investigations which have been carried out on the exchange reactions between olefines and deuterium [1] have indicated that exchange proceeds through an associative mechanism, *e.g.*



$$\begin{array}{cc} \mathrm{CH_2} & \!\!\text{—}\mathrm{CH_2} \\ | & | \\ \mathrm{Ni} & \mathrm{Ni} \end{array} \xrightarrow{+\mathrm{D}} \begin{array}{c} \mathrm{CH_2D} \\ | \\ \mathrm{CH_2} \\ | \\ \mathrm{Ni} \end{array} \xrightarrow{-\mathrm{H}} \begin{array}{cc} \mathrm{CH_2} & \!\!\text{—}\mathrm{CHD} \\ | & | \\ \mathrm{Ni} & \mathrm{Ni} \end{array}$$

This implies that when the olefine is chemisorbed on the catalyst, the double bond is opened and attachment takes places between the two carbon atoms of the double bond and two nickel atoms. It is therefore of interest to calculate how ethylene and higher olefines fit in this manner to a nickel surface.

The first calculation is concerned with the fitting of the olefine molecule between the two nickel atoms (Figs. 1 (*a*) and (*b*)). The ethylene molecule is used for these calculations as the interatomic distances are not appreciably affected by substitution of alkyl groups for hydrogen atoms on the double bond. The ethylene then fits to the catalyst as shown in Figs. 1 (*a*) and (*b*).

The following values for the lengths of the bonds are used :—

(*a*) Ni—Ni 2·47 A. (Davy, *Physic. Rev.*, 1925, 25, 753).

(*b*) Ni—C 1·82 A. (Crawford and Cross, *J. Chem. Physics*, 1938, 6, 525).

(*c*) C—C 1·52 A. (Brockway, *Rev. Mod. Physics*, 1936, 8, 261).

Since the nickel crystal has a face-centred cubic structure, there are two nickel-nickel distances to be considered, the distance of closest

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[1] Twigg and Rideal, *Proc. Roy. Soc., A*, 1939, 171, 55; Twigg, *Trans. Faraday Soc.*, 1939, 35, 934.

packing 2·47 A. and the unit cell side 3·50 A. (Davy, *loc. cit.*). It can be shown that the distance 3·50 A is too great for adsorption in the manner postulated above; adsorption must therefore take place on the 2·47 A. distance. The nickel-carbon distance is not easy to determine; it is taken here as being equal to the Ni—C distance in nickel carbonyl $Ni(CO)_4$. The C—C distance is taken as the single bond distance in paraffins. From Fig. 1 (*a*) it is seen that $a = c - 2b \cos \theta$ and substituting for a, b, and c, we find $\theta = 105°4'$, in place of the tetrahedral angle 109° 28′ which one would expect. Thus by a slight decrease of the angle, the molecule fits very well to the surface. The change in the angle θ from the tetrahedral angle required for a good fit will actually be much less, as the molecule can accommodate itself by twisting slightly so that the C—C axis lies at a small angle to the Ni—Ni axis. It is also possible that the process of forming an active catalyst, by oxidation followed by reduction, causes an increase in the interatomic distance. The promotion of nickel catalysts by oxygen [2] may be due to the oxygen atoms maintaining the crystal lattice in an expanded state.

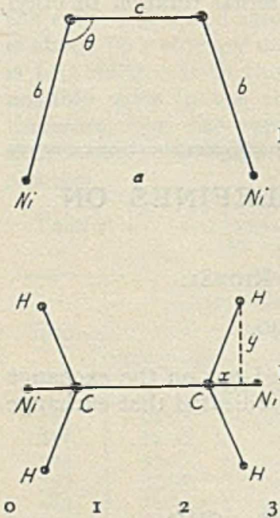

FIG. 1*a*.

FIG. 1*b*.

FIG. 1.—(*a*) Chemisorbed ethylene molecule—side view.
(*b*) Chemisorbed ethylene molecule—plan.

The interatomic distance of the catalyst atoms appears to be an important factor in determining the activity of the catalyst, whether on account of the fitting of the adsorbed molecules as discussed above or because of distortion of the lattice changing the properties of the catalyst atoms. The experiments of Maxted and co-workers [3] suggest that the activity of a catalyst is not due to isolated active atoms, but is present in relatively large areas of the catalyst. The low temperature at which activation of a nickel catalyst by oxidation and reduction (90° C. in one experiment here) can be brought about militates against the view that isolated highly unsaturated atoms are being produced. Activation is then probably due, not only to an increase in area, but also to an alteration in interatomic distance.

In the chemisorption of olefines in the manner described above, if the angles between the valences were the tetrahedral angles, the distance between the nickel atoms would have to be 2·73 A. This may be taken as approximately an upper limit for the catalyst spacing. This agrees with the fact that catalysts active in hydrogenation have interatomic distances (distances of closest approach) lying between 2·47 A. and 2·54 A. (Fe, Ni, Co, Cu) and between 2·7 A. and 2·8 A. (Pt, Pd). It is noteworthy that in the latter group where the distance is near the maximum, the form of the crystal lattice has become important, for only those metals with

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[2] Juliard and Herbro, *Bull. Soc. Chim. Belgique*, 1938, 47, 717; Ablezova and Zellinskaja, *J. Physic. Chem. Russ.*, 1937, 9, 252.
[3] *J.C.S.*, 1928, 1600.

interatomic distance between 2·7 A. and 2·8 A. which have also a face centred cubic lattice are active in hydrogenation. The greater activity of the face centred cubic crystal lattice was shown by Long, Frazer and Ott,[4] using alloys, to exist also for the other group of metals (Fe, Ni, Co, Cu).

That the fitting of the olefine to the catalyst surface is an important factor in such a reaction as hydrogenation seems to be shown by a preliminary experiment which was made with a tungsten catalyst.* Under very rigorous conditions of cleanliness a wire catalyst was obtained very active for the para-hydrogen conversion (high temperature mechanism); the half life of the conversion was 5 minutes at — 130° C. A mixture of ethylene and hydrogen in contact with this catalyst showed no appreciable hydrogenation in half an hour during which the temperature of the catalyst was raised from — 130° C. to 200° C. The absence of reaction was due not to the inability of the catalyst to "activate" hydrogen, but to its inability to "activate" the ethylene which in turn seems bound up with the question of catalyst spacing.

The interatomic spacing must therefore exert a considerable influence on the ability of substances to catalyse reactions, though it is not suggested that this is the complete explanation.

The second calculation which has been made on the fitting of the olefine molecules to the surface concerns the interaction of neighbouring adsorbed molecules. Fig. 1 (*b*) represents a plane projection of the adsorbed ethylene molecule from a point above the surface.

The various distances and positions of the atoms have been calculated as follows. It has been assumed that all the angles between the valences of the carbon atoms are equal to the tetrahedral angle 109° 28′. Then, if d is the length of the C—H bond,[5] 1·09 A., the distance x is given by $x = d/3 = 0{\cdot}36$ A., and the distance y by $y = d\sqrt{2/3} = 0{\cdot}89$ A.

In order to find out whether there is any interaction between the adsorbed olefine molecules, a plan of the adsorption on the 110 and 111 nickel planes has been drawn to scale (Fig. 2) using the above distances.

These planes were chosen for calculation since it has been shown (E. C. Williams, private communication) by means of experiments on evaporated nickel films, that the 110 nickel plane was catalytically active whereas the 100 plane was quite inactive.

The adsorption of ethylene on these two planes is demonstrated in Fig. 2; the effective sizes of the hydrogen atoms have been drawn in (full circles). The effective diameter of the hydrogen atom is taken as the diameter of the hydrogen molecule from viscosity, etc., measurements, less the internuclear distance. Taking the diameter [6] as 2·3 A., and the internuclear distance [7] as 0·75 A., this gives 0·78 A. for the radius of the hydrogen atom. It will be seen that if the molecules are adsorbed on the 111 nickel plane (Fig. 2A), there is a certain amount of interaction between them, though this may not be sufficient to prevent ethylene covering the whole surface. On the other hand, if adsorption is on the 110 plane (Fig. 2B) there is no interaction between neighbouring adsorbed molecules, and the ethylene can easily cover the whole surface,

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[4] *J.A.C.S.*, 1934, **56**, 1101.

* This experiment was carried out in collaboration with Mr. D. D. Eley of this department.

[5] Sutherland, *Ann. Reports Chem. Soc.*, 1936, **33**, 55.

[6] Farkas and Melville, *Experimental Methods in Gas Reactions*, p. 2, Macmillan & Co., London, 1939.

[7] Mecke, *Hand- Jahrbuch chem. Physik*, 1934, **9**, 283.

as has been shown experimentally to be the case up to 160° C. (Twigg and Rideal).[1] There may, of course, be holes in the ethylene layer owing to the two-point contact required for the ethylene molecule.[8]

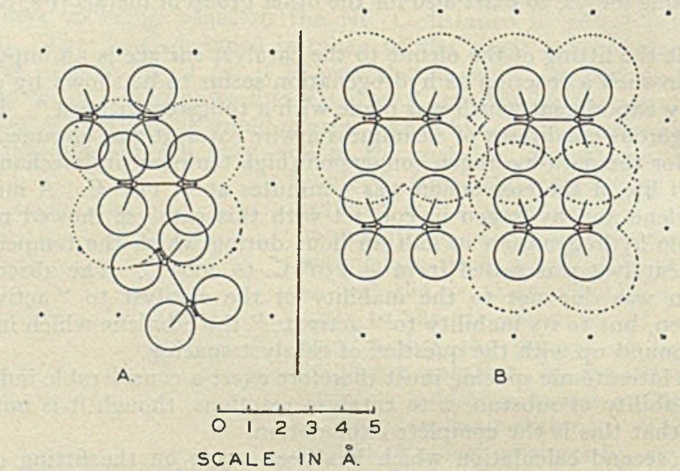

FIG. 2.—Plan of chemisorbed ethylene and methyl ethylenes on the nickel surface. A on the 111 plane. B on the 110 plane.

In the case of the methyl substituted ethylenes, interaction between neighbouring adsorbed molecules is very great, particularly if adsorption is on the 111 plane. The size of the —CH_3 group is indicated by the dotted circles in Fig. 2. The diameter of the —CH_3 group is taken as the same as that of the methane molecule,[9] 3·06 A. It will be seen that interaction between adsorbed methyl substituted ethylenes, even on the 110 plane would be so great that the whole surface could not be completely covered. It can also be seen from the fact that the dotted circles of the methyl groups overlap with the full circles of the hydrogen atoms, that even in the case of propylene with only one methyl group, there will be considerable interaction between the adsorbed molecules. This calculation then shows that despite their higher molecular weights, the substituted ethylenes should be less strongly adsorbed in quantity than ethylene itself, that they should be unable to cover the whole surface and that there should be bare surface on which the equilibration reaction $H_2 + D_2 \rightleftarrows 2HD$ can take place.

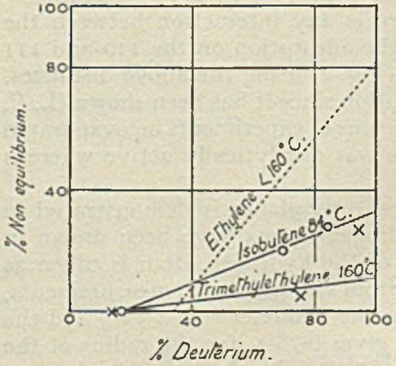

FIG. 3.—Equilibration of hydrogen during exchange reactions. x in presence of trimethylethylene at 160° C. o in presence of isobutene at 84° C.

These conclusions were tested by means of the technique described previously (Twigg and Rideal).[1] The olefine and deuterium were allowed

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[8] *Cf.* Roberts, *Proc. Roy. Soc.*, *A*, 1935, 152, 464.

[9] Braune and Linke, *Z. physik. Chem.*, *A*, 1930, 148, 195.

to interact on the catalyst, and the course of the exchange and equilibration reactions was followed simultaneously. The deuterium content u of the hydrogen was graphed against the non-equilibrium content $1 - x$. The results obtained are shown in Fig. 3.

Using ethylene, the points obtained at temperatures below 160° C. lie on the dotted line, showing that the ethylene covers the whole surface up to that temperature. Above that temperature the slope of the line decreases owing to displacement of the ethylene by hydrogen. With trimethylethylene at 160° C., however, the lowest line was obtained. Here equilibration is proceeding very fast, showing that the surface is considerably bare. The same phenomenon is illustrated by the other line which was obtained by using isobutene at as low as 84° C. The rapid equilibration confirms the conclusions drawn above, that the methyl substituted ethylenes, because of interaction between neighbouring adsorbed molecules, are unable to cover completely the whole catalyst surface.

Summary.

Information derived from exchange reactions showed that olefines are chemisorbed to a nickel surface with opening of the double bond and adsorption to two nickel atoms. Calculations have been made which show that this mode of adsorption is possible with very little distortion of the adsorbed molecule. The effect of the interatomic spacing of the catalyst atoms is discussed and the view is advanced that this will be an important factor in the hydrogenation of double bonds where two point contact is required.

Calculations were also made qualitatively of the interaction between neighbouring adsorbed olefine molecules. It has been shown that for ethylene there is little or no interaction, especially when adsorption is on the 110 crystal plane; ethylene can therefore cover the whole catalyst surface. For the higher olefines, however, interaction is considerable and these molecules cannot cover the whole surface. The experimental evidence confirms these conclusions.

We have to thank the Carnegie Trust for a Fellowship to one of us (G. H. T.) and Dr. H. Melville for a microconductivity gauge.

Dept. of Colloid Science,
Free School Lane,
Cambridge.

ELASTIC RECOVERY AND PLASTIC FLOW IN RAW RUBBER.

By L. R. G. Treloar.

Received 18th January, 1940.

1. Purpose of the Work.

A satisfactory theory of the structure of raw rubber must be able to account for all the physical phenomena displayed by this material. It is of importance, therefore, that its physical behaviour should be carefully studied and described in the most direct and accurate manner possible. Experimental studies of this kind may also be of assistance in suggesting the most hopeful lines of approach to the theoretical study of the problem.*

The first specific problem which appeared to require examination was that of the separation of the elastic and plastic effects which in general take place simultaneously when raw rubber is subjected to a deformation. The existing information on this subject is scanty. True, numerous studies of plasticity have been carried out, but these have been concerned almost entirely with masticated rubber, with which it is not proposed to deal here. Stress-strain curves for raw rubber at different temperatures have been given by Rosbaud and Schmid.[1] In contrast to those for vulcanised rubber, these show a great dependence on the temperature and on the rate of extension, effects which have generally been attributed to the occurrence of plastic flow, although the magnitude of the flow has not been determined. On the other hand, several workers, including in particular Feuchter,[2] have drawn attention to the fact that raw rubber, when stretched quickly to about 600 % elongation, recovers on warming practically to its original length, *i.e.*, there is no plastic flow in this case. Perhaps the most successful attempt to distinguish the plastic from the elastic deformation was made by Whitby[3] who clearly demonstrated the kind of difficulty encountered in an investigation of this kind. Whitby maintained specimens of raw rubber extended to a constant length for given times at various temperatures. They were then allowed to recover for several days at room temperature, until the length had ceased to change, but on subsequently raising the temperature to 100° C. a further contraction was observed. The " set " remaining after this treatment was regarded as a plastic deformation. This view will be shown not to have been entirely justified.

In the present work Whitby's methods have been taken as a starting-point, but greater care has been exercised in securing the complete removal of elastic strain. The data cover the following aspects of the behaviour of rubber :—

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* A review of existing knowledge of the physical properties of raw rubber is to be found in Chapter II, by G. S. Whitby, in *The Chemistry and Technology of Rubber* (New York, 1937).

[1] F. Rosbaud and E. Schmid, *Z. techn. Physik*, 1928, **9**, 98.

[2] H. Feuchter, *Kautschuk*, 1926, **2**, 260, 282.

[3] G. S. Whitby, *J. Physic. Chem.*, 1932, **36**, 198.

1. The elastic recovery at constant temperature.
2. Further recovery on raising the temperature.
3. The non-recoverable extension or plastic flow.
4. The decay of tension at constant extension.

Finally an attempt is made to draw certain inferences from the results of these experiments concerning the structure of raw rubber.

2. Experimental Methods.

The rubber used in these experiments was Malayan crepe. Its average molecular weight (M) was determined from viscosity measurements in dilute benzene solutions. The ratio of specific viscosity (η_{sp}) to concentration (c), expressed in g. per 100 c.c. solution, extrapolated to infinite dilution was 7·0. Applying Staudinger's equation

$$k\frac{\eta_{sp}}{c} = M$$

and assuming his value [4] of the constant k for rubber, *i.e.*, 22,000, a figure of 154,000 was obtained for the average molecular weight.

Preparation of Specimens.—One difficulty experienced in working with raw rubber is to obtain the material in a form suitable for carrying out mechanical tests. For this purpose it is important that the rubber should be of uniform texture and thickness. In these respects crepe in its commercial form is unsuitable. To overcome this difficulty films were prepared by pouring a 4 % solution of the rubber in benzene on to a flat surface and drying off the solvent. In the first attempts the solution was poured into a frame standing on a glass plate, but films prepared in this way were found to be in a state of internal strain which arose from the inability of the solvent-swollen rubber to contract freely during drying owing to its adhesion to the glass. This was a serious difficulty, for the strain thus introduced could not easily be removed, and it is clearly of the utmost importance in experiments of the kind contemplated that the material worked on shall be strain-free initially. The difficulty was overcome by pouring the solution on to a mercury surface with a confining boundary consisting of a zig-zag paper strip floating edgewise on the mercury, as depicted in Fig. 1. Such a boundary offers no appreciable resistance to the uniform contraction of the film during drying, the contraction actually obtained amounting to 35 % of the linear dimensions. Films prepared by this process were practically strain-free, as judged by the methods to be described later.

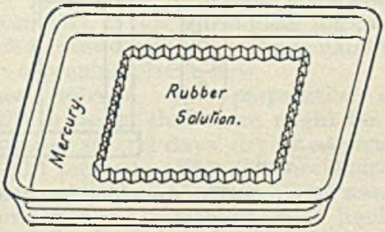

FIG 1.—Preparation of rubber films from solution.

From the films thus prepared, whose thickness was in the neighbourhood of 0·3 mm., straight test-pieces 40 mm. long and 5 mm. wide were cut. In the experiments a free length of 30 mm. between grips was used, measurements being taken on a marked length of 10 mm. in the middle of the specimen.

The Stretching Machine.—The essential details of the stretching machine employed are shown in Fig. 2. The upper grip G_1 was hung by a steel wire from the flat steel spring S the deflection of which could be read on the scale C. The lower grip G_2 was connected by a cord passing round pulleys P_1 P_2 P_3 to the 1 Kg. weight W. The release of this weight by

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[4] H. Staudinger, *Ann.*, 1931, 488, 127 ; *Ber.*, 1930, 63, 921.

means of the trigger T caused a rapid extension of the test-piece. The supporting rod R was of glass, a material preferred to metal on account of its lower thermal conductivity. The specimen could be surrounded by a tube A which was immersed in a constant-temperature bath. In no case was liquid used in direct contact with the rubber.

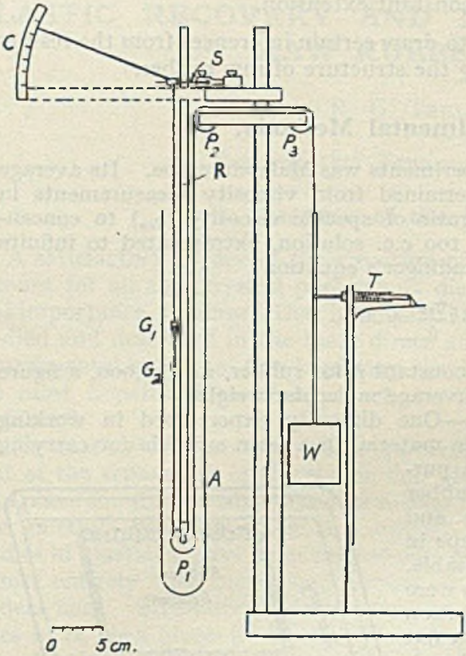

FIG. 2.—The stretching machine.

By this arrangement the tension could be observed whilst the specimen was stretched approximately to a constant length. There was, of course, a small change of length due to the movement of the spring; this was not more than 2 % of the stretched length of the specimen during any experiment.

In carrying out the experiments the unstretched specimen was inserted in the thermostat, and after a suitable warming-up time the weight was released. Commencing 5 seconds after releasing the weight, readings of tension were taken at suitable intervals throughout the period of extension. At the end of this time the stand was lifted so as to remove the specimen, still stretched, from the thermostat, and an interval, generally 5 minutes, was allowed for the rubber to cool down below 25° C. The tension was then released, the lower end of the specimen cut off below the marking to remove unnecessary weight, and the specimen transferred to the 25° C. thermostat. Subsequent changes of length were then noted over a 20-hour period.

3. The Removal of Strain from Stretched Rubber.

The general nature of the recovery phenomena observed after raw rubber has been stretched are shown in Fig. 3, curve (*a*), which depicts the behaviour of a specimen of crepe after stretching at 50° C. for 1 hour at an elongation of 390 %. At 25° C. there was an immediate recovery to 260 % elongation on releasing the tension. Thereafter there was a further recovery, rapid at first, then progressively slower, over a period of 20 hours. Increas-

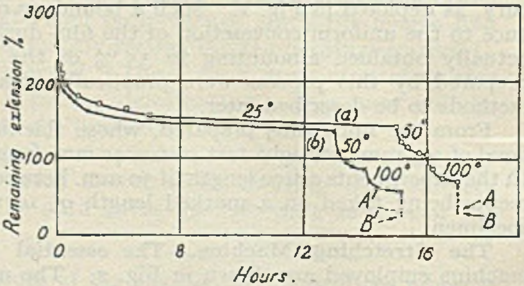

FIG. 3.—Elastic recovery of crepe at temperatures indicated after stretching to 390 % extension for 1 hour at 50° C.
(*a*) Normal.
(*b*) Vacuum treated.

ing the temperature to 50° C. caused a sharp increase in the rate of recovery, but with continued heating the rate again slowly diminished. At 100° C. the same phenomenon was repeated. Even then the elastic recovery was not complete. For the further removal of strain two methods were tried, both depending on the swelling action of a solvent. In the first method the specimen was hung in a vessel containing some benzene and the vapour allowed to act on the rubber for a certain time, after which it was removed and dried. The permissible swelling was limited by the tendency of the rubber to sag, so that several successive treatments were usually necessary to secure constancy of length. In the second and preferred method the rubber was immersed in a liquid benzene-alcohol mixture, removed after a suitable time, and dried. This method avoids the sagging difficulty and also permits of a control over the amount of swelling by variation of the benzene content of the mixture. The results obtained by the two methods were in close agreement.

In Fig. 3 the point A represents the remaining extension after treatment for 16 hours by a mixture containing equal volumes of benzene and alcohol. The point B represents a further treatment for the same time by a mixture containing 60 % of benzene. It will be noted that these treatments led to a reduction of the residual extension by more than 50 %. It is hardly possible to use a mixture containing a higher percentage of benzene, owing to the difficulty of handling such highly-swollen rubber. However, since the effect of the 60 % mixture was not very much greater than that of the 50 % mixture, it may be assumed with some confidence that the final length of the rubber represents, if not a complete removal of elastic strain, at least a close approach to that condition. The remaining extension may therefore be regarded as a genuine plastic flow.

Possible Effects due to Retained Solvent.—The preparation of specimens from solutions is open to the criticism that there might be a trace of solvent left in the rubber even after several days' drying at room temperature, the presence of which might seriously affect the mechanical properties. To meet this criticism a piece of rubber prepared in the usual way was heated to 50° C. for 8 hours in a high vacuum, with liquid air applied to the evacuated tube, a treatment which should have been sufficient to remove any remaining solvent. The rubber was stretched at 50° C. by means of a falling weight, and the recovery was observed first at 25° C. and then at higher temperatures, both the stretching and recovery being completed without admitting air to the tube. The rubber was then removed and treated with benzene-alcohol mixture in the usual way. The result of this experiment is shown in Fig. 3, curve (*b*), from which it is clear that the precautions taken made no marked difference either to the amount of the elastic recovery at any temperature or to the plastic flow, and it may therefore be concluded that the results reported are not in error on account of absorbed solvent. At the same time this experiment proves that the possible presence in the rubber of water absorbed from the atmosphere was not having an important effect.

4. The Phenomena of Elastic Recovery.

Recovery at 25° C. after Stretching at 25° C.—Fig. 4 shows the recovery curves obtained at 25° C. for samples stretched for 1 hour at 25° C. to various elongations. Noteworthy features of these curves are that for the higher elongations there is no further recovery after the first half-hour, whilst for the lower elongations the recovery is more gradual, and also more complete.

Recovery at 25° C. after Stretching at 50° C.—Similar data for samples stretched for 1 hour at 50° C. are given in Fig. 5. It will be observed that the gradualness of the recovery is more noticeable at this stretching temperature than at 25° C., and that the absence of gradual recovery is apparent only after relatively high initial elongations.

Recovery at Temperatures above 25° C. Crystallisation.—The recovery curves at 25° C. thus fall into two main classes. In the first the recovery after releasing the tension is relatively small and ceases within about 30 minutes, whilst in the second the recovery is relatively large, and continues at a diminishing rate for at least 20 hours. The high extensions yield recovery curves of the first type, and the low extensions those of the second. Increase of stretching temperature favours the second type.

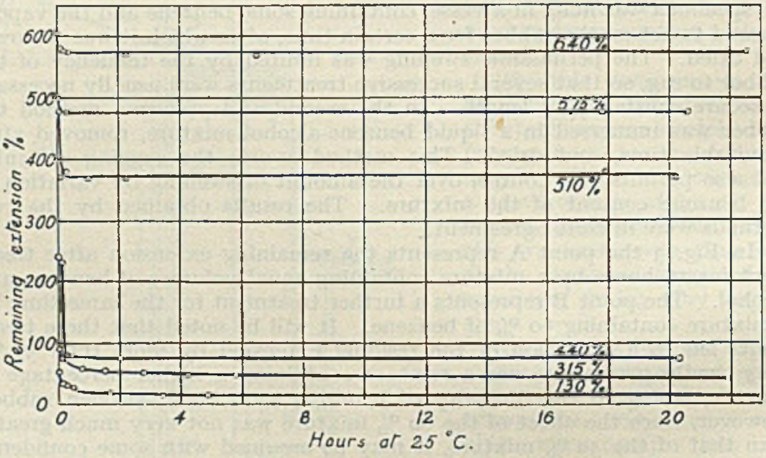

FIG. 4.—Recovery at 25° C. after stretching 1 hour at 25° C. Elongations as marked.

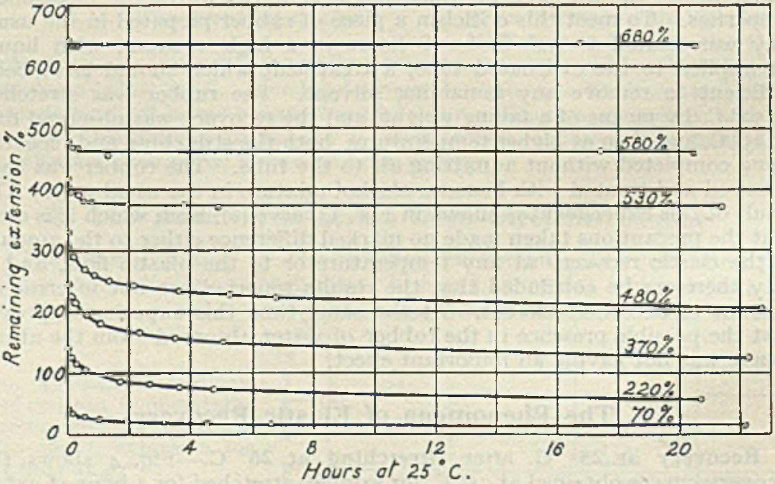

FIG. 5.—Recovery at 25° C. after stretching 1 hour at 50° C. Elongations as marked.

Two types of behaviour are also observed when the recovery at higher temperatures is examined. There is the type of behaviour represented in Fig. 3, in which each increase in temperature gives a slight increase in the recovery; this type of behaviour corresponds with the lower degrees of extension. An entirely different type of behaviour is depicted in Fig. 6, which shows the effect of raising the temperature at the rate of about 1° C. per 3 minutes. The specimens represented in this figure had been extended at 25° C. for 1 hour and subsequently allowed to recover for 20 hours at 25°. For the higher extensions practically the whole of the subsequent recovery occurred quite quickly over a temperature interval of only 1° C.

Similar experiments on specimens stretched at 50° C. are more interesting because they show clearly the transition between the gradual and the critical-temperature types of recovery (Fig. 7). For the highest extension the temperature range over which most of the recovery occurred was as narrow as for a stretching temperature of 25°, but as the initial elongation was reduced the recovery range showed a corresponding broadening, until for an initial elongation of 480 % all signs of a special recovery temperature had disappeared.

These phenomena have been observed by a number of authors, in greater or less degree, and an explanation of the sharpness of the recovery temperature for highly-extended rubber has been given by Feuchter and Hauser.[5] These workers found that on storing rubber "racked" to 600 % extension the recovery range narrowed from 11° to 1°, and at the same time there was an increase in density of the rubber and an increase in the intensity of the X-ray "fibre" pattern. They concluded that these phenomena were associated with a high degree of crystallinity. On this view the recovery temperature is to be identified with the melting-point of the crystals formed on stretching.

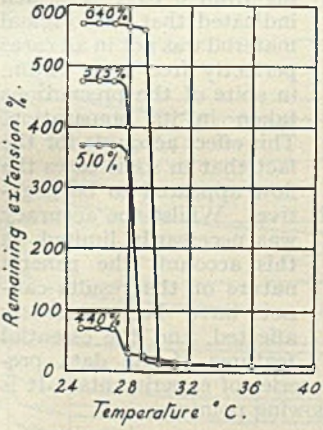

FIG. 6.—Recovery with rising temperature after stretching for 1 hour at 25° C. to extensions indicated.

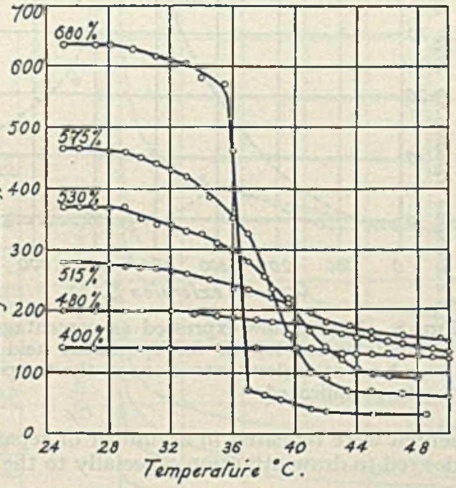

FIG. 7.—Recovery with rising temperature after stretching for 1 hour at 50° C. to extensions indicated.

