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OPTICAL SENSITISATION AND ADSORPTION OF DYES ON SILVER HALIDE: THE STATE OF THE ADSORBED DYE.*

By E. P. Davey.

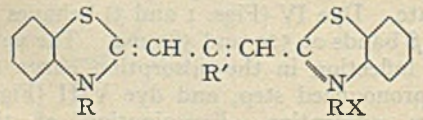
Received in original form 20th July, 1939, and as amended 17th November, 1939.

Recently a considerable advance has been made in the study of the theory of the optical sensitisation of silver halide by dyes. In particular papers by Leermakers, Carroll and Staud,[1, 2, 3] by Sheppard, Lambert and Walker,[4] by Sheppard,[5] are of great interest, and will be referred to often in this study.

Experimental.

The adsorbing medium was a photographic silver bromide emulsion containing about 3 % of silver iodide, of moderate speed, and chosen because it responded well to optical sensitisation. 5 c.c. of methyl alcohol containing the required amount of dye was added from a pipette to 50 c.c. of emulsion, with stirring, at 45° C., and left at this temperature for half an hour with stirring. 25 c.c. of this sensitised emulsion was diluted to 100 c.c. with warm water and centrifuged. The dilution of the emulsion introduced no error under the conditions of experiment, since no dye was found to redissolve during centrifuging. The dye was extracted from the halide by taking the latter up in 100 c.c. of water, fixing out with 50 c.c. of 40 % sodium thiosulphate, and extracting with 50 c.c. of *n*-butyl alcohol. In the presence of the thiosulphate, extraction was very nearly complete. The alcohol layer was separated, made up to 50 c.c. (necessary because of the partial mutual solubility between butyl alcohol and water), and the dye was estimated colorimetrically. For alcohol solutions, Beer's Law holds.

Certain sensitising cyanine dyes were used. The numbering adopted here corresponds, as far as possible, to that used by Leermakers *et al.* Dyes II, IV and VIII were thiacarbocyanines of the general formula:



* Communication No. H740 from the Kodak Research Laboratory, Wealdstone, Harrow, Middlesex.

[1] J. A. Leermakers, B. H. Carroll, and C. J. Staud, *J. Chem. Physics*, 1937, 5, 878.

[2] J. A. Leermakers, *ibid.*, 889.

[3] J. A. Leermakers, B. H. Carroll, and C. J. Staud, *ibid.*, 893.

[4] S. E. Sheppard, R. H. Lambert, and R. D. Walker, *ibid.*, 1939, 7, 265.

[5] S. E. Sheppard, *Optical Sensitising of the Silver Halides*, 8th Congress of Chemistry, Rome, 1938, 1, 234-283.

in which R is an alkyl group, R′ is alkyl or hydrogen, and X is a halide ion. Dye IX was similar, but benzselenazole rings replaced the benzthiazole. Dye VII was pinacyanol, having two quinoline rings, and dye V a cyanine, with only one methine group in the conjugate chain. Details are as follows :—

Dye II.	2 : 2′-dimethyl-8-ethylthiacarbocyanine bromide.
Dye IV.	8-methyl-2 : 2′-diethylthiacarbocyanine bromide.
Dye V.	1 : 1′-diethyl-2 : 2′-cyanine iodide.
Dye VII.	1 : 1′-diethyl-2 : 2′-carbocyanine iodide.
Dye VIII.	5 : 5′-dichloro-2 : 2′ : 8-triethylthiacarbocyanine iodide.
Dye IX.	2 : 2′ : 8-triethylselenacarbocyanine iodide.
Dye X.	1 : 1′-dimethyl-2 : 2′-carbocyanine iodide.

Parallel with the adsorption measurements, photographic tests were made on plates coated with the dyed emulsion. Spectrograms showing spectral sensitivity were obtained by exposing the plate in a wedge spectrograph, in which an image of a spectrum is projected on the plate, and a measure of relative spectral sensitivity is obtained by having a neutral wedge over the slit. These spectrograms may be used as an estimate of spectral absorption as well as of spectral sensitivity, since it has been shown,[1] for some of the dyes used here, that the two properties are parallel.

The adsorption curves obtained are shown in Figs. 1 and 2, and some corresponding spectrograms in Figs. 3 and 4. (The divisions in the latter figures represent an increase of ten times in the incident intensity and hence in the sensitivity.)

Discussion.

According to Sheppard, on sensitising a silver halide emulsion with a dye, equilibrium is not reached before 18 hours, using an emulsion diluted by 1 : 25. For the accurate study of adsorption such treatment is necessary, but it is felt that though the results shown here will not correspond to true equilibrium, they will have a closer relation to the practical sensitising results.

The adsorption and sensitising curves of dye V are shown in Figs. 1 and 4. The adsorption curve of this dye is smooth and follows Langmuir's adsorption isotherm, though this latter point is probably fortuitous. The spectrogram shows two regions of sensitivity and therefore light adsorption in addition to the original sensitivity region of the silver halide, with maxima at 520 and 570 mμ, called here, after Sheppard *et al.*,[4] the α and β bands respectively. With increasing concentration the relative sensitivity of the two bands increases at about the same rate. Dye IV (Figs. 1 and 3) behaves in the same way, having the α and β bands at 520 and 580 mμ. The very similar dye II, however, has an inflection in the adsorption curve (Fig. 1), dye IX (Fig. 2) a more pronounced step, and dye VIII (Fig. 1) a still more definite two-stage adsorption. Examination of the spectrograms (Figs. 3 and 4) show that dye II exhibits principally the α band at quite low concentration, the β band appearing at higher concentrations. With dyes IX and VIII the β band appears later in the concentration series, parallel with the increased clearness of the two steps in the adsorption curve. It is concluded from these results that the dye is adsorbed in two forms in all cases, but that, as with dyes II, VIII and IX, the α form is first adsorbed, and then the β form, with, however, more or less overlapping.

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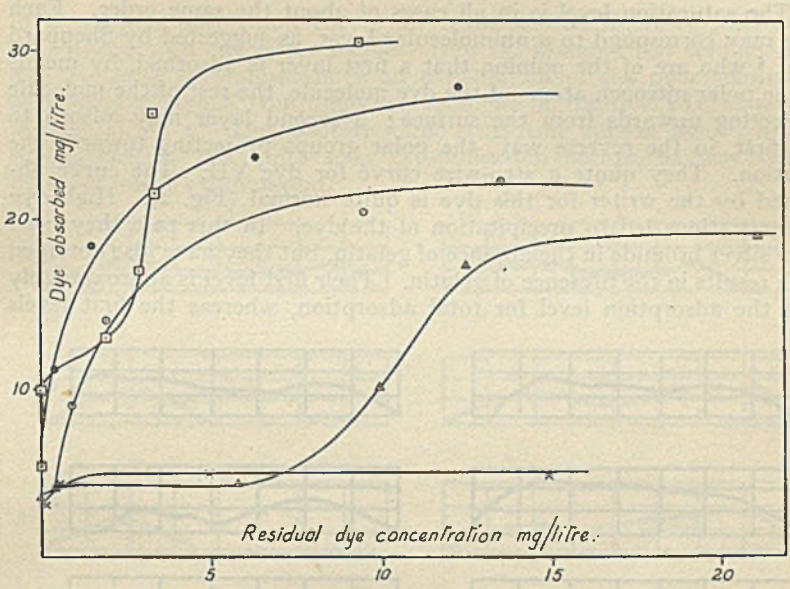

FIG. 1.—Absorption of dyes II, IV, V and VIII.

⊙ Dye V. × Dye V (β Band depressed).
⊡ ,, II. ● ,, IV. △ Dye VIII.

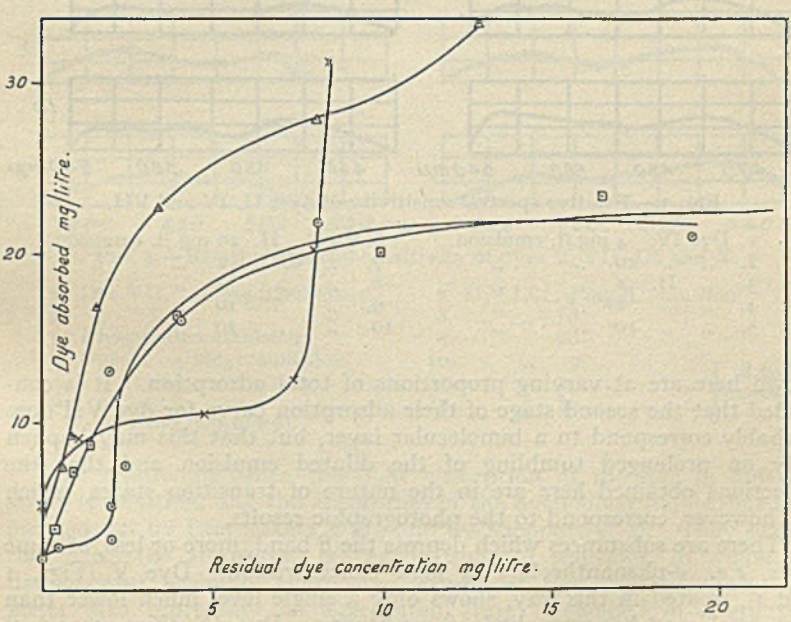

FIG. 2.—Absorption of dyes VII, IX and X.

⊙ Dye IX. ⊡ Dye VII.
× ,, ,, (β band depressed). △ ,, X

The saturation level is in all cases of about the same order. Each step may correspond to a unimolecular layer, as suggested by Sheppard *et al.*,[4] who are of the opinion that a first layer is adsorbed, by means of the polar nitrogen atoms of the dye molecule, the rest of the molecule projecting upwards from the surface; a second layer may adsorb to the first, in the reverse way, the polar groups projecting towards the solution. They quote a step-wise curve for dye VII. The curve obtained by the writer for this dye is quite normal (Fig. 2). High dye concentrations led to precipitation of the dye. In this case they used pure silver bromide in the absence of gelatin, but they have also obtained such results in the presence of gelatin. Their first level is approximately half the adsorption level for total adsorption, whereas the first levels

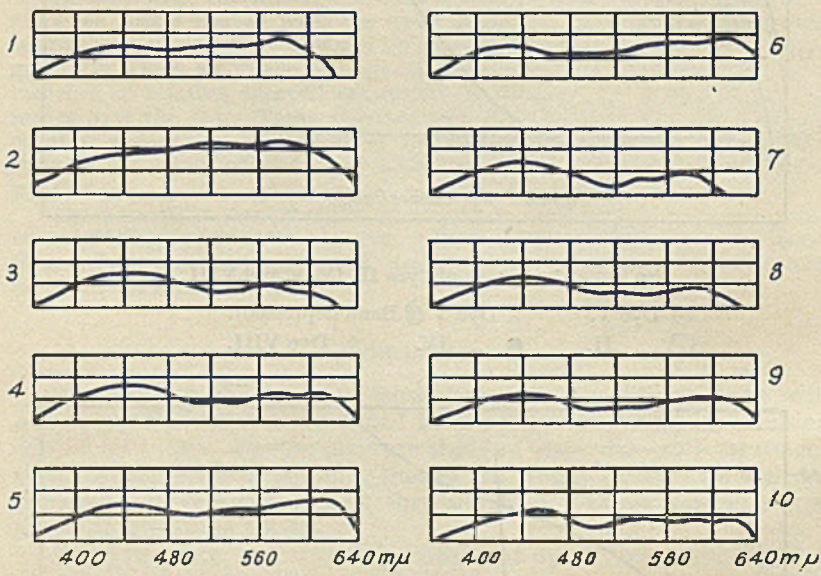

FIG. 3.—Relative spectral sensitivity of dyes II, IV and VII.

1.	Dye	IV.	4	mg./l.	emulsion.	6.	Dye	II.	20 mg./l. emulsion.
2.	,,	,,	20	,,	,,	7.	,,	VIII.	2 ,, ,,
3.	,,	II.	1	,,	,,	8.	,,	,,	4 ,, ,,
4.	,,	,,	2	,,	,,	9.	,,	,,	10 ,, ,,
5.	,,	,,	10	,,	,,	10.	,,	,,	20 ,, ,,

shown here are at varying proportions of total adsorption. It is concluded that the second stage of their adsorption curve for dye VII does probably correspond to a bimolecular layer, but that this may happen only on prolonged tumbling of the diluted emulsion and that the inflections obtained here are in the nature of transition states, which do, however, correspond to the photographic results.

There are substances which depress the β band, more or less, of some dyes, *e.g.*, *o*-phenanthroline in high concentration. Dye V (Figs. 1 and 4), treated in this way, shows only a single level much lower than the usual, and has very little β sensitivity. Dye IX (Figs. 2 and 4) also has a first level only in such circumstances, though higher, corresponding to the higher sensitivity of the α band, and there is no true saturation level; instead, crystallisation of the dye took place, resulting

in a spurious adsorption curve, for many of the micro-crystals were centrifuged with the silver halide. Dye IX is much less soluble than dye V. Such crystallisation is an explanation of the poor sensitising behaviour of dye X, the dimethyl analogue of the dye VII, as shown in Figs. 2 and 4. The adsorption and sensitising appear weakly at low concentrations, but quite soon crystallisation occurs, as was shown by microscopic examination.

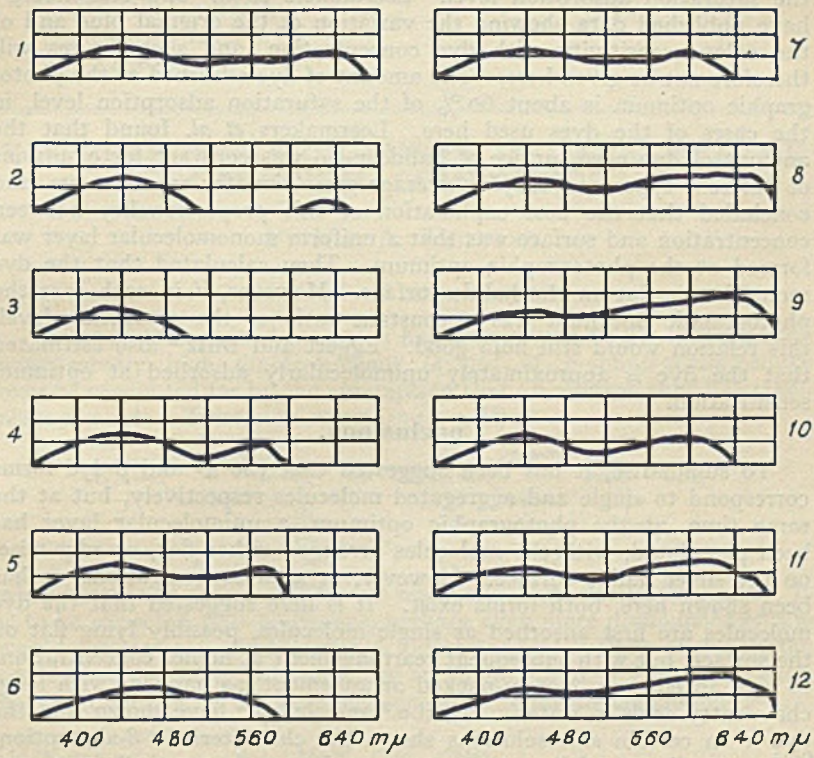

FIG. 4.—Relative spectral sensitivity of dyes V, VII, IX and X.

1. Dye VII. 10 mg./l. emulsion.
2. ,, X. ,, ,, ,,
3. Unsensitised emulsion.
4. Dye V. 4 mg./l. emulsion.
5. ,, ,, 20 ,, ,,
6. ,, ,, ,, ,, ,,
(β band depressed).

7. Dye IX. 4 mg./l. emulsion.
8. ,, ,, 10 ,, ,,
9. ,, ,, 20 ,, ,,
10. ,, ,, 9 ,, ,,
11. ,, ,, 10 ,, ,,
12. ,, ,, 20 ,, ,,
} β band depressed.

The relation between the light absorption of the dye in different states in solution, and the absorption of the dyed silver halide, has been pointed out by Leermakers *et al.*, and by Sheppard *et al.* They suggest that since the absorption of certain aqueous solutions, in which the dye is most probably aggregated, resembles that of the β form, the latter also represents an aggregated state. Scheibe,[9] in a study of the absorption spectra of various dye solutions, concludes that the separate maxima are due to different states of aggregation. Adsorption from alcoholic solution or from very dilute aqueous solution leads to the α form only, and hence the latter is assumed to be a unimolecular

form. It need not necessarily be assumed that the state in solution determines the state of the adsorbed dye; the writer has found that successive very small additions of dye II give first the α form and then the $\alpha + \beta$ forms, in precisely the same way as when the whole of the dye is added at once. The dye can therefore be adsorbed in single units, whatever the final state on the surface.

The optimum photographic dye concentration is always short of the saturation adsorption level. Leermakers *et al.*[3] and Heisenberg [7] have published data showing the variation of the original blue and of the colour sensitivity with dye concentration, and such figures will therefore not be given here. The amount of dye adsorbed at the photographic optimum is about 60 % of the saturation adsorption level, in the cases of the dyes used here. Leermakers *et al.* found that the amount of dye used/surface of halide ratio was constant for emulsions of different types and varying average grain-size, for any one dye, and concluded that the best explanation of this proportionality between concentration and surface was that a uniform monomolecular layer was formed at the photographic optimum. They calculated that the dye molecules lie flat on the halide surface. However, if in each case the photographic optimum was a constant ratio of the saturation level, this relation would still hold good. Eggert and Biltz [8] also estimated that the dye is approximately unimolecularly adsorbed at optimum sensitisation.

Conclusions.

To summarise, it has been suggested that the α- and β-dye forms correspond to single and aggregated molecules respectively, but at the same time, at the photographic optimum, a unimolecular layer has been postulated, with the molecules arranged either flat, or edge-wise, on the silver halide surface. However, at such concentrations, as has been shown here, both forms exist. It is here suggested that the dye molecules are first adsorbed as single molecules, possibly lying flat on the surface, but with subsequent rearrangement at higher concentrations to give an edge-on, closely-packed arrangement, as happens with long-chain fatty acids in water. Scheibe [9] and Jelley [6] have shown that the dye V in certain salt solutions shows the characteristic β-absorption, and, according to Jelley, this may pass into a "nematic" form consisting of thread-like particles oriented in one direction only (as in a pack of cards), and still possessing the β-absorption. Hence the α form, adsorbed singly, has a light absorption characteristic of the molecule, while the β form, adsorbed edge-on, and packed in a parallel fashion, has an adsorption characteristic of the aggregated or Jelley's nematic form. Cases of suppression of the β form may be explained by assuming that the interfering substance prevents close parallel packing.

Summary.

Adsorption and sensitising data have been obtained for certain sensitising dyes adsorbed to silver halide. These particular dyes are adsorbed in two forms, each having a distinct absorption, and the two forms are often shown up by two stages in the adsorption curve. From the avail-

[6] E. E. Jelley, *Nature*, 1937, **139**, 631.
[7] E. Heisenberg, *Veroff. Agfa*, 1933, **3**, 115.
[8] J. Eggert and M. Biltz, *Trans. Faraday Soc.*, 1938, **34**, 892.
[9] Scheibe, *Koll. Z.*, 1938, **82**, 1.

able data it is suggested that these dyes are adsorbed partly as single molecules attached by the nitrogen atoms to the surface, but possibly lying flat, and partly as molecules oriented as units packed in a parallel fashion, adsorbed edge-on, again by the nitrogen atoms. The influence of factors which may affect this orientation is discussed.

The author wishes to thank Dr. E. E. Jelley and Dr. S. E. Sheppard for helpful criticisms.

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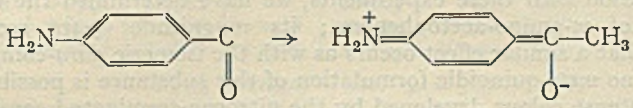
ZWITTERION-STRUCTURES IN UNSATURATED CARBONYL COMPOUNDS.

By Miss A. Weizmann.

Received 1st August, 1939.

In a previous paper,[1] attention has been drawn to the fact that the unexpectedly high dipole-moment (4·29D) of *p*-amino-acetophenone may be accounted for by the assumption that an electron shift has taken place towards a Zwitterion-structure (I → II) :



I. II.

which naturally would exhibit an unusually high electric moment. It is to be expected that analogous, perhaps even more pronounced effects would appear in α, β-unsaturated aldehydes and ketones in which the conjugated system is terminated by an amino group.[2] This expectation has been verified by the investigation of the following compounds :—

p-dimethylamido-benzaldehyde	$Me_2N . C_6H_4 . CHO$	5·6D
p-dimethylamido-cinnamic aldehyde	$Me_2N . C_6H_4 . CH{=}CH . CHO$	5·4D
p-dimethylamido-benzylidene-acetone	$Me_2N . C_6H_4 . CH{=}CH . CO . CH_3$	5·3D
p-dimethylamido-cinnamylidene-acetone m.p. 120°	$Me_2N . C_6H_4 . CH{=}CH . CH{=}CH . CO . CH_3$	6·7D
p-dimethylamido-benzalacetophenone	$Me_2N . C_6H_4 . CH{=}CH . CO . C_6H_5$	4·3D
p-dimethylamido-cinnamylidene-acetophenone	$Me_2N . C_6H_4 . CH{=}CH . CH{=}CH . CO . C_6H_5$	5·4D

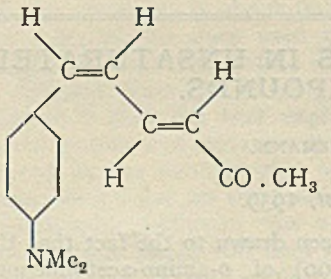
The effect appears to be more marked with increasing number of double bonds in the conjugated system of the ketones. The same seems to be true for the pair

ethyl *p*-amino-benzoate	$H_2N . C_6H_4 . COOC_2H_5$	4·0[3]
ethyl *p*-dimethylamino-cinnamate	$Me_2N . C_6H_4 . CH{=}CH . COOC_2H_5$	4·6 ;

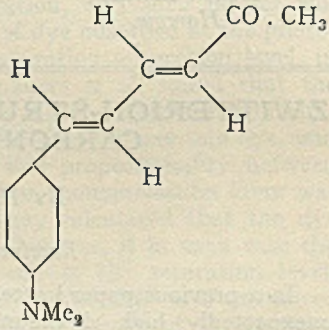
[1] Bergmann and Weizmann, *Trans. Faraday Soc.*, 1936, **32**, 1318.
[2] Compare Burawoy, *Ber.*, 1932, **65**, 941, 947.
[3] Estermann (*Z. physik. Chem. B.*, 1938, **1**, 134) reported the dipole moment 3·3D for methyl *p*-amino-benzoate.

in this case, too, the figures are higher than simple addition of the moments of the amino and the carbethoxy groups would let us expect. In this respect, the C=O group of the carboxyl behaves like an aldehydic or ketonic carbonyl.