The data here brought forward generally tend to substantiate this view. It is to be expected, and it has been demonstrated by von Susich[6] from X-ray evidence, that the appearance of crystallisation requires a higher degree of extension the higher the temperature at which the extension is carried out. Hence the critical-temperature type of recovery would be expected to occur more readily at a lower than at a higher temperature, as is indeed found to be the case. There is, however, one feature of the experimental results for which no obvious explanation can be found, namely that the recovery temperature depends on the temperature at which the stretching is performed (*cf.* Figs. 6 and 7). One would not expect the

[5] H. Feuchter and E. A. Hauser, *Kautschuk*, 1929, 5, 194, 218, 245, 276.
[6] G. von Susich, *Naturwiss.*, 1930, 18, 915.

melting-point of the crystals to depend on the temperature at which they were formed.

5. Plastic Flow.

After recovery at 25°, followed in some cases by further recovery at higher temperatures, the samples were treated by a benzene-alcohol mixture containing 50 % of benzene for 16 hours, followed by a further treatment with a 60 % benzene mixture for the same time. The extensions remaining after this treatment, representing plastic flow, are shown in Fig. 8, for stretching temperatures of 25° and 50° C. respectively. A number of control specimens, not stretched, which were subjected to the same benzene-alcohol treatment, showed contractions ranging from 0 to 3 %, which indicated that the original material was not in all cases perfectly free from strain, in spite of the precautions taken in its preparation. This effect accounts for the fact that in some cases the flow appeared to be negative. Whilst the accuracy was necessarily limited on this account, the general nature of the results cannot have been seriously affected, and the essential features of the data presented were repeated in a number of separate series of experiments. It is desired to draw attention especially to the following points :—

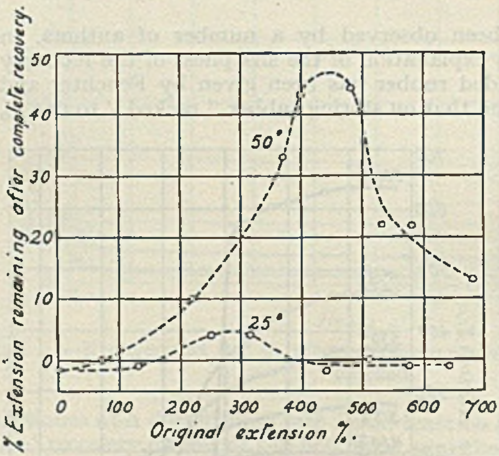

FIG. 8.—Plastic flow expressed as percentage of undeformed length for specimens held for 1 hour at various extensions at the temperatures indicated.

1. The plastic flow increased to a maximum at intermediate extensions, and fell again at higher extensions.

2. The maximum flow on stretching at 25° C. occurred at an elongation of about 300 %, and amounted only to about 2 % of the original extension.

3. For a stretching temperature of 25° the flow was negligibly small for extensions exceeding 400 %.

4. For a higher stretching temperature, *i.e.*, 50° C., the maximum flow occurred at a higher elongation, and the flow at any given elongation was higher.

If we accept the view that the total effect of cohesion between molecules in a crystalline lattice is greater than that between molecules in the disordered state, the reduction of flow which occurred when a certain extension was exceeded may be explained as being due to the occurrence of crystallisation. The fact that the maximum flow occurred at a higher elongation at the higher temperature would appear to be a direct result of the lesser degree of crystallinity at any given elongation. The general features of the flow phenomena are thus explicable on the same basis as the general features of the recovery phenomena dealt with in section 4.

Whitby, from his experiments,[3] drew the conclusion that the amount of flow increased with the elongation. However, he worked only up to 350 % elongation, *i.e.*, on one side only of the maximum in the flow-elongation curve.

Some Consequences of the Observed Flow Phenomena.

Besides being of interest from the theoretical point of view the peculiar relation between plastic flow and initial elongation leads to certain considerations of practical importance. Since the flow is greatest at intermediate extensions, it is necessary that the intermediate region should be passed through as quickly as possible if the smaller flow characteristic of the higher elongations is to be observed. This is one of the reasons for the adoption, in the present work, of an automatic method of securing rapid extension of the rubber. Moreover, the effect undoubtedly has a bearing on the shape of the stress-strain curves obtained by Rosbaud and Schmid.[1] It accounts also for the observation of Hauser[7] that an X-ray fibre diagram could not be obtained when raw rubber was stretched very slowly, for in this case the region of maximum flow may never have been passed through and the molecular extension necessary for crystallisation thus not achieved. Finally, it reveals the importance of making a careful study of the accompanying flow before attempting to discuss the meaning of the variations in the shape of stress-strain curves obtained at different temperatures and rates of elongation, and of the hysteresis observed in the stress-strain relationship. These effects are further complicated by the variation of tension with time, even when the flow is negligible. (See below.)

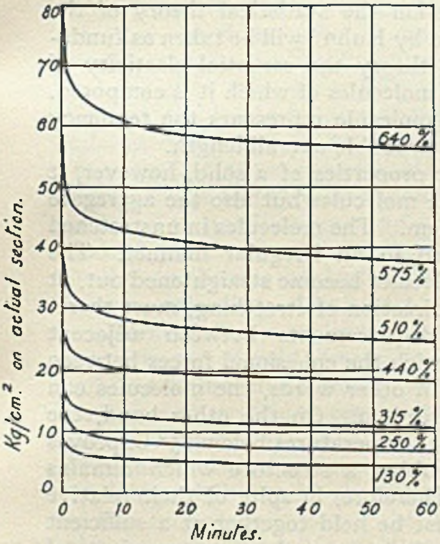

Fig. 9.—Decay of tension at constant extension at 25° C.

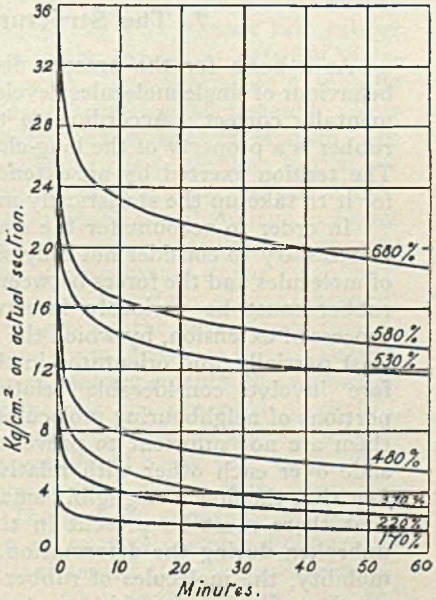

Fig. 10.—Decay of tension at constant extension at 50° C.

6. The Decay of Tension during Extension.

The change of tension with time, for specimens held at constant length, is shown in Figs. 9 and 10. In plotting these curves the observed tensions have been converted to Kg. per cm.² referred to the strained cross-section, assuming the density to remain unaltered by the extension. Two features of these curves call for special comment. Firstly, for a given elongation the relative fall of tension is greater at the higher temperature, whilst at

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[7] E. A. Hauser, *Kautschuk*, 1927, 3, 288; *Ind. Eng. Chem.*, 1927, 19, 169

a given temperature it diminishes with increasing elongation. Secondly, the tension for a given elongation at 50° is in all cases very much lower than for the same elongation at 25°. This second result is not consistent with what is deduced from the simplest application of the statistical theory of rubber elasticity developed by Kuhn[8] among others, according to which the tension at constant elongation is directly proportional to the absolute temperature. A linear rate of increase of tension with temperature has indeed been observed by Hauk and Neumann[9] for a number of vulcanised rubbers. The discrepancy cannot be disposed of by taking account of the plastic flow during stretching, this effect being much too small. A difficulty arises also in explaining the fall of tension at a fixed extension. For example, reference to Figs. 8 and 9 shows that a fall of 30 % may occur in the course of 1 hour for rubber elongated by 510 % at 25°, though the flow under these conditions is negligible. How, then, is the fall to be explained ?

7. The Structure of Raw Rubber.

As a basis for the present discussion the statistical theory of the behaviour of single molecules developed by Kuhn[8] will be taken as fundamentally correct. According to this theory the essential elasticity of rubber is a property of the long-chain molecules of which it is composed. The tension exerted by an extended molecule represents the tendency for it to take up the statistically most probable overall length.

In order to account for the elastic properties of a solid, however, it is necessary to consider not only single molecules but also the aggregate of molecules and the forces between them. The molecules in unstretched rubber must be variously intertwined in an irregular manner. The process of extension, by which the molecules become straightened out, at least partially, and orientated in the direction of stretching, must therefore involve considerable relative displacements between adjacent portions of neighbouring molecules, which the cohesional forces between them are not sufficient to prevent. In other words, the molecules can slide over each other with relative freedom. On the other hand, the fact that the flow is negligibly small at temperatures below 25° C. proves that there must be present in the rubber a structure which remains unbroken during the deformation. Therefore, in spite of their relative mobility, the molecules of rubber must be held together at a sufficient number of points for this structure to be preserved. The experimental evidence thus leads directly to the following important conclusion :—

The molecules of rubber are held together at certain points, or over certain regions, so as to form a three-dimensional structure. On deformation at a temperature not exceeding 25° *C. a sufficient number of these points of linkage or cohesion are maintained for this structure to remain substantially unchanged.*

It is not suggested that the postulation of a structure of this kind to account for the behaviour of elastic bodies is either new or original, but in view of the fact that raw rubber has been commonly regarded as being very imperfectly elastic, it does seem important that the above conclusion should be explicitly stated. By way of comparison, it is of interest to quote the conclusions arrived at by Busse[10] regarding the necessary conditions for the occurrence of high-elasticity in general. These conditions are :— *

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[8] W. Kuhn, *Koll. Z.*, 1936, **76**, 258.

[9] V. Hauk and W. Neumann, *Z. physik. Chem.*, *A*, 1938, **182**, 285.

[10] W. F. Busse, *J. Physic. Chem.*, 1932, **36**, 2862.

* *Cf.* also *First Report on Viscosity and Plasticity*, 2nd Edition, p. 98.

1. " The presence of groups of atoms which form strong, somewhat flexible, fibrous units,
2. " weak or uniform cohesive forces around the fibres,
3. " an interlocking of the fibres at a few places along their length to form a 3-dimensional network. This interlocking may occur through chemical combination, by secondary valence forces, or by mechanical entanglement, and
4. " A means of storing up free energy in the fibres during deformation."

The Nature of the Cohesive Links between Molecules.—The results brought forward in this paper show that the links between the rubber molecules (*i.e.*, those referred to under Busse's 3rd condition) begin to break down at an appreciable rate at about 50° C. Therefore they cannot be primary chemical bonds. In this respect raw rubber differs from the vulcanised product, in which the bonds between molecules are of high energy. In raw rubber, the links (condition 3) may be due either to van der Waals' forces or to mechanical entanglements. Now we have seen that when fully extended, raw rubber crystallises. In this case the forces holding the molecules in the crystalline lattice are undoubtedly of the van der Waals' type, for there are no others available. Yet, even in this very favourable case, in which the alignment increases the efficacy of the van der Waals' forces between molecules, the crystals are found to break down completely at a temperature in the neighbourhood of 30° C. Such a mechanism cannot therefore *of itself* account for the persistence at higher temperatures of the links (condition 3) between molecules. It is necessary therefore to introduce Busse's suggestion, namely the conception of mechanical entanglements, *in conjunction with van der Waals' forces*, to account for the observed properties. Such entanglement-cohesions would possess a wide range of energies, hence at any stretching temperature some would break very much more quickly than others. Flow would occur when the number remaining unbroken fell below a certain value. There would appear to be a strong *a priori* probability of the formation of relatively stable linkages by mechanical entanglement if the view is accepted that the rubber molecules are very long (length/diameter $>$ 1000), that they are arranged entirely at random with respect to each other but are at the same time densely packed. Under such conditions two or more molecules might very well bcome twisted together or looped through each other in such a way that on the application of a shearing force a long time would elapse before separation occurred. Or, to put the matter in another way, the entanglements may be regarded as regions possessing an exceptionally high resistance to flow. If a number of such regions were interconnected by extensible (but unbreakable) molecules, the high viscosity characteristic of these regions would be retained as a property of the substance in bulk, whilst at the same time the general mobility of the individual molecules between the points of entanglement would remain.

A mechanism of this kind accounts qualitatively for a number of features of the mechanical behaviour of raw rubber. Considering first the tension, we have to account for (*a*) a continuous fall of tension at constant length, without plastic flow, and (*b*) a lower tension after a given time at any extension at the higher temperature. With regard to (*a*), a fall of tension of the type shown in Fig. 9 is just what would be expected from a series of links representing a wide range of binding energies. The low-energy links would break quickly, those of higher energy less quickly, and those of still higher energy (*i.e.*, involving considerable entanglement) very slowly or not at all. Consequently, the tension would fall rapidly at first, and thereafter more and more slowly. The same mechanism accounts for (*b*), for at a higher temperature all the links would break more quickly.*

Consider now the recovery phenomena. During extension, simultaneously with the breaking of the original entanglement-cohesions between molecules, there will occur a formation of weaker entanglement-cohesions in the deformed state. The greater the degree of mechanical entanglement formed in the stretched condition, the greater will be the energy required to release the strain thus introduced. An increase of temperature will increase the possibility of the formation of new entanglement-cohesions, firstly because of the greater rate of release of the original linkages, and secondly because of the greater thermal agitation of the molecules. On the other hand, the emergence of a crystalline state will tend to reduce the formation of cohesions of the entanglement type.

These considerations lead to a fuller understanding of the recovery phenomena. The new entanglements formed in the stretched condition, though of the same kind as those originally present in the unstretched rubber, will be less complex, and therefore more readily broken down. As with the original linkages, there will be a wide range of cohesional energies, but the average energy will be lower. Hence on releasing the applied tension the force of retraction resident in the individual molecules will cause the breaking down of the new rather than of the original entanglements. There will be a rapid reduction of length corresponding to the breaking of entanglements of low energy, followed by a progressively more and more gradual recovery, corresponding to the release of those of higher energy. An increase of temperature will clearly increase the rate of recovery, without altering its nature.

The theory, of course, accounts for the recovery phenomena only when crystallisation is not present to an important extent, for under these circumstances, as was pointed out above, the behaviour is controlled by van der Waals' forces rather than by entanglement-cohesions.

Summary.

In considering existing information on the mechanical properties of raw rubber, it is not generally possible to distinguish between the effects of elastic and of plastic deformation. In the experiments described great care was taken to secure the complete removal of elastic strain, after stretching to various extensions at different temperatures. The plastic flow increased to a maximum with increasing elongation and fell again at higher elongations, an effect attributed to the increase of crystallisation with increasing extension. For rubber held extended for one hour at 25° C. the flow was never greater than 2 % of the original extension, whilst for extensions greater than 440 % or less than 130 % it was negligibly small.

Curves showing the decay of tension at constant extension, and the recovery of length after stretching, in conjunction with the observations on plastic flow, are interpreted in terms of a theory proposed by Busse, according to which the rubber molecules are held together at certain points

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* For a discussion of the rôle of molecular entangelement in vulcanised rubber the reader is referred to the work of Long, Singer and Davey. (*Ind. Eng. Chem.*, 1934, **26**, 543) on the time lag in the formation of the X-ray fibre pattern on stretching.

by cohesional linkages of low energy, some of which are broken down during stretching.

The author desires to express his indebtedness to Professor E. K. Rideal who provided facilities at the Laboratory of Colloid Science, Cambridge, for carrying out part of this work, and also to Dr. J. K. Roberts of the same laboratory, who was responsible for directing the course of the research and whose advice and criticism have proved invaluable.

The above work has been carried out as part of the programme of fundamental research on rubber undertaken by the Board of the British Rubber Producers' Research Association.

British Rubber Producers' Research Association,
48 Tewin Road, Welwyn Garden City, Herts.

NUCLEAR GOLD SOLS. III. LOWER LIMIT OF PARTICLE SIZE.

BY A. BAKER AND F. L. USHER.

Received 12th February, 1940.

The very few published investigations relating to particle size in nuclear gold sols have been made, with one exception, with sols prepared by reduction with phosphorus in ether (Faraday's method). In the earliest of these Zsigmondy[1] found that the smallest detectable particles contained $9{\cdot}7 \times 10^{-20}$ g. of gold, corresponding with a spherical radius[2] just over 1 mμ, a figure substantially confirmed later by Scherrer[3] by X-ray methods. In 1909 Svedberg[4] measured the diffusion coefficient of amicronic particles and arrived at a value for the radius of 0·94 or 2·16 mμ, according to the formula used; but this must be considered a rough approximation, and the figure itself too small, since no account was taken of the osmotic effect of the counter-ions. Reitstötter,[5] in a much fuller study of nuclear sols, examined the effect of varying the conditions of preparation (purification of materials, use of different solvents), and of diluting the initial gold solution. He found that the quantity of gold per particle could be reduced from $4{\cdot}9 \times 10^{-19}$ to 3×10^{-19} g. by a twenty-fold dilution of the original solution, which contained $1{\cdot}25 \times 10^{-5}$ g. Au per c.c.; the smallest particles obtained in this way had a radius of 1·5 mμ. Thiessen,[6] using potassium thiocyanate as the reducing agent, estimated by an ingenious but inexact method that the smallest nuclei capable of growth had a radius about 1 mμ. The evidence now available can still be summarised appropriately as was done by Zsigmondy and Thiessen :

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[1] Zsigmondy, *Z. Elektrochem.*, 1906, 12, 633.

[2] It should be noted that in the German literature linear dimensions or "diameters" often refer to the length of a cube edge, not to a spherical radius.

[3] Scherrer, *Nachr. K. Ges. Wiss. Göttingen*, 1918, 98 (*Chem. Centr.*, 1919, 1, 322).

[4] Svedberg, *Z. physikal. Chem.*, 1909, 67, 105.

[5] Reitstötter, *Kolloid Beih.*, 1917, 9, 221.

[6] Thiessen, *Z. anorg. Chem.*, 1929, 180, 110.

> "Up to now gold particles with linear dimensions less than 1·5 mμ have not with certainty been shown to exist, and it is questionable whether particles of metal with fewer than about 300 gold atoms are capable of existence and can form part of a very homogeneous gold sol. . . . We must assume that in the production of gold hydrosols the region that lies between simple gold molecules and aggregates with more than about 300 gold atoms is skipped over rapidly. Particles of intermediate size are not known." [7]

The smallest detectable nuclei, whatever their size, are built up from gold atoms liberated in the chemical reaction, and it is hardly conceivable that this process should take place by encounters of about 300 atoms simultaneously. The alternatives are to assume (1) that the particles are built up atom by atom, or (2) that they are built up by a process analogous to coagulation. In the former event particles of all possible degrees of complexity, and in the latter of a considerable number, must have a transient existence in the region referred to by Zsigmondy. Failure to detect such particles can be easily understood when it is remembered that the magnitude of the stabilising charge increases with the size of the particles, and may be considered, to a first approximation, proportional to their surfaces. There must therefore be a critical size, depending on the experimental conditions, at which the adsorbed ionogenic layer just suffices to confer permanent stability. Particles of smaller size will grow, either by the acquisition of gold atoms or by coagulation with other particles, until the critical size is reached or exceeded. If this view is correct the critical size, and consequently the size of the smallest stable particles, should be influenced by (*a*) introducing into the reaction mixture ions which might be expected to promote stabilisation, and (*b*) diluting the reaction mixture so as to reduce the total amount of electrolyte present. Experiments dealing with these two points will now be described.

Influence of Added Ions.

The ions used were aurocyanide and iodide. The first is relatively stable and should be readily adsorbable on gold because of its chemical structure, whilst iodide has been shown to increase the stability of ordinary gold sols towards electrolytes.[8]

Effect of Aurocyanide.—$NaAu(CN)_2$ was made by digesting excess of freshly precipitated AuCN with a solution of NaCN. A slightly alkaline solution of $KAuCl_4$ was divided into three parts, one of which (*A*) was made 0·007 M., and another (*B*) 0·0007 M. with respect to $NaAu(CN)_2$, whilst the third (*C*) contained none. All three were then reduced with phosphine under otherwise identical conditions, the resulting nuclear sols containing 10^{-5} g. Au per c.c. The size of the nuclei was determined in each of the three sols by the method described in Part I.[9] The results were: Sol *A*, r = 1·49, 1·54, 1·64, 1·68, mean 1·6 mμ; sol *B*, r = 1·81, 1·79, 1·86, 1·90, 1·80, mean 1·85 mμ; sol *C*, r = 1·66, 1·52, 1·65, mean 1·6 mμ. Thus the particle size was not smaller in the presence of aurocyanide. The sols *A* and *B* began to turn purple after several days and showed signs of sedimentation after a month, whilst *C* remained quite stable. It is evident that aurocyanide lessens the stability of gold sols.

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[7] Zsigmondy and Thiessen, *Das kolloide Gold*, Leipzig, 1925, 84.

[8] Kruyt and Nierstrasz, *Kolloid Z.*, 1937, 78, 26.

[9] Usher, *Trans. Faraday Soc.*, 1938, 34, 1230.

Effect of Iodide.—Three solutions of $KAuCl_4$, each containing 10^{-5} g. Au per c.c., were made 0, 2×10^{-5}, and 2×10^{-4} M. with respect to KI, and reduced with phosphine. After standing overnight the sols containing iodide were still yellow, whilst the other had turned pink. On boiling, all three were red. The respective particle sizes were 2·8, 3·0, and 4·8 mμ. It is thus clear that the size is slightly increased by the presence of potassium iodide. The sols with iodide became purple after a month but showed no sign of sedimentation.

An attempt was made to determine the effect of aurate ions, but the aurate was found to be reduced by phosphine to an extent depending on the *p*H of the solution, and no trustworthy inference could be drawn. In no experiment was any decrease of size found.

Influence of Dilution.

Reitstötter's experiments[5] were made with solutions containing $1{\cdot}25 \times 10^{-5}$ g. Au per c.c. which were diluted in four stages to a final concentration of $6{\cdot}25 \times 10^{-7}$ g. per c.c., whilst the amount of phosphorus used for reduction was kept constant. It was argued that if reduction took place at the surface of the colloidal phosphorus particles the mass of the individual gold nuclei would decrease proportionally with dilution, since the number of reducing centres would remain approximately the same. The actual effect of the dilution, however, was to reduce the number of nuclei from $2{\cdot}6 \times 10^{13}$ to $2{\cdot}1 \times 10^{12}$ per c.c., corresponding with a decrease in radius from 1·8 to 1·5 mμ. This decrease of size, corresponding with a difference of 60 per cent. in the quantities actually measured (*i.e.* the number of particles derived from a given weight of gold), is well beyond the limits of experimental error and must be considered real. Its significance consists in showing that dilution is one means by which the size of gold nuclei can be diminished ; no other has yet been discovered. The twenty-fold range of concentration studied by Reitstötter enabled him to prove that no obvious relation existed between the number of phosphorus particles and the number of gold nuclei, but to gain a satisfactory insight into the relation between concentration and particle size it is clearly desirable to extend the range considerably. The experiments described below were made with this object.

Two series of measurements were made, the nuclear sols being prepared by the phosphine method[10] in the first and by the hydrogen sulphide method[10] in the second. The sols were made by adding the phosphine or hydrogen sulphide solution to 30 c.c. of a solution of $KAuCl_4$, suitably diluted, and slightly alkaline in the first case but neutral in the second ; the final volume was always 50 c.c. In every case the sols were boiled for 5 minutes and air was bubbled through them for 30 minutes to remove the excess of the reducing agent (PH_3 or H_2S). The range of concentration studied was 2×10^{-4} to 2×10^{-9} g. Au per c.c. in the phosphine series and 8×10^{-4} to 2×10^{-9} g. per c.c. in the hydrogen sulphide series. For the size determinations a solution of $KAuCl_4$ containing 1 mg. of gold was mixed with such a quantity of the diluted nuclear sol as would furnish particles in the size range corresponding with a purple colour, and the colour of the resulting sol was matched in the way described in Part I.[9] To ensure even growth and to reduce the chance of fresh nuclei being formed during reduction, the hydroxylamine (12·5 c.c. of a solution containing 0·27 g. NH_2OH, HCl per litre) was added very slowly from a Jena glass burette with ungreased stopcock at the rate of 1 drop every 5 seconds for the first half and at twice this rate for the second half of the reduction.

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[10] Baker and Usher, *Trans. Faraday Soc.*, 1940, 36, 385.

The mixture undergoing reduction was contained in a 100 c.c. Pyrex flask clamped to a tilted base which was mechanically shaken while the mouth of the flask remained stationary under the burette. Since the colour of the grown sols is determined only by the particle size the number of particles is obtained by a simple calculation, and if this number can be assumed to be the same as that of the nuclei in the added nuclear sol the size of the particles in the latter can be calculated from the known weight of gold contained in it. If, however, the operations involved in growing the sols cause the formation of any fresh nuclei, the number ultimately found will be too large, and the calculated size too small. It is therefore necessary first to determine the magnitude of the correction to be applied if this source of error is present.

Formation of Fresh Nuclei During Reduction.—Although hydroxylamine is a reducing agent of the " non-nuclear " type, nuclei are in fact produced when it is mixed with a gold solution to which no ready-formed nuclei have been added. Westgren[11] showed that if the concentration of ready-formed nuclei in the reaction mixture falls below about 2×10^{10} per c.c. some fresh nuclei are formed when hydrogen peroxide is used as the reducing agent, but that if this concentration is exceeded all the gold formed in the reaction is deposited on the nuclei already present and the total number of particles remains the same. Hydroxylamine has a smaller tendency than hydrogen peroxide to produce nuclei, but no figures are available for it. However, it is possible to fix an upper limit from the data for one of the sols made in the course of calibrating the colour standard used in this investigation. This sol was made by reducing 1 mg. of gold as $KAuCl_4$ in the presence of a small quantity of nuclear sol, and the resulting particles were found from the rate of sedimentation to have a radius of 84 mμ. This size corresponds with 2×10^{10} particles, the volume of the sol being 40-50 c.c. Since the calculated number of particles in the original nuclear sol agreed with that obtained from other similar experiments in which a larger proportion of nuclear sol was used, it is certain that no extraneous nuclei were present, and it can therefore be safely assumed that the concentration of nuclei produced by hydroxylamine under these particular conditions does not exceed 5×10^{8} per c.c., and is probably smaller. The correction to be applied on this account in any of the determinations given below is smaller than the experimental error. A further possibility has now to be considered. The reducing agents used in the preparation of the nuclear sols, *viz.*, phosphine and hydrogen sulphide, are specially active in promoting the formation of nuclei, and any trace of them remaining in the nuclear sol will cause some fresh nuclei to be formed as soon as the gold solution used for growing the particles is added. The procedure regularly adopted to remove the gases from solution, *viz.*, to boil the liquid for 5 minutes and then to pass air through them for half an hour, cannot be expected to be completely effective, and it was therefore necessary to carry out blank experiments in which particles were grown by the standard method in the presence of measured quantities of a " nuclear sol " which had been treated exactly as described above, but which contained no gold. When this was done, fresh nuclei were formed in numbers nearly proportional to the amount of blank " nuclear sol " used, and these numbers were used as corrections to those found when real nuclear sols were substituted for the blank one. The results are in Table I.

There are thus two sources of unwanted nuclei : one is the conductivity water and other reagents, which are responsible for about 2×10^{10} with the quantities used in these experiments, and the other is the residual traces of reducing gas present in the nuclear sols, which give rise to $4{\cdot}7 \times 10^{11}$ and $2{\cdot}8 \times 10^{11}$ per c.c. of the phosphine and sulphide sols respectively ; these make up the total (*i.e.*, the number actually determined)

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[11] Westgren, *Z. anorg. Chem.*, 1915, 93, 156.

shown in the third column of Table I. In experiments made to determine the amount of gold (w_n) in each particle of a particular nuclear sol the corrected value is then $w_n = cvw_g/(10^{-3} - kvw_g)$, where w_g is the experimentally determined weight of each particle in the grown sol, c is the concentration (g. per c.c.) of gold in the nuclear sol, v the (undiluted) volume of the latter, and k the number of extra nuclei produced by 1 c.c. of nuclear sol, as derived from the data in Table I; the 10^{-3} represents the total weight, 1 mg., of gold used in every case. The correction thus introduced is a maximum correction, since it implies that all the extra nuclei found when a blank "nuclear sol" is used are also formed in the presence of added nuclei. The results are shown in Table II to two significant figures.

It has been shown[10] that gold sulphide nuclei, which are present in the nuclear sols used in the second series of measurements, form effective condensation centres for metallic gold. The particles grown on these nuclei contained from 2000 to 2,000,000 times as much gold as the nuclei themselves, and were of course indistinguishable from particles grown on metallic nuclei. The results in this series are less regular than those in the first, but are otherwise similar. The obvious misfits ($N7$, $N15$, $N26$ and $N28$) are not due to any error of measurement; they are probably to be attributed to accidental variations in the rate of mixing the reacting solutions, or in the concentration of the solution of reducing agent used in making the sols.

TABLE I.

Reducing Agent.	Blank Nuclear Sol. (c.c.).	Radius of Particles from 1 mg. Au $m\mu$.	Total No. of Particles formed ($\times 10^{11}$).	No. of Particles per c.c. of Blank Sol ($\times 10^{11}$).
Phosphine . .	1·0	29	5·02	5·0
,, . .	0·5	37	2·41	4·8
,, . .	0·33	40·5	1·84	5·5
				Mean . 5·1
Hydrogen sulphide	2·0	28	5·59	2·8
,, ,,	1·5	30·5	4·31	2·9
,, ,,	1·0	34·5	2·98	3·0
,, ,,	0·67	38·5	2·14	3·2
				Mean . 3·0

After making allowance for these irregularities and for experimental errors, the figures leave no doubt that the particle size decreases with dilution of the reacting solutions down to an apparent limit where the number of atoms per particle is approximately the same as the number constituting a unit cell of crystalline gold. No useful purpose would be served in carrying the dilution still further, since the correction would then become considerably larger than the quantity being measured and the results would have little value.

The Formation and Stability of Nuclei.

The distinction generally recognised between the formation of nuclei and their subsequent growth to larger particles is justified on practical grounds, since these two phases of the formation of a colloidal particle are often affected in different ways by a particular set of conditions. This distinction, as well as the use of the terms "nuclei" and "primary particles" with reference either to aerosols or to hydrosols, unfortunately tends to obscure the essential unity of the processes by which particles of any size are evolved from their parent atoms or molecules. These processes are collision and the mutual adhesion of the units that have collided. In an unstable system such as an aerosol the whole process of building up large particles from molecules is continuous, and must be

TABLE II.

Designation and Concn. of Nuclear Sol (g. Au per c.c.).	Wt. of Nuclei Uncorr. (g. × 10^{21}).	Wt. of Nuclei Corr. (g. × 10^{21}).	No. of Au Atoms per Nucleus.		Designation and Concn. of Nuclear Sol (g. Au per c.c.).	Wt. of Nuclei Uncorr. (g. × 10^{11})	Wt. of Nuclei Corr. (g. × $10)^{11}$.	No. of Au Atoms per Nucleus.	
Sols made with Phosphine :									
				Mean.					Mean.
*N*12	5400	5400	17000		*N*16	30	33	100	
2×10^{-4}	6200	6300	19000		2×10^{-7}	38	42	130	
	6700	6800	21000			37	41	130	
	6000	6100	19000	19000		40	45	140	130
*N*13	1100	1100	3500		*N*17	27	31	96	
8×10^{-5}	1000	1000	3100		10^{-7}	34	41	130	
	1000	1000	3100			40	50	150	
	1000	1000	3000	3200		39	49	150	120
*N*7	1900	2100	6300		*N*18	17	20	63	
10^{-5}	1800	2000	6000		5×10^{-8}	16	19	60	
	1600	1800	5400			15	18	54	
	1600	1800	5400	5800		13	15	46	56
*N*2	690	750	2300		*N*19	9·0	11·7	36	
$4 \cdot 1 \times 10^{-6}$	670	730	2200		2×10^{-8}	7·6	9·3	29	
	650	710	2200			7·2	8·7	27	
	450 *	480 *	1500 *			8·3	10·4	32	31
	660	720	2200	2200	*N*20	3·0	4·9	15	
*N*14	180	200	610		4×10^{-9}	3·1	5·0	16	
10^{-6}	180	200	600			3·2	5·3	16	
	140	150	470	560		2·7	4·2	13	15
*N*15	140	160	500		*N*21	2·3	5·7	17	
5×10^{-7}	170	210	650		2×10^{-9}	2·0	4·3	13	
	190	230	700			2·1	4·5	14	
	180	220	680	630		2·2	5·2	16	15
Sols made with Hydrogen Sulphide :									
*N*24	700	710	2200		*N*29	47	66	200	
2×10^{-5}	720	730	2300		5×10^{-8}	56	84	260	
	660	670	2100			60	93	280	
	600	600	1900			49	68	210	240
	630	630	2000		*N*30	45	79	240	
	610	620	1900	2100	2×10^{3}	37	85	260	
*N*25	420	430	1300			37	81	250	
10^{-5}	410	410	1300			35	73	230	240
	390	400	1200		*N*31	13	22	69	
	380	390	1200	1200	10^{-8}	16	29	88	
*N*26	530	550	1700			20	49	150	
4×10^{-6}	520	540	1700			18	40	120	100
	470	480	1500		*N*32	6·0	11	33	
	440	460	1400	1600	4×10^{-9}	6·8	14	43	
*N*27	140	150	470			6·1	11	35	
8×10^{-7}	140	150	460			5·5	9·4	29	35
	150	160	480		*N*33	2·3	3·4	11	
	160	170	520	480	2×10^{-9}	2·1	3·1	9	
*N*28	34	36	110			2·1	3·2	10	
2×10^{-7}	29	30	92			2·4	3·9	12	10
	30	31	96	99					

* Rejected.

presumed to conform in all its stages to purely kinetic principles. The same is true of a stable hydrosol as far as the production of the smallest stable particles—the so-called nuclei; beyond this point collisions are not followed by adhesion, owing to the electric charge which is acquired when a certain degree of complexity has been reached. The stabilising charge is generally understood to be due to either autogenous or adsorbed ions, and Pauli and others[12] have shown that in the case of gold the stabilising ion is probably $AuCl_2'$ or $Au(OH)Cl'$, presumably formed by the partial reduction of the original gold compound. Unfortunately the effect of varying the concentration of this ion in the reaction mixture cannot be studied, since there is no known way of controlling the amount produced. Attempts such as are recorded in this paper to impart a heavier charge, or to impart a charge at an earlier stage of growth, by the addition of other ions which might be expected to be effective, have led to diminished rather than improved stability, as shown by the increased size of the particles. It seems probable either that the stabilising ion that happens to be formed in the reaction is specially effective, or that the sols themselves are unusually sensitive to very small concentrations of electrolyte even when the latter contains an adsorbable anion.

The data presented in Table II show that the size of the smallest stable particles is greatly affected by the concentration of the solution undergoing reduction; the mass of the resulting nuclei is very roughly proportional to the square root of the gold concentration in both the sulphide and the phosphine series. The figures given for the size of the smallest nuclei are subject to an error perhaps as large as 40 per cent. on account of the relatively large correction involved, but it still remains evident that particles of about the size of a unit cell, *i.e.* 14 atoms, can exist and can be detected in a stable sol.

A survey of the course of events leading to the formation of nuclei indicates that the influence of dilution on particle size cannot be explained on purely kinetic grounds. The addition of the reducing agent causes a sudden appearance of gold atoms at a certain concentration n_0, and these atoms will at once begin to form aggregates by a process analogous to ordinary coagulation. If no stabilising factor is present the particle size will continue to increase indefinitely, but if, as is here assumed, the particles after reaching a certain degree of complexity begin to adsorb stabilising ions, the process must slow down when that stage is reached, and must eventually come to a stop when stabilisation is complete, when no fruitful collisions will occur. It is clear that the influence of n_0 will be strictly confined to determining the frequency of collisions, and that the effectiveness of these must depend on other factors. The observed effect of dilution must therefore be due to some factor other than the mere decrease in the initial concentration of gold atoms, and an explanation of it may be found in the parallel decrease in the concentration of electrolytes. Thiessen[13] showed that the stability of gold sols towards electrolytes increases as the size of the particles decreases over the range 70 — 20 $m\mu$; but it is also known that the stability vanishes altogether at a still lower size; there must therefore be some intermediate size for which the stability is a maximum. Hence in the early stages of growth before this maximum is reached the same degree of

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[12] Eirich and Pauli, *Kolloid Beih.*, 1930, **30**, 113; Pauli, Russer, and Brunner, *Kolloid Z.*, 1925, **72**, 26.

[13] Thiessen, Thater, and Kandelaky, *Z. anorg. Chem.*, 1929, **180**, 11.

stability will be attained by a particle in the presence of a certain concentration of foreign electrolyte as is possessed by a smaller particle in the presence of a smaller concentration. These considerations offer a simple and adequate explanation of the experimental results, if it can be assumed that the stability of gold sols really decreases with increasing concentration of electrolyte at the very small concentrations prevailing during their preparation. Evidence for this is to be found in Zsigmondy and Thiessen's statement[14] that gold sols may be concentrated by evaporation to a maximum of about 0·1 per cent., but only if the evaporation is accompanied by dialysis. The more efficient methods of electrodialysis and electrodecantation have recently enabled Pauli and others[15] to achieve still higher concentrations, up to 5 per cent. Thus it is clear that the stability of gold sols is increased by the removal of electrolyte up to the extreme limits made possible by modern technique. Another possible factor, which may be important at very low concentrations, is the relative quantity of the stabilising ion formed during reduction. Nothing is known as to how this varies with the experimental conditions, but it should be kept in view as a factor the effectiveness of which may vary with the dilution of the gold compound as such, independently of that of the accompanying electrolyte.

The question how far the results obtained with gold may be expected to hold for other substances can be answered only in general terms. It is characteristic of colloidal solutions of gold and other noble metals that their stability increases with the progressive removal of electrolytes, and it is for this reason that in them the smallest particles are formed in sols made from the most dilute solutions. On the other hand substances whose colloidal solutions become unstable or less stable under prolonged dialysis would form the smallest particles at some intermediate dilution. It is clear that each sol must be considered by itself in the light of information about the effect of dilution of the reacting solutions on its stability, an effect which may be due to alteration of the quantity or the composition of the stabilising ion, as well as to the removal of non-stabilising or " foreign " electrolytes.

Homogeneity and Stability of Nuclear Sols.

With reference to the preparation of unidisperse gold sols it is often tacitly assumed that the nuclear sol used for this purpose is itself unidisperse. This assumption is unfounded. Only if the nuclei were formed by the building up of aggregates atom by atom would the process stop when all the aggregates were of approximately equal size. Such a process is hardly conceivable, since the proportion of single atoms becomes very small at an early stage, and further growth must therefore occur chiefly by the union of aggregates; the inevitable result of this is the formation of more complex aggregates whose sizes will be distributed over a considerable range. There can be little doubt that the size distribution in a nuclear sol, though possibly less symmetrical, is otherwise similar to that found in an ordinary sol made without any special precautions. This inference has a practical bearing on the preparation of unidisperse sols, for if the size distribution curves of nuclear sols with different average sizes are of similar shape, it is clearly advantageous to grow a sol on nuclei of the smallest possible average size, since it is

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[14] Zsigmondy and Thiessen, *op. cit.*[7], 47.

[15] Pauli, Szper and Szper, *Trans. Faraday Soc.*, 1939, 35, 1178.

the absolute and not the percentage variation in linear dimensions that is reproduced in the grown particles; and for similar distributions the absolute variation will be proportional to the average size.

A further consequence of the suggested mode of evolution of a nuclear sol is that the freshly prepared sol will be only just stable and will therefore be very sensitive to small additions of electrolyte. For a similar reason slight variation in the conditions prevailing while the sol is being prepared may (for example by altering the amount of stabilising agent formed) cause a marked change in the average particle size. This is perhaps the chief cause of the few irregularities appearing in the results quoted in Table II. It has been found on several occasions that the particle concentration of an undiluted nuclear sol has decreased after the lapse of a few months, presumably because even with the strictest precautions some increase in electrolyte content occurs during storage in glass vessels. Changes of this kind can be avoided by diluting the sol with conductivity water immediately after preparation.

Summary.

1. Previous work on the minimum size of gold nuclei is reviewed.

2. Attempts to reduce the size of nuclei by the addition of adsorbable anions were unsuccessful.

3. Progressive dilution of the reacting solutions over an extensive range resulted in the production of stable nuclei of less than one-tenth the size of the smallest hitherto believed to exist. These nuclei are of approximately the size of a unit cell of crystalline gold.

4. The experimental results are in agreement with the view that the formation of colloidal particles from atoms or molecules is a continuous process governed by the same kinetic principles as are used to explain coagulation. The terms "nuclei" and "primary particles" have no significance apart from their use to describe the smallest particles that are stable or detectable under existing conditions.

The University,
Leeds.

VISCOSITY OF ELECTROLYTIC MIXTURES IN DILUTE SOLUTION.

By A. S. Chacravarti and B. Prasad.

Received 12th February, 1940.

The study of the viscosity of simple electrolytic solutions has received much attention since Jones and Dole[1] proposed their equation $\eta/\eta_0 = 1 + A\sqrt{c} + Bc$ and Falkenhagen, Dole and Vernon[2] gave a theoretical interpretation of "A" in terms of the interionic attraction theory, and found out a mathematical expression for it involving dielectric constant and viscosity of solvent and the mobility and electric charges of the ions. The problem of solutions containing more than

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[1] Jones and Dole, *J. Amer. Chem. Soc.*, 1929, **51**, 2950.

[2] Falkenhagen and Dole, *Z. physik. Chem. B* 1929, **6**, 159; *Physik. Z.*, 1929, **30**, 611; Falkenhagen and Vernon, *Phil. Mag.*, 1932, **14**, 537.

two species of ions with respect to viscosity has not been studied experimentally as yet in the light of the interionic attraction theory. Such works as those of Stearn,[3] Yajnik and Uberoy,[4] Ruby and Kawai,[5] Tollert,[6] Banchetti [7] and Ishikawa [8] are concerned with either the study of complex salt formation or the application of one or the other of the various mixture law formulæ to the viscosity of mixed electrolytes in solution. Onsager and Fuoss [9] are the only workers who have tackled the problem from a theoretical standpoint, but their treatment is so highly mathematical that their analysis has not been able to stimulate the interest the subject deserves. The net result of their analysis is that in the case of mixtures of electrolytes also " the electrostatic contribution to viscosity is proportional to the square root of concentration."

The idea underlying the present investigation was to examine how a mixture of two electrolytes (with a common ion) in a definite proportion behaved with respect to viscosity when the concentration was changed without affecting the proportion of the components of the mixture by diluting with water and whether the variation in viscosity could be represented by an equation of the Jones and Dole type. The salt pairs examined were (*a*) sodium chloride and barium chloride, and (*b*) sodium chloride and magnesium chloride. In each case a number of mixtures containing the two salts in different proportions were examined.

Experimental.

The experimental technique and procedure have been described in previous communications.[10] [11] The viscometer used had a capillary of 10 cm. length and 0·028 cm. diameter with an upper bulb of 5 c.c. capacity. The approximate time of efflux of water was 29 minutes. No kinetic or surface tension correction was considered necessary. Three readings for the time of flow were taken with a Venner time switch graduated in tenths of seconds, agreeing with one another within 0·2 sec. The time for water was determined before and after each solution. The pyknometer was one of about 64 c.c. capacity. The density figures are the results of two determinations, differing by less than 1 mg., the weights being reduced to vacuum standard.[12] Double distilled water was used in all the experiments. The thermostat was maintained at 35° ± 0·005 C. The error in viscosity measurements is expected to be less than three parts in ten thousand and densities are accurate to sixteen parts in a million.

Merck's *pro-analysi* $BaCl_2$, reagent quality $MgCl_2$ and *pro-analysi* NaCl were used. Standard solutions of these salts were prepared and their strengths were determined. Barium chloride was estimated gravimetrically as BaSO, $MgCl_2$ as AgCl after eliminating Mg by precipitation as $MgCO_3$ and NaCl by direct weighing after drying in an air oven at 130° C. Mixtures having the two salts in different proportions were prepared by mixing the solutions in proper proportion. The mixtures were then diluted to decrease their concentration to the required level.

The results are tabulated below. Total concentrations are given in gram moles per litre and densities are expressed in grams per c.c. η/η_0(obs.)

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[3] Stearn, *J. Amer. Chem. Soc.*, 1922, **44**, 670.
[4] Yajnik and Uberoy, *ibid.*, 1924, **46**, 802.
[5] Ruby and Kawai, *ibid.*, 1926, **48**, 1120.
[6] Tollert, *Z. physik. Chem.*, *A*, 1935, **172**, 129.
[7] Banchetti, *Gazz. Chim. Ital.*, 1934, **64**, 229 ; 1935, **65**, 159 ; 1936, **66**, 446.
[8] Ishikawa, *Bull. Chem. Soc. Japan*, 1937, **12**(1), 16.
[9] Onsager and Fuoss, *J. Physic. Chem.*, 1932, **36**, 2689.
[10] Srinivasan and Prasad, *Trans. Faraday Soc.*, 1938, **34**, 1139.
[11] Chacravarti and Prasad, *ibid.*, 1939, **35**, 1466.
[12] Srinivasan and Prasad, *ibid.*, 1462.

and η/η_0(calc.) are the relative viscosities, observed and calculated from the equation. The divergence (Δ) between the two is given in the last column.

TABLE I.

Pure NaCl; $\eta/\eta_0 = 1 + 0{\cdot}006\sqrt{c} + 0{\cdot}102c$.

Total Concentration.	Density.	η/η_0 (obs.).	η/η_0 (calc.).	$\Delta \times 10^4$.
0·0100	0·994478	1·0016	1·0016	0
0·0200	0·994870	1·0030	1·0028	+2
0·0300	0·995255	1·0041	1·0041	0
0·0400	0·995669	1·0053	1·0053	0
0·0500	0·996076	1·0065	1·0064	+1
0·0600	0·996467	1·0076	1·0076	0
0·0700	0·996872	1·0087	1·0087	0

[NaCl]/[BaCl$_2$] = 3; $\eta/\eta_0 = 1 + 0{\cdot}009\sqrt{c} + 0{\cdot}132c$.

Total Concentration.	Density.	η/η_0 (obs.).	η/η_0 (calc.).	$\Delta \times 10^4$.
0·0100	0·994771	1·0020	1·0022	−2
0·0200	0·995511	1·0039	1·0039	0
0·0300	0·996270	1·0056	1·0056	0
0·0400	0·997033	1·0074	1·0071	+3
0·0500	0·997767	1·0086	1·0086	0
0·0600	0·998508	1·0101	1·0101	0
0·0700	0·999257	1·0115	1·0116	−1

[NaCl]/[BaCl$_2$] = 1; $\eta/\eta_0 = 1 + 0{\cdot}011\sqrt{c} + 0{\cdot}170c$.

Total Concentration.	Density.	η/η_0 (obs.).	η/η_0 (calc.).	$\Delta \times 10^4$.
0·0100	0·995136	1·0026	1·0028	−2
0·0200	0·996236	1·0048	1·0050	−2
0·0300	0·997344	1·0069	1·0070	−1
0·0400	0·998421	1·0090	1·0090	0
0·0500	0·999519	1·0112	1·0110	+2
0·0600	1·000595	1·0129	1·0129	0
0·0700	1·001687	1·0150	1·0148	+2

[NaCl]/[BaCl$_2$] = 1/3; $\eta/\eta_0 = 1 + 0{\cdot}015\sqrt{c} + 0{\cdot}205c$.

Total Concentration.	Density.	η/η_0 (obs.).	η/η_0 (calc.).	$\Delta \times 10^4$.
0·0100	0·995479	1·0034	1·0036	−2
0·0200	0·996866	1·0062	1·0062	0
0·0300	0·998319	1·0086	1·0088	−2
0·0400	0·999720	1·0114	1·0112	+2
0·0500	1·001152	1·0137	1·0137	0
0·0600	1·002580	1·0159	1·0160	−1
0·0700	1·003987	1·0183	1·0184	−1

[NaCl]/[MgCl$_2$] = 4; $\eta/\eta_0 = 1 + 0{\cdot}009\sqrt{c} + 0{\cdot}165c$.

Total Concentration.	Density.	η/η_0 (obs.).	η/η_0 (calc.).	$\Delta \times 10^4$.
0·0100	0·994547	1·0027	1·0026	+1
0·0200	0·995020	1·0046	1·0046	0
0·0300	0·995518	1·0067	1·0066	+1
0·0400	0·995999	1·0083	1·0084	−1
0·0500	0·996499	1·0102	1·0103	−1
0·0600	0·996982	1·0122	1·0121	+1
0·0700	0·997468	1·0140	1·0140	0

[NaCl]/[MgCl$_2$] = 3/2; $\eta/\eta_0 = 1 + 0{\cdot}011\sqrt{c} + 0{\cdot}220c$.

Total Concentration.	Density.	η/η_0 (obs.).	η/η_0 (calc.).	$\Delta \times 10^4$.
0·0100	0·994624	1·0034	1·0033	−1
0·0200	0·995181	1·0059	1·0060	−1
0·0300	0·995762	1·0083	1·0085	−2
0·0400	0·996306	1·0109	1·0110	−1
0·0500	0·996880	1·0134	1·0135	−1
0·0600	0·997429	1·0160	1·0159	+1
0·0700	0·997998	1·0182	1·0183	−1

[NaCl]/[MgCl$_2$] = 2/3; $\eta/\eta_0 = 1 + 0{\cdot}013\sqrt{c} + 0{\cdot}282c$.

Total Concentration.	Density.	η/η_0 (obs.).	η/η_0 (calc.).	$\Delta \times 10^4$.
0·0100	0·994690	1·0042	1·0041	+1
0·0200	0·995327	1·0077	1·0074	+3
0·0300	0·995963	1·0107	1·0107	0
0·0400	0·996605	1·0138	1·0139	−1
0·0500	0·997248	1·0167	1·0170	−3
0·0600	0·997930	1·0198	1·0201	−3
0·0700	0·998582	1·0230	1·0231	−1

Discussion.

The applicability or otherwise of the Jones and Dole equation in case of any mixture having the two salts in a fixed proportion was tested by plotting $(\eta/\eta_0 - 1)/\sqrt{c}$ against $\sqrt{c}$, where "c" is the total concentration of electrolyte in gram moles per litre. In every case a straight line was obtained, showing the applicability of the equation. The coefficients "A" and "B" for any such mixture were determined as usual from the plot. Onsager and Fuoss's expectation, *viz.* the existence of a square root term in the viscosity-concentration relation of electrolytic mixtures, thus receives the first experimental verification. Of course, it has to be borne in mind that here, as in the case of single substances, the law is correct only for dilute solutions.

Another behaviour which has been noticed is that the value of " A " in case of a mixture of two electrolytes changes linearly with increase or decrease of the fractional molar concentration $c/(c_1 + c_2)$ for one of the electrolytes. The following figure will make this point clear. As the lines obtained in the cases of sodium chloride-barium chloride and sodium chloride-magnesium chloride mixtures are similar, only one of them is given. The values of " A " for pure barium chloride and magnesium chloride are taken from a previous paper.[11]

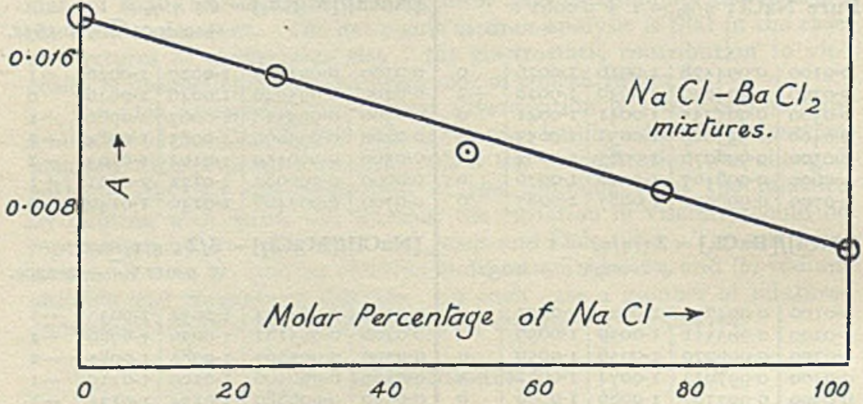

FIG. 1.

Thus, it follows that the value of " A " for any mixture containing the salts in the ratio c_1/c_2 is given by the expression $A = xA_1 + (1 - x)A_2$, where x, *i.e.* $c_1/(c_1 + c_2)$ is the fractional molar concentration of the first component and A_1 and A_2 are the values of " A " for the first and second component respectively.

Further work on the viscosity of mixed electrolytic solutions is in progress. The additivity of the values of " B " for mixtures will be discussed in a subsequent communication.

One of us (A. S. C.) wishes to record his thanks to the Government of Orissa for the award of a Research Scholarship.

Summary.

1. Viscosity and density of mixed solutions of barium chloride with sodium chloride and magnesium chloride with sodium chloride in three different proportions as well as the values for pure sodium chloride are reported.

2. Onsager and Fuoss's limiting law for mixed ionic solutions has been established in these cases.

3. An equation of the Jones and Dole type has been applied with success to all the mixed solutions.

4. The coefficient of the square root term " A " has been shown to be a linear function of composition.

Chemical Laboratory,
Ravenshaw College,
Cuttack, India.

THE EFFECT OF HYDROCHLORIC ACID ON THE VISCOSITY OF BARIUM AND MAGNESIUM CHLORIDE SOLUTIONS.

By A. S. Chacravarti and B. Prasad.

Received 12*th February*, 1940.

A good deal of work has been done on the viscosity of dilute solutions of electrolytes in order to test the Jones and Dole[1] equation :

$$\eta/\eta_0 = 1 + A\sqrt{c} + Bc,$$

as well as to compare the experimental value of " *A* " with that obtained from Falkenhagen and Vernon's[2] equation. Generally, the agreement has been good. Discrepancies have been observed in the cases of lanthanum chloride,[3] magnesium sulphate,[3] and nickel chloride.[4] When the salts are likely to be hydrolysed, some authors add a small amount of acid to repress hydrolysis. Thus, Cox and Wolfenden[3] added small amounts of hydrochloric acid to lanthanum chloride solutions. The present authors, while studying the effect of hydrochloric acid on the value of " *A* " for cadmium chloride,[5] found that the value of " *A* " was appreciably depressed in dilute solutions of hydrochloric acid. The Jones and Dole equation had not been expected to hold good with hydrochloric acid as solvent, as there is no allowance in Falkenhagen and Vernon's treatment for the electrical field due to charged ions from the solvent itself, even for the most dilute solutions. It was considered probable that the validity of the equation as well as the lowering of the value of " *A* " might be due to the formation of complex $CdCl_4^{--}$ ions, and that the equation might break down if solutions of barium chloride or magnesium chloride in dilute hydrochloric acid were tried, as there was no possibility of complex ions being formed in these cases. With this object in view as well as with the idea of studying the change in the value of " *A* " with change in concentration of hydrochloric acid in case the Jones and Dole equation happened to hold good, it was decided to measure the viscosity of barium chloride and magnesium chloride in solutions containing hydrochloric acid, whose concentration was kept stationary for one set of measurements.

Experimental.

The experimental procedure is the same as that described in previous papers.[6] [4] The temperature was maintained at 35° ± 0·005 C. Double distilled water was used in all the experiments. No kinetic or surface tension correction was necessary with the viscometer used. The length of the capillary tube of the viscometer was 10 cm., its diameter 0·028 cm.,

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[1] Jones and Dole, *J. Amer. Chem. Soc.*, 1929, **51**, 2950.

[2] Falkenhagen and Vernon, *Phil. Mag.*, 1932, **14**, 537.

[3] Cox and Wolfenden, *Proc. Roy. Soc., A*, 1934, **145**, 475.

[4] Chacravarti and Prasad, *Trans. Faraday Soc.*, 1939, **35**, 1466.

[5] Chacravarti and Prasad, *J. Ind. Chem. Soc.*, 1938, **15**, 479.

[6] Srinivasan and Prasad, *Trans. Faraday Soc.*, 1938, **34**, 1139.

TABLE I.

Concentration.* (g. moles./litre).	Density (g./c.c.).	Relative Viscosity (observed).	Relative Viscosity (calculated).
1. HCl; $\eta/\eta_0 = 1 + 0{\cdot}006\sqrt{c} + 0{\cdot}060c$.			
0·0020	0·994087	1·0005	1·0004
0·0040	0·994127	1·0007	1·0006
0·0070	0·994170	1·0007	1·0009
0·0100	0·994233	1·0010	1·0012
0·0150	0·994315	1·0018	1·0016
0·0500	0·994949	1·0047	1·0044
0·1000	0·995834	1·0081	1·0079
2. $BaCl_2$ in 0·0020M. HCl; $\eta/\eta_0 = 1{\cdot}0004 + 0{\cdot}014\sqrt{c} + 0{\cdot}240c$.			
0·0025	0·994503	1·0015	1·0018
0·0050	0·994969	1·0026	1·0027
0·0150	0·996711	1·0062	1·0058
0·0250	0·998463	1·0087	1·0087
0·0400	1·001101	1·0126	1·0129
3. $BaCl_2$ in 0·0040M. HCl; $\eta/\eta_0 = 1{\cdot}0006 + 0{\cdot}012\sqrt{c} + 0{\cdot}260c$.			
0·0010	0·994307	1·0013	1·0013
0·0040	0·994848	1·0023	1·0024
0·0100	0·995902	1·0044	1·0044
0·0180	0·997322	1·0071	1·0069
0·0250	0·998506	1·0090	1·0090
0·0400	1·001155	1·0134	1·0134
4. $BaCl_2$ in 0·0070M. HCl; $\eta/\eta_0 = 1{\cdot}0009 + 0{\cdot}009\sqrt{c} + 0{\cdot}280c$.			
0·0025	0·994621	1·0023	1·0021
0·0050	0·995063	1·0031	1·0029
0·0150	0·996876	1·0060	1·0061
0·0250	0·998681	1·0096	1·0093
0·0400	1·001338	1·0137	1·0139
5. $BaCl_2$ in 0·0100M. HCl; $\eta/\eta_0 = 1{\cdot}0012 + 0{\cdot}006\sqrt{c} + 0{\cdot}270c$.			
0·0010	0·994415	1·0014	1·0017
0·0025	0·994681	1·0021	1·0022
0·0040	0·994912	1·0025	1·0027
0·0075	0·995543	1·0040	1·0037
0·0150	0·996856	1·0060	1·0059
0·0250	0·998614	1·0086	1·0089
0·0400	1·001232	1·0132	1·0132
6. $BaCl_2$ in 0·0150M. HCl; $\eta/\eta_0 = 1{\cdot}0016 + 0{\cdot}322c$.			
0·0025	0·994746	1·0024	1·0024
0·0050	0·995223	1·0030	1·0032
0·0150	0·997007	1·0065	1·0064
0·0250	0·998839	1·0101	1·0097
0·0400	1·001534	1·0141	1·0145
7. $BaCl_2$ in 0·0500M. HCl; $\eta/\eta_0 = 1{\cdot}0044 + 0{\cdot}295c$.			
0·0010	0·995132	1·0048	1·0047
0·0040	0·995659	1·0060	1·0056
0·0075	0·996251	1·0067	1·0066
0·0150	0·997587	1·0090	1·0088
0·0250	0·999317	1·0117	1·0118
0·0400	1·001954	1·0159	1·0162
8. $MgCl_2$ in 0·0025M. HCl; $\eta/\eta_0 = 1{\cdot}0005 + 0{\cdot}014\sqrt{c} + 0{\cdot}400c$.			
0·0100	0·994861	1·0059	1·0059
0·0200	0·995669	1·0107	1·0105
0·0300	0·996467	1·0147	1·0149
0·0400	0·997239	1·0193	1·0193
0·0500	0·998046	1·0238	1·0236
9. $MgCl_2$ in 0·0050M. HCl; $\eta/\eta_0 = 1{\cdot}0007 + 0{\cdot}011\sqrt{c} + 0{\cdot}415c$.			
0·0100	0·994866	1·0059	1·0060
0·0200	0·995665	1·0109	1·0106
0·0300	0·996456	1·0149	1·0151
0·0400	0·997251	1·0195	1·0195
0·0475	0·997831	1·0226	1·0228
10. $MgCl_2$ in 0·0075M. HCl; $\eta/\eta_0 = 1{\cdot}0010 + 0{\cdot}008\sqrt{c} + 0{\cdot}430c$.			
0·0100	0·994905	1·0060	1·0061
0·0200	0·995684	1·0110	1·0106
0·0300	0·996481	1·0153	1·0153
0·0400	0·997276	1·0194	1·0198
0·0500	0·998059	1·0240	1·0243
11. $MgCl_2$ in 0·0100M. HCl; $\eta/\eta_0 = 1{\cdot}0012 + 0{\cdot}004\sqrt{c} + 0{\cdot}445c$.			
0·0025	0·994394	1·0022	1·0025
0·0100	0·995007	1·0061	1·0061
0·0150	0·995400	1·0080	1·0084
0·0200	0·995799	1·0109	1·0107
0·0300	0·996590	1·0153	1·0153
0·0400	0·997396	1·0198	1·0198
12. $MgCl_2$ in 0·0125M. HCl; $\eta/\eta_0 = 1{\cdot}0014 + 0{\cdot}002\sqrt{c} + 0{\cdot}450c$.			
0·0100	0·994988	1·0064	1·0061
0·0200	0·995773	1·0107	1·0107
0·0300	0·996571	1·0153	1·0152
0·0400	0·997352	1·0195	1·0198
0·0500	0·998136	1·0239	1·0243
13. $MgCl_2$ in 0·0500M. HCl; $\eta/\eta_0 = 1{\cdot}0044 + 0{\cdot}430c$.			
0·0100	0·995648	1·0089	1·0087
0·0200	0·996434	1·0130	1·0130
0·0300	0·997236	1·0174	1·0173
0·0400	0·998029	1·0215	1·0216
0·0500	0·998784	1·0257	1·0259

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* For (1)—of HCl; for (2)-(7)—of $BaCl_2$; for (8)-(13)—of $MgCl_2$.

and the approximate time of efflux for water was 29 minutes. Three readings for the time of flow generally agreeing within 0·2 sec. were taken with a Venner time switch marked off in tenths of seconds. The mass of a definite volume of the solution was determined in a pyknometer (about 64 c.c.), described before.[4] The density figures are results of two determinations, the weights being reduced to vacuum as described in a previous communication.[7] In every case, relative viscosity η/η_0 (viscosity of solution/viscosity of water) was calculated as usual. Viscosity is accurate to 3 parts in 10,000 and density 16 in a million.