Of *p*-dimethylamido-cinnamylidene-acetone, we have been able to isolate besides the substance listed in the above table a second of the four possible geometric isomers; m.p. 215°. Its dipole moment is distinctly lower (2·4D). This is understood if the polar groups occupy a *c is*-position with regard to each other, *e.g.* III instead of IV.



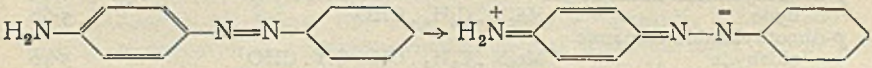
III.



IV.

In connection with these experiments, we have determined the electric moment of *m*-amino-acetophenone; its magnitude (5·4D) seems to indicate that a similar effect occurs as with the isomeric *para*-compound, although no *meta*-quinoidic formulation of this substance is possible.

The intense colour developed by the nitrogen-terminated conjugated systems in, *e.g.*, sulphuric acid, may well be ascribed to a stabilisation of the quinoidic arrangement by addition of the elements of the acid to the charged system.[4] In this connection attention may be drawn to the salt-formation of amino-azo-dyes; for these substances, we have advanced previously the suggestion that they, too, undergo an electron shift in accordance with the scheme V → VI.



V. VI.

On addition of HX, V would give the yellow salt, whereas VI, by reaction on the terminal atoms of the charged system, gives the violet isomer, discovered by Hantzsch.[5]

Experimental.

The figures in the tables have the following significance: c molar fraction, ρ density, ϵ dielectric constant, n refractive index, $P_{\frac{1}{2}}$ total polarisation ($P_{E\frac{1}{2}}$ electronic polarisation) for the solution, $P(P_E)$ the same for the solute, P_{A+O} atomic and orientation polarisation, which is either graphically extrapolated to infinite dilution or of which the average is taken.

[4] Compare, for a similar case, Wizinger, *Z. angew. Chem.*, 1927, **40**, 939.

[5] Hantzsch, *Ber.*, 1909, **42**, 2129. It may, however, be noted that according to Kehrmann (*Ber.*, 1915, **48**, 1933; *Ber.*, 1917, **50**, 856) the violet salts need not necessarily be formulated as quinoidic substances.

c.	ρ.	ε.	n^2.	$P_{\frac{1}{2}}$.	$P_{E\frac{1}{2}}$.	P.	P_E.	P_{A+O}.
p-Dimethylamido-benzaldehyde[6] (*t* = 17·5° *Benzene*).								
0	0·8816	2·2830	2·2251	26·589	—	—	—	—
0·00345	0·8831	2·4815	2·2255	29·291	—	809	calcd.	763
0·00679	0·8846	2·5813	2·2258	30·624	—	621	46	575
0·00878	0·8855	2.7300	2·2261	32·479	—	698	—	652
P_{A+O} (average) = 664. μ = 5·6D.								
p-Dimethylamido-cinnamic aldehyde[7] (*t* = 21·3° *Benzene*).								
0	0·8771	2·2813	2·2457	26·611	26·092	—	—	—
0·00178	0·8788	2·3447	2·2494	27·530	26·153	543	60	483
0·00279	0·8798	2·3990	2·2503	28·295	26·172	630	55	575
								(*t* = 27·4°).
0	0·8699	2·2691	2·2323	26·656	26·108	—	—	—
0·00316	0·8713	2·4123	2·2380	28·767	26·254	694	72	622
P_{A+O} (average) = 598. μ = 5·4D.								
p-Dimethylamido-benzylidene-acetone[8] (*t* = 24·2° *Benzene*).								
0	0·8737	2·2754	2·2380	26·632	26·079	—	—	—
0·00280	0·8741	2·3861	—	28·313	—	627	(86)	541
0·00503	0·8744	2·5197	2·2471	30·210	26·382	738	87	651
0·00706	0·8747	2·5878	2·2500	31·169	26·492	669	85	584
P_{A+O} (average) = 592. μ = 5·3D.								
p-Dimethylamido-cinnamylidene-acetone[9]; **m.p. 120/2°** (*t* = 25·4° *Benzene*).								
0	1·0273	2·2385	2·0116	25·031	21·601	—	—	—
0·00136	1·0269	2·3294	2·0140	26·365	21·692	1006	89	917
0·00196	1·0268	2·3767	2·0150	27·034	21·727	1045	85	960
P_{A+O} (average) = 939. μ = 6·7D.								

[6] Commercial sample; recrystallised from light-petroleum (b.p. 80-100°); m.p. 63°.

[7] Koenig and Schramek, *Ber.*, 1928, **61**, 2078. From alcohol, leaflets, m.p. 141°.

[8] In order to obtain *p*-dimethylamido-benzal-acetone, it is necessary to change the conditions stated by Sachs and Lewin (*Ber.*, 1902, **35**, 3576): 3 g. dimethylamido-benzaldehyde and 10 c.c. acetone were condensed in 6 c.c. alcohol in presence of some drops of sodium hydroxide solution. From alcohol, m.p. 135-136°. If the aldehyde is condensed with 1·5 g. acetone only, the condensation product, recrystallised from benzene-light petroleum, melts at 191-192° and is bis-(*p*-dimethylamido-benzal)-acetone (Sachs and Lewin, *l.c.*).

[9] When to a mixture of dimethylamido-cinnamic aldehyde (1·3 g.), acetone (0·3 g.) and alcohol (12 c.c.), a few drops of NaOH solution were added, crystals separated on standing which after treatment with butyl alcohol and recrystallisation from acetone, melted at 215°. The analytical figures concord with the formula of dimethylamido-cinnamylidene-acetone (Found: C, 78·1; H, 6·5. $C_{14}H_{17}ON$ requires: C, 78·1; H, 7·9 %).

In an experiment, in which 2·5 g. of the aldehyde and 10 c.c. of acetone in 12 c.c. of alcohol were condensed, the reaction product, after recrystallisation from benzene, had m.p. 120-122° and gave the same analytical figures (Found: C, 77·4; H, 7·6. $C_{14}H_{17}ON$ requires: C, 78·1; H, 7·9 %).

c.	ρ.	ε.	n^2.	$P_{\frac{1}{2}}$.	$P_{E_{\frac{1}{2}}}$.	P.	P_E.	P_{A+O}.
p-Dimethylamido-benzal-acetophenone[10] (t = 20·3° *Benzene*).								
0	0·8783	2·2834	2·2440	26·609	26·061	—	—	—
0·00276	0·8791	2·3536	2·2515	27·799	26·279	457	105	352
0·00316	0·8794	2·3927	2·2533	28·358	26·355	491	104	387
0·00642	0·8801	2·5056	2·2596	30·034	26·578	560	106	454
P_{A+O} (average) = 398. μ = 4·4D.								
p-Dimethylamido-cinnamylidene-acetophenone[11] (t = 26·0° *Dioxan*).								
0	1·0272	2·2301	2·0135	24·911	21·634	—	—	—
0·00147	1·0279	2·2917	2·0203	25·848	21·796	660	132	528
0·00216	1·0282	2·3431	2·0224	26·590	21·855	803	124	679
0·00324	1·0286	2·3806	2·0278	27·151	21·983	716	129	587
P_{A+O} (average) = 598. μ = 5·4D,								
Ethyl p-amino-benzoate[12] (t = 19·4° *Benzene*).								
0	0·8794	2·2852	2·2500	26·603	26·088	—	—	—
0·00386	0·8813	2·3962	2·2524	28·229	26·174	447	48	399
0·00620	0·8825	2·4311	2·2512	28·743	26·193	372	49	323
0·00848	0·8837	2·4659	2·2536	29·247	26·260	339	46	293
P_{A+O} (average) = 340. μ = 4·0D.								
Ethyl p-dimethylamino-cinnamate[13] (t = 18·8° *Benzene*).								
0	0·8801	2·2964	2·2407	26·599	25·929	—	—	—
0·00480	0·8828	2·4541	2·2545	29·097	26·280	547	99	448
0·00676	0·8838	2·5312	2·2563	30·188	26·368	556	91	465
P_{A+O} (average) = 457. μ = 4·6D.								
p-Dimethylamido-cinnamylidene-acetone (m.p. 215°)[9] (t = 20·0° *Dioxan*).								
0	1·0284	2·3141	2·0170	26·065	21·664	—	—	—
0·00040	1·0314	2·3239	2·0218	26·138	21·690	210	87	123
μ = 2·4D								
m-Amino-acetophenone[14] (t = 18·2° *Benzene*).								
0	0·8808	2·2876	2·2515	26·995	26·069	—	—	—
0·00457	0·8827	2·4541	2·2530	28·945	26·122	541	38	503
0·00747	0·8839	2·4999	2·2536	29·574	26·151	426	37	389
0·01078	0·8852	2·5435	2·2560	30·165	26·208	363	39	324
P_{A+O} (average) = 635. μ = 5·4D.								

[10] Sachs and Lewin, *l.c.*[8] From alcohol, m.p. 114°.

[11] Dimethylamido-cinnamic aldehyde (1 g.) and acetophenone (1·5 g.) were gently heated in alcohol (10 c.c.) in presence of a few drops of NaOH solution for 5 minutes. On cooling, brown, shiny needles separated, which after recrystallisation from methyl alcohol, had m.p. 155-157°; yield 0·6 g. (Found: C, 83·0; H, 6·3. $C_{19}H_{19}ON$ requires: C, 82·3; H, 7·0 %).

[12] Commercial sample; from alcohol, m.p. 91-92°.

[13] Sodium wire (2·3 g.) is suspended in ethyl acetate (20 g.) and a solution of *p*-dimethylamido-benzaldehyde (14·9 g.) in ethyl acetate (30 g.) is added. The reaction is slow, but goes to complete solution of the sodium. Glacial acetic acid (6 g.) is added, the product washed with water, dried with sodium sulphate and evaporated. The residue is recrystallised from light-petroleum (b.p. 80-100°); m.p. 70°. Weil, *Monatshefte*, 1908, **29**, 900.

[14] Acetophenone was nitrated according to Elson, Gibson and Johnson (*J. Chem. Soc.*, 1930, 1130) and the *m*-nitro-compound reduced in the following way: 10·5 g. were mixed with 24 g. granulated tin and gently heated. Then concentrated hydrochloric acid was added in small quantities, until all the metal had dissolved. Alkali was added and the amino-compound isolated by extraction with ether (yield, 5 g.). Recrystallisation from benzene gave slightly yellowish plates, m.p. 99°.