The $BaCl_2$ used was Merck's *pro-analysi* quality, $MgCl_2$ was Merck's reagent quality, and HCl was Schering-Kahlbaum's *pro-analysi* quality. A stock solution was prepared in each case whose strength was found gravimetrically. This solution was diluted to the proper concentrations. The results are given in the tables on opposite page.

Discussion.

In the case of hydrochloric acid, " *A* " and " *B* " are obtained by plotting $(\eta_{\text{HCl}}/\eta_0 - 1)/\sqrt{c}$ against $\sqrt{c}$. The intercept on the ordinate gives " *A* " and the slope of the straight line gives " *B* ".

In case of barium and magnesium chloride solutions in presence of a fixed concentration of hydrochloric acid $(\eta/\eta_0 - \eta_{\text{HCl}}/\eta_0)/\sqrt{c}$ plotted against $\sqrt{c}$ gives straight lines. Hence, these results can be represented by an equation of the same kind as in aqueous solutions;

$$\eta/\eta_0 = \eta_{\text{HCl}}/\eta_0 + A\sqrt{c} + Bc.$$

Only " 1 ", the relative viscosity of water is replaced by η_{HCl}/η_0, the relative viscosity of the hydrochloric acid solution, that is the solvent in these cases. " *A* " and " *B* " in acid solutions are found as in aqueous solutions. As for the value of η_{HCl}/η_0 (*i.e.*, the relative viscosity of the hydrochloric acid solution), it was calculated by means of the " *A* " and " *B* " constants for hydrochloric acid, which were obtained from the measurements on pure HCl solutions given in the table.

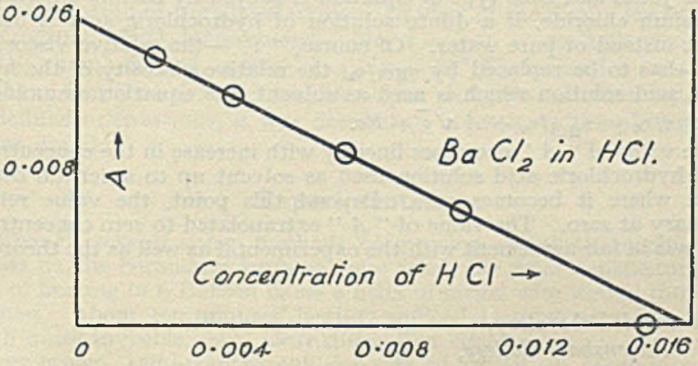

Fig. 1.

The surprising result that we get is that the Jones and Dole equation holds good even when dilute solutions of hydrochloric acid are used as solvents. The electrical field due to the ions from the acid does not make the Jones and Dole equation inapplicable. The equation holds

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[7] Srinivasan and Prasad, *Trans. Faraday Soc.*, 1939, 35, 1462.

good, but the value of "A" steadily decreases as the concentration of hydrochloric acid increases, as is seen in the figure. As the lines obtained for barium chloride and magnesium chloride are similar, only one of them is shown. It can be seen from the figure that the decrease is linear up to a certain concentration of hydrochloric acid beyond which "A" becomes zero.

The value of "A" extrapolated to zero concentration of acid is in fair agreement with the experimental [4] as well as the theoretical [2] value. This behaviour may be utilised in determining the value of "A" for salts which hydrolyse in aqueous solution. The value of "A" in aqueous solution for these salts can be found indirectly by making measurements in hydrochloric acid solutions of several fixed concentrations and extrapolating the straight line obtained therefrom to zero concentration of acid. Some tri-univalent salts will be taken up to examine the possibility of this method.

	Theoretical.	Experimental.	Extrapolated.
"A" for $BaCl_2$	0·015	0·018	0·016
"A" for $MgCl_2$	0·017	0·017	0·017

One of us (A. S. C.) wishes to record his thanks to the Government of Orissa for the grant of a Research Scholarship.

Summary.

The Jones and Dole type of equation is obeyed by barium chloride and magnesium chloride, if a dilute solution of hydrochloric acid is used as solvent instead of pure water. Of course, "1"—the relative viscosity of water—has to be replaced by η_{HCl}/η_0, the relative viscosity of the hydrochloric acid solution which is used as solvent, the equation assuming the form: $\eta/\eta_0 = \eta_{HCl}/\eta_0 + A\sqrt{c} + Bc$.

The value of "A" decreases linearly with increase in the concentration of the hydrochloric acid solution used as solvent up to a certain concentration where it becomes zero. Beyond this point, the value remains stationary at zero. The value of "A" extrapolated to zero concentration of acids is in fair agreement with the experimental as well as the theoretical value.

Chemical Laboratory,
Ravenshaw College,
Cuttack, India.

AN ELECTRON DIFFRACTION STUDY OF THE SURFACE REACTION BETWEEN NICKEL OXIDE AND CORUNDUM.

By H. R. Thirsk and E. J. Whitmore.*

Received 18*th January*, 1940.

The structure and orientation of deposits of substances evaporated on to single crystal substrates have recently been the subject of some research. Most of the investigations have been devoted to the study of metallic films formed on ionic crystals. The present paper, however, is mainly concerned with an example of a kind of orientation not previously observed, namely that of a non-metallic film condensed on to a crystal not definitely ionic. The example is that of nickel oxide deposited on corundum single crystal surfaces. Interest in this was first aroused by the observation of some remarkable electron-diffraction patterns yielded by a specimen of corundum which had been used for certain experiments on the effect of heat on the structure of the polish layer. The patterns were then identified as being due to nickel oxide originating from a nickel wire support used during an experimental heat treatment. The orientation of the nickel oxide crystals was such as to suggest that the oxide had been formed prior to deposition, and that the corundum surface was in effect an active substrate in that it determined the nature of the orientation of the nickel oxide. In view of the dissimilarity of the two structures (NiO, face-centred cubic, $a = 4{\cdot}17$ A., rocksalt structure; α-Al_2O_3, rhombohedral, $a = 5{\cdot}13$ A., $\alpha = 55^\circ\ 6'$, hæmatite structure), and of the fact that the electron diffraction patterns indicated unusually well-defined orientations, it was decided to investigate the phenomenon in some detail.

Experimental.

Although several other methods of growing orientated nickel oxide deposits on the corundum surfaces were tried, the most satisfactory consisted of heating in a Bunsen flame a helix of nickel wire wound round the specimen. About ten minutes' heating sufficed to produce a film which, though quite invisible, gave clear diffraction effects.

Grey-brown, semi-transparent deposits of nickel on corundum were obtained by heating a nickel filament in vacuo near the surface of the heated specimen. These films could readily be oxidised by heating in air, when they became transparent and colourless. Films of similar appearance, but consisting of a mixture of nickel and nickel oxide were obtained by evaporation in air at about 10^{-2} mm. pressure.

The corundum crystals were in the form of rectangular blocks, each of which had one face highly polished. These faces were cut so that their normals were at approximately 0°, 30°, 60°, or 90° to the optic axis. They yielded electron diffraction patterns of diffuse spots. After etching (with a mixture of concentrated nitric and sulphuric acids) or annealing at about

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* For Figs. 1-4 see Plate VII; Figs. 7, 8, 10, 11, 12 and 15 see Plate VIII, and Figs. 16-19 see Plate IX.

1000° C. these surfaces yielded the Kikuchi line patterns characteristic of well-formed single crystals.

A camera length of 22·5 cm. and various accelerating potentials near 50 KV. were used.

Results.

Nickel films evaporated on to corundum were found to consist of completely random crystals, together with a few having one degree of orientation, that is one type of net plane being parallel to the surface but the crystals otherwise at random. Nickel oxide films prepared in the manner outlined above consisted mainly of crystals exhibiting two degrees of orientation, that is, having certain specific positions relative to the underlying crystal. Films of nickel on corundum heated in air became colourless and transparent, and were found to consist of unorientated nickel oxide. Films prepared in a very limited supply of air consisted of a mixed deposit of nickel and nickel oxide, of which the nickel was random, and the nickel oxide orientated. Hence it was clear that orientation in two dimensions of nickel oxide crystals on corundum is only possible when the deposit is built up from the vapour, *i.e.* molecule by molecule. Evidently the nature of the orientation observed in this case is determined by the crystal structure of corundum and its relationship to that of nickel oxide.

Of the eight polished corundum surfaces employed, five were crystallographically different and four approximated closely to important planes in the crystal. These planes were approximately the basal plane $\{000,1\}$, the prisms $\{11\bar{2},0\}$, and $\{10\bar{1},0\}$, and the rhombohedron $\{10\bar{1},1\}$. The fifth surface contained a basal axis of the crystal, and was inclined by about 30° to the basal plane.

The Kikuchi line pattern served for the accurate identification of the crystallographic directions of the corundum surfaces. Thus, if in the Kikuchi line pattern from a triclinic crystal having axes a, b, c, and interaxial angles α, β, γ, the trace of a lattice row $[\lambda\mu\nu]$ approximately normal to the plate be chosen as origin, the trace of a plane (uvw) containing $[\lambda\mu\nu]$ be taken as the x-axis and the normal to it as the y-axis, then the equation of the median of the pair of Kikuchi lines arising from the plane (hkl) is given by

$$Px + Ry + L = 0,$$

where

$$P = \frac{d_{uvw}}{V(\lambda h + \mu k + \nu l)} \begin{vmatrix} \lambda a^2 + \mu ab\cos\gamma & \mu b^2 + \nu bc\cos\alpha & \nu c^2 + \lambda ca\cos\beta \\ + \nu ca\cos\beta, & + \lambda ab\cos\alpha, & + \mu bc\cos\alpha \\ u & v & w \\ h & k & l \end{vmatrix}.$$

and

$$R = \frac{D_{\lambda\mu\nu}\quad d_{uvw}}{V^2(\lambda h + \mu k + \nu l)}\left[\sum_{abc} uhb^2c^2\sin^2\alpha - \sum_{abc}(kw + lv)a^2bc(\cos\alpha - \cos\beta\cos\gamma)\right];$$

and, further,

L = camera length,

V = volume of unit cell $= abc\sqrt{1 - \Sigma\cos^2\alpha + 2\cos\alpha\cos\beta\cos\alpha}$,

d_{uvw} = net plane spacing of (uvw)

$$= V/\sqrt{\Sigma u^2b^2c^2\sin^2\alpha - \Sigma 2vwa^2bc\,(\cos\alpha - \cos\beta\cos\gamma)},$$

and $D_{\lambda\mu\nu}$ = spacing of lattice row $[\lambda\mu\nu] = \sqrt{\Sigma\lambda^2a^2 + 2\Sigma\mu\nu bc\cos\alpha}$.

In the case of corundum it is simpler to use a hexagonal unit cell,

$$a = b,\ c/a = c_0,\ \alpha = \beta = 90°,\ \gamma = 120°.$$

Hence $P = \begin{vmatrix} \lambda - \frac{1}{2}\mu & \mu - \frac{1}{2}\lambda & \nu c_0^2 \\ u & v & w \\ h & k & l \end{vmatrix} \div (\lambda h + \mu k + \nu l)\sqrt{(u^2 + uv + v^2)c_0^2 + \frac{3}{4}w^2}$.

$$\text{and } R = \frac{2\sqrt{\lambda^2 - \lambda\mu + \mu^2 + \nu c_0{}^2}\left[u(h + \tfrac{1}{2}k) + v(k + \tfrac{1}{2}h) + \tfrac{3}{4}w\dfrac{l}{c_0{}^2}\right]}{(\lambda h + \mu k + \nu l)\,.\,\sqrt{3}\,.\,\sqrt{u^2 + uv + v^2 + \dfrac{3}{4}\dfrac{w^2}{c_0{}^2}}}.$$

For a prism face (11$\bar{2}$,0) and the [001] azimuth

$$P = \frac{c_0(k-h)}{\sqrt{3}\,.\,l},$$

$$R = \frac{(h+k)c_0}{l}.$$

The equation of the median of a pair of Kikuchi lines in the pattern (Fig. 18) is thus

$$(k-h)x + \sqrt{3}(k+h)y + \sqrt{3}\,.\,lL/c_0 = 0.$$

The first surface used was within 2° of the prism face (11$\bar{2}$,0), and Figs. 1 and 3 are electron diffraction patterns from nickel oxide films deposited thereon. Fig. 1 was obtained with the beam in the direction of the *c*-axis azimuth, and similar patterns occurred at each 60° azimuth from this direction, while the pattern (Fig. 3), was obtained at 30°, 90°, etc. The principal spot pattern can readily be indexed from the diagrams, Figs. 2 and 4. These patterns indicate that the nickel oxide crystals are for the most part orientated with {111} planes parallel to the prism face, and ⟨11$\bar{2}$⟩ lattice rows parallel to the *c*-axis of the corundum. Two equivalent orientations fulfil these conditions, and the superposition of the two corresponding patterns in each azimuth results in the patterns shown. In Fig. 1 the spots from crystals in the two orientations coincide in the zero-, third-, etc., order Laue zones. Fig. 2 is the index diagram corresponding to Fig. 1, and

$$\mp\, 2H' = h - k,$$
$$K' = h + k + l,$$
$$\pm\, 2L' = h + k - 2l; \text{ and}$$

Fig. 4 is the index diagram of the pattern Fig. 3,

where
$$\pm\, 2H' = h + k - 2l,$$
$$K' = h + k + l$$
$$\pm\, 2L' = h - k.$$

A second prism face cut less accurately than the first was also used. In this case the *c*-axis was inclined by about 6° to the surface (Fig. 18). Again a similar orientation was obtained, the {111} planes of the nickel oxide being parallel to the prism face, and not to the surface of the specimen.

It will be noticed that there is present in Fig. 1 a faint pattern of spots similar to the pattern of strong spots in Fig. 3, and *vice versa;* thus some of the nickel oxide crystals are orientated with the {111} planes parallel to the prism face and the ⟨1$\bar{1}$0⟩ lattice row parallel to the *c*-axis, *i.e.* at 90° to the prevalent orientation. Furthermore, there are present a series of what are apparently very faint half-order diffractions, which are slightly drawn out towards the shadow edge. A complete explanation of the appearance of these will be given subsequently. Again in Fig. 3 there are diffractions for which $H' = 0$, 6, 12, etc., when $K' = 1$, 2, 4, 5, 7, 8, etc., and for $H' = 1$, 2, 4, 5, 7, 8, etc., when $K' = 0$, 3, 6, etc. These give values of h, k, and l which differ by $\frac{1}{3}$ from integers. Thus these might at first sight be supposed to be due to some kind of submicroscopic twinning, as has been postulated in the case of silver films on rocksalt,[1] but if this were the case, certain of them, for example those in the plane of incidence, should appear in Fig. 1 (which was obtained from the same

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[1] G. Menzer, *Z. Krist.*, 1938, **99**, 378; O. Goche and H. Wilman, *Proc. Physic. Soc.*, 1939, **51**, 625.

specimen) whereas they are absent. A satisfactory explanation of their appearance in Fig. 3 is provided by "double diffraction," the re-diffraction by a crystal in one orientation of a beam arising from diffraction by a crystal in the other orientation. It is worthy of note that in the patterns from silver films condensed on to rocksalt those of the "extra" spots which are not due to simple twinning may be explained in the same way.

In Fig. 5 the arrangement of lattice points in the junction planes of the two crystals are superposed. The corundum lattice is regarded as being "body-centred" rhombohedral; this is not quite accurate, since the two molecules in this "body-centred" unit cell are rotated with respect to one another by 180° about the three-fold axis. It will be seen from the figure that there is no close fit of the two lattices along the plane of junction. The reason for the similarity in dimensions between the spot patterns of the nickel oxide and of the corundum in the [001] azimuth of the latter lies in the coincidence in spacing of the net planes parallel to the surface and to the plane of incidence in the two structures. Thus for corundum the spacings of the $(11\bar{2},0)$ and $(10\bar{1},0)$ planes respectively are 2·38 and 1·37 A., while for nickel oxide the spacings of the $\{111\}$ and $\{1\bar{1}0\}$ planes which are parallel to these are 2·41 and 1·47 A. respectively. If the arrangement of oxygen atoms in a $(11\bar{2},0)$ plane is considered, it is found that they form a network similar to that in the octahedral plane of nickel oxide (Fig. 6), and the two structures fit by virtue of this similarity.

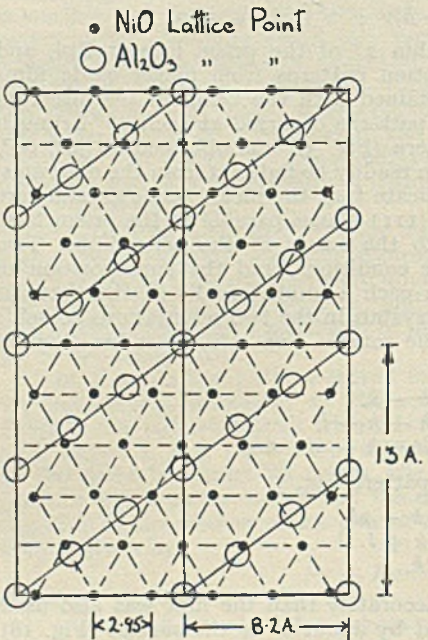
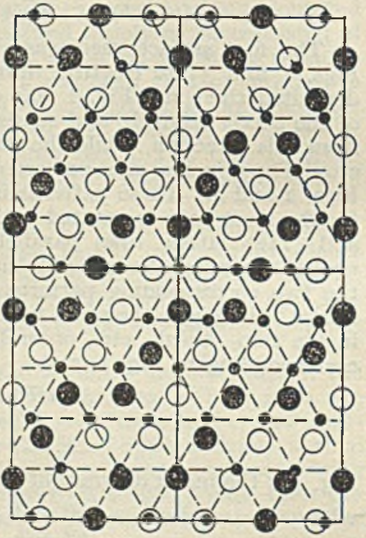


FIG. 5.—(111) net of nickel oxide and $(11\bar{2},0)$ net of corundum in their relative positions.



○ Oxygen atoms of molecules in one $(11\bar{2},0)$ net plane of Al_2O_3.

⬤ Oxygen atoms of molecules in the adjacent $(11\bar{2},0)$ net plane of Al_2O_3.

● Oxygen atoms of nickel oxide.

FIG. 6.—As Fig. 5, but showing the oxygen arrangement of corundum.

A peculiar feature of this case of orientation is that although the two predominant orientations of the nickel oxide crystals are equivalent, there is a decided tendency for one of them to occur more strongly than the other. This was especially the case in very thin films; moreover, it is always the same orientation that is preferred on a given specimen.

Figs. 7 and 8 are diffraction patterns obtained from a nickel oxide film formed on the basal plane (000,1) of corundum. It was immediately apparent that these patterns were similar to Figs. 1 and 3. In this case the {111} plane of nickel oxide is parallel to the basal plane and the $\langle 11\bar{2}\rangle$ lattice row parallel to the *a*-direction of the corundum. Extra diffractions similar to those obtained from films on the prism face are also present, but the apparently half-order diffractions are fainter. There are also present continuous rings, probably as a result of incomplete annealing of the substrate crystal. The two lattices fit fairly well along the junction plane, as shown in Fig. 9.

The two orientations of nickel oxide on corundum so far described, *viz.*, those on the prism $\{11\bar{2},0\}$ and the base {000,1} are entirely different as regards crystallographic direction. Thus unlike the epitaxy of sodium nitrate on calcite,[2] there is no single definite orientation of deposit and substrate which is independent of the direction of the substrate surface. It is therefore of interest to note that both of these orientations can occur on the surfaces inclined by as much as 30° to the plane defining the orientation. For example, on a surface containing an *a*-axis of the corundum, but inclined by about 30° to the basal plane, nickel oxide films are orientated in exactly the same way as on the basal plane. When the electron beam is parallel to the *a*-axis, therefore, a diffraction pattern (Fig. 12) similar to Fig. 7, is obtained, except that it is tilted by 30° to the shadow edge. Further, the orientation observed on the prism $\{11\bar{2},0\}$ also occurs on the prism $\{10\bar{1},0\}$. Nickel oxide crystals with octahedral planes parallel to the two prisms of the type $\{11\bar{2},0\}$ adjacent to and making angles of 30° with surface occur. Thus there are present four positions with the $\langle 11\bar{2}\rangle$ lattice row of nickel oxide parallel to the *c*-axis of the corundum. It was observed that both on the plane inclined by 30° to the basal plane and on the prism $\{10\bar{1}, 0\}$ the patterns consisted of arcs rather than spots.

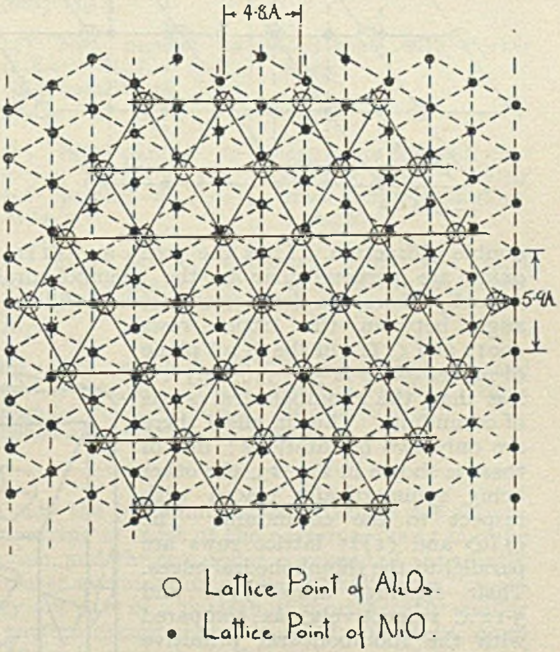


FIG. 9.—(111) net of nickel oxide and (000,1) net of corundum in their relative positions.

One other kind of orientation of nickel oxide on corundum was observed. A surface cut so that it was inclined by about 65° to the basal plane, and containing an *a*-axis of the crystal was found to be about 5° from the rhombohedron $\{10\bar{1},1\}$. Nickel oxide films crystallised on this surface with {110} planes parallel to the rhombohedron. Symmetrical spot patterns were obtained in both the *a*-axis azimuth and the azimuth normal to it. At azimuths $27\frac{1}{2}$° from the *a*-axis, *i.e.* 90° from the rhombohedral edges, almost symmetrical patterns were obtained (*e.g.*, Fig. 10). This

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[2] Finch and Whitmore, *Trans. Faraday Soc.*, 1938, 34, 640.

pattern consists of a square and a hexagonal pattern of spots (from the $\langle 001\rangle$ and $\langle 1\bar{1}1\rangle$ azimuths of nickel oxide respectively) superposed (Fig. 11). The spots in the zero-order Laue zone not thus accounted for are due to double diffraction. Thus the $\langle 001\rangle$ and $\langle 1\bar{1}1\rangle$ lattice rows of the nickel oxide are perpendicular to the rhombohedral edge of the corundum. Actually there are four orientations fulfilling these conditions, but the angle between the lattice rows $\langle 001\rangle$ and $\langle 1\bar{1}1\rangle$ in the {110} plane of nickel oxide is 54° 55′, only 12′ less than the rhombohedral angle of corundum. Thus in effect there are only two orientations; one of these is shown in Fig. 13, the other being symmetrically placed with respect to the corundum. The $\langle 1\bar{1}0\rangle$ and $\langle 1\bar{1}2\rangle$ lattice rows are parallel to the rhombohedral edges. Their spacings are 2·95 A. and 5·12 A. respectively, as compared with the rhombohedral primitive translation of corundum of 5·13 A. Thus, on the rhombohedron there is a close fit of the lattices along the junction plane, both in angle and dimensions.

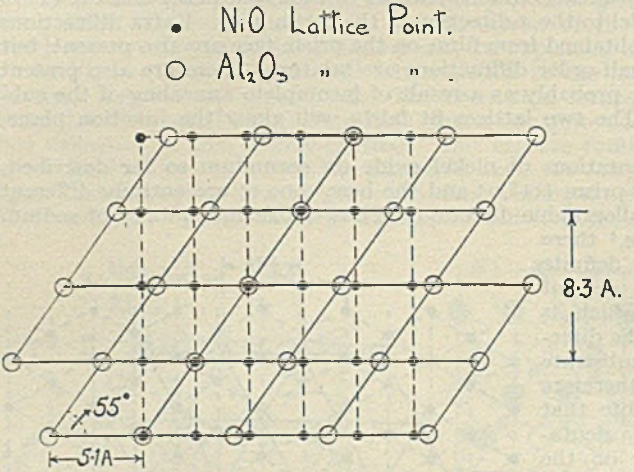


FIG. 13. — (110) net of nickel oxide and (10$\bar{1}$,1) net of corundum in their relative positions.

The above experiments show that corundum is an active substrate for nickel oxide. Three different relative orientations of the two lattices were observed. In two of these there was a close coincidence of the lattice dimensions in directions parallel to the planes defining the orientation. In the third case a fit of the two structures could be obtained by a consideration of the arrangements of their oxygen atoms. Fig. 14 shows a corundum crystal which has all the faces described above, approximately the basal plane *c* {000,1}, the prisms *a* {11$\bar{2}$,0}, and *m* {10$\bar{1}$,0}, and the

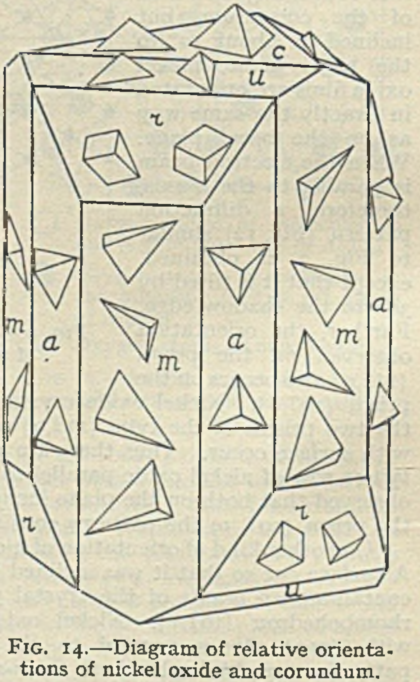


FIG. 14.—Diagram of relative orientations of nickel oxide and corundum.

rhombohedra *r* $\{10\bar{1},1\}$ and *u* $\{10\bar{1},4\}$. Cubic crystals of nickel oxide are shown in positions representing the orientations found. The results are summarised in Table I.

TABLE I.

Indices of Corundum Faces.	Orientation of Nickel Oxide.	Description of Typical Pattern.
$\{11\bar{2},0\}$	$\{111\}$ NiO parallel to $(11\bar{2},0)$ Al_2O_3 . $\langle 11\bar{2}\rangle$ NiO parallel to $[001]$ Al_2O_3, also traces of $\langle 1\bar{1}0\rangle$ NiO parallel to $[001]$ Al_2O_3.	Sharp spots, thin films usually formed, and pattern due to substrate showing; (Figs. 1 and 3)
$\{10\bar{1},0\}$	$\{111\}$ NiO parallel to $(11\bar{2},0)$ Al_2O_3 . $\langle 11\bar{2}\rangle$ NiO parallel to $[001]$ Al_2O_3.	Arced spots with thicker films.
$\{000,1\}$	$\{111\}$ NiO parallel to $(000,1)$ Al_2O_3 . $\langle 11\bar{2}\rangle$ NiO parallel to $[001]$ Al_2O_3.	Sharp spots on faint, continuous rings. Fairly thick films formed. (Figs. 7 and 8).
$\{10\bar{1},4\}$ approx., *i.e.*, plane at 30° to basal plane containing an *a*-axis.	$\{111\}$ NiO parallel to $(000,1)$ Al_2O_3 $\langle 11\bar{2}\rangle$ NiO parallel to the $[001]$ Al_2O_3.	Sharp spots and faint arcs. Fairly thick films. (Fig. 12).
$\{10\bar{1},1\}$	$\{110\}$ NiO parallel to $(10\bar{1},1)$ Al_2O_3 . $\langle 1\bar{1}0\rangle$ parallel to the rhombohedral edge $[1\bar{2}1]$.	Pattern of short arcs and spots. Fairly thick films. (Fig. 10).

On the prism *a* $\{11\bar{2},0\}$ only the predominant orientations are shown. Of the extra diffractions appearing in most of the patterns, many may be explained by double diffraction, and the remainder consisted of apparently half-order diffractions. A closer examination of these " half-order " spots show that in every case they are part of a pattern of spots exactly similar to the normal nickel oxide pattern except that it is about 3 per cent. more than half the size. Thus there is present in these films a substance of cubic structure for which the unit cell has $a = 8{\cdot}1$ A. This immediately suggests a substance of the spinel type. Of the possible substances having this structure, only nickel aluminate, $NiAl_2O_4$, can be looked for under the conditions of the experiment. Moreover, its known lattice dimensions agree very well with the dimensions of the patterns in question. The appearance of the nickel spinel pattern, together with the fact that its diffraction spots sometimes show refractive index effects suggests that the formation of orientated nickel oxide films may depend on the presence of a junction layer of the mixed oxide.

In general, it was found that the more rapid the evaporation, the less the proportion of nickel aluminate. It was noted that thin films yielding little or no trace of nickel aluminate were just as highly orientated as those in which there was a large proportion of this substance. The tendency to form the spinel was particularly noticeable on the prism $\{11\bar{2},0\}$ and it was also observed that the thickness of the nickel oxide film formed in a given time was less on this face than on any other.

Heating in air at 900° C. of specimens of nickel oxide on corundum caused the general fading of the nickel oxide pattern and the corresponding strengthening of the nickel spinel pattern (see Figs. 16 and 17, and compare with Figs. 7 and 8). On all faces the spinel had the same orientations as the nickel oxide, except that on the prism $\{11\bar{2},0\}$ only one of the two principal orientations occurred. The spots due to spinel usually had the same form as those due to the nickel oxide; thus Fig. 17 consists of arced spots, as does Fig. 8. On the prism face $\{11\bar{2},0\}$, however, the spots due to the spinel were extended towards the shadow edge, whereas the nickel oxide spots were more or less circular. Also in this case there were found to be anomalous Kikuchi lines in the corundum Kikuchi line pattern which accompanied the cross-grating spot patterns (Fig. 19). It is possible that these were due to double diffraction, but if this were so, it would have to be supposed that a beam corresponding to each point of one of the normal Kikuchi lines acted as a primary beam for a cross-grating pattern of nickel aluminate spots. This would fail to explain the considerable intensity of the extra lines, and so it seems that they may be the 111 bands of the spinel on the surface.