Summary.

The occurrence of Zwitterion-structure is detected in compounds of the *p*-dimethyl-amido-benzaldehyde, *p*-dimethylamido-benzal-acetophenone and ethyl *p*-amino-benzoate type by means of dipole-moment measurements. The difference in electric moment of two isomeric dimethylamido-cinnamylidene-acetones obtained is discussed.

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AN INFRA-RED STUDY OF CHLORAL HYDRATE AND RELATED COMPOUNDS.

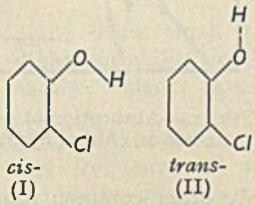
By Mansel M. Davies.

Received 14th August, 1939.

The inter- and intra-molecular interactions of polar groups have recently been the subject of many spectroscopic investigations.[1] In particular, the influence of both molecular association and of adjacent substituents upon the valence vibration of the OH group has been observed in infra-red absorption spectra. The present paper is principally concerned with the second mode of interaction. It may be taken in three sections: the first presents some new experimental observations on absorption spectra of this type; the second is concerned with the evaluation of bond-energy differences from frequency changes; whilst the third discusses the probable origin of these energy differences.

PART I.

The clearest example of the effects studied is that of *o*-chlorophenol [2] where the interaction of the Cl and OH groups leads to two orientations of the latter, the *cis*- form (I) being favoured with respect to the *trans*- (II) by an amount corresponding to an energy difference of about 1400 cal./g. mol. It is now to be established that a similar interaction is responsible for the peculiar stability of chloral hydrate, $CCl_3 . CH(OH)_2$. This compound and its analogue bromal hydrate are the only two common stable derivatives in which two hydroxyl groups are attached to the same carbon atom.



cis- (I) *trans*- (II)

Experimental.

The methods were essentially those previously described.[3] A Nernst glower was throughout the source of radiation. Quartz, fluorite, and rock-salt prisms have been employed in the present measurements and a rock-

[1] Sutherland, *Ann. Rep. Chem. Soc.*, 1938, **35**, 38.
[2] Pauling, *J. Amer. Chem. Soc.*, 1936, **58**, 94. Davies, *Trans. Faraday Soc.*, 1938, **34**, 1427.
[3] Davies and Sutherland, *J. Chem. Physics*, 1938, **6**, 755.

salt cell of similar construction to the fluorite ones has been used beyond 10 μ. Analar solvents were used without further purification. The solvent corrections were repeatedly checked between the runs made with the solutions, and all the absorption curves reproduced have been corrected for the cell and solvent effects. The chloral and bromal hydrates were purchased from Messrs. Harringtons: careful recrystallisation from CS_2 had no noticeable effect on their absorption spectra. The setting of the prisms was done with the visible lines from a small Hg-discharge tube, and subsequently checked on the sharp OH absorption band in dilute CCl_4 solutions of benzyl alcohol at 2·764 μ: for the fluorite and rock-salt prisms the 4·26 μ atmospheric CO_2 band was plotted for confirmation.

Results.

A determination of the absorption of chloral hydrate in the region 2·6 μ to 3·0 μ in CCl_4 shows the significant result that the OH band in this molecule is centred at 2·82 μ. Fig. 1 shows a typical curve for a saturated solution in CCl_4. The main band is located at 2·82 μ, whilst weaker peaks appear at 2·70 μ and 2·90 μ. Of these feebler absorptions, that at 2·70 μ is certainly an overtone or combination band characteristic of the CCl_3 group, as it occurs in all the compounds containing this structure which have been examined;[3] the shoulder at 2·90 μ is probably a combination band involving the C—O frequencies.

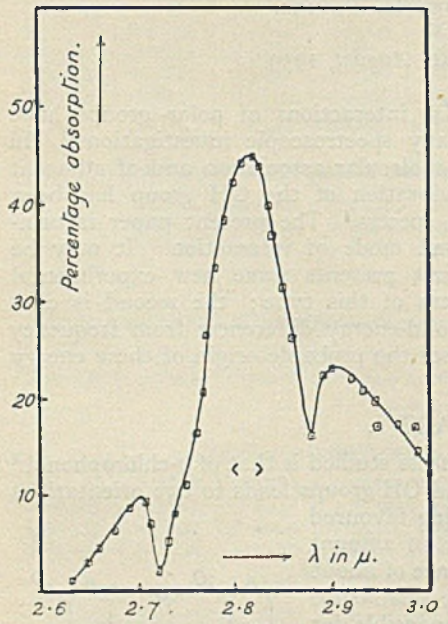
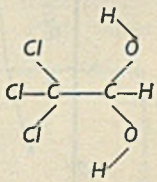


Fig. 1.—Absorption of 5·0 mm. layer of 0·006 M. chloral hydrate in CCl_4.

The position and intensity of the 2·82 μ band leave no doubt as to its origin. The concentration of the chloral hydrate in the solution used was estimated as about 0·0060 M., and the considerable intensity of the band under these conditions is typical of the OH group. The only other common fundamentals occurring in this region are those of the C—H bond which appears in the range 3·25 μ (aromatic) to 3·45 μ (aliphatic), and of the NH group which is near 3·00 μ. Attempts to confirm the origin of the 2·82 μ absorption by observations on CCl_4 solutions of chloral ($CCl_3 . CHO$) in the same region failed because these solutions rapidly became saturated with the hydrate due to absorption of atmospheric moisture during the filling of the cell. Only by twice distilling the hydrate from concentrated H_2SO_4 in an all-glass apparatus protected by a stream of dry air could the chloral be satisfactorily freed from the hydrate and exposure to moist air quickly led to the formation of sufficient hydrate for this to crystallise out. Chloroform, $HCCl_3$, and ethyl ether, $C_2H_5 . O . C_2H_5$, which together contain

all the groups and bonds present in chloral hydrate other than the hydroxyl, show at concentrations 100 times greater than those of the hydrate no signs of an absorption centred near 2·82 μ.

It is now well established[4] that simple alcohols in dilute CCl_4 solution have a sharp absorption band arising from the valence OH vibration the peak of which is within the range 2·750 μ to 2·770 μ. On the attachment of a carbonyl oxygen to the same carbon atom as the hydroxyl, *i.e.*, in $-C\begin{matrix}\diagup\!\!\!\!\diagup O \\ \diagdown\!\!\!\!\diagdown OH\end{matrix}$ the interaction of the C=O and O—H groups shifts the fundamental band of the latter to 2·84 μ. Compared with a simple hydroxylic compound such as methyl alcohol, $CH_3-O\begin{matrix}\diagup H \\ \diagdown\end{matrix}$, where the potential barrier restricting free rotation of the hydrogen about the C—O bond is small,[5] in the carboxyl structure the OH group is now locked in the *cis*-position.[6] The same shift to longer wavelengths of the OH fundamental is also apparent as between *trans*- and *cis*-*o*-chlorophenol (from 2·775 μ to 2·825 μ). It seems certain that the location of the OH fundamental in chloral hydrate at 2·82 μ arises from circumstances similar to those just mentioned. It suggests that the OH groups are again clamped in a position corresponding to maximum interaction with the adjacent dipoles, each OH group lying in the plane defined by a $Cl\diagdown C-C$ group, with the hydrogens tied towards the chlorines (III). It can easily be seen that if the hydrogens were free to rotate about the C—O bonds they might approach one another very closely and the elimination of H_2O would then be a simple process. Several careful plots of the band havef ailed to show any indication of even a shoulder in the absorption curve near 2·76 μ so that the occurrence of structures, in which one of the OH groups is free, is not detectable. The band does appear to be broader than that for a monohydroxylic alcohol examined under the same conditions. It may be that, the restoring force governing the vibrations of the hydrogens perpendicular to the $Cl\diagdown C-C\diagup O$ -plane being small, the amplitude of this vibration is responsible for a slight variability in the force-constant of the valence O—H vibration.



(III)

(IV)

(V)

Having established the distinctive change in the OH frequency, it was of interest to investigate whether the interaction was also noticeable by its influence on the CCl_3 group. A major uncertainty in the interpretation of these results lies in the assignment of the CCl_3 frequencies which, in the absence of a complete vibrational analysis, has to be made largely by comparison

[4] Fox and Martin, *Proc. Roy. Soc.*, *A*, 1937, **162**, 419.
[5] Borden and Barker, *J. Chem. Physics*, 1938, **6**, 553.
[6] Bauer and Badger, *ibid.*, 1937, **5**, 852. Morino and Mizushima, *Proc. Instit. Phys. Chem. Research, Tokyo*, 1937, **32**, 33. Davies and Sutherland,[3] p. 762. See, however, Coop, Davidson and Sutton, *J. Chem. Physics*, 1938, **6**, 905.

with the simpler molecule, $CHCl_3$. According to Kohlrausch[7] the two valence vibrations for $CHCl_3$ (IV and V) (of which ν_{23} is doubly degenerate) are to be assigned as $\nu_1 = 668$ cm.$^{-1}$, $\nu_{23} = 760$ cm.,[8] which would correspond to absorption bands at 15·0 μ and 13·2 μ respectively.

A careful examination of the absorptions of chloral hydrate and trichloracetic acid in the region 11 μ to 15 μ was made using a rock-salt prism: trichloracetic acid was chosen for comparison as being the molecule nearest in structure to chloral hydrate. Several measurements of trichloracetic acid in CS_2 (Fig. 2) show two distinct bands. One, centred at 14·25 $\pm$ 0·1 μ seems to be the equivalent of ν_1 in $CHCl_3$: its contour suggests the appearance of the *P*-, *Q*-, and *R*- branches of a parallel vibration. The second has its main peak at 12·2 μ with a subsidiary at 12·7 μ: a doublet nature is to be expected for ν_{23} in this case, as the degeneracy is now removed. Absorption curves for chloral hydrate in CS_2 (Fig. 3) similarly showed peaks at 12·35 μ and 12·75 μ

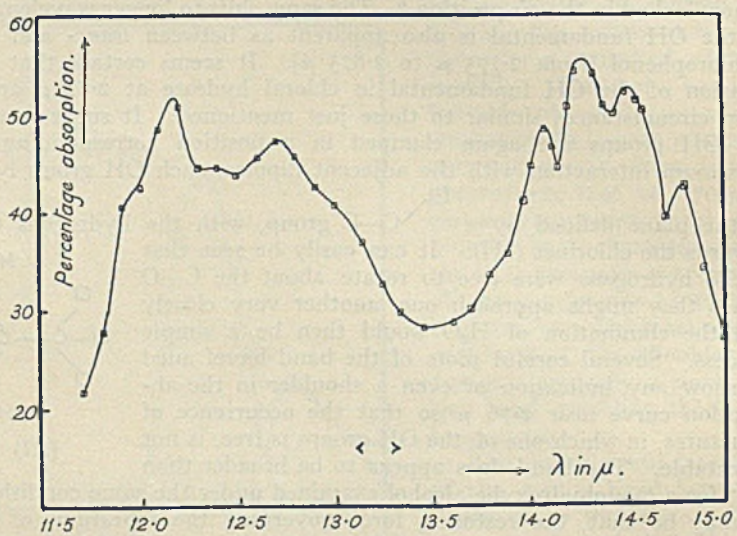


FIG. 2.—Absorption of 1·5 mm. of 0·057 M. trichloracetic acid in CS_2.