Continued heating of these specimens at 900° C. did not result in any decrease in intensity of the nickel spinel pattern; moreover, the thickness of the spinel film was certainly not less than that of the original nickel oxide film, as adjudged by the appearance of the background pattern of the corundum Kikuchi lines. Random nickel oxide films could be prepared on corundum by evaporation from a film with the substrate at 500° C. or less. When the specimens were strongly heated in air, no nickel aluminate rings appear, but the ring pattern of the nickel oxide gradually decreased in intensity and at the same time the intensity of the spot pattern of the corundum increased.

Thus nickel oxide once orientated on to corundum cannot easily be removed by evaporation, and once all the nickel oxide is combined with the alumina, further heating has no effect and does not cause the nickel oxide to diffuse right into the corundum. It appears that the reaction $NiO + Al_2O_3 \rightarrow NiAl_2O_4$ can only occur when the nickel oxide is orientated with respect to the corundum. Arcs due to the nickel spinel were always sharp, and corresponded to the same lattice dimensions ($a_0 = 8{\cdot}08$ A.) These observations indicate that there is no phase of variable lattice dimensions.

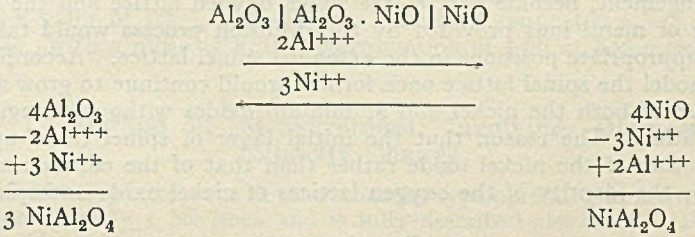
Discussion.

It is evident that the prism face of corundum behaves differently from other faces in respect of the orientation of nickel oxide crystals by condensation from the vapour on the surface. The differences may be summarised as follows:

(i) The orientation of the nickel oxide and of the spinel is most perfect on the prism face $\{11\bar{2}, 0\}$, sharp spot patterns without arcs or rings usually being obtained.
(ii) A considerable proportion of the nickel spinel is always present in the films on the prism face.
(iii) The rate of adsorption of nickel oxide is slower on the prism face.
(iv) There is no close lattice fit of the nickel oxide and corundum structures on this plane, although the two structures fit fairly well as regards the oxygen structures.
(v) The spinel orientation does not entirely follow that of the nickel oxide crystals on this face, only one of two equivalent orientations being present (Fig. 15).
(vi) The diffraction spots due to the spinel differ from those of the nickel oxide in showing an extension perpendicular to the shadow edge, due to refraction of the diffracted beams.

It appears that there is some fundamental difference in the nature of the orientating influences on the prism faces from that on other corundum surfaces. The two kinds of orientations observed on faces other than the prisms may be regarded as being of the Royer type, in that the lattices fit on the plane of junction without the formation of an intermediate mixed oxide, *i.e.* spinel, layer.

The probable mechanism of the surface reaction on the basal plane of corundum may be pictured from a consideration of the structural relations at the interface. The oxygen atoms in the corundum structure consist approximately of plane hexagonally packed layers perpendicular to the three-fold axis, the mean oxygen spacing being 2·75 A. The oxygen atoms in the nickel oxide structure also consist of hexagonally packed layers with packing distance = 2·95 A. Thus the nickel oxide may be regarded as sharing an oxygen layer with the substrate. The oxygen structure of spinel is identical with that of nickel oxide except that the dimensions of the unit cell are slightly smaller, the oxygen atom separation being 2·85 A. Thus the formation of the spinel may be pictured as interdiffusion of the metal ions in the two lattices involving only a slight change in the dimensions of the stationary oxygen framework. The reaction then proceeds according to the following scheme:



A reaction between nickel and aluminium oxides in the solid state has been observed by Hedvall.[3] The mechanism of the formation of the spinel structure has been discussed by Barth and Posnjak,[4] and a summary on this and related subjects is given by Wagner.[5] The investigation of Wollan [6] on the electron distribution in the magnesium oxide lattice indicated that lattices of the MgO type are non-ionic. Some experiments by the authors (not yet published) on the orientation of silver films condensed on to magnesium oxide suggest, however, that the latter becomes ionic, at least to some extent, at temperatures above 500° C.

As has been mentioned, the array of oxygen atoms in a plane $\{11\bar{2},0\}$ of corundum is approximately hexagonal (Fig. 6). Half of these atoms, however, belong to molecules in one layer and half to the layer below. Thus, if corundum be regarded as a molecular structure, the prism face would contain only half of the oxygen atoms shown in the figure, and unless the spaces were filled with adsorbed oxygen atoms, the " sharing " of an oxygen layer with the nickel oxide crystals would not occur on this surface. It is evident, however, that in this case also a relatively slight change in the oxygen structure of the corundum is necessary for the formation of spinel. It is possible that

[3] Hedvall, *Z. anorg. Chem.*, 1915, 92, 381.
[4] T. W. Barth and E. Posnjak, *Z. Krist.*, 1932, 82, 325.
[5] C. Wagner, *Angewandte Chemie*, 1936, 49, 735.
[6] E. O. Wollan, *Physic. Rev.*, 1930, 35, 1019.

the formation of an orientated film of nickel oxide on the prism face depends on the formation of a thin layer of spinel by the first few molecular layers of nickel oxide.

The reaction scheme shown above satisfactorily accounts for the ease of formation of the orientated spinel layer on the (000,1) plane of corundum. On the other faces of the corundum there should be formed a double layer of spinel, one layer having the orientation of the nickel oxide, and beneath that a layer having an orientation depending solely on that of the aluminium oxide. The picture is unsatisfactory because (i) no trace of a second kind of orientation of spinel was found, (ii) if nickel and aluminium ions can diffuse across the spinel-corundum interface there appears to be no reason why the reaction should cease when all the nickel oxide is combined, and (iii) it affords no reasonable explanation as to why the spinel takes up only one of the two nickel oxide orientations on the prism face.

These difficulties can be resolved to some extent if it be supposed that diffusion can only occur in the spinel lattice. In this case only those metal ions in the uncombined oxides that are immediately adjacent to the spinel layer could leave the oxide lattice to diffuse into the spinel. The oxygen atoms " freed " by this process would, by a very slight rearrangement, become part of the spinel oxygen lattice and the slight excess of metal ions provided by the diffusion process would take up their appropriate positions in the extended spinel lattice. According to this model the spinel lattice once formed would continue to grow at the expense of both the nickel and aluminium oxides without changing in orientation. The reason that the initial layer of spinel takes up the orientation of the nickel oxide rather than that of the corundum may well be the identity of the oxygen lattices of nickel oxide and spinel.

Summary.

The structure, orientation and spinel-formation of crystalline nickel oxide films condensed on to heated corundum single crystals have been studied by electron diffraction.

It was found that the nickel oxide crystals take up, with respect to the substrate crystal, certain special orientations according to the crystallographic direction of the corundum surface. These orientations have been explained in terms of geometrical similarities between the two crystals in important planes near the junction surface. The nickel oxide was shown to react slowly at about 900° C. with the corundum to form nickel spinel, which takes up orientations similar to those of the nickel oxide. Certain of these results can be explained on the assumption that the spinel lattice is the only one of the three in which appreciable diffusion of metal ions can occur.

The authors wish to express their indebtedness for awards from Messrs. E. G. Acheson Ltd. (H. R. T.) and the Department of Scientific and Industrial Research (E. J. W.).

Applied Physical Chemistry Laboratories,
Imperial College,
London, S.W.7.

THE DIELECTRIC CONSTANT OF DIAMOND.

By L. G. Groves and A. E. Martin.

Received 22nd February, 1940.

An investigation of the optical and photoelectric properties of diamond[1, 2] has disclosed the existence of at least two forms (types 1 and 2), and a preliminary measurement of the dielectric constant was reported in the first of these publications. It was established that both types of diamond had the same dielectric constant within experimental error, but the absolute value could not at that time be determined with the accuracy desired, owing to the lack of a suitable standard micro-condenser.

Reference to the literature reveals a wide range of values. Pirani[3] gives a value of 16·5, Schmidt[4] a value of 5·5, Coehn and Raydt[5] values between 5·18 and 8·0. More recently, Whitehead and Hackett[6] have found a value of 5·7 ± 2 % over the frequency range 300 c./sec. to 1·6 Mc./sec., with a most accurate determination of 5·66 at 800 c./sec. and 27·8° C.

Part I. Method of Measurement Involving Diamond/Air Capacity Change.

The first apparatus was of the resonance type operating at a frequency of approximately 1 Mc./sec., and is fully described elsewhere.[7] For use with solids a micrometer condenser cell, Fig. 1, was constructed from a micrometer head, circular parallel brass plates 16 mm. diameter being used for the electrodes. Unworked diamonds, such as were employed here, are usually available as cleavage plates up to a few mm. in thickness and less than 1 sq. cm. in area, and can be sandwiched between the plates of the micrometer cell. In the resonance apparatus, variation in the capacity of the condenser due to introduction of the solid caused a change in the rectified current of the valve-voltmeter, and the actual capacity change was found by adjustment of a standard variable condenser (Sullivan, 70-1200 $\mu\mu$F) in series with a small fixed condenser (10-20 $\mu\mu$F) until the original current reading was established. The small fixed capacity

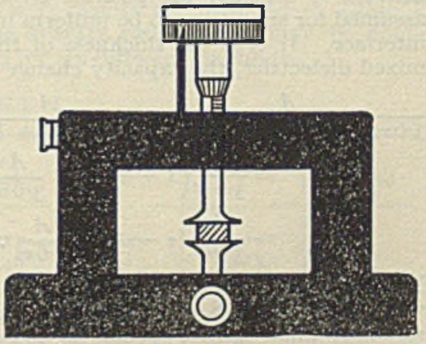


Fig. 1.

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[1] Robertson, Fox and Martin, *Phil. Trans., A*, 1934, **232**, 463.

[2] Robertson, Fox, and Martin, *Proc. Roy. Soc., A*, 1936, **157**, 579.

[3] Pirani, *Dissertation*, Berlin (1903).

[4] Schmidt, *Ann. Physik*, 1903, **11**, 114.

[5] Coehn and Raydt, *ibid.*, 1909, **30**, 777.

[6] Whitehead and Hackett, *Proc. Physic. Soc.*, 1939, **51**, 173.

[7] Groves and Sugden, *J. Chem. Soc.*, 1934, 1094.

is chosen so that a considerable portion of the standard variable condenser is required to compensate for the capacity change in the cell, but the exact measurement of this small fixed capacity provides the chief difficulty associated with the method. In practice it was determined by varying the air capacity of the micrometer cell : the capacity change on varying the air gap from t_1 to t_2 cm. is $\frac{A}{3\cdot6\pi}\left(\frac{1}{t_2}-\frac{1}{t_1}\right)$ μμF, where A is the area of either electrode in cm.^{2}

This calibration was found to be somewhat in error owing to changes in stray capacities associated with the backs and edges of the brass electrodes, and it was decided that the construction of a standard micro-variable-condenser was the only satisfactory method of overcoming the difficulty. At this stage in the work a change in electrical apparatus was made.

Description of Improved Apparatus.

This operated on the heterodyne principle at the same frequency as the first apparatus and made use of certain methods of frequency stabilisation ; it was also equipped with a standard micrometer variable condenser of calibration constant 1·862 μμF per cm. travel, the reading being estimated to 10^{-4} cm., *viz.*, about 2×10^{-4} μμF.

A further refinement was the substitution of a cathode-ray oscillograph as a means of observing the heterodyne beat frequency, in place of the tuning fork methods usually employed in this type of work. The whole apparatus has been described in detail by one of us (L. G. G.),[8] in connection with the measurements of the electric moments of vapours. The cell, Fig. 1, was again used for the solids, but the increase in capacity caused by their insertion was measured by direct replacement with the micro-variable condenser, *i.e.* $\frac{A}{3\cdot6\pi t}(\epsilon-1)=\delta C$, where A is the area of the solid (cm.^{2}), t its thickness (cm.), and ϵ the dielectric constant. It is of interest to consider the possible error in the results due to an air film, assumed for simplicity to be uniform in thickness, at an insulator-electrode interface. If δt is the thickness of the air film, then from the theory of mixed dielectrics, the capacity change on introduction of the solid is :

$$\frac{A}{3\cdot6\pi\{t+\delta t-t(1-1/\epsilon)\}}-\frac{A}{3\cdot6\pi(t+\delta t)}$$

$$=\frac{A\epsilon}{3\cdot6\pi t}\left(1-\frac{\delta t}{t}\epsilon\right)-\frac{A}{3\cdot6\pi t}\left(1-\frac{\delta t}{t}\right)\text{ very nearly}$$

$$=\frac{A}{3\cdot6\pi t}(\epsilon-1)-\frac{A}{3\cdot6\pi t}\cdot\frac{\delta t}{t}(\epsilon^2-1)\text{ instead of }\frac{A}{3\cdot6\pi t}(\epsilon-1).$$

If the air film is 1 % of the thickness of the solid, the value found for ϵ will be $(\epsilon-1/\epsilon)$ % low, and since the air film is likely to be much the same for thick or thin specimens, it is desirable, where controllable, to use as thick a plate of solid dielectric as will give a reasonable change in capacity of the cell.

Measurements and Results.

Several specimens of diamond were available, and we would like here to express our thanks to Professor W. T. Gordon for the loan of these. Of the type 1 diamonds, figures are given in Table I for one only (D1), this being the most suitable in form of those available. It was an equilateral triangular plate, of side about 10 mm. length, and 3·11 mm. in thickness. Others of this type, but with less suitable dimensions, gave

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[8] Groves, *J. Chem. Soc.*, 1939, 1144.

similar values for ϵ. Only one moderately suitable specimen of type 2 diamond (No. 2) could be obtained, but unfortunately had a stepped edge. This may be considered approximately as being composed of a plane parallel part of area A_1 and a wedged portion of area A_2, Fig. 2, and the capacity change due to insertion between the electrodes can be shown to be nearly $\frac{A_1}{3{\cdot}6\pi t}(\epsilon - 1) + \frac{A_2}{3{\cdot}6\pi t}\left[\frac{\ln \epsilon}{1 - 1/\epsilon} - 1\right]$, from which ϵ may be found. As it is possible that the edge irregularities of the diamonds of both types, though inside the volume bounded by the cell plates, may cause some error in the measured values of ϵ, it was thought advisable to check this point. Accurate glass models of the diamonds were made and their apparent values of ϵ compared with an accurate value for the same glass in the form of regular plates. (The models were made by Mr. F. S. Benge of this laboratory.)

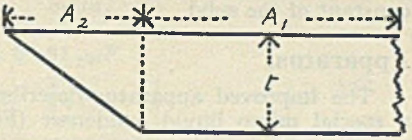

FIG. 2.

The several ratios are as follows :—

$$\frac{\text{Capacity change for diamond No. 1}}{\text{Capacity change for glass model}} = 0{\cdot}789$$

$$\frac{\text{Capacity change for diamond No. 2}}{\text{Capacity change for glass model}} = 0{\cdot}813$$

$$\frac{\text{Measured } \epsilon \text{ for diamond No. 1}}{\text{Measured } \epsilon \text{ for glass of models}} = 0{\cdot}796$$

It thus appears that the dielectric constants directly measured for the two diamonds are satisfactory and that the difference between them is within the limits of experimental error ; ϵ for diamond No. 1, 5·26, is the value preferred since this diamond had the more regular form.

As a further check on the method, measurements were made on three plane parallel plates of fused silica, the individual values for which were in good mutual agreement. These results are included in Table I with those for the diamond D_1. The average result, 3·69, may be compared with Jaeger's [9] values 3·57-3·80 for six different methods.

TABLE I.

Substance.	A (cm.^{2}).	t (cm.)	C ($\mu\mu F.$)	ϵ.	ϵ (Mean.)
Diamond D_1 . .	0·598	0·311	0·725	5·26	
Silica 1 . . .	0·945	0·249	0·913	3·72	3·69
,, 2 . . .	0·575	0·256	0·533	3·69	
,, 3 . . .	0·339	0·254	0·315	3·67	

Part II.—Method of Measurement Involving Diamond/Liquid Capacity Change.

In view of the fact that our value of 5·26 for diamond differs considerably from 5·7 found by Whitehead and Hackett at our frequency of measurement, it was decided to repeat the determination with a liquid replacement method to eliminate air films, mentioned above as a source of error.

Briefly, this consists in measuring the dielectric constants of a range of liquids of lower and higher dielectric constant than that of the solid, alone

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[9] Jaeger, *Dissertation*, Berlin (1917).

and with the solid immersed in them. If ϵ_l is the dielectric constant of the liquid, and ϵ_m the dielectric constant of the same liquid with the solid immersed in it, then the dielectric constant of the solid is given by that value of ϵ_m which satisfies the relation $\epsilon_m/\epsilon_l = 1$. Accordingly, therefore, if such measurements are carried out with a range of liquids and ϵ_m/ϵ_l is plotted against ϵ_m (abscissa), then the value of ϵ_m corresponding with the point of intersection of the curve with the line $\epsilon_m/\epsilon_l = 1$ gives the dielectric constant of the solid.

Apparatus.

The improved apparatus described in Part I was used, except that a special micro liquid condenser (Fig. 3) replaced the micrometer cell. This liquid cell was made from two circular brass plates and a ring of synthetic resin about 3·5 cm. diameter. Both surfaces of the ring and the inner surfaces of the brass plates were polished flat. The inner diameter of the ring was 2 cm., its thickness about 4 mm., and the inner wall of the ring was carefully turned so that it made an angle of 90° with each inner surface of the brass plates. The three components were assembled with a trace of fish glue and then bolted together with three bolts tapped into the insulator. The three bolts formed the corners of an equilateral triangle, two being inserted from one electrode and the third from the other. In either brass plate large clearance holes were drilled opposite the ends of the bolts to keep insulation high. The combination of electrodes and insulating ring was then sawn into unequal segments such that the larger provided a cell of vertical inner depth 1·3 cm., and of volume about 0·95 c.c. The cut surface of this cell was polished flat and was at right angles to the inner surfaces of the electrodes. A rectangular glass slab (6 cm. × 3 cm. × 4 mm.) with one face optically flat was used to cover the cell, being adjusted symmetrically over the cell aperture. A heavy brass rod provided a means of clamping the cell and was connected to earth; the other plate was joined by a rigid fine wire to the electrical apparatus. The completed cell provides a condenser of constant boundary conditions, the capacity changes of which when filled with an insulating liquid of dielectric constant ϵ_l will be directly proportional to $\epsilon_l - 1$. To check this point, the replaceable capacity was determined by calibration with benzene at 20° C., and using the cell constant, C_0, so obtained, the dielectric constant of chlorobenzene at 25° C. was measured. The value used for benzene at 20° was 2·283 (Hartshorn and Oliver) [10] and the value obtained for chlorobenzene at 25° was 5·61; *cf.* Sugden's [11] value of 5·612 obtained by a method which gave results for benzene in agreement with Hartshorn and Oliver's figure at 25°. These measurements are set out in Table II.

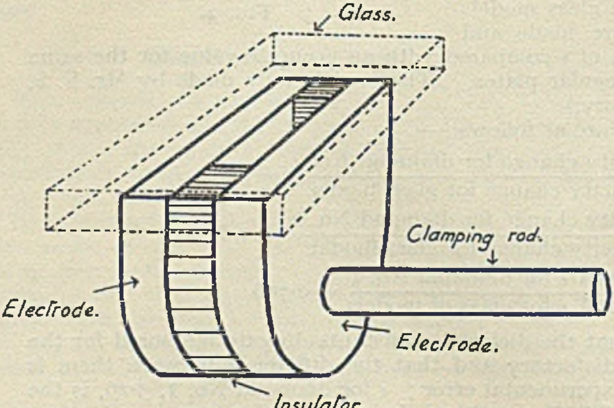

FIG. 3.

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[10] Hartshorn and Oliver, *Proc. Roy. Soc., A*, 1929, **123**, 664.

[11] Sugden, *J. Chem. Soc.*, 1933, 773.

TABLE II.

M_0 (mm.).	M_l (mm.)	$M_l - M_0$ (mm.)	δC. ($\mu\mu$F.)	C_0 ($\mu\mu$F.)	ϵ.
Calibration with benzene at 20° C.					
1·445	4·763	3·318	0·618	0·481	
1·476	4·792	3·316	0·617		
1·594	4·911	3·317	0·618		
ϵ at 25° for chlorobenzene using $C_0 = 0{\cdot}481\ \mu\mu F$.					
5·405	17·309	11·904	2·217		5·61
5·538	17·449	11·911	2·218		

C_0 and ϵ are separately obtained from the relation $\delta C = C_0 \,.\, \overline{\epsilon - 1}$ by insertion of the appropriate values.

M_0 and M_l are the micro-condenser readings with cell empty, and filled with liquid.

$$\delta C = (M_l - M_0) \times 0{\cdot}1862\ \mu\mu\text{F}.$$

Method of Measurement.

With cell empty and glass cover plate in position the micrometer standard condenser is read. Liquid is then pipetted into the cell and the glass plate replaced, overflow being removed with cotton wool. The condenser is adjusted to compensate for the increase in capacity and re-read. The plate is again removed, the solid dropped into the cell, and a reading taken on the condenser after compensation for further change in capacity. The cycle of operations is then reversed, *i.e.*, solid removed and cell refilled with liquid, liquid removed and cell dried out, readings on the condenser being taken at each stage. Averages of the two readings at "cell empty" and at "cell + liquid," and the single reading at "cell + liquid + solid" yield three figures which are sensibly free from small changes due to zero drift in the apparatus over the time taken to carry out one complete set of measurements.

The liquids were made up from dried samples of *n*-heptane, carbon tetrachloride, and 1 : 2-dichloro-ethane of approximate dielectric constant at 20° C. respectively, 1·97, 2·24, and 10·4. The room which contained the apparatus was kept at 20° C. throughout the experiments except for the chlorobenzene calibration, when it was maintained at 25° C.

The advantages of the above procedure are that the dielectric constants of both liquid and solid are measured in the same cell, and that the replaceable part of the condenser is wholly free from edge effects. The diamonds available for this series of measurements were D_{16} and D_2, both type 2 diamonds, separately occupying about 20 % of the volume of the cell, and D_{26}, a type 1 diamond of considerably smaller dimensions. Considerable care was taken to obtain a liquid mixture of the same dielectric constant as D_{16}, the largest diamond (for which detailed results are given), and having obtained it, no change in capacity was observed upon immersion of either D_{26} or D_2. It is thus shown that both types of diamond have the same dielectric constant.

The value obtained, 5·35, is in good agreement with that derived from the earlier direct replacement method, *viz.*, 5·26, but is probably the more correct figure as uncertainties due to air films are eliminated; ϵ was also determined for the largest fused silica disc, which occupied about 25 % of the volume of the cell. The value obtained was 3·60. The measurements with D_{16} are set out in Table III. Detailed results for the silica are not given, but the $\epsilon_m/\epsilon_l - \epsilon_m$ curve for this substance is shown in Fig. 4 along with that for the diamond.

TABLE III.

M_o (mm.)	M_l (mm.)	M_m (mm.)	$M_l - M_o$ (mm.)	$M_m - M_o$ (mm.)	ε_m	ε_l	$\varepsilon_m/\varepsilon_l$
Liquid No. 1.							
4·295 4·300	12·425 12·435	12·857 12·863	8·130 8·135	8·562 8·563	4·31	4·15	1·040
Liquid No. 2.							
4·686 4·670	13·319 13·315	13·700 13·680	8·633 8·645	9·014 9·010	4·49	4·34	1·033
Liquid No. 3.							
3·358 4·121	13·858 14·607	13·976 14·727	10·500 10·486	10·618 10·606	5·11	5·06	1·009
Liquid No. 4.							
4·326 4·771	15·573 16·010	15·570 16·015	11·247 11·239	11·244 11·244	5·35	5·35	1·000
Liquid No. 5.							
3·904 3·760	15·804 15·646	15·677 15·549	11·900 11·886	11·773 11·789	5·56	5·60	0·992

M_o, M_l and M_m are respectively the micro-condenser readings with cell empty, filled with liquid, and filled with liquid + solid.

$$\epsilon = 1 + \frac{0{\cdot}1862(M - M_o)}{0{\cdot}481}.$$

All measurements in both Parts I and II were made at a frequency of approximately one megacycle per second.

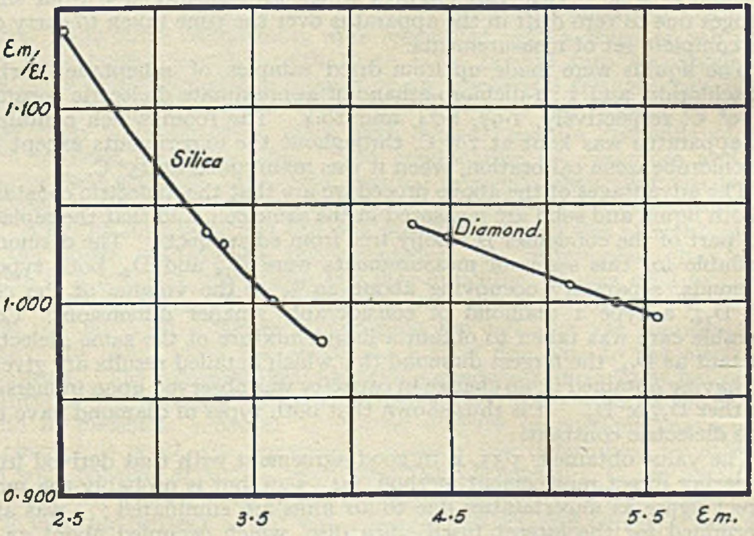

FIG. 4.

The authors wish to thank Dr. J. J. Fox, C.B., O.B.E., for facilities afforded to carry out the work, and for permission to publish.

Summary.

The dielectric constant of diamond has been determined by two methods, (1) involving solid-air capacity changes and employing a micrometer cell of variable capacity with the diamond sandwiched between the electrodes; (2) involving solid-liquid capacity changes and employing a micro cell of fixed air capacity, with constant boundary conditions irrespective of the nature of the replaceable dielectric medium.

The capacity changes have been measured by direct compensation with a micrometer variable condenser in the tuned circuit of one oscillator of a heterodyne apparatus, the condenser readings being estimated to 2×10^{-4} μμF.

The accuracy of the second method has been checked by an independent determination of the dielectric constant of chlorobenzene at 25° C.

The values of the dielectric constant of diamond obtained by the two methods are 5·26 and 5·35 respectively, the latter being the preferred figure.

No difference has been observed between the dielectric constants of the two types of diamond discussed by Robertson, Fox and Martin.

Government Laboratory,
Clement's Inn Passage,
London, W.C. 2.

THE LATENT PHOTOGRAPHIC IMAGE: ADDITIVITY OF PART-EXPOSURES AND MICRO-CRYSTALLINE STATE OF SILVER HALIDE GRAINS. †

BY J. C. M. BRENTANO and S. BAXTER.

Received 30*th November*, 1939.

The present paper describes, firstly, experiments on the formation of the latent photographic image in which the additive effect of part exposures is examined near the threshold and for higher densities. Their interpretation leads to an X-ray examination of the crystalline structure of photographic emulsions and to further experiments on the additive effect of exposures with different wave-lengths. These are discussed in the later part.

The original planning of the experiments was largely determined by the recent theory of Gurney and Mott[1] and reference may therefore be made to those features of the theory which have a particular bearing on our work.*

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† The results of this paper were presented at the Conference on Photography, held in Manchester, 3rd and 4th July, 1939, reported in *Nature*, 1939, 144, 356.

[1] Gurney and Mott, *Proc. Roy. Soc.*, *A*, 1938, 164, 151.

* The authors are aware that alternative interpretations of the results could be considered; *e.g.* they could be interpreted on the basis of secondary processes which accompany the formation of neutral halogen atoms within the grains and their migration, views developed in numerous papers. Our primary purpose was to examine how far the more recent wave-mechanical theory could account for the particular group of phenomena to which it had not been applied. It seemed thus best to use this and its development as a working hypothesis throughout. A different course, which would have led to a comparative study of a classical and of a wave-mechanical theory, was outside the scope of this work.

1. The Wave Mechanical Theory of Latent Image Formation.

The latent photographic image is generally assumed to consist of small specks of metallic silver in the silver halide grains of the emulsion. These specks bring about a reduction of the grains to metallic silver by the chemical action of the developer. For brevity and to distinguish such specks from the sensitivity specks, referred to later, we call such specks "active silver specks." Gurney and Mott assumed that these active silver specks result from the following process: when light is absorbed, electrons are lifted into the conduction level or conduction band of the silver halide crystals composing the grains. From the conduction band, the electrons can drop into the levels of the sensitivity specks. These sensitivity specks may consist of Ag_2S or of silver; they are assumed to pre-exist in the grains of the emulsion, prior to exposure to light. The effect of the negative charge given by the electrons to the specks, is that they attract positive silver ions. The negative charge is thus neutralised and the resulting Ag atoms form specks of metallic Ag or increase the size of silver specks already existing. As more electrons are lifted into the conduction levels of the halide crystal, this process continues and the silver specks grow. The formation of the active silver specks comprises thus two processes; one depending on the displacement of electrons, the other on the displacement of ions.

Of the more specialised picture foreseen by the theory, the following points are of particular interest for the present discussion: (1) In terms of the original theory of Gurney and Mott, an electron lifted into the conduction band of the halide crystal can leave it in two ways: it can either pass to the sensitivity specks in the way we have described; or alternatively it can fall back into the halogen atom created by its removal from a halide ion by the action of light, or into an equivalent atom formed by the removal of another electron; in which case the electron does not take part in the mechanism leading to the formation of an active silver speck. (2) The transition of electrons between the conduction levels of the halide crystal and of the sensitivity specks is similar to the transition of molecules between the liquid and gas phase of a substance, in so far as the theory assumes a finite probability for an electron to escape from the speck, while the probability that the speck may capture an electron increases with the density of the electrons in the conduction levels of the halide crystal.* In addition, as the negative charge of the speck increases, the repelling action of this charge makes any further increase difficult. In this way, the continued condensation of electrons on the sensitivity specks depends firstly on a certain minimum density of electrons being reached in the conduction band of the crystal, and secondly on the negative charge of the specks being neutralised by positive ions.

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* At the Conference on Photography held in Manchester, 3rd and 4th July, 1939, after this paper was written, Professor Mott announced a modified form of the theory in the sense that an electron could not leave an active speck without the supply of additional energy greater than could be supplied by heat motion. Such energy supplied by infra-red radiation would account for the Herschel effect. At this conference Professor Mott also expressed his agreement with an explanation of the failure of the reciprocity law for low intensities proposed by Webb and Evans[2] as an alternative to the one originally proposed by Gurney and Mott; we shall refer to this later.

[2] Webb and Evans, *J. Opt. Soc. Am.*, 1938, 28, 431.

2. The Photographic Threshold.

By the photographic threshold we mean the fact that an exposure in the visible must reach a certain minimum value before the action of the developer can produce any appreciable effect. This threshold is less marked with dye-sensitized and highly sensitive emulsions than with blue sensitive emulsions of the straight type. The common feature, however, is that there is an initial range for which very little change of density with exposure takes place. From the range of practically constant density there is a more or less gradual transition to the range where, with the usual logarithmic plotting, the characteristic density-exposure curve is approximately linear.

We might interpret this threshold in the terms of the original Gurney-Mott theory as that exposure necessary before an electron concentration in the conductivity level of the crystal is reached, which is sufficient for a sustained transition of electrons to the sensitivity-specks. This would bring the phenomenon in line with the failure of the reciprocity law for low intensities, where Gurney and Mott assumed that since the electrons may return to the vacated places, their concentration in the conduction level of the halide crystal for weak illuminations remains small, so that an efficient transition of electrons to the sensitivity specks does not then take place.

From these considerations the experiments on the additive effect of part-exposures, described in the following sections, took their origin.

3. Experimental Arrangement.

The source of light for the exposures was a tungsten filament lamp with a blue filter transmitting the wave band from 3700 to 5200 A. Constancy of the source was obtained by the use of a glow discharge stabiliser. As an alternative, large storage batteries, set apart for these exposures, were used, and for experiments requiring a lesser accuracy, a Solus stabiliser unit. Great attention was paid to the constancy of the source of illumination, since part of the exposures comprised time intervals of several hours. The exposure times were fixed by a rotating shutter; the intensity of illumination could be varied by varying the distance from the source. A grey wedge comprising an extreme density range of 0·2 was placed in front of the film; in this way the required exposures could be obtained within close limits. A sliding gate was used in front of the film, so that comparative exposures were taken on several strips of film. The strips ran in the direction of the gradation of the wedge, so that each intensity value was recorded in several parts of the film area. Variations of illumination as well as irregularities of coating could thus be eliminated.

Densities in the lower range were evaluated by a scatter method, described previously,[3, 4] the particular merit of which is that by substituting the measurement of a direct effect, *viz.*, the quantity of light scattered by the silver grains, for the measurement of a difference-effect (as given by the usual absorption densitometry), higher accuracy in the range of small densities is reached. The scatter method measures essentially the number of grains, not their absorbing power. The measurements were made with a microphotometer which uses a photo-electric cell with valve amplification. Higher densities were determined by absorption photometry.

The individual exposures consisted of flashes varying in duration from 0·1″ to 8″, the intensities of which could be varied by adjusting the distance between source and film, a wedge being inserted, as already

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[3] Brentano, *Z. Physik*, 1931, 70, 74.

[4] Brentano, Baxter and Cotton, *Phil. Mag.*, 1934, 17, 370.

indicated, so as to obtain with one exposure a range of intensity values. When comparing the densities from single and from added part-exposures, the corresponding intensities and the total exposure times were always equal.

4. The Summation of Part-Exposures Separated by Varying Time Intervals.

Numerous investigations have been made concerning interrupted exposures, in the form of regularly intermittent exposures. The present work is concerned with the effect of single breaks which lead to a simpler interpretation in terms of the wave-mechanical model.*

TABLE I.

Exposures.	Density for Contin. Exp.	Density for Interr. Exp.
110	0·0041	0·0042
127	0·0051	0·0051
137	0·0057	0·0055
145	0·0073	0·0062

In a first group of experiments conditions were chosen so that the densities were just on the rising part of the characteristic curve, they were distinctly above the fog level and rose with increasing rate. Such exposures are just past the threshold value; those for which the increase of density with exposure is still negligible or small we call sub-threshold exposures. Table I shows the total exposures in arbitrary units, the densities above the fog level for a continuous exposure and the densities obtained for two exposures separated by a time interval of 20′, the first being one-third, the second two-thirds of the total. While for each table densities are inter-related, exposures on thin emulsions were used for part of the work evaluated by scatter; numerical density values have then a different meaning than when observed with normal emulsions by absorption. The emulsion used was Ilford Fine Grain Ordinary, a blue sensitive material.

It will be seen that for small exposures, the densities obtained from the superposition of the two sub-threshold exposures are substantially the same as those obtained from one continuous exposure. Exact numerical agreement between the values in the two columns is fortuitous; the order of accuracy is ± 5 per cent. The general result, that two sub-threshold exposures are additive, was confirmed for intervals separating the exposures up to 300 hours; this was also found when the part exposures were given in the ratios 1 : 1 and 2 : 1, the longer exposure in the latter case being given first. The same result was found for other types of emulsions. Ilford Line Film, Kodak Panatomic and Agfa Isopan F.

The results of similar experiments in the range of greater exposures and higher densities are represented by Fig. 1, in which we have plotted the densities resulting respectively from one continuous exposure, and from two part exposures of the same total value, the latter being given in the ratio, 1 : 2, separated by a time interval of 20′. The emulsion used was again Ilford Fine Grain Ordinary. The curves comprise results

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* For more general references on the intermittence effect, see, for instance, Kochs.[5] Regarding the effect of single interruptions, Long, Germann and Blair examined the superposition of part exposures for Azo paper. Brush, Norman and Albersheim[6] observed the change of the effect of pre-exposure with time; Brush found a decrease for very small pre-exposures and additivity for larger exposures; Norman found a decrease of the sensitizing action for intervals from 3–20 hours, while Albersheim examined the change on the modulation of a sound track.

[5] Kochs, *Z. wiss. Phot.*, 1937, **36**, 97.

[6] Long, Germann and Blair, *J. Opt. Soc. Am.*, 1935, **25**, 382; Brush, *Physic. Rev.*, 1910, **31**, 241; Norman, *J. Opt. Soc. Am.*, 1936, **26**, 407; Albersheim, *J. Soc. Motion Picture Eng.*, 1939, **32**, 73.

obtained from several plates, and to interlink these results, a curve has been traced from a limited number of density steps which were all recorded on one plate and marked by ⊙ : on this curve the relative densities for single exposures and for exposures given in parts are marked by a cross and a dot respectively.

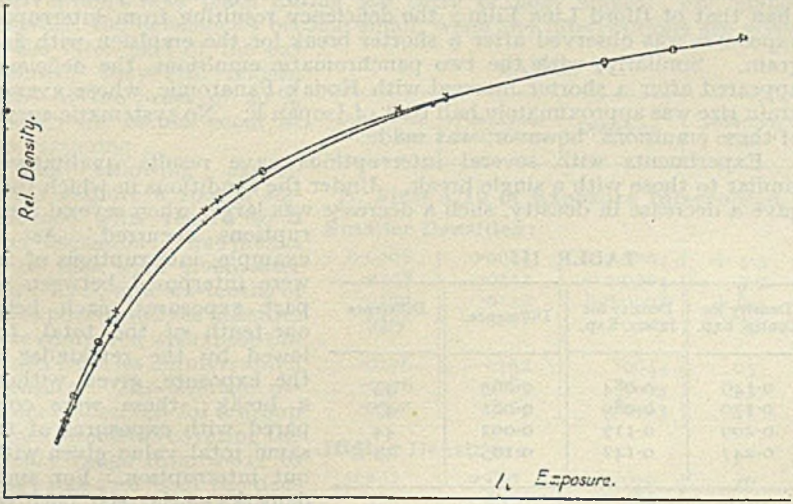

FIG. 1.

In the range of greater exposures, the density obtained from two part exposures is less than that obtained from the equivalent exposure given without interruption. The deficiency is greatest in the range of medium densities where the decrease in density is of the order of 20 per cent. ; it falls off for small and for high densities.

The effect of the interruption in reducing the density attains approximately its full value for an interval of 20′ between the part exposures. This is shown in Table II, where the densities obtained for medium exposures are shown for time intervals of various lengths. The emulsion used was again Ilford Fine Grain Ordinary.

TABLE II.

Interval between Exposures.	Density for Contin. Exp.	Density for Interr. Exp.	Difference.
2′	0·234	0·237	− 0·003
5′	0·246	0·234	+ 0·012
20′	0·278	0·254	0·024
60′	0·260	0·239	0·021
360′	0·244	0·222	0·022

The small increase for the interval of 2′ has no real significance ; it falls within the limits of error. The result of a great number of observations is that no change was observable for intervals less than 2′ 30″, for 5′ it was very distinct, for 15′ it had almost acquired its full value. From there on only a very slow change with density took place. These times vary greatly with different emulsions.*

Experiments, in which the ratios between the first and second exposure were 1 : 1 and 2 : 1—the longer exposure in this case being given first—gave qualitatively similar results to those shown in Fig. 1.

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* We must consider how far the deficiency observed with interrupted exposures is possibly affected by the fact that the time interval between exposure and development is necessarily lengthened for part of the exposures in those experiments where the exposure is interrupted. Various results are recorded on

Experiments with other emulsions, Ilford Line Film which is blue sensitive, Kodak Panatomic and Agfa Isopan F, which are panchromatic, also gave a deficiency of density for interrupted exposures. The average grain size of Ilford Fine Grain Ordinary is approximately 2·5 times larger than that of Ilford Line Film; the deficiency resulting from interrupted exposures was observed after a shorter break for the emulsion with finer grain. Similarly, with the two panchromatic emulsions, the deficiency appeared after a shorter interval with Kodak Panatomic, whose average grain size was approximately half that of Isopan F. No systematic survey of these emulsions, however, was made.

Experiments with several interruptions gave results qualitatively similar to those with a single break. Under the conditions in which these gave a decrease in density, such a decrease was larger when several interruptions occurred. As an example, interruptions of 20′ were interposed between six part exposures, each being one-tenth of the total, followed by the remainder of the exposure, given without a break; these were compared with exposures of the same total value given without interruption. For small densities — the six part exposures then falling within the sub-threshold range—no decrease in density was observed; this agrees with corresponding experiments with a single break. For higher densities, losses of density were observed (Table III) of the order of 43 %-47 %, considerably greater than those observed with one single interruption, when the greatest density loss was 20 per cent.

TABLE III.

Density for Contin. Exp.	Density for Interr. Exp.	Difference.	Difference (%).
0·149	0·084	0·065	43
0·170	0·089	0·081	47
0·209	0·117	0·092	44
0·247	0·142	0·105	43

Table IV shows the comparative effect of interruptions in the early and in the later part of the exposure; in (A) the first four-tenths of the exposure were given in four separate parts at intervals of 20′, and the remainder in one unit. In the experiments recorded in (B), the early part of the exposure was given without a break, while the last four-tenths of the exposure were given in separate parts at intervals of 20′. Again, it will

the effect of the time between exposure and development on density.[7] In general, it is found that such an effect becomes noticeable only after longer time intervals than those used in our experiments and that it would tend to produce a density change opposite to that observed by us. Tests which we made under the conditions of our experiments, gave the results shown in the accompanying table, where the three vertical columns show the densities obtained. The film was equally exposed for each of the three values given in one column, while the time between exposure and beginning of development varied as indicated. The film used was Ilford Fine Grain Ordinary.

Time between Exposure and Development.	Densities.		
25″	0·512	0·530	0·608
20′	0·515	0·532	0·605
40′	0·517	0·534	0·602

It will be seen that the values for each column agree within 1 per cent.; a 20′ period between exposure and development should thus not appreciably affect the results. This interval was used in most of our experiments on interrupted exposures.

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[7] Hylan and Blair, *J. Opt. Soc. Am.*, 1935, **25**, 246; Brush, *Physic. Rev.*, 1910, **31**, 241; Carroll, *J. Physic. Chem.*, 1925, **29**, 693; Jausseran, *Sci. Ind. Phot.*, 1929, **9**, 85, 167; Narbutt, *Z. wiss. Phot.*, 1932, **31**, 146; Blair and Leighton, *J. Physic. Chem.*, 1932, **36**, 1649; Bullock, *Sci. Ind. Phot.*, 1932 (2), **3**, 201; 1933 (2), **4**, 33.

be seen that for the smallest densities, no appreciable or only small density losses are produced by the repeated breaks at the beginning or the end of the exposures. For somewhat greater densities, deficiencies of about 30 % are observed, and are appreciably the same, whether the interruptions take place during the early or later stages. For higher densities, the deficiencies become small, when the interruptions are given in the later part of the exposures; they still remain high—of the order of 20 %—when the breaks occur at the beginning.

TABLE IV.

Density for Contin. Exp.	Density for Interr. Exp.	Difference.	Difference (%).
A. First 4/10 of Exposure Interrupted.			
Smaller Densities :			
0·0088	0·0084	+ 0·0004	+ 4·5
·0108	·0112	− 0·0004	− 3·7
·0120	·0112	+ 0·0008	+ 6·5
·0128	·0111	·0017	13
·0176	·0132	·0044	25
·0276	·0183	·0093	33
·0390	·0267	·0123	32
Higher Densities :			
0·237	0·167	0·070	30
·323	·237	·086	27
·410	·301	·109	27
·546	·432	·114	21
B. Last 4/10 of Exposure Interrupted.			
Smaller Densities :			
0·0066	0·0068	− 0·0002	− 3·0
·0074	·0072	+ 0·0002	+ 2·7
·0082	·0080	·0002	2·5
·0096	·0089	·0007	7
·0120	·0104	·0016	13
·0140	·0098	·0042	29
·0199	·0148	·0051	26
·0304	·0216	·0088	30
Higher Densities :			
0·214	0·190	0·024	11
·301	·285	·016	5
·374	·362	·012	3
·477	·461	·016	3

The following experiments acquire a special significance with regard to a later discussion: Three breaks of 20′ each were given after four-, five-, and six-tenths of the exposure and the densities were compared with those obtained from an uninterrupted exposure. The average deficiency observed for a group of measurements covering the density range from 0·022 to 0·055 was 27·8 % of the density. An experiment was made covering the same density range, but with one break of 60′ after the first half of the exposure ; * the average deficiency was then only 15·5 %. In a third experiment, with a single break after the first half of the exposure, but of 20′ duration only, the average deficiency was also 15·5 %. The total exposures were the same for the three experiments and were so small, that the part-exposures falling between the two consecutive breaks in the first experiment were of the order of the threshold. It is seen that the deficiency produced by a single break is the same whether it lasts for 20′ or for 60′, whilst repeated breaks produce a considerably larger deficiency than one single break of the same total duration.

5. Discussion of the Experiments on the Summation of Part Exposures Separated by Time Intervals.

The essential result for small densities is that in the neighbourhood of the threshold part exposures are additive, even when separated by

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* The interruptions were placed in the middle part of the exposure because in one particular interpretation specks broken up with the interruption may be rebuilt during the final exposure. This process, which is difficult to allow for quantitatively, is small so long as the final exposure is not longer than the first.

long time intervals, and that the effect of the initial exposure—which then falls within the sub-threshold range—possesses a considerable degree of stability. Considered on the tentative model of the threshold indicated in Section (2), it would be expected that the initial stages of an exposure should serve primarily to build up the electron concentration in the conduction level for an efficient transition of electrons to the sensitivity specks to take place. If an exposure were interrupted at this point the electrons should fall back to their original positions in the lattice of the halide crystal without contributing, except to a limited extent, to the formation of active specks. A second exposure after a sufficient time interval should find the grains substantially in the same state as if no previous exposure had been given. For sufficiently long time intervals between the part exposures there should thus be a decrease of density and, in fact, the experiments were originally undertaken with the object of thus measuring the average time of retention of electrons in the conduction level. This time should be of the order of one hour,* considerably shorter than the time-interval used in some of our experiments. Since, for the production of small densities sub-threshold exposures are additive, the threshold cannot be accounted for by an accumulation of electrons in the conduction level. It seems thus improbable that a process of this kind should play any large part in the phenomena with which we are here concerned.

For larger exposures a deficiency in density was observed, increasing with the time interval separating the part exposures up to a certain value, which for one particular emulsion was of the order of 20′. This would be in reasonable agreement with the time which electrons may be expected to require to leave the conduction level of the halide crystal and to revert to their original positions, so that we could interpret the phenomena on the basis of the model we have just discussed, except for the fact that the same model would not account for the phenomena observed for very low densities.

On the assumption that the same model should apply to the phenomena near the threshold and at higher densities we can here also refer to the effect of low temperatures discussed in Section (6), where it is found that the density decrease or regression disappears at temperatures below — 90° C. The falling back of electrons from the conduction level into their original positions in the halide crystal should take place also at the lower temperatures. It will thus be seen that this process cannot, at any rate alone, account for the phenomena where a regression is observed.

Another way of interpreting the experiments is to assume a general instability of small silver specks, leading to the break-up and loss of specks during the early stages of their growth. Such instability, due to thermal energy, has been suggested by Webb and Evans,[3] in order to account for the low intensity reciprocity law failure which they and Weinland[8] observed. They assumed the probability of such a thermal disintegration to be higher for a small than for a large speck and " that the stability of the latent image speck does depend upon its size, and

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* In the original Gurney-Mott theory which forms the basis of this discussion the time for electrons to be retained in the conduction level can be estimated from the discussion given in one of the papers [1] and more directly from the time over which an exposure must be extended in order to show a marked low-intensity deviation from reciprocity law.

[8] Weinland, *J. Opt. Soc., A.*, 1928, 16, 295.

when it has reached about half its final size, then it is perfectly stable and does not disintegrate under temperature motion" (p. 434). Applying this model to our experiments, we might interpret the regression as due to the loss of those specks which are unstable. The rate of disintegration for some group of specks, as determined by the fact that the model accounts for the low intensity reciprocity law failure, could well agree in order of magnitude with the regression period for an interrupted exposure. One point to be considered, however, is that for the smallest specks we should expect a very rapid disintegration, decreasing gradually for those specks near the size at which they are stable, which initially would decay very slowly. There should thus be a very marked regression for very short interruptions with a gradual protracted increase for longer periods; this does not correspond with what we have observed.

If we compare the effect of repeated breaks with that of single interruptions (see the group of experiments discussed at the end of Section (4)), it is noted that repeated interruptions, separated by only small intermediate exposures, give a regression considerably greater than that produced by one single interruption of the same total duration. In terms of a general break-up of small specks this implies a very short range of instability, since otherwise with three and with one interruption essentially the same specks should have been affected. From our experiments, the range of instability of the specks can be expressed by the intermediate exposure between successive interruptions necessary for the additional density loss to acquire its full value; for larger intermediate exposures the number of additional new specks is balanced by a corresponding number of specks lost. The experiments show then that this range is very small. It is then reasonable to place this range of instability in the early stages of the speck's growth, so that these specks which can be lost with an interruption of the exposure are essentially those which originated in the small exposure range immediately preceding the break. We have seen in Section (4) that one single interruption can produce a density loss of 20 %, which in the range of medium exposures represents the loss of a considerable number of specks, and that the interruption can take place at various stages of the exposure, so that each stage at which an interruption is effective in producing a considerable density loss should be preceded by a narrow range in which a large number of specks originate. It is difficult to co-ordinate this narrow range of instability with the fact that an interruption, whether in the early or in the later part of the exposure, can produce a marked density loss. This difficulty is accentuated if we assume that the majority of active specks result from a cumulative process * involving many quanta, when on statistical grounds the initial stages of their growth should mostly take place during the early part of an exposure. An interruption outside this early part should not then be effective in producing a regression.

We can arrive at a formal interpretation ot the results, in which a gradual formation of active silver specks by a cumulative action is actually demanded, if we assume that the interruption of the exposure produces a certain regression or "stepping back," in the sense that at the

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* While the older theories largely assumed such a cumulative action, some recent authors, *e.g.* Silverstein and Trivelli,[9] favour the view that only one or two quanta need be received by a sensitive speck in order to produce an active development centre. We shall revert to this point in a later section.

[9] Silverstein and Trivelli, *J. Opt. Soc., A.*, 1938, 28, 441.

beginning of the second exposure the specks are no longer in the state they had reached when the first exposure was interrupted ; in this way, the second exposure could only contribute to the further growth of the silver specks after a certain amount of leeway, as it were, had been made good. Such an effect should take place for the early stages of the growth of the specks, and should lead, not to their complete disappearance, but merely to a limited regression. We can then understand that the density loss increases with the number of breaks ; furthermore, in the case of exposures not exceeding the limit within which the particles are susceptible to regression, a later break may have a similar effect to an interruption in the earlier part of the exposure. By assuming that specks which have already attained a considerable size, or which result from a process of very gradual growth, are not subjected to such a regression, we can understand that an interruption in the later part of a large exposure is less effective. The regression should be most noticeable at those densities at which the number of active silver specks increases most rapidly with the exposure and when the interruption takes place within the critical stage of their growth. This accords with Fig. 1. The density loss falls off for small and for very high densities, because (1) when the number of developable grains increases slowly with exposure, a stepping back by a small amount—equivalent to a certain loss of exposure time—affects the formation of few active specks only ; (2) in both the extreme regions an interruption only affects specks which are already large.

In an alternative formal interpretation, we avoid the difficulties found with a general break-up and loss of small specks by substituting a more specialised process which provides that : (1) at any stage of the exposure only a limited number of specks can break up and for these specks the rate of disintegration is high, while the remainder of the specks are stable ; and (2) specks liable to break up are found throughout the greater part of the exposure range. Such a mechanism gives results formally almost equivalent to those of the stepping back action.

We may consider whether a physical significance could be given to one or the other of these models. We can account for the " stepping back action " if it is possible to assume that electrons and ions on joining a small speck do not at once take up their fully consolidated positions and that, say, the last electron may be unstable and in a position to leave the speck with thermal energy. As to the alternative, a breaking-up process satisfying the two conditions last mentioned could be found in a two-quantam process, when specks with but one electron would be definitely unstable and would possibly lose and regain this electron repeatedly. Such a process would also avoid the crowding of the initial stages of the formation of specks into the early part of the exposure, which results from a cumulative process involving many quanta.

6. The Effect of Low Temperatures on the Regression.

In these experiments the photographic material was kept at a low temperature during the interval between the part exposures. Cooling took place in less than 40″ and the period of warming was approximately 50″ ; the total time during which the emulsion was not at low temperature was thus less than the time required for any appreciable regression to take place. Experiments were carried out at liquid air temperature and at somewhat higher temperatures up to − 90° C, and no appreciable regression could be observed. In one typical experiment, the interval between the first third of the exposure and the remaining two-thirds was increased to 6 hours, while the temperature was maintained between − 90° C. and − 79° C.; the densities of the interrupted exposure agreed with those of a continuous exposure within 2 %, the limits of error.

The loss of electrons from the conduction level of the halide crystal by direct return to their original positions, considered in Section (2) with regard to the threshold, should not show such a change with temperature. The experiments prove thus that this process by itself could not account for the regression effect, but that regression must depend on processes involving the mobility of ions or the supply of thermal energy for the escape of electrons.

7. The Effect of Infra-Red Radiation on the Regression.

In these experiments we flooded the photographic material with infra-red radiation during the interval between the part exposures. Two sources were used corresponding to emitters at 590° K. and 540° K. With the source of higher temperature (590° K.) a distinct Herschel effect took place, which could be observed from comparing density-marks obtained with single exposures given before and after the irradiation with infra-red. Within the limits of accuracy the irradiation between the part exposures produced, however, no increase of the regression, after making allowance for the normal Herschel effect on the fully formed developing centres. Corresponding exposures under identical conditions but with the source at 540° K. gave no observable normal Herschel effect and produced also no increase of the regression as compared with experiments where between the part exposures no flooding with infra-red had taken place.

8. The Cumulative Effect and the Threshold.

The tentative interpretation of the threshold discussed in Section (2) is essentially a specialised way of interpreting it as a statistical effect. The problem has a wider significance in view of the point raised in Section (5) as to whether the formation of active specks results from a process involving only two or a larger number of quanta. The following sections refer to this question.

If an active silver speck is produced by the absorption of a single light quantum, then for the early stages of an exposure proportionality should exist between the exposure and the number of active silver specks produced. This is found for exposures with X-rays of high frequency, when one X-ray quantum supplies the energy necessary for the formation of one speck, the absorption taking place by way of the formation of secondaries. Not only is no threshold then observed, but proportionality exists between exposure and the increase in the number of developable grains. Accurate measurements for very small densities were made on this point, using the scatter method for determining the number of developed grains.

When, on the other hand, the formation of an active silver speck requires the absorption of a large number n of light quanta, then it is improbable that these n quanta will be absorbed within the volume of the grain or of a crystallite forming part of a grain in the course of an exposure smaller than the average exposure required for the absorption of n quanta within this volume; and it becomes the more improbable the more the exposure in terms of this average value is small and the number n is great. If all grains were alike and each required the absorption of the same number of quanta, then the probable fluctuation in the exposures required for producing a developable grain should extend through a range of $1/\sqrt{n}$ of the exposure. With increasing n it becomes extremely improbable that these n quanta should be absorbed during an exposure considerably shorter than the average exposure required. With a large value n, a well-defined threshold range should thus be observed.

Fig. 2 shows a characteristic curve for Ilford Fine Grain Ordinary giving the density against the logarithm of exposure,* and also curves giving the distribution of the probability for the absorption of n quanta for $n = 5$ and $n = 10$, the scale being again logarithmic and the abscissæ being so adjusted that the probable absorption of 5 and 10 respectively are made to coincide with the middle of the steep rise of the characteristic curve. It will be seen that the run of the characteristic curve falls somewhat between that of the probability distribution curve for $n = 10$ and $n = 5$. Nothing more than a rough qualitative correspondence can be expected, since different values of n apply to different grains, tending to smooth out the rise of the characteristic curve. The comparison of the calculated curves would suggest that the average value of n should be of the order of 10.

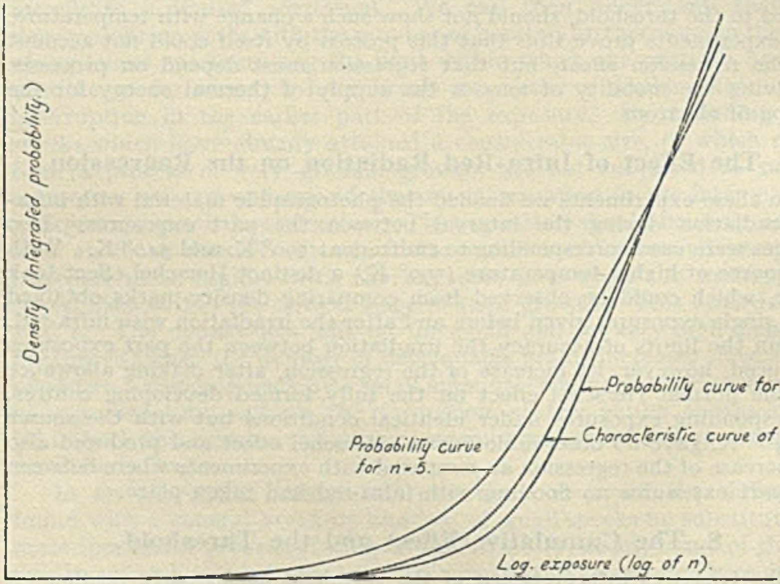

FIG. 2.

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* *Added in Proof:* The same statistical method is discussed in two papers by Webb,[10] which appeared after the Manchester Conference. The first may also be referred to for earlier literature. In the second paper Webb shows by a detailed analysis that with appropriate assumptions *H* and *D* curves can be accurately accounted for on a statistical basis. Our aim was essentially to account for the threshold, and to use the *H* and *D* curve for finding whether the formation of active specks comprises two or more stages. Nothing more than a very approximative answer appears justified, so long as the various parameters (size and sensitivity distribution, absorption in the emulsion), are not actually known from data which should be independent of this particular interpretation. To reduce this uncertainty we considered in the first place the foot of the *H* and *D* curve (see the account of the Manchester Conference in *Nature*), where the effect of absorption is less disturbing, while Webb, in his analysis, considers the general steepness. We do not, however, suggest that differences in findings should be attributed to differences of method, but rather to the different character of the emulsions; we used an emulsion with steep gradation. To discuss the theory of latent image formation, it seemed best to apply it to the greatest variety of data obtained for one and the same photographic material: one of simple and uniform type was chosen.

[10] Webb, *J. Opt. Soc. Am.*, 1939, **29**, 309 and 314.

9. X-Ray Examination of the Microcrystalline State of the Grains of Photographic Emulsions.

We examined the relation between sensitivity and the state of crystalline subdivision of the grains by determining the average size of the crystallites composing the grains of various emulsions. The experimental details regarding these measurements will be reported in a separate paper. The general finding, which is of interest here, was that emulsions with coarse grains gave broader X-ray lines indicating that the crystallites composing the grains were either smaller or more highly deformed. This was found in particular with regard to coarse grain emulsions of high sensitivity, the grains of the more sensitive emulsions showing a state of greater distortion or a higher degree of sub-division.

Apart from measurements made on commercial emulsions experiments were made on the effect of sensitizers upon the condition of the crystallites. Two particular instances may be quoted : when Ag_2S was introduced in such a way as to act as an efficient sensitizer the X-ray lines were broader than those from a similar emulsion of the same average grain size of pure AgBr, and broader also than those of a similar emulsion containing Ag_2S but introduced in such a way as not to act as a sensitizing agent. When an emulsion was exposed to the action of mercury vapour, under such conditions as to act as a sensitizer then with the increase of sensitivity also a decrease in the regularity of the crystalline state of the grains could be observed. These experiments do not establish that the increase of sensitivity produced by the action of a sensitizer is caused by the deterioration of the microcrystalline structure ; both phenomena may go parallel without one being the cause of the other. We have, in fact, some evidence that in certain cases a specific sensitizing action can take place with but little or no deterioration of the lattice. What can safely be said is that the coarse grains of sensitive emulsions are largely subdivided or deformed.

The breaking up of grains into smaller units and the formation of more internal boundaries may actually affect the sensitivity in different ways. It might decrease the sensitivity in so far as active silver specks can act as developing centres only when situated near the external surfaces of the grain, while internal boundaries may give the opportunity for electrons to collect and specks to form in the interior in places which are not accessible to the developer. On the other hand, it might increase the sensitivity in so far as the subdivision enhances locally favourable conditions to have full effect ; this would be in accordance with the theory of Gurney and Mott.*

10. The Summation of Exposures with Different Wave-lengths.

An alternative interpretation of the threshold could arise if during the early stages of the exposure some other process took place preceding the formation of active specks. Such a process could be imagined to consist in the trapping of electrons at some intermediate levels. In regard to the

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* According to this theory, as indicated in section (2), large n numbers might be associated with large grains. The discussion in section (8) would then suggest that the threshold value should be particularly great, while it is generally found that for coarse grain emulsions the initial sensitivity is high and the threshold small. The X-ray examination shows that such grains are actually subdivided into small crystallites and this would account for the n numbers being small. It should not be overlooked that another reason for the high sensitivity of coarse grains may result from the inequality of the specks : a limited number of specks with enhanced sensitivity would provide a larger contribution to the resulting density when the grains are large, since each active speck entails the development of a whole grain.

existence of such electron traps, the following experiments were made : * Two exposures with different wave-lengths were given in succession. It could be expected that if a first exposure with a short wave-length had brought electrons into some intermediate levels, a subsequent exposure with longer wave-lengths, so long as not to be very efficient in lifting electrons from their original places into the conduction band, would be more effective in producing active silver specks than when the exposures were given in the reversed order; the opposite effect would arise with electrons trapped very firmly. A wave-band in the blue and in the yellow were used (the yellow one being chosen so that a prolonged exposure would still yield a high density) and the intensities were so adjusted that for the single exposures equal densities were obtained for equal exposure times. If for each of the two wave-lengths the action of light were the same, the deviation from the reciprocity law should be equal in each case. It was then found that for low densities the resulting density was independent of the sequence of the exposures (and this applies also when the added effect of the two exposures just exceeded the threshold), but that for high densities there was a distinct difference suggesting a small amount of trapping at deep levels. Webb,[11] who made an extensive examination of the additive effect of exposure with two wave-lengths, did not observe this effect. It is very small and not noticeable outside the range of high densities, and was possibly not observed in earlier work for this reason.