almost coinciding with those in the acid. The centre of what has been taken as the ν_1 band, however, is now located at 13·7 μ which is far removed from its position in trichloracetic acid, amounting to a frequency shift of 28 cm.$^{-1}$. The higher frequency of ν_1 in chloral hydrate compared with the acid is not what would have been expected if the interaction in the former merely led to the C—Cl bond being stretched along its length. The result may mean that the principal effect consists in a lateral displacement of the Cl atoms opposite the hydrogens, which in itself would probably result in a steeper potential curve along the C—Cl direction. It is to be noted that the present interpretation of these results does not conflict with the Raman data for these molecules.[8a]

There is a further fundamental of the CCl_3 group, which Kohlrausch surprisingly assigns to a deformation vibration, at 1215 cm.$^{-1}$, *i.e.*,

[7] *Z. physik. Chem.*, *B*, 1935, **28**, 340.
[8] Cabannes and Rousset, *Ann. Physique*, 1933, **19**, 229; and ref. 7.
[8a] Parthasarathy, *Phil. Mag.*, 1934, **17**, 471. Kohlrausch, Koppl and Pongretz, *Z. physik. Chem.*, *B*, 1933, **21**, 242.

within the experimental infra-red range, at 8·2 μ. The region 7·5 μ to 8·5 μ was examined, using a fluorite prism. The absorption curve

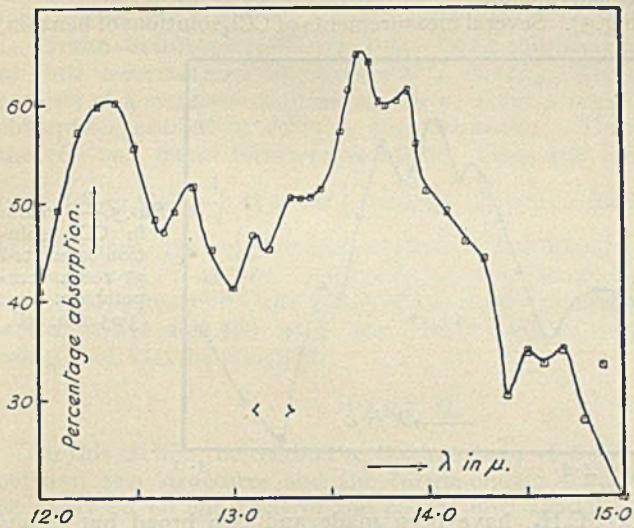


FIG. 3.—Absorption of saturated solution chloral hydrate in CS_2. Cell thickness = 1·5 mm.

for trichloracetic acid was found to have a strong band at 7·96 μ with shoulders at 7·87 μ, 8·16 μ, and 8·24 μ, the central peak, from its intensity, almost certainly corresponding to a fundamental. Plots made of chloral hydrate showed the main absorption at 8·21 $\pm$ 0·01 μ, but subsidiary bands in the neighbourhood are so numerous as to make interpretation far too speculative.

Bromal Hydrate. (Fig. 4). This compound has been examined only in the short-wave region of the OH fundamental. In both CS_2 and CCl_4 solutions the main absorption is at 2·81 $\pm$ 0·01 μ. In the five plots of this absorption which have been made there are indications, although these are admittedly slight, of an irregularity corresponding to an absorption at 2·76 μ. The latter might well arise from a small proportion of "free" OH groups, the presence of which would coincide with the lower stability of bromal hydrate relative to chloral hydrate. The published measurements on water in these two solvents [9] show that in

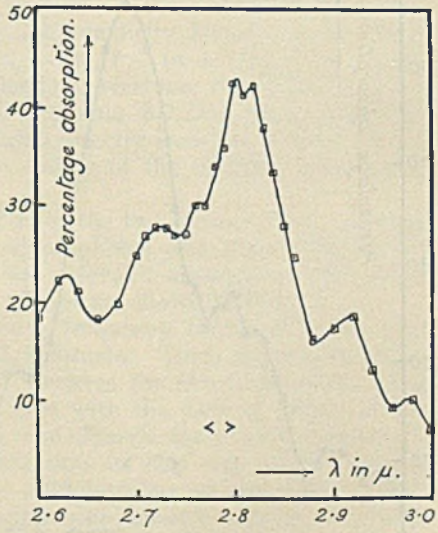


FIG. 4.—Absorption of bromal hydrate in CS_2. Nearly saturated solution in 25 mm. cell.

[9] Borst, Buswell and Rodebush, *J. Chem. Physics*, 1938, **6**, 61. Kinsey and Ellis, *Physic. Rev.*, 1937, **51**, 1074.

CCl_4 it gives only a single absorption at 2·70 μ, whilst in CS_2 the absorption of a saturated solution is far too small to have been recorded in the present measurements.

Benzoin. (Fig. 5). Several measurements of CCl_4 solutions of benzoin,

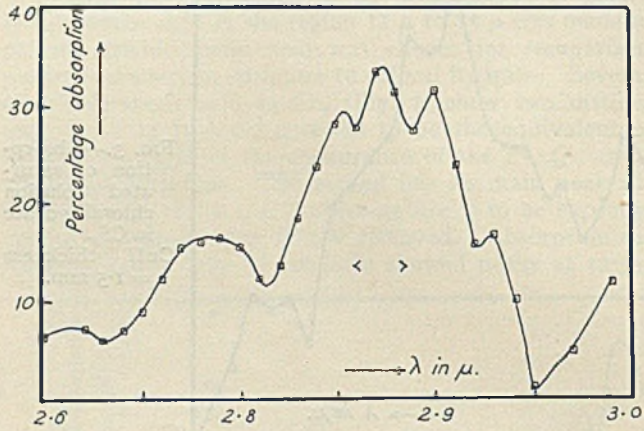


FIG. 5.—Benzoin in CCl_4 solution saturated at room temperature. 3·05 mm. cell.

$C_6H_5 . CHOH . CO . C_6H_5$, have been made and two broad but easily separable absorptions were found near 2·78 μ and 2·89 μ; these must be attributed to the different orientations of the OH group with respect to the C=O group. The abnormal breadth of these OH absorptions is also apparent in the overtone region,[10] and the one at 2·89 μ has now been resolved into a number of peaks. So different is this from the usual appearance of these bands that their identification was confirmed by examining benzophenone, $C_6H_5 . CO . C_6H_5$ in the same region, throughout which it was found to have no appreciable absorption. The peculiar width of the bands is presumably due to the coupling of the OH frequencies with other much lower frequencies in the molecule, but why this should be so pronounced

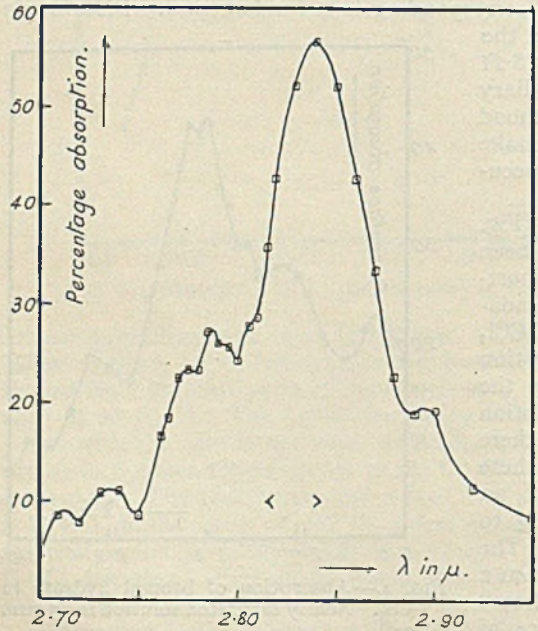


FIG. 6.—0·090 M. *o*-bromophenol in CCl_4 at 17°C. 3·05 mm. cell.

[10] Wulf and Liddel, *J. Amer. Chem. Soc.*, 1935, **57**, 1464.

in the present instance is not clear. Although the estimate of the band intensities was not very reliable owing to their width, it sufficed to show the increase of the 2·78 μ absorption relative to the 2·89 μ with rising temperature.

Ortho-bromophenol. (Fig. 6). This solute was carefully examined at both room temperature and at 75° C. in CCl_4. The main absorption consists of a symmetrical peak at 2·84 μ, whilst a small but less regular absorption, centred at 2·785 μ, was also shown. These correspond to the *cis-* and *trans-* forms respectively. From the integrated absorptions $\left(\delta = \int \log_{10} \frac{I_0}{I}\, d\lambda = kcl\right)$, making allowance for the overlapping of the bands, the relative concentrations were found to be 4·31 : 1 at 17° and 2·95 : 1 at 75°. Assuming an equilibrium determined by a statistical factor $c^{E/RT}$, the values of the energy difference of the isomers would be 850 and 760 cal./g. mol., from which a mean value of 800 cal./g. mol. may be accepted.

PART II.

In this section the relation of the frequency change in the OH group between two structures and the corresponding energy difference will be discussed on the basis of the results now available. The lowering in frequency on association of the alcohols was linked by Fox and Martin [11] with the energy involved on the basis of the Morse potential function. The latter gives for the energy of dissociation from the vibrationless evel, $D = \frac{h\omega_e(1 - x)^2}{4x}$, where ω_e is the vibration frequency for ideally small displacements and x is the anharmonicity factor: ω_e is related to the observed frequencies by $\nu_n = n\omega_e[1 - (n + 1)x]$, where $n = 1$ for the fundamental, $n = 2$ for the first overtone, etc. Clearly if x is the same for the two forms of the molecule, $\delta D/D = \delta\omega_e/\omega_e$ and their energy difference δD can be estimated directly from $\delta\omega_e$ using a reasonable value for D, the dissociation energy of the hydroxyl group (*e.g.*, 113 k. cal./g.mol.).

A direct test of the identity of x for the two forms of each molecule is very desirable, but only for *o*-chlorophenol and *o*-bromophenol are the locations of the origins of the relevant absorptions sufficiently precise to give significant results. These are shown in Table I.

The figures in brackets involve a frequency observed in the pure substance: the others refer to CCl_4 solutions. There seems little doubt that x varies by about 10 per cent. between the two forms of the same molecule. It has been confirmed that with the data at present available (*e.g.*, for benzoin, monomeric and dimeric acetic acid, monomeric and associated alcohols) the evaluation in this way of the energy difference between two molecular configurations as the simple difference of their D values gives only such meaningless results as in Table I, where these differences have the wrong sign. This general anomaly partly results from the fact that the anharmonicity factor is found to be larger for the form in which interaction occurs.

Returning to the simplified relation used by Fox and Martin, Table II shows the values of $\delta D = \frac{\delta\omega_e}{\frac{1}{2}(\omega_1 + \omega_2)} \times 113$ k. cal./g. mol.

[11] See ref. [4].

The corresponding values to δD from other methods are given in the last column.

The spectroscopic estimates of the energy differences are obviously only of the correct order of magnitude, although it must be emphasised that, except in the case of the carboxylic dimer, more accurate values are also desirable for the last column.

TABLE I.*

Compound.	Frequency (cm.$^{-1}$).	$x \cdot 10^2$.	ω_e.	D (k. cal./g. mol.).
Cis-chlorophenol . .	3540 6910 10086	2·29 2·34 } 2·34	3714	107·7
	(12993)	2·60		
Trans-chlorophenol . .	3603 7050 10331	2·08 2·12 } 2·10	3760	122·1
	(13328)	2·39		
Cis-bromophenol . .	3520 10001	2·51	3710	99·95
Trans-bromophenol . .	3595 10317	2·08	3760	123·37

* (Data taken from Freymann, *J. Physique et Radium*, 1938, **9**, 517; Davies, *Trans. Faraday Soc.*, 1938, **34**, 1427.)

A linear relation between δD and $\frac{\delta\omega_e/\omega_e}{\omega_e}$ is also to be expected on the basis of a simple potential function recently suggested by Sutherland [12] as a useful representation of the conditions in diatomic linkages. This is partly borne out by the fact that the spectroscopic values in Table II are about double the estimates otherwise made. This empirical correspondence is probably the best which can be attained at present.

TABLE II.

Molecule.	Structure.	ν(fundamental).	$x \times 10^2$.	ω_e.	δD.	δE.
o-Chlorophenol	*cis*- *trans*-	3540 3603	2·22	3704 3772	2·06	1·4 to 1·7
o-Bromophenol	*cis*- *trans*-	3520 3595	2·30	3690 3768	2·31	0·8
Benzoin .	*cis*- *trans*-	3454 3604	2·20	3613 3770	4·80	—
Acetic acid .	monomer dimer	3525 3030	2·00	3672 3155	17·2	7·8
Ethyl alcohol .	monomer associated	3634 3373	2·20	3802 3529	8·42	4·0

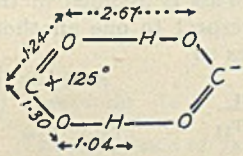
PART III.

Perhaps the major interest in the molecular systems being discussed lies in the determination of the origin of the interaction energies concerned. It is the object of the present section to indicate that in many

[12] *Proc. Indian Acad. Sci.*, 1938, **8**, 341.

cases, at least, these may be accounted for by dipole interactions with the addition of the induction and possibly dispersion effects. The origin and magnitude of these forces have been clearly discussed in a summarising paper by London.[13]

In this respect the carboxylic acid dimer is the most instructive example, as both its structure and the experimental value of δE are accurately known. For the former the data[14] lead to the representation shown (VI), where distances are in Angstrom units. In the subsequent calculations, unless otherwise specified, interatomic distances and dipole moments have been taken from Pauling's book,[15] and most of the group polarisabilities (α) from Waters.[16] In the present instance, we have taken $\mu_{C=O} = 2{\cdot}50$D, $\mu_{O-H} = 1{\cdot}66$D, $\mu_{C-O} = 0{\cdot}7$D (the last



(VI)

TABLE III.

In (B) ↓ \ In (A) →	O—H.	C—O.	C=O.
C=O	−5955	+883	−1680
C—O	+ 455	−144	+ 883
O—H	− 148	+455	−5955

from Sidgwick and Bowen[17]); $\alpha_{C=O} = 1{\cdot}35$, $\alpha_{O-H} = 1{\cdot}0$, $\alpha_{C-O} = 2{\cdot}0$, in units of 10^{-24} c.c. In calculating the interactions an accurate scale model of the planar group has been drawn and the distances required obtained from this. For the simple dipole interaction the moments have been resolved into point charges located at the appropriate atomic centres. Taking the separate interactions of each group in one half (A) of the carboxylic dimer with those in the other half (B), a total Coulombic contribution to δE of $-11{,}200$ cal./g. mol. is obtained, distributed as in Table III:

The value -5955 cal. for the C=O and OH interaction is in agreement with the similar values for this factor previously calculated by a different method by Moelwyn-Hughes.[18]

The induction effect for a dipole μ_1 orientated at an angle θ_1 to the line joining its centre to that of a group of polarisability α_{11} is given by $U = -\frac{\alpha_{11}}{2} \cdot \frac{\mu_1^2}{R^6}(1 + 3\cos^2\theta_1)$: R is the distance between the centres of the interacting systems. This energy, being necessarily negative, invariably corresponds to an attraction. For the total interaction between two groups the contributions of μ_1 and α_{11}, μ_{11} and α_1 must be added. Thus, the total energy in the present instance will be the sum of eighteen terms of the form above, and this total is found to be 2240 cal./g. mol.

It remains to evaluate the dispersion interaction for which London, in the same circumstances as the above, has given the expression $U = -m_1^2/3hR^6 \cdot (1 + 3\cos^2\theta_1) \cdot \sum \frac{m_2^2\nu_2}{\nu_2^2 - \nu_1^2}$. Here m_1 is the "oscil-

[13] *Trans. Faraday Soc.*, 1937, **33**, 8.
[14] Pauling and Brockway, *Proc. Nat. Acad. Sci.*, 1934, **20**, 336.
[15] *The Nature of the Chemical Bond*, Cornell Univ. Press, 1939, p. 146.
[16] *J. Chem. Soc.*, 1933, 1551.
[17] *Ann. Rep. Chem. Soc.*, 1931, **28**, 402.
[18] *J. Chem. Soc.*, 1938, 1243.

lator strength" appearing in the simple dispersion formula which gives the polarisability α_1 of the group, of which ν_1 is the resonance electronic frequency. To evaluate these terms, the approximate relation $m_1^2 = 3h\nu_1\alpha_1/2$ is combined with the assumption that ν_1 may be identified with the frequency corresponding to the ionisation potential (V_1) of the same group ($h\nu_1 = \epsilon V_1$): at the same time this involves the replacement of the summation by a single term. It is obvious from the appearance of the term ($\nu_2^2 - \nu_1^2$) that the net interaction of two groups will be the difference of two terms: *e.g.*, the C=O group acting on the OH of the opposite molecule leads to $U = -7380$ cal.: the OH acting on the C=O gives $U = +10{,}590$ cal. This gives the impossible result of a net repulsion of 3210 cal. between these two groups: impossible, because the dispersion effect must necessarily lead to an attraction. A great proportion of the error in this evaluation is introduced in the substitution used for m_1^2. This is avoided in the case of two groups at random orientation with respect to one another, for which the total dispersion interaction simplifies to

$$U = -3h/2R^6 \,.\, \alpha_1\alpha_{11} \,.\, \frac{\nu_1\nu_{11}}{\nu_1 + \nu_{11}}.$$

At their distance apart, the groups mentioned (if at random orientation) would yield an attractive energy of 1090 cal./g. mol. This is certainly a better estimate of the true order of magnitude of the dispersion energy. For the other groups, owing to the R^{-6} term, this contribution is bound to be much smaller, and for the present it is neglected.

It is noticeable in these circumstances that the dipole interaction is certainly much greater than the dispersion effect. This order is contrary to their contribution to the van der Waals forces in many instances.[19] But the reason is not far to seek. The interatomic distances here dealt with are too small to make the condition $\frac{\mu_1\mu_2}{R^3} \ll kT$ necessitated in London's comparison of these forces of any further validity. Thus, for the C=O and O—H groups, $\frac{\mu_1\mu_2}{R^3} = 26{\cdot}5 \times 10^{-14}$ ergs per molecule, compared with $kT = 4{\cdot}0 \times 10^{-14}$ at room temperatures. Further, the fixed orientation of the dipoles with respect to one another, means that their interaction approaches the maximum possible $\left(U = -\frac{2\mu_1\mu_2}{R^3}\right)$ where the dependence is upon R^{-3}, rather than R^{-6} as occurs for the random orientation at large distances involved in the van der Waals forces.

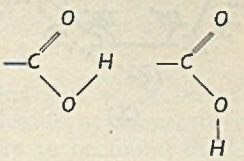
It has been found that the simple and induced dipole effects together give an interaction energy of 13,440 cal./g. mol., compared with a measured δE for formic and acetic acids in the gas phase[20] near 15500 cal./g. mol. In the first place, it may safely be suggested that the difference, 2060 cal. or 13 per cent., may be attributed to the dispersion forces. This proportion might well be used as a fair estimate of the relative contribution of this effect as between orientated groups in molecular structures: for the 13 per cent. in the present instance is the mean over several groups at various distances. Further, the fact

[19] London, *loc. cit.* [13], p. 19.

[20] MacDougall, *J. Amer. Chem. Soc.*, 1936, **58**, 2585. Coolidge, *ibid.*, 1928, **50**, 2166.

that 87 per cent. of the observed interaction energy can be accounted for on the simple basis of electrostatic forces makes the introduction of any resonance effects connected with a "hydrogen bond" of small import in this case. This conclusion agrees with the general sense of the spectroscopic analysis of this structure.[3]

The Monomeric COOH Group. A simpler example of the operation of the foregoing effects is found in the structure of the monomeric carboxyl group. This might be expected to occur in the *cis*- and *trans*- forms, (VII) and (VIII). Calculation of the interaction of the two groups C=O and O—H in these cases, using the same data as for the dimer except that the O—H bond distance is 0·96A, and < COH = 110° gives the following results (cal./g. mol.):



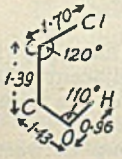
(VII) (VIII)

	Dipole interaction	*Induction effect.*	*Total.*
(*a*) *Cis*-form . .	−10,960	−3490	−14,450
(*b*) *Trans*-form . .	− 4,100	−2930	− 7,030

The difference of 7420 cal. in these totals may be taken as a measure of the stability of (VII) relative to (VIII). Using a factor of $e^{\delta E/RT}$, it may be estimated that at room temperatures the relative frequency of occurrence of the two forms is $3{\cdot}62 \times 10^5 : 1$. This conforms with the complete absence of the structure (VIII) as indicated by spectroscopic analysis.[21]

Benzoin. Another molecule in which the same two groups interact is benzoin, $C_6H_5CHOH . CO . C_6H_5$. Here, the interposition of the C—C bond reduces the calculated energy difference to 3530 cal./g. mol.:

	Dipole interaction.	*Induction effect.*	*Total.*
Cis-form . . .	3790	515	4305
Trans-form . . .	556	220	776



(IX)

This value of δE is of the same order as that (4800) estimated in Part II from the frequency shift between the two forms.

o-Chlorophenol. In treating this molecule the electron diffraction value of the C—Cl distance in chlorobenzene has been used,[22] and the moments $\mu_{Cl-C} = 1{\cdot}56D$, $\mu_{O-H} = 1{\cdot}73D$:

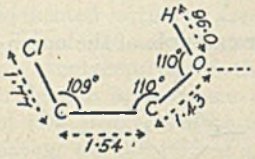
	Dipole interaction.	*Induction effect.*	*Total.*
Cis-form . . .	2040	468	2508
Trans-form . . .	432	293	725

The estimated difference of 1780 cal./g. mol. is in reasonable agreement with the value of 1400-1700 cal. deduced from estimates of the relative intensities of the absorptions corresponding to the two forms of the molecule.

o-Bromophenol. The energy values are very near those in chlorophenol, and give an estimated energy difference of 1630 cal./g. mol.:

[21] Bauer and Badger, *J. Chem. Physics*, 1937, **51**, 852.
[22] Glasstone, *Ann. Rep. Chem. Soc.*, 1936, **33**, 76.