11. Discussion of the Experiments of Sections 6 to 10.

In Section 5 we have summarised our results by reference to the two alternative working hypotheses, *viz.*, that the regression may be due to the loss of specific electrons, or to a "specialised" break-up which could be accounted for by a two-quantum process.

The fact that the regression disappears on lowering the temperature shows that it must depend on some phenomenon requiring thermal energy, this could apply to either the loss by the speck of specific loosely held electrons or the break-up of small specks.

On this latter view, flooding with infra-red should have increased the regression, in view particularly of Mott's interpretation of the Herschel effect as the breaking up of fully formed active silver specks. In analogy a somewhat smaller energy should considerably enhance the disintegration of smaller specks, for which according to the model of Webb and Evans the chance for disintegration should gradually increase with decreasing size of the specks. If, on the other hand, the regression consisted in the loss of specific incompletely consolidated electrons or ions, leaving the speck by thermal energy alone, flooding with long wave infrared should not alter the number of electrons lost. This view would thus conform with the results of the experiments.

In this model, which foresees that some specific electrons are unstable, the time during which the regression increases can then be taken as the average time for such losses of electrons to occur through their thermal energy. In a modified interpretation we may assume that the incompletely consolidated electrons are much less stable than is

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* The experiments on the additive effect of exposures to two different wave-lengths, here reported, were first undertaken in the range of small densities by one of us (J. C. M. B.) in collaboration with W. J. Meredith and formed part of the thesis (1936) of the latter. For the later experiments in the range of higher densities one of the writers (J. C. M. B.) had the collaboration of J. B. Sharples and J. R. Whitehead. Recently Berg reported in these *Transactions* (1939, 35, 445), on analogous experiments in the range of low temperatures.

[11] Webb, *Phot. J.*, 1936, 76, 78.

indicated by the regression period, but that they are replaced on the specks so long as a sufficient electron density is maintained in the conduction level. The maintenance of such a state and the regression period would then essentially be determined by the time during which the electrons remain in the conduction level before falling back into their original positions in the crystal lattice. To account for the disappearance of the regression at lower temperature we then assume that at low temperatures the electrons do not possess the necessary energy for leaving the speck. We do not wish to attach to one or the other version any other significance than that of correlating the experiments. Regarding the alternative model, we have indicated the conditions under which a break-up and loss of small specks could account for them. These could be satisfied by a break-up essentially restricted to definite groups (the initial stages). Repeated transitions of electrons between speck and conduction band, of the kind indicated in the second version of the model just discussed, could then determine a regression period. The forming of an appreciable number of active specks, right from the initial stages, becomes possible if specks were made in only two or few stages. The following discussion leads to this point:—

Section (8) which is primarily concerned with the threshold, shows that it can be accounted for on a statistical basis, and that the assumption of a cumulative effect for the formation of active silver specks (which also forms the basis of the theory of Gurney and Mott) is sufficient to account for the threshold and the early rise of the density-exposure curve. On this statistical interpretation, for a blue sensitive material, the majority of active specks should result from a gradual growth involving more than two, and on the average approximately ten quanta. X-ray determinations show that, in general, increased sensitivity goes parallel with a more highly deformed or more highly subdivided microcrystalline structure. This may be due to the fact that, with a division of the grain in smaller units, locally favourable conditions are given greater weight. It may also be due to the formation of intermediate electron levels at which electrons can be trapped, and which can have the effect of increasing the sensitivity. The initial accumulation of electrons in such traps could provide an alternative interpretation for the threshold which should then not necessarily be considered as resulting from a cumulative effect. The experiments on the summation of part exposures with different wave-lengths showed differences which can be interpreted as trapping, although only for high densities.* While this is of interest, it fails to account for the phenomena at low densities and at the threshold.

With regard to the formation of active specks and the particular assumption, that they result from a two-quantum process and that breaking up occurs while only one quantum has been received, the fact that, on a statistical basis, the threshold can be accounted for by a cumulative process involving a greater number of steps and not by a two-quantum process does in itself not disprove such a process, so long as the threshold can be accounted for in an alternative way. The one here considered is that electron traps may exist at intermediate levels; the experiments

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* In referring to the results in this way, we do not exclude that other reasons may account for any change of the densities with the order of the exposures; but the fact that no such change was observed in the range of low densities justifies the interpretation in the sense that in the initial stages no trapping occurs.

do not confirm the existence of such traps for exposure near the threshold. This does not preclude that the threshold may be accounted for on a different basis.

12. Conclusions.

The examination of the photographic action of part exposures showed that part exposures are additive even when separated by time intervals of 300 hours, when their summation produces a density of low value indicating a marked stability of the effect of sub-threshold exposures. In the range of higher densities a deficiency or regression of density is observed ; for one particular emulsion this becomes noticeable when the interruption exceeds 3′ and attains a finite value for an interval of 20′. This regression is greatest in the range where the density increases most rapidly with exposure ; it falls off in the range of small and of high densities. It increases with the number of interruptions. No regression is observed when the photographic material is maintained at a temperature below − 90° C. The regression is not modified by flooding the photographic material with infra-red radiation.

An X-ray examination of the microcrystalline structure of the grains showed that in general the grains of more sensitive emulsions consist of more deformed or more highly subdivided crystallites.

Experiments on the summation of exposures to light of different wave-lengths showed that for large exposures the densities depend on the order in which they are given. For small exposures no such effect was observed.

The various results with regard to the threshold and to the regression effect can be co-ordinated by assuming that for a blue sensitive material the large majority of active specks results from a process of gradual growth involving approximately ten steps, and that the interruption of an exposure is followed by the loss of a limited number of electrons, either from specks which are small or from specks on which they are held in unstable positions. An alternative assumption of a break-up of small specks, limited to the early stages of a process of growth involving two or few steps only, is contingent to finding that the threshold can be accounted for without recurring to a multi-quantum process.

Summary.

Experiments on the formation of the latent photographic image, in particular the threshold and a regression or deficiency observed in the addition of part-exposures, are described.

The dependence of this regression on density, on the length and number of interruptions, and the manner in which it is affected by cooling and by flooding with infra-red are examined.

Subsidiary experiments comprise a statistical discussion of the threshold, an X-ray examination of the micro-crystalline state of the grains of photographic emulsions and experiments on the super-position of radiations with different wave-lengths.

The results are discussed with regard to possible interpretations derived from a wave-mechanical model.

The authors wish to express their thanks to Professor Mott, Professor Peierls and Dr. Gurney for discussions and suggestions received during the course of this work. They are also grateful to Professor Mott for the privilege of perusing MSS. of his papers and receiving first-hand information on the development of the theory and to Dr. Berg for various valuable indications and for drawing their attention to papers which were not easily accessible.

They are also greatly indebted to Dr. Bloch and to Messrs. Ilford Ltd. for having provided a number of special photographic materials which were most valuable in carrying out this work.

One of us (S. B.), is indebted to the Department of Scientific and Industrial Research for a grant which enabled him to devote his time to the investigations described.

MONOLAYERS OF COMPOUNDS WITH BRANCHED HYDROCARBON CHAINS. I. DI-SUBSTITUTED ACETIC ACIDS.

By Einar Stenhagen.*

Received 15*th February*, 1940.

The properties of insoluble monolayers of compounds with normal hydrocarbon chains and different polar groups are well known. This knowledge is largely due to the systematic researches of Adam and his associates.[1] No work has been carried out, however, on compounds with branched hydrocarbon chains. Carboxylic acids with branched chains are important from the biological point of view. Adams and collaborators [2] have shown that certain acids of this type have a bactericidal action against certain bacteria, and other investigators have shown that branched acids are normal constituents of several bacteria. The most remarkable discovery is perhaps that one acid of this type, isolated from the tubercle bacillus by Anderson and Chargaff,[3] and called the phthioic acid, is responsible for the tissue reaction characteristic of tuberculosis.[4]

A study of the surface film properties of different branched chain acids may, in favourable cases, give valuable information as to the structure of naturally occurring acids, by comparing the data obtained with the acid of unknown structure with those obtained with acids of known constitution. Furthermore, by the technique developed by Schulman and Rideal and associates [5] it is possible to study their interaction with other chemical compounds in surface films.

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* Rockefeller Foundation Fellow, 1938-39.

[1] N. K. Adam, *The Physics and Chemistry of Surfaces*, 2nd edition, Oxford, 1938.

[2] (*a*) R. Adams, W. M. Stanley and H. A. Stearns, *J. Amer. Chem. Soc.*, 1928, **50**, 1475. (*b*) G. R. Yoke and R. Adams, *ibid.*, 1928, **50**, 1503. (*c*) J. A. Arvin and R. Adams, *ibid.*, 1928, **50**, 1983. (*d*) L. A. Davies and R. Adams, *ibid.*, 1928, **50**, 2297; (*e*) W. M. Stanley, M. S. Jay and R. Adams, *ibid.*, 1929, **51**, 1261. (*f*) S. G. Ford and R. Adams, *ibid.*, 1930, **52**, 1259. (*g*) B. F. Armendt and R. Adams, *ibid.*, 1930, **52**, 1289. (*h*) C. M. Greer and R. Adams, *ibid.*, 1930, **52**, 2540.

[3] (*a*) R. J. Anderson and E. Chargaff, *J. Biol. Chem.*, 1929-30, **85**, 77. (*b*) R. J. Anderson, *ibid.*, 1932, **97**, 639.

[4] F. Sabin, *Physiol. Rev.*, 1932, **12**, 141.

[5] (*a*) J. H. Schulman and E. K. Rideal, *Proc. Roy. Soc.*, *B*, 1937, **122**, 29 and 46. (*b*) J. H. Schulman and E. Stenhagen, *ibid.*, 1938, **126**, 356. (*c*) E. G. Cockbain and J. H. Schulman, *Trans. Faraday Soc.*, 1939, **35**, 716.

Technique.

The measurements were carried out using a Langmuir-Adam trough in the usual manner. The surface potential was measured by means of a polonium electrode and a Lindemann electrometer, as described by Schulman and Rideal.[6] A trough of Pyrex glass and a mica boom were employed, in order to avoid heavy metal ions. The water used was free from copper ions and the chemicals were of " Analar " grade. The material to be spread was dissolved in redistilled petrol ether (B.D.H., Bp. 60-80° C.) and spread by means of an " Agla " micrometer syringe.

The torsion wire balance was sensitive to 0·1 dynes. Due to the relatively low sensitivity of the apparatus used, the investigation of the acids at very low surface pressures was left for future work.

At least two separate sets of measurements were carried out with freshly prepared petrol ether solutions, and it is considered that the *F-A* curves are accurate within 2-4 per cent. The nature of several of the acids used does not allow extreme accuracy to be obtained. The time interval between different points on the *F-A* curves is about 45 sec. ; with different rates of compression slightly different areas will be found, in general, slightly smaller areas will be obtained on very slow compression. The difference will be significant only in cases where the acids collapse readily at higher pressures, in such cases the *F-A* curves are dotted.

The surface potentials were read to the nearest millivolt, and each point on the curves is the mean of measurements on three different points on the surface. Above 1 dyne pressure, the potentials were uniform to 4 mv.

The measurements were carried out at a temperature of 18 ± 1° C.

In order to simplify the figures and conserve space, the acids are characterised only by the number of carbon atoms in the two branches, if these have normal chains. The 2 : 10 acid is thus ethyl-decyl-acetic acid, and the 0 : 15 acid the straight chain margaric acid.

Material Used.

This work was made possible by the generosity of Professor Roger Adams, University of Illinois, who placed a large number of synthetic acids at the author's disposal. Details of the synthesis, purification and physical constants of the various acids will be found in the original papers by Adams and collaborators.[2]

In addition, the C_{26} acids and the ethyl-tetradecyl-acetic acid were obtained from Dr. E. Chargaff, New York,[7] the margaric acid from Professor F. Francis, Bristol, and the di-octadecyl-acetic acid from Dr. A. S. C. Lawrence, Cambridge.

The ethyl-dodecyl-acetic acid (Mp. 20-21° C.) and the decyl-dodecyl-acetic acid (Mp. 47° C.) were prepared by Mr. H. K. King, Cambridge.

To all these gentlemen the author wishes to express his thanks.

Results

A. Acids in undissociated form on acid (0·01 N HCl) substrate.

1. Effect of displacing the carboxyl group along a chain of 16 carbon atoms. Isomeric heptadecanoic acids.[2(a)]—Fig. 1 shows that even the introduction of a methyl side chain in the 1 : 14 acid leads to a considerable expansion of the monolayer. This expansion increases with further increase in the length of the shorter chain to reach its maximum in the 7 : 8 acid, where the carboxyl group is as near the middle of chain

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[6] J. H. Schulman and E. K. Rideal, *Proc. Roy. Soc., A*, 1931, **130**, 259.

[7] E. Chargaff, *Berichte, B*, 1932, **65**, 745.

as possible. The monolayers are liquid and fairly stable, but exhibit in general a slow collapse on standing when the pressure is above 12-15 dynes. As the acids from the 2 : 13 acid on either have their three dimensional melting-points near the temperature of the experiments or are liquids at that temperature, the compression curves show flat collapses due to equilibrium between lenses on the surface and the monolayer. No real equilibrium seems to exist, however, on prolonged standing the pressure usually falls several dynes below the initial collapse pressure. They are thus not very good as piston oils. The initial collapse pressures are fairly reproducible. The limiting area of the 5 : 10 acid, shown in the figure to be at 83 A², is uncertain, as this acid expands on standing at low pressures (indicated by small arrows in the figure). The curve in Fig. 1 was obtained on compression immediately after spreading. The same tendency is also found, although less pronounced, in some of the other acids, and has also been found in normal chain acids.[8]

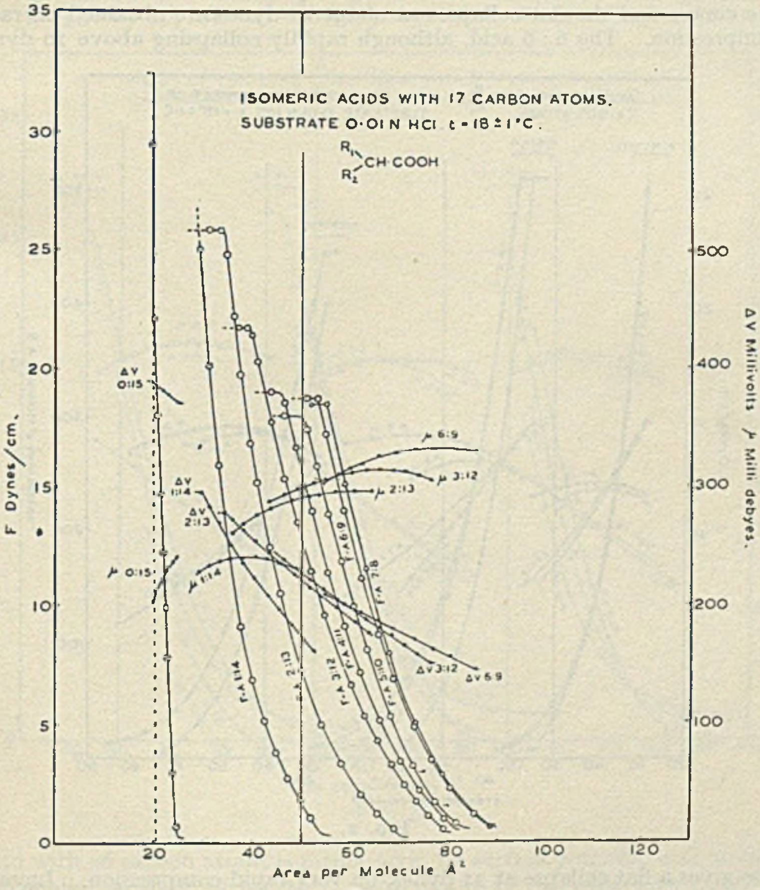

Fig. 1.

The surface moment μ for the 1 : 14 acid is nearly the same as for the straight chain acid, but it increases with increasing expansion and is around 300 millidebyes for the more symmetrical acids. On compression the moment increases first, passes through a maximum and then falls.

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[8] G. C. Nutting and W. D. Harkins, *J. Amer. Chem. Soc.*, 1939, 61, 1180.

This behaviour is characteristic for most di-substituted acetic acids. In order not to overcrowd the figure some of the intermediate ΔV and μ curves are left out. ΔV and μ for the 7 : 8 acid are very similar to those of the 6 : 9 acid.

2. Effect of increase of the number of carbon atoms in the molecule when the length of the shorter side chain is constant. C_{14}-C_{26} acids [2(a), (g), (h), 7].—Figs. 2 and 3 show sets of curves obtained with acids with the shorter chain 1-6 carbons long. The isomeric acids containing 14 carbon atoms (4 : 8, 5 : 7, 6 : 6 of Fig. 3) tend to the vapour expanded state and are unstable at higher pressures. The dotted part of the curves and the flat collapses at about 21 dynes are obtained on rapid compression. The 6 : 6 acid, although rapidly collapsing above 10 dynes, also gives a flat collapse at 21 dynes, on very rapid compression. Increase in the total number of carbon atoms has in all cases a condensing effect on the lower part of the curve. At higher pressures there is a condensing effect with 1-3 carbons in the short chain and a tendency to expansion when the side chain is longer. The expansion with increasing length of the short chain is illustrated by the increasing height at which the sets of curves cut the vertical line drawn through the 50 A² mark on the abscissa. The 4 : 20 acid, which has a total of 26 carbon atoms, collapses against 0·1 dynes pressure at 18° C. The lateral adhesion between the C_{20} chains is probably sufficient to remove the polar group from the water when the monolayer is compressed. The adhesion can be reduced by increasing the temperature and at 40° C. to the monolayer withstands 3 dynes pressure (Fig. 3).—The difference in the area occupied by the 2 : 14 and the 2 : 13 acids appears a little large for a difference of only one carbon

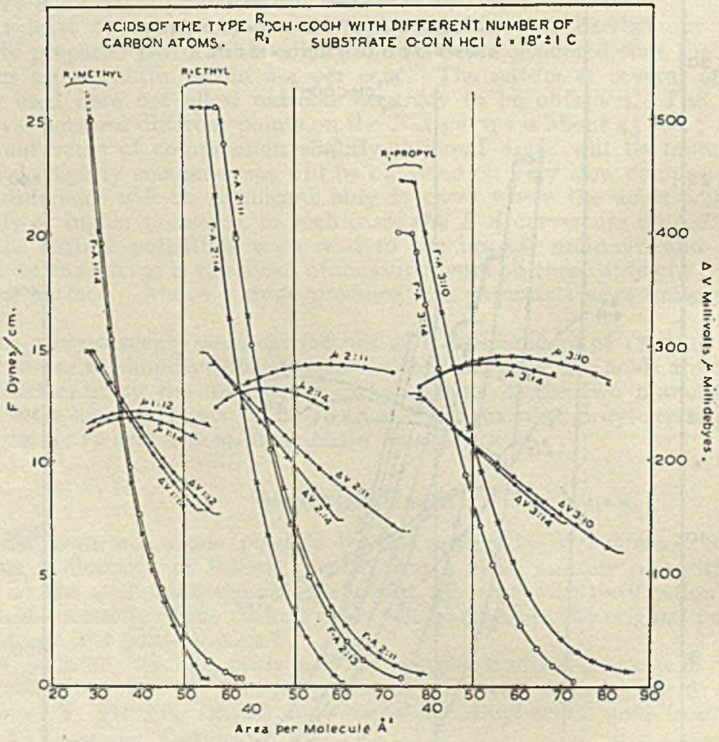

FIG. 2.

atom. It has, however, been repeatedly obtained with the specimen available.

The 10 : 12 acid has a limiting area of 76 A², and collapses at an area of 61 A² and a pressure of 11 dynes.

The moments increase from methyl to propyl side chains and are then rather constant around 300 millidebyes.

3. Symmetrical acids with different number of carbon atoms.—The condensing effect at low pressure and the expansion at higher pressure (*i.e.* the decreasing compressibility) with increasing number of carbon atoms are well illustrated by the curves in Fig. 4. The compressibility per CH_2 group appears to be roughly constant. The stability of the 12 : 12 acid with 26 carbon atoms is rather poor, its surface potential and moment are similar to those of the 10 : 14 acid. The 18 : 18 acid with 38 carbon atoms was found to give no stable monolayer.

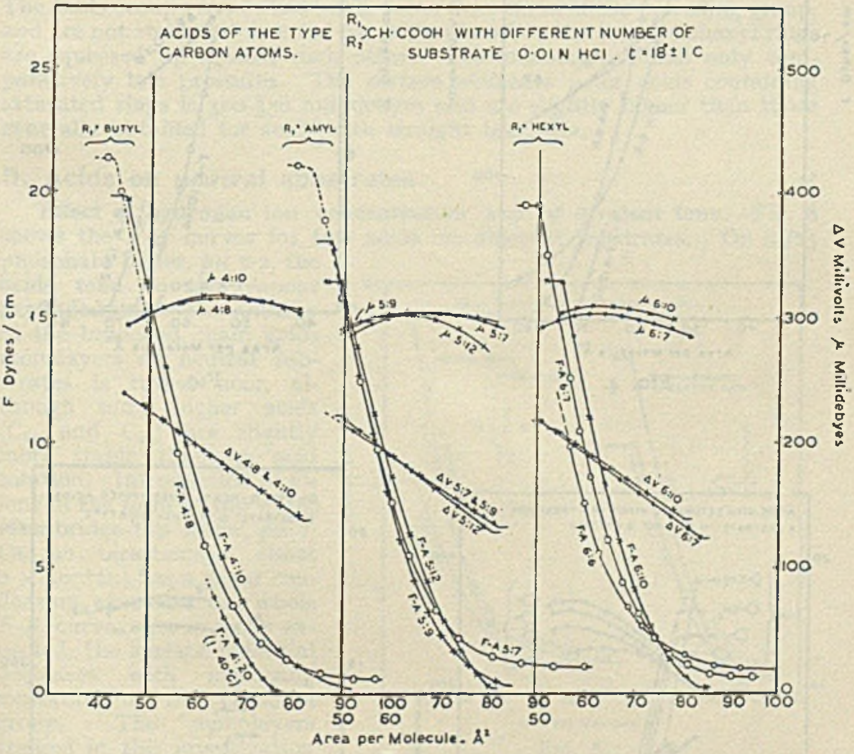

FIG. 3.

4. Isomeric acids with 26 carbon atoms.[7]—With 26 carbon atoms (Fig. 5) the hydrophobic part of the molecule outweighs the hydrophilic group and the monolayers are rather unstable. The stability in this case seems to be greatest when the number of carbon atoms in the longer chain is twice that of the shorter chain. Even in this case the most symmetrical acid is the most expanded.

5. Acids with saturated hydrocarbon rings in α-position [2(a), (b), (c), (f)]. **Cyclopropylmethyl-tetra-decanoic and cyclopentyl-tridecanoic acids (C_{18}) and cyclobutylmethyl-tetradecanoic and cyclohexyl-tridecanoic acids (C_{19}).**—Fig. 6 shows that cyclopentyl and cyclobutylmethyl in α-position give almost identical curves, which is to be expected. Cyclopropylmethyl decreases and cyclohexyl increases the expansion

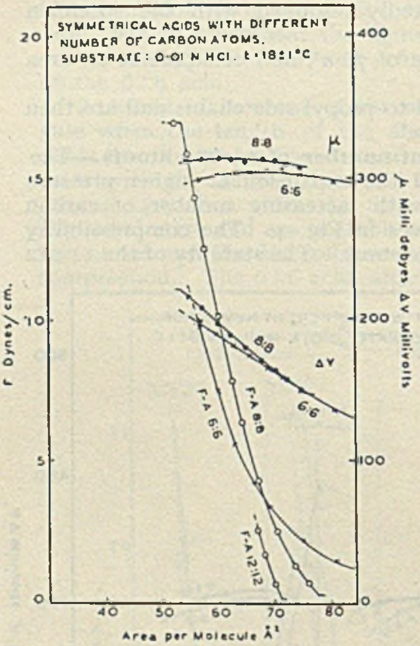

FIG. 4.

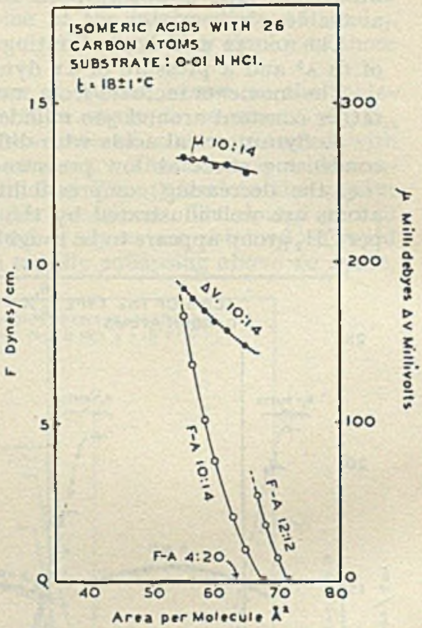

FIG. 5

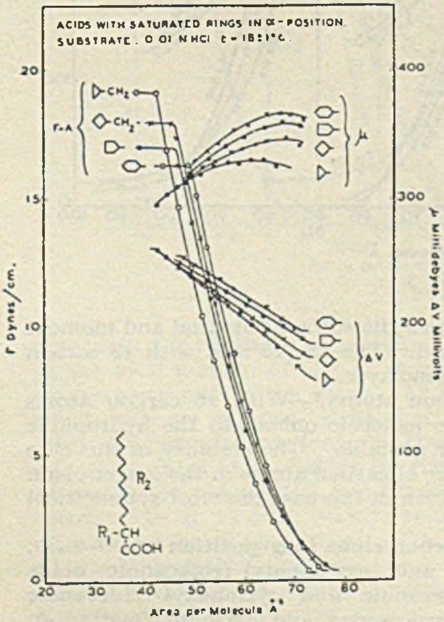

FIG. 6

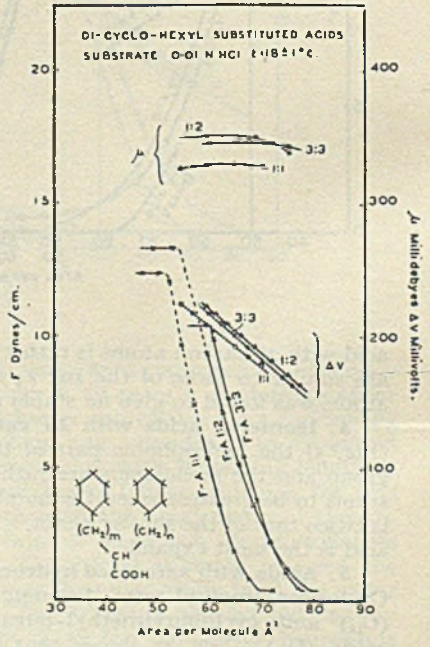

FIG. 7.

slightly. The area of the cyclohexyl ring is 30 A^2 according to measurements by Danielli[9] on long chain cyclohexanols. The α-cyclohexyl-tridecanoic acid collapses at just below 50 A^2, which corresponds roughly to the area of a cyclohexyl group + a hydrocarbon chain. The *F-A* curve of this acid is completely reversible; even if the acid has been compressed beyond the collapsing point, the pressure on expansion falls along the original compression curve. In general, the acids studied on expansion after collapse give slightly smaller areas than on the initial compression. The area so obtained also depends on the rate of expansion.

6. Di-cyclohexyl substituted acids.[2(d)]—(The numbers in Fig. 7 refer to the number of—CH$_2$—groups in the two branches respectively.) The acids occupy somewhat larger areas than those of the preceding group, and are not stable below 60 A^2 per molecule, when the two cyclohexyl rings are squeezed up against each other. The monolayers stand only comparatively low pressures. The surface moments μ for acids containing saturated rings is 300-350 millidebyes and are slightly higher than those generally obtained for acids with straight branches.

B. Acids on neutral substrates.

Effect of hydrogen ion concentration and of divalent ions.—Fig. 8 shows the *F-A* curves for two acids on different substrates. On M./25 phosphate buffer, *p*H 7·2, the acids tend to the vapour expanded state. The stability of the branched chain acids monolayers on neutral substrates is rather poor, although some higher acids (C_{24} and C_{26}) are slightly more stable than on acid solution. Introduction of Ca ions in the form of tap water (Cambridge tap water, *p*H 8, Ca as bicarbonate about 2×10^{-5} M.) has a slight condensing effect on the whole *F-A* curve. As is to be expected, the surface potential decreases with increasing ionisation of the carboxyl group. The monolayers studied in this investigation are nearly all of the liquid expanded type. Fig. 8 shows the thermal expansion of a typical acid. The curves are obtained without use of enclosed constant temperature apparatus, and show only the general type of expansion obtained.

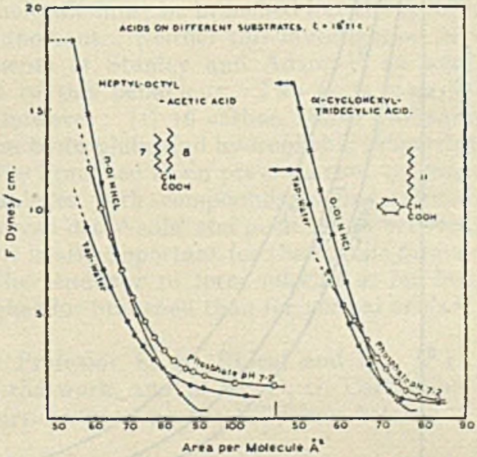

FIG. 8.

The 6 : 6, 7 : 8 and 1 : 14 acids have also been examined using the automatic registrating Wilhelmy surface balance described by Dervichian.[10] The results confirmed those obtained in the ordinary way.

Discussion.

The fact that the monolayers tend to expand with increasing number of carbon atoms, when the shorter chain contains more than 3 or 4 carbons, shows that two long hydrocarbon chains attached to a common (tertiary) carbon atom do not arrange themselves side by side easily.

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[9] N. K. Adam, J. F. Danielli, et al., *Biochem. J.*, 1932, **26**, 1233.

[10] (*a*) D. G. Dervichian, Thèses, Paris, 1936, Masson et C^{ie}; (*b*) *idem. J. Physique*, 1935, **6**, 221.

This is particularly marked in the symmetrical acids shown in Fig. 4. One would expect the 12 : 12 acid to be more condensed than the 8 : 8 acid due to increased adhesion between the two longer chains, but on the contrary it is rather more expanded. The areas are very much larger than that occupied by two closely packed chains, 40 A². This behaviour will be further discussed in Part II.