	Dipole interaction.	*Induction effect.*	*Total.*
Cis-form . . .	1820	638	2458
Trans-form . . .	482	350	832



(X)

Chloral Hydrate. It is very probable that owing to the interaction of the O—H and C—Cl groups the structure will be in or near one plane. Accordingly, the form depicted has been assumed for this system. Taking the *cis*- and *trans*- orientations as corresponding to the clamped and free forms of the O—H group, and calculating the two contributions as before :

	Dipole interaction.	*Induction effect.*	*Total.*
Cis-form . . .	3760	1080	4840
Trans-form . . .	90	430	520

It is seen that the *cis*-orientation of each OH group is stabilised by an interaction energy of about 4300 cal. which would correspond to a frequency distribution of 1700 : 1 in favour of the clamped position, or of $2{\cdot}9 \times 10^6 : 1$ as between the structure with the two hydroxyls towards the chlorines and that with them both in the opposite orientation.

Summarising these results, it is clear that simple electrostatic forces are sufficient to account for a considerable variety of interactions involving the OH group. Provided the interactions are endowed with the requisite energy their other characteristics follow, and these appear in a continuous range from the simple *cis-trans*- distribution in *o*-chlorophenol to the formation of a new molecular species of considerable stability in the case of the carboxyl dimer. There seems to be no strong practical reason for the introduction of a special mechanism of a " hydrogen bond " to account for the observed energy effects, and although the existence of a resonance contribution is an *a priori* likelihood in most cases, its magnitude would often appear to be negligible.

Summary.

(i) Infra-red measurements on chloral hydrate in solution have shown a considerable interaction between the OH groups and the adjacent CCl_3 radical. This interaction is related to the peculiar stability of the compound and similar results for analogous structures are presented.

(ii) The relation of the frequency change in the OH group between two structures and the corresponding energy difference is discussed. The unsatisfactory nature of those estimates assuming identical anharmonicity factors in the two structures is indicated.

(iii) Electrostatic energies are evaluated for interactions involving the OH group. With reasonable assumptions, these are found to account for the observed effects in a considerable variety of cases, and it is suggested that the magnitude of the resonance contribution to the stability of the " hydrogen bond " may often be negligible.

The author owes the suggestion of examining chloral hydrate in the infra-red to a discussion with Dr. T. P. Hughes. He is also indebted to the Department of Scientific and Industrial Research for a Senior Award, and to the Chemical Society for a grant.

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THE VAPOUR PRESSURE OF OLEUM.

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In addition to the vapour pressure determinations of McDavid[1] for oleum containing up to 40 % of pure sulphur trioxide, at temperatures between 10° and 50°, two other series of data are to be found in the literature. The first was published by Knietsch in his well-known paper of 1902[2] and the second was contributed to the International Critical Tables (Vol. III) by the Eastern Laboratory of Messrs. E. I. duPont. Both series cover most of the temperature range 20°-100° C. and of the concentration range 0-100 % free trioxide, but in neither case are the actual experimental results given, or the method by which the figures in the tables are derived from them. Knietsch indeed has stated that "On this account" (that mercury is attacked by pure sulphur trioxide) "the measurement was carried out in an iron apparatus by means of a manometer, which was quite accurate enough for experimental purposes." Below the title is given "($\frac{3}{4}$ vol. Oleum + $\frac{1}{4}$ vol. Air)" from which it appears that the containing vessel was only $\frac{3}{4}$ filled with acid, having air above the acid presumably at one atmosphere pressure. The pressures recorded are evidently the excess over about an atmosphere, but whether any deduction has been made for the increase of the air-pressure at higher temperatures, or what the temperature was at which the instrument was filled, or whether the pressure of air was exactly one atmosphere when the filling was done (most unlikely, in view of the high vapour pressure of the stronger oleum), is quite impossible to find out. Other peculiarities of this set of figures will be mentioned later.

The duPont figures cover the range of free sulphur trioxide 0-66 % and are limited to temperatures which vary between 55° (for 66·9 %) and 90° C. (for 33·3 %). The divergence between this set and Knietsch's is very wide and is not always in the same sense. Oleum of 30 %, for instance, shows 152 mm. pressure at 60° according to Knietsch; according to duPont the pressure of 31 % oleum at the same temperature is 74 mm. On the other hand, for 40 % at 75° the pressure recorded by Knietsch is 360 mm.; that given by duPont is 539·5 mm. Again, the two values are respectively, for 60 % acid at 55°, 730 mm. and 512 mm.

Redetermination was clearly necessary. Choice of methods lay between the dynamic method of boiling under various definite pressures and the static method of measuring pressures at definite temperatures. The latter was preferred, although the presence of air dissolved in the liquid is a source of error and the most stringent precautions possible must be taken on this account. It was decided therefore to synthesise the oleum by distilling pure sulphur trioxide into the bulb of the vapour pressure apparatus containing sulphuric acid (98·5 % H_2SO_4) which had been degassed by stirring and heating *in vacuo*. By adding further portions of sulphuric acid to the oleum it was hoped to carry out several

[1] *J.S.C.I.*, 1924, 43, 57T. [2] *Ber.*, 1902, 34, 4112.

series of determinations in succession for several varieties of oleum, but the manipulation required to admit the sulphuric acid and to exclude all air was found impracticable and each variety of oleum was made up from its components, the apparatus being cut open and sealed up again for each series of determinations.

The field of the measurements was limited on two sides. The temperature could not safely be raised above 175° C. because of the soldered joints of the air-bath, and the maximum pressure which could be recorded on the mercury manometer was 950 mm. In this field, however, lie all the data which are likely to be of any technical interest. Complete series of determinations were made for the following concentrations: 6·9 %, 12·7 %, 21·1 %, 32·3 %, 48·2 % and 64·9 %, and since the apparatus was very suitable for the redetermination of the vapour pressure of pure sulphur trioxide, this was undertaken also, the manometer being doubled for the purpose in order to record pressures of about two metres.

Experimental.

General.—As SO_3 attacks Hg, it was not possible to measure the vapour pressure of oleum directly on a Hg manometer. It was therefore decided to introduce a glass Bourdon gauge between the oleum and the manometer, by passing air into, or withdrawing air from, the space between the gauge and the manometer. When the needle of the gauge

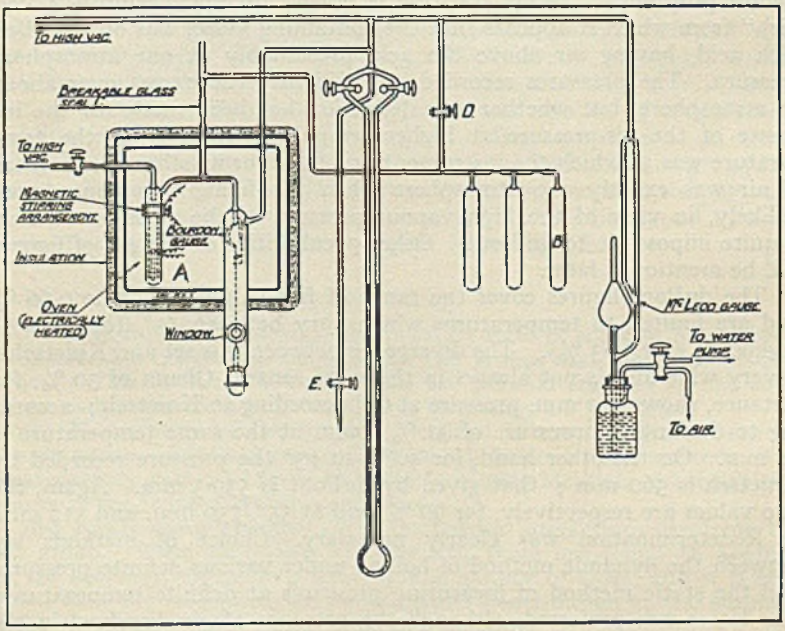

Fig. 1.

was at zero position, the vapour pressure of the oleum was the same as that indicated on the manometer.

The gauge as used for HNO_3 vapour pressure determination could not be used in this case as it is not possible to make one of this kind which would withstand the very large pressure differences encountered, and at the same time be sufficiently accurate for our purpose. A modified

form of Bourdon gauge which was devised by B. S. Foord [3] proved to be sensitive to 0·1 mm. of Hg, and yet able to bear more than an atmosphere difference of pressure between the two sides.

A diagrammatic representation of the final set-up of the apparatus is given on Fig. 1.

The measurements were carried out in a large electrically heated air oven, heated on all six sides so as to give an even temperature throughout. A liquid bath would have given better temperature control, but no common liquid except H_2SO_4 can safely be used to withstand the risk of mixing with hot SO_3; water was considered to be out of the question.

The temperature was measured by means of thermo-couples, one in a tube which was passed under the surface of the oleum, and one fixed to the wall of the bath. Two thermo-couples were used, because it was found that there was considerable divergence between the temperature of the oleum and the surrounding air, particularly after the apparatus had been heated or cooled in order to take readings at another temperature. Readings were taken only when the temperature of the bath wall and of the oleum were the same. For greater accuracy in measurement the "cold" junctions of the thermo-couple were placed in an oil bath, the temperature of which could be read on a thermometer, and could be adjusted to give a "null" deflection on the galvanometer. Temperatures could thus be determined to less than 0·2° C.

Method of Stirring.—It was important that the oleum be efficiently stirred, because of the fact that trioxide tended to escape only from the surface layers when the temperature was increased, and to condense only on the surface layers when it was lowered. Thus in the first case the surface layer should have a lower concentration and therefore a lower vapour pressure than that of the remainder of the oleum. In the second, the effect should be reversed. The oleum was therefore stirred by a magnetic stirring arrangement, with an automatic make and break, such that a metal stirrer covered with platinum was pulled up by an electro magnet when the circuit was completed, and allowed to fall gently when the circuit was broken. The stirrer was not worked continuously because of the heat which resulted from the passage of an electric current through the coil of the magnet, and tended to overheat that part of the apparatus in close proximity to the coil.

Preparation of Oleum.—In order to free the oleum and glass apparatus from air and other adsorbed gases, the following procedure was adopted.

Concentrated H_2SO_4 of known strength was weighed into the tube A (Fig. 1) and then sealed on to the rest of the apparatus, the air which was used to expand the joints in glass blowing being dried by passing through calcium chloride tubes. The glass bulb B was then weighed and a known weight of 65 % oleum introduced. This bulb was now sealed on to the apparatus, using dried air.

The oleum was then cooled down in a paste of solid CO_2 and acetone, in order to reduce its vapour pressure to a very low value, and both halves of the apparatus, *i.e.* on both sides of the breakable glass seal C, were evacuated by the mechanical and Hg vapour pumps. When the pressure as shown on the McLeod gauge was fairly low (about 10^{-2}), the stopcock D was closed. The freezing mixture was now applied to the second bulb, and the bulb B heated slightly (to 40° C. or less) using a bath of concentrated sulphuric acid. When sufficient SO_3 had distilled over, the bulb B was sealed off at the constriction and the weight of residual oleum found. Stopcock D was opened and any air which might now be present in the apparatus was removed by pumping, using the high vacuum system. Stopcock D was then again closed, and sulphur trioxide distilled from the second to the third bulb by cooling the third and heating the second bulb. The latter was then sealed off.