The apparent surface dipole moment μ increases with increasing expansion. This has also been found in other cases, for instance for esters and methyl ketones,[11] and can be attributed to reorientation of the dipole axis with increased expansion and possibly also a change in the dielectric constant at the interphase. The moment of a normal chain acid as the myristic acid in the expanded state is around 200 millidebyes,[12] and does not differ appreciably from that of normal chain acids in the condensed state.

The considerable increase of the moment in branched acids at corresponding areas is therefore probably due to a change in orientation of the polar group caused by the α-substitution, when the substituent is larger than a methyl group. For the same degree of expansion the C_{24} and C_{26} acids show slightly smaller moments than their lower homologues.

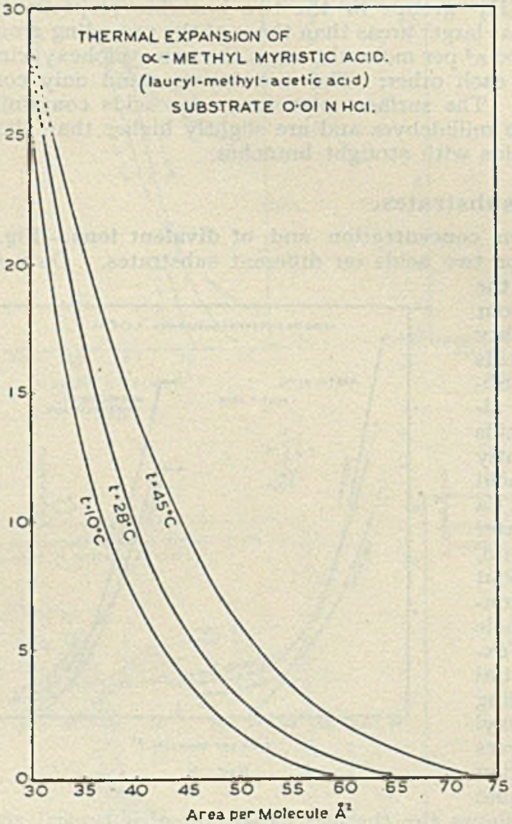

FIG. 9.

The relative expansion at low surface pressures and contraction at higher pressures on a neutral substrate seems to be a general phenomenon for expanded fatty acids; it occurs both in cases of thermal expansion as in the myristic acid [13] and of expansion due to steric reasons as in unsaturated acids,[14] and in the branched chain acids under discussion.

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[11] (*a*) J. H. Schulman and A. H. Hughes, *Proc. Roy. Soc.*, *A*, 1932, 138, 430. (*b*) A. E. Alexander and J. H. Schulman, *ibid.*, *A*, 1937, 161, 115. (*c*) N. K. Adam, J. F. Danielli and J. B. Harding, *ibid.*, 1934, 147, 491.

[12] *Loc. cit.* 11ᵃ and *loc. cit.* 10ᵃ.

[13] W. D. Harkins and R. J. Myers, *J. Chemical Physics*, 1936, 4, 716.

[14] J. Marsden and E. K. Rideal, *J. Chem. Soc.*, 1939, 1163.

The expansion at low pressure was attributed by Harkins and Myers [13] to repulsion of ionised head groups but the reason for the contraction is more obscure. Marsden and Rideal [14] attribute it to accumulation of bound ions on compression of the monolayer and to association as found in acid soaps. It is doubtful if this can be the cause in branched acids where the area of the monolayer at collapse is more than 50 A^2 per molecule, *i.e.* the distance between the polar groups is large, but the slight general contraction when calcium ions are present in the substrate indicates effects of ions even when the distance between the heads is large. Calcium ions are not, however, sufficient to condense the acids at low pressures, the strong condensing effect found for straight chain acids being entirely absent.

In the fully ionised state, *p*H 11 or higher, branched chain acids give vapour films due to the strong repulsion between the head groups, while straight chain acids, probably due to salt effects,[15] give vapour films only on extremely alkaline solutions.

Adams and collaborators found that a number of their synthetic acids had the same action as chaulmogric acid on the leprosy bacillus.[16] Very dilute soap solutions of the acids killed the bacillus in vitro. It was found that acids with 16 carbon atoms were the most effective. The hydrocarbon part of the molecule must be branched but the special configuration does not seem important. Neither this investigation nor the surface tension measurements of Stanley and Adams [17] on soap solutions give any direct clue to this behaviour. Two facts may be important in this connection, however: (1) 16 carbon atoms probably give an optimal balance between hydrophilic and hydrophobic properties of a carboxylic acid; and (2) the branched chain prevents close packing and formation of strong complexes with compounds having normal chains, due to weakening of the van der Waals' and polar forces between the molecules. The latter point is also important for the micelle formation in the soap solutions. The tendency to form micelles is far less and the water solubility far higher for branched than for normal acids.[17]

The author is indebted to Professor E. K. Rideal and Dr. J. H. Schulman for their interest in the work, and to Dr. D. G. Dervichian, Paris, for carrying out the experiments using the Wilhelmy balance.

Summary.

Force-area and surface potential—area relations are given for a number of branched chain carboxylic acids of the di-substituted acetic acid type, with a total number of carbon atoms from 14 to 38. For unionised aliphatic acids the following applies:

(*a*) The monolayers are of the liquid expanded type, with the exception of the C_{14} acids, which are vapour expanded.

(*b*) For a given number of carbon atoms the monolayers become more expanded with the displacement of the carboxyl group from the end to the middle of the chain, *i.e.* with increasing symmetry of the di-substituted acetic acid.

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[15] (*a*) N. K. Adam and J. Miller, *Proc. Roy. Soc., A*, 1933, **142**, 401. (*b*) J. Marsden and J. H. Schulman, *Trans. Faraday Soc.*, 1938, **34**, 748.

[16] *Loc. cit.* [2] and W. M. Stanley, G. H. Coleman, C. M. Greer, J. Sacks and R. Adams, *J. Pharmacol.*, June, 1932.

[17] W. M. Stanley and R. Adams, *J. Amer. Chem. Soc.*, 1932, **54**, 1548.

(*c*) Increase in the total number of carbon atoms has a condensing effect at low surface pressures, and also at higher pressures if the short chain contains less than 4 carbon atoms ; if longer, expansion occurs at higher pressures.

(*d*) The apparent surface moment μ tends to increase with increasing expansion.

Acids containing alicyclic rings are, due to the size of the rings, very expanded, and show comparatively high surface moments.

On neutral substrates the monolayers undergo a relative expansion at low pressures, and a contraction at higher pressures. Ions of divalent metals have a slight condensing effect on the whole force-area curve.

In the fully ionised state, on substrates having a *p*H of 11 or higher, the acids give vapour films.

The Colloid-Science Department,
The University,
Cambridge.

NOTE ON HEATS OF FORMATION OF ETHYL AND PROPYL PEROXIDES.

By E. C. Stathis and A. C. Egerton.

Received 28th February, 1940.

Although the measurements given in this note are only of a perliminary kind, it seems worth while to record them, as it may not be possible for some time to complete the investigation of the thermal properties of these peroxides as was intended.

The peroxides were made by methods described elsewhere, A. C. Egerton, F. L. Smith, A. R. Ubbelohde, *Phil. Trans*, 1934, 234, p. 433 ; E. J. Harris and A. C. Egerton, *Proc. Roy. Soc. A*, 1938, 168, p. 1 ; E. J. Harris, *Proc. Roy. Soc. A*, 1939, 173, p. 126.

The heats of combustion were determined in a bomb calorimeter. About 0·5 gram of the peroxide was weighed into very thin glass bulbs with ground-in stoppers, which it filled completely. The bulb was placed in a small porcelain crucible ; a cover glass perforated with a central hole held it in position. Ignition was started by an iron wire touching 0·1 gram sugar spread on the tray formed by the cover glass. A number of experiments led to the following results for the heats of combustion at 298° K. and 1 atmos. :—

$(C_2H_5)_2O_2$	7155 ± 200 cal. per gram.
$C_2H_5O_2H$	5400 ± 200 ,, ,,
$C_3H_7O_2H$	6300 ± 200 ,, ,,

These results provide values for the heat of formation of the vapours, which are only little different from the values for the corresponding ether and alcohols :—

$(C_2H_5)_2O_2$	68 Kg. cal. per mol.	$(C_2H_5)_2O$	65 Kg. cal. per mol.
$C_2H_5O_2H$	50 ,, ,, ,,	C_2H_5OH	57 ,, ,, ,,
$C_3H_7O_2H$	60 ,, ,, ,,	C_3H_7OH	63·5 ,, ,, ,,

It was hoped to check and obtain more reliable figures by hydrogenation and other methods, so that the energy associated with the peroxide bond could be assessed.

Imperial College of Science and Technology,
South Kensington, S.W. 7.

REVIEWS OF BOOKS.

Ephraim's Inorganic Chemistry. 3rd English Edition. By P. C. L. Thorne and A. M. Ward. (London: Gurney and Jackson, 1939. Pp. xii + 911. Price 28s. net.)

This edition of Ephraim is some forty pages longer than the previous one. It has been well brought up to date and, in addition to numerous references to recent papers on the various aspects of the subject treated, there are several entirely new sub-chapters.

Ephraim is now so well established as an advanced text-book and book of reference that extensive review is not called for. Suffice it to say that the standard of the previous edition is fully maintained.

The volume is excellently documented so that the reader can readily refer to the source of any particular piece of information. Well printed and soundly bound, this book is splendid value.

Statistical Thermodynamics. By R. H. Fowler and E. A. Guggenheim. (Cambridge: at the University Press, 1939. 26 × 17 cm.; pp. x + 693. Price, 40s.)

Fowler's *Statistical Mechanics*, the second edition of which was published towards the end of 1936, is remarkable not only for the rigour of the mathematical technique by which the statistical formulæ are developed from the basic quantum mechanical postulates, but also for the vast range of applications which are considered in detail. For most physicists and chemists, however, the book is somewhat formidable, a contributory factor to this being the avoidance of relatively familiar thermodynamic methods. Many will welcome a modified version in which, as the authors state in their preface, the theory is developed so as to be complementary to a presentation of thermodynamics, mathematical details of proofs are taken for granted, and the applications are confined to terrestrial physics and chemistry. Guggenheim's profound grasp of thermodynamical methods, as shown in his *Modern Thermodynamics* (1933), and his wide interests in the general field, shown by his papers, make him eminently fitted for collaboration in the task of providing this modified version of statistical mechanics.

The general approach and character of the treatment follow closely the lines of Fowler's earlier book, many sections of which are taken over with little change. Even in these, however, the changes that have been made suggest that the whole of the material has been subjected to extremely careful revision. Except for the omission of the previous discussions on problems of stellar atmospheres and interiors, and on fluctuations, the field of applications covered is much the same. There has, however, been a tightening up in the general arrangement, the more recent work is fully discussed, and a considerable amount of previously unpublished material is included. A chapter which has no counterpart in the earlier book is that on generalised partition functions and the related thermodynamic functions and their applications.

The first two of the fourteen chapters discuss the basic assumptions of statistical mechanics, enunciate the general theorems required, and develop the connections between the statistical and thermodynamic formulæ. The statistical procedure used is that of determining average, rather than most probable, values for an assembly, using the elegant contour integration method. Although details of proofs are omitted, the method is fully explained. The statistical problem, in connection with a particular assembly, is reduced to that of constructing and evaluating a partition function ; from this the various thermodynamic functions can be derived, and the theoretical molar characteristics of the assembly determined, to be compared with observed molar properties. The second law of thermodynamics is formulated by reference to the (Helmholtz) free energy function (rather than the entropy function), and by a process of identification of the terms in a statistical function which is shown to have the same properties, the thermodynamic significance of the parameters occurring in the statistical treatment is obtained.

Applications are first made to permanent perfect gases. There is a clear discussion of nuclear symmetry effects, and detailed treatments are given of the rotational and vibrational heat capacities for a large number of molecules. Crystals are then considered, primarily on the lines of the Debye treatment, with discussions on the character and effect of the approximations made. A long chapter on chemical equilibria and evaporation concludes with a clear and detailed discussion of the status of Nernst's heat theorem. The account of grand partition functions which follows should be of value in clarifying the physical meaning of various generalised partition functions and the associated thermodynamic functions, and in showing the circumstances in which alternatives to the usual partition functions may advantageously be employed. The discussion of imperfect gases includes an analysis of interaction energies, and accounts of very recent work on condensation. Liquids are treated in two chapters, dealing with non-electrolytes and electrolytes. The more recent work in which a liquid is regarded as quasi-crystalline rather than as quasi-gaseous is fully described, and an account is given of the application of grand partition functions to liquid mixtures. There is an excellent presentation and critical discussion of the Debye-Hückel treatment of electrolytes, and of later theoretical developments. In the chapter on surface layers, mobile and localised monolayers are discussed.

The basic principles of the modern electron theory of metals are considered, the fundamental formulæ are derived, and applications are made to electronic heat capacities, thermionic emission and the photo-electric effect. Here and in the last chapter use is made of the formulæ essentially characteristic of Fermi-Dirac statistics ; in all the applications in other chapters the quasi-classical approximations are adequate.

Very properly, a chapter on chemical kinetics has been included. This is not only of interest in itself, but is almost indispensable for providing a quantitative guide as to the conditions for applicability of the results of equilibrium theory with which the book is primarily concerned.

The range and power of statistical methods is shown clearly in the last two long chapters. The first of these deals with lattice imperfections, and order-disorder phenomena in alloys. The chapter is notable for the very detailed account of the relation between the treatments of order-disorder effects due to Bragg and Williams, Kirkwood, and Bethe, and the development of a new " quasi-chemical " treatment which enables a good approximation to be obtained without undue complexity of mathematical method. The final chapter deals with electric and magnetic properties. The treatment of electric and magnetic susceptibility includes a review of crystalline field effects in paramagnetic salts, a discussion of the magnetic cooling method, and some account of the interpretation of phenomena in the very low temperature region. An account is also given of the collective electron treatment of ferromagnetism.

The above indication of the topics treated can give but an inadequate impression of the character and content of this book. Each chapter may be said to constitute a monograph on the subject with which it is concerned, giving a detailed presentation of theoretical investigations, and an adequate summary of relevant experimental data. Although the book has, in one sense, the character of an extended series of reports, in another it is original throughout, for all the work discussed is presented from the unifying standpoint provided by the general statistical treatment.

Attention should perhaps be directed to the point that, when the book is described in a sub-title as " a version of Statistical Mechanics for Students of Physics and Chemistry ", the wider meaning of " students " must be understood. In no sense is this an introductory treatise. It could hardly serve as a guide to students making a first approach to the subject, and it is not concerned, save incidentally, with the historical development. It is an exposition of a technique for the application of statistical mechanics to physico-chemical problems, and of a large number of the applications which have been made, the character of the treatment implying the assumption of much more than elementary knowledge of the field on the part of readers. The general methods used, moreover, though they are, from the standpoint of mathematical rigour, perhaps the most satisfactory available, will undoubtedly make severe demands on many physicists and chemists. Readers will, however, be amply repaid for such efforts as are required of them. A growing appreciation of this book for the magnificent achievement which it is will go hand in hand with a clearer and more profound understanding of the wide range of physico-chemical phenomena with which it deals.

E. C. S.

Molecular Spectra and Molecular Structure. I. Diatomic Molecules. By G. HERZBERG. Translated by J. W. T. SPINKS. (New York: Prentice-Hall, Inc., 1939. Pp. xxvi + 592, with numerous illustrations and tables. Price $6.50.)

This comprehensive work has already received attention in these *Transactions*, at the time of its issue in the original German edition. It is therefore unnecessary to enlarge upon its merits, which are there for all to see. The translation which has now appeared has been undertaken with the author's co-operation, an advantage which is manifested by the way in which the sense of continuity of style has been happily preserved. A book of this calibre should be a stimulus to refined experiment, because what is most urgent in molecular spectroscopy to-day is the provision of data of the greatest possible degree of precision, combined with the highest resolving power. This is what the theorist needs, and this volume illustrates what he can do with it as soon as it is forthcoming.

F. I. G. R.

Kinetik der Phasenbildung. By M. Volmer. (Pp. xii and 220. Verlags. Theodor Steinkopff, Dresden, 1939. Price R.M. 14.25 : bound 15.0.)

This book forms the fourth volume of a series with the general title *Die Chemische Reaktion*, issued under the editorship of Professor Bonhoeffer.

It deals in as systematic a way as possible with the phenomena which accompany the passage of matter from one to another of its states of aggregation. The treatment is clear and balanced. Mathematical calculations are given throughout, but they do not outweigh the qualitative and descriptive part of the book.

After a historical introduction the transitions gas-liquid, gas-solid, crystal I-crystal II, and so on, are discussed in order : then delayed transitions and nucleus formation are dealt with and drop and bubble formation treated at length. Finally, there are short chapters on the rule of " steps " and on the structure of new phases (crystallite size and so on).

The book is a very useful contribution to the literature of molecular processes ; numerous topics of importance are discussed in a logical and judicial manner. The difficult task of a really synthetic treatment of the whole is not attempted ; the author would probably not regard this as possible or desirable at the present time.

ERRATA.

P. 329. Formula 1. The methyl radical of the acetyl group has been omitted.

P. 506. Line 7 from bottom. *For* " specification " *read* " specific action ".

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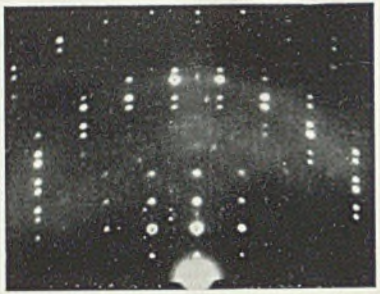

FIG. 1.—Nickel oxide condensed on to heated corundum; $(11\bar{2},0)$ face [001] azimuth of the corundum; {111} face $\langle 11\bar{2}\rangle$ azimuth of the nickel oxide.

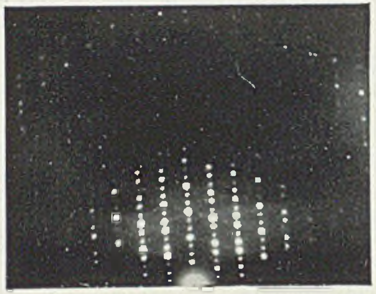

FIG. 3.—Surface as for Fig. 1. Azimuth 30° from Fig. 1.

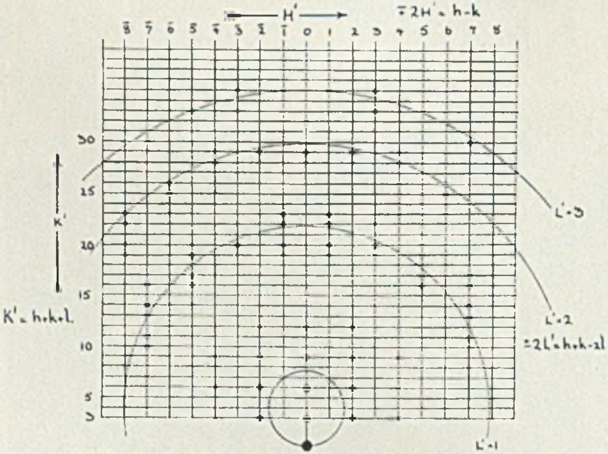

FIG. 2.—Index diagram to Fig. 1.

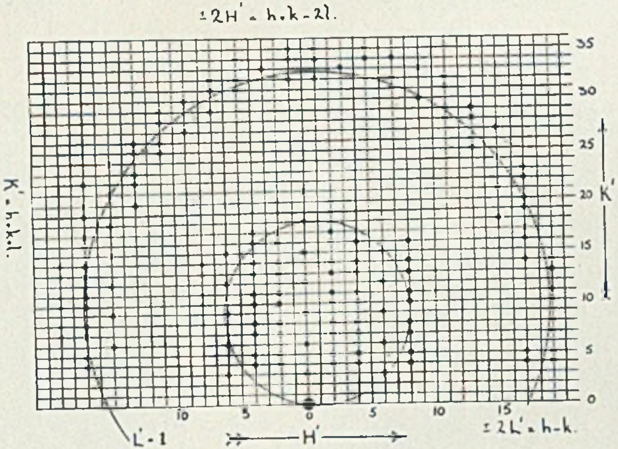

FIG. 4.—Index diagram to Fig. 3.

PLATE VIII.

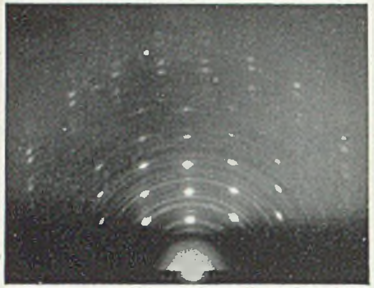

FIG. 7.—Nickel oxide condensed on to corundum; (000,1) face [100] azimuth of corundum; {111} plane $\langle 11\bar{2} \rangle$ azimuth of nickel oxide.

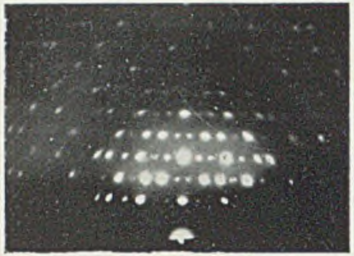

FIG. 10.—Nickel oxide condensed on to corundum $(10\bar{1},1)$ face and azimuth 90° from the rhombohedral edge $[1\bar{2}1]$ of the corundum; {110} plane ⟨001⟩ and $\langle 1\bar{1}1 \rangle$ azimuths of nickel oxide.

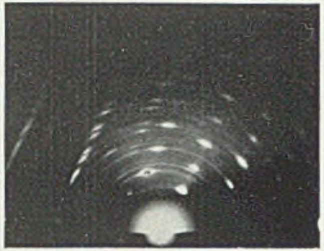

FIG. 12.—Nickel oxide on a plane of corundum inclined by 30° to the basal plane. [100] azimuth of corundum, $[11\bar{2}]$ of nickel oxide. *Cf.* Fig. 7.

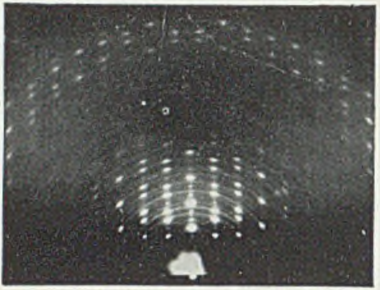

FIG. 8.—Azimuth 30° from Fig. 7.

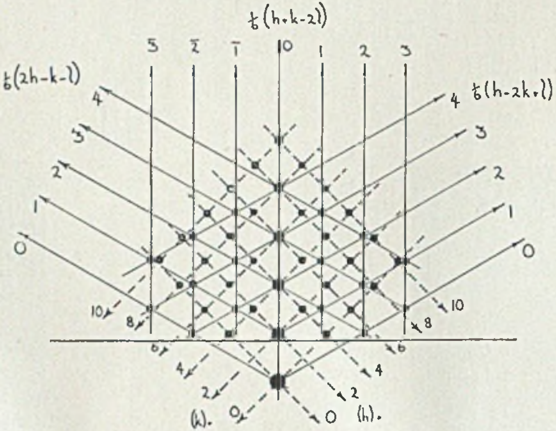

FIG. 11.—Index diagram to Fig. 10.

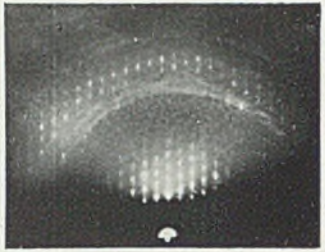

FIG. 15.—Pattern from specimen of Fig. 3 after heating. [110] azimuth of nickel aluminate, only one orientation present.

PLATE IX.

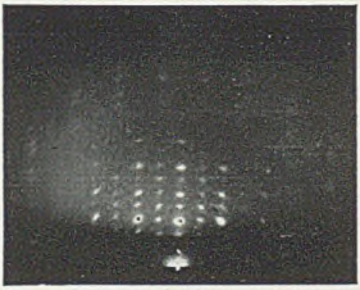

FIG. 16.—Pattern from specimen of Figs. 7 and 8 after heating, $\langle 11\bar{2} \rangle$ azimuths of nickel oxide and aluminate.

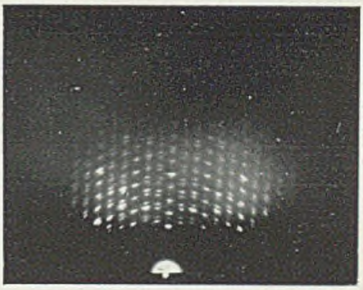

FIG. 17.—Pattern from specimen of Fig. 16 after further heating, $\langle 110 \rangle$ azimuth of nickel aluminate; nickel oxide pattern faintly visible.

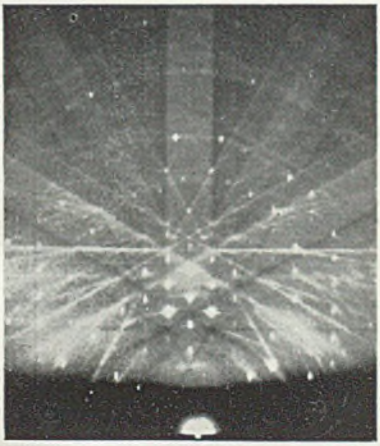

FIG. 18.—Kikuchi-line pattern from corundum surface about 6° from $\{11\bar{2},0\}$, after polishing, "annealing," and lightly etching. Prominent zone axis is [001]. Bands at 0° 60° and 120° from horizontal are $11\bar{2},0$ type, and those at 30°, 90°, and 150° are $10\bar{1},0$ type.

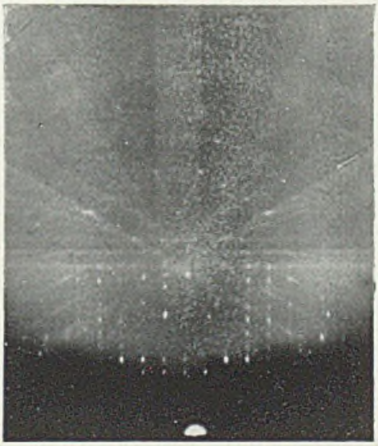

FIG. 19.—Pattern from specimen of Fig. 18 with a thin film of nickel aluminate on the surface.

The Faraday Society.

THE HYDROGEN BOND.

A meeting at which papers will be read on the above subject will be held in London (probably in the Royal School of Mines Building, Imperial College of Science and Technology, S. Kensington) on Friday, 17th, and Saturday, 18th May next.

Papers have already been promised by the following :—

Dr. W. T. Astbury.
Dr. C. E. H. Bawn, Prof. E. L. Hirst and Dr. G. T. Young.
Dr. J. J. Fox and Dr. A. E. Martin.
Dr. J. M. Robertson.
Dr. G. B. B. M. Sutherland.

Arrangements are being made for an informal dinner to be held at the Rembrandt Hotel on the Friday evening. (Price 6s. 6d., exclusive of wines.) The Rembrandt Hotel will give the special terms of 10s. 6d. for bed and breakfast for those members attending the meeting who wish to stay in London on the Friday night. It is desirable that those wishing to stay in the Hotel should make early application to the Manager, The Rembrandt Hotel, Thurloe Place, London, S.W. 7; otherwise it may be difficult to secure accommodation.

A Secretary's room will be available in the Hotel for those who wish to discuss in comfort matters personal and scientific.

Further particulars of the papers will be circulated to members at a later date.

The Electrochemical Society.

LIST OF PREPRINTS.

No. 77— 9. "Some Experiments showing the Directional Reactivities of Single Crystals of Copper." By A. T. Gwathmey and A. F. Benton.
" "—10. "A Theory for the Passivity of Chromium." By S. M. A. Ryan and H. Heinrich.
" "—11. "Irreversible Electrode Phenomena of Thallium. I. Hydrogen Overvoltage in Sulphuric Acid." By I. M. Le Baron and A. R. Choppin.
" "—12. "X-Ray Analysis of Corrosion Products from Galvanized Sheets." By F. R. Morral.
" "—13. "Photoelectric Cells Sensitive to Long Wave Length Radiation. The Bismuth Sulfide Cell." By C. G. Fink and J. S. Mackay.
" "—14. "Oxidation-Reduction Potentials and their Applications. A Review." By S. Glasstone.
" "—15. "Stainless Steel Rolled Products." By P. B. Greenawald.
" "—16. "Stress in Electrodeposited Copper as Determined by X-Rays." By E. M. Mahla.
" "—17. "The Application of Electromotive Force Measurements to Binary Metal Systems." By H. Seltz.

Transactions of the Faraday Society

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Authors submitting papers for publication are requested to note the following particulars:—

i. All communications made to the Society are the property of the Society. When papers have been accepted for publication, authors are not at liberty, save by permission of the Council, to publish them elsewhere. Such permission will not be unreasonably withheld. Communications which have appeared in any other Journal may not usually be published in the Transactions.

ii. (*a*) **Papers should be as brief as is compatible with clarity,** and no experimental details should be included which are not necessary for the understanding of the paper or for verifying any conclusions that may be drawn. Paragraphs should not be unnecessarily sub-divided.

(*b*) Tables should be reduced to a minimum and, where possible, results should be shown by means of curves rather than tables. Only in exceptional cases may tables be published as well as graphical representations of their contents.

(*c*) Each paper should include a brief summary indicating in general terms its purpose and conclusions.

iii. (*a*) Papers must be typewritten, with double spacing, on one side only of the paper, with a good margin on the left side.

(*b*) **References** should be typed in numerical order (and in the following sequence: journal; date; volume number; page) at the end of the paper; the necessary reference numbers only should appear in the text.

(*c*) Symbols, formulæ and equations should be written or typewritten with great care. The symbols recommended in the Report of the Joint committee of the Chemical Society, the Faraday Society and the Physical Society should be employed.

iv. (*a*) **Line drawings** may in the first instance be submitted in sketch form. For publication, however, they must be made with Indian ink on Bristol-board or preferably tracing *cloth*. Freehand must not be employed and all lines must be firmly and evenly drawn. Drawings should, generally, be capable of reduction to about one-half scale, depending on their nature and complexity; all drawings relating to one paper should be so made that they will all be reduced to the same extent. In the case of curves the ordinates and abscissæ must be drawn in ink and reliance must not be placed on the printed lines of scale paper.

(*b*) Where possible, lettering should be outside the diagram. Lettering should be put in lightly with lead pencil.

(v) **Rapidity of publication** is facilitated if papers are submitted in duplicate with duplicate photographs or tracings of diagrams, so that each paper with its drawings and photographs will go into a foolscap envelope.

(vi) Authors must retain copies of their communications.

Correction of Proofs.—The address to which proofs are to be sent should be written on every paper. Authors resident overseas may name agents in Britain to whom may be referred matters concerning their papers, including the correction of proofs, in order that delay in publication may be avoided.

Two galley proofs are provided, one of which duly corrected should be returned to the Editor. Authors are required to submit their communications in such form that corrections other than of printer's errors will be unnecessary. **Authors making other corrections will be required to bear the cost thereof.**

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