[3] *J. Sc. Instr.*, 1934, 11, 126.

Meanwhile the concentrated H_2SO_4 in bulb A was being freed from air by connection to the diffusion pump and heating to about 80° C., while being stirred intermittently by means of the magnetic stirring arrangement. The glass seal C was now broken by a metal plunger which was pulled up by a magnet and then allowed to fall on to the seal. The freezing mixture was removed from the third bulb, applied to the tube A, and distillation of SO_3 carried on until sufficient was judged to have passed over into the concentrated H_2SO_4 to give an oleum of the required concentration. The third bulb was then sealed off as close to the wall of the bath as possible, and after a thorough evacuation of the oleum at low temperature the bulb A was detached from the pump by sealing off close to the wall at the constriction. Much delay was caused and many runs spoilt by the cracking of the oleum bulb when the SO_3, which had been frozen in it, was melted. This could not always be prevented, but happened much less often when the melting was carried out by surrounding the bulb with H_2SO_4 and manipulating in such a way that the SO_3 was liquefied first at the upper surface, so that the enclosure of liquid by a solid plug above was avoided.

Fixing the Zero of the Bourdon Gauge.—In order to have a fine end on the moveable pointer of the gauge a short length of very fine wire was fixed to it by means of cement, and its lateral movement was observed against a similar wire attached to a rigid piece of glass rod. This movement was observed through a small low power lens. Owing to the great difficulty of fixing these wires so that they were exactly in line when the pointer was in a zero position, it was found to be more practicable to fix the wires fairly close together and then to find the pressure required to bring them into line with each other. This was done for each set of measurements by cooling the oleum to reduce its vapour pressure to as low a value as possible (about 10^{-3} mm.), completely evacuating the apparatus on the other side of the gauge, and then admitting air slowly through the stopcock E to the left hand limb, which was in direct contact with one side of the Bourdon gauge, until the wires on the gauge coincided. This pressure was read off on the manometer, and subtracted from all subsequent readings.

Measurement of Vapour Pressure.

The bath was now raised to the required temperature, the oleum being stirred now and then with the magnetic stirrer, particularly before each pressure reading. When the temperature of the oleum and of the bath walls was the same, the vapour pressure of the oleum was measured by admitting air to the left-hand limb of the manometer and one side of the Bourdon gauge through the stopcock E until the crosswires coincided, As there was a high vacuum in the right-hand limb of the manometer, the difference between the cathetometer reading of the mercury in the two limbs, less the correction, was equal to the vapour pressure of the oleum in millimetres of mercury at the measured temperature.

Measurement of Concentration.

To determine the concentration of SO_3, the acid was weighed in single-stemmed "oleum bulbs." The weighed bulb was heated slightly in a Bunsen flame, and the open end of the capillary inserted under the surface of the oleum. When sufficient oleum had been sucked in, the end of the capillary was sealed off in a flame. Thereafter the oleum was estimated by breaking under water in a closed glass-stoppered bottle and titrating with normal sodium hydroxide solution.

From the known weight of 65 % oleum which was originally taken for each series of measurements, from the total weight of oleum and SO_3 remaining in the bulbs which were removed after sealing off, and from the

weight of H_2SO_4 put into the measurement bulb, the composition of the oleum synthesised could be estimated fairly closely. In Table I are given the final analytical figures, together with the compositions estimated from the weights.

TABLE I.

Composition from Weights taken.	*Composition by Analysis.*
6·65 % free SO_3	6·91 free SO_3 6·89
13·4 known to be inaccurate	12·69 12·96
21·35	21·08
33·55	32·34 32·29
(38·50)	(38·98)
48·50	48·20
65·50	64·62 64·78

Vapour Pressure of Pure Sulphur Trioxide.

It was found necessary to make minor alterations in the apparatus in order to obtain anhydrous SO_3. It is important that the trioxide be kept free from small quantities of water, as the presence of water in extremely small amounts favours the production of the "asbestos" form of SO_3, which has a higher melting-point, than the normal form melting at 16·8° C. and boiling at 44·5° C.

The concentrated oleum was introduced as before into bulb A (Fig. 2), the system evacuated through stopcock D, and SO_3 distilled as before into bulb B. Both tube A and tube B were now cooled simultaneously in carbon dioxide and acetone and the whole system again evacuated, after which the first constriction was closed. Thus, the portion of the apparatus which remained was glass-sealed without stopcocks, and there was no risk of contamination of the trioxide by any products of its action on stopcock grease.

The trioxide in bulb B was now distilled in the usual fashion over P_2O_5 into the bulb C, and the tube B removed by sealing at the con-

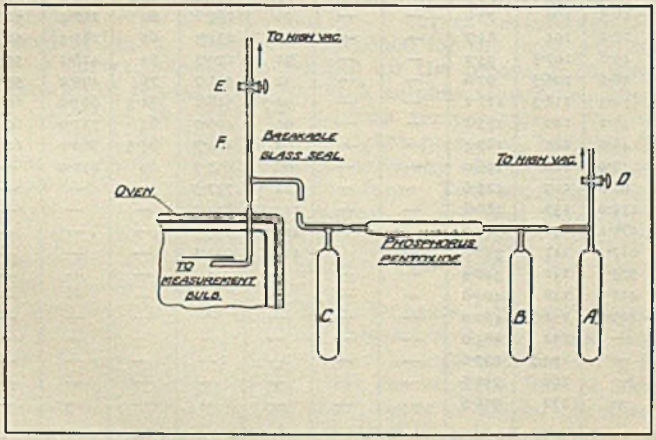

FIG. 2.

striction. Some of the trioxide in bulb C was now redistilled into the measurement bulb and the bulb C sealed off. In order to remove any air or other gas which might have been given off during these distillations, the measurement bulb and its contents were thoroughly frozen, the breakable glass seal F was broken, and the apparatus thoroughly evacuated through the stopcock E, after which the constriction close to the wall of the bath was sealed off.

It was found that the trioxide tended to volatilise and condense on the side tubes and Bourdon gauge, particularly when the temperature

of the bath was being lowered. This seemed to be due to the fact that the mass had a greater temperature-lag than the rest of the apparatus, and this caused distillation on to the colder side tubes and gauge. The latter were therefore wound with fine resistance wire held between layers of asbestos paper. During vapour pressure measurements a small electric current, sufficient to maintain the temperature *slightly* above that of the SO_3, was passed through the wire. Care was taken to see that the surface of the liquid was not overheated in this way.

TABLE II——Vapour Pressure of Oleum.

6·89 % SO_3.		12·7 % SO_3.		21·08 % SO_3.		32·3 % SO_3.		48·2 % SO_3.		64·7 % SO_3.	
t (°C.).	*p* (mm. Hg).	*t* (°C.).	*p* (mm. Hg).	*t* (°C.).	*p* (mm. Hg).	*t* (°C.).	*p* (mm. Hg).	*t* (°C.).	*p* (mm. Hg).	*t* (°C.).	*p* (mm. Hg).
20	2·1	28	2·5	17·5	2·3	18·5	3·7	14·5	15·3	1·5	25·4
28	2·9	34	3·7	20	2·9	20	5·2	18	21·5	8·2	43·8
34·3	3·3	43	4·7	47	9·5	34	10·7	18·5	21·6	9·3	54·2
37	3·7	58	12·1	61	23·7	36	12·9	24·5	28·0	11·4	61·5
42	4·4	59·5	12·7	81·2	70·6	38	15·9	27·5	36·4	15	80·1
43	4·5	60	13·5	93·0	109·1	41	18·8	32	47·7	18	92·2
46	5·1	62	14·7	101·2	160·7	44·5	22·1	39	70·2	19·8	107·0
55	7·4	65	16·0	117	269·3	45	24·0	41	78·3	23·4	131·1
57	7·8	70	21·3	127·5	410·0	49	29·8	44	96·1	25	150·8
60	8·8	71·5	22·2	132	520·0	52	37·2	46	106·9	31·5	210·9
61	9·2	81·5	29·0	137	667·0	55	43·9	47	118·9	34	241·5
64	10·0	87	44·7	140·5	790·0	61	54·8	51	136·5	35·3	263·1
66	10·8	98	64·9	143	901·3	70	98·1	54	169·3	42·6	389·2
67	11·1	99	71·5	—	—	77	138·1	58·5	204·0	46	445·2
80	16·3	100	73·8	—	—	79	163·6	62	257·4	52	594·6
81	17·1	104	84·7	—	—	86	234·3	65	285·3	52·8	619·7
85	19·8	107·5	93·2	—	—	91	290·5	73	418·2	55·5	706·9
94	26·6	108·5	97·6	—	—	92	311·7	76	499·2	59·6	832·7
100	32·3	112·5	117·2	—	—	92·5	318·1	82·3	663·6	60	862·4
105	39·2	120	153·2	—	—	99	406·0	85	741·0	60·8	873·4
108	46·1	125	187·4	—	—	102	474·7	85·5	760·0	61·1	890·7
109	47·0	126	199·0	—	—	108	603·7	89	871·0	—	—
118	68·0	129	225·6	—	—	112	737·5	—	—	—	—
131	114·0	137	286·8	—	—	113·5	814·5	—	—	—	—
144	179·1	140	319·6	—	—	115	899·5	—	—	—	—
149	217·3	141	336·0	—	—	117	931·5	—	—	—	—
164	375·3	142	346·9	—	—	—	—	—	—	—	—
167	417·4	148	420·6	—	—	—	—	—	—	—	—
170	465·1	151·7	480·0	—	—	—	—	—	—	—	—
—	—	152	484·0	—	—	—	—	—	—	—	—
—	—	159·7	607·6	—	—	—	—	—	—	—	—
—	—	166	756·6	—	—	—	—	—	—	—	—
—	—	172	926·6	—	—	—	—	—	—	—	—

In order to get readings of pressures higher than one atmosphere, the right-hand limb of the U-tube manometer was filled with air at atmospheric temperature and pressure before being closed instead of being evacuated. The vapour pressure of the SO_3 was therefore equal to the pressure of this air plus the difference of mercury levels. The pressure in the closed limb was easily calculated from the change in volume as it was compressed. A thermometer was strapped to the tube and read to make sure that no significant change of temperature took place during this compression. It was not considered advisable to go higher than about 2½ atmospheres.

Results.

All the readings of the vapour pressures of the six different concentrations of oleum with the temperatures at which they were made are included in Table II. Table III gives the results for pure sulphur trioxide.

TABLE III.—VAPOUR PRESSURE OF SULPHUR TRIOXIDE.

Readings with Ordinary Manometer.		Readings with Pressure Manometer.	
t (°C.).	p (mm. Hg).	t (°C.).	p (mm. Hg).
17·5	148	47·1	858
21	193	49·7	989
25·3	259	49·8	989
27·2	293	50·0	1007
28·1	307	50·5	1035
32·4	398	54·5	1241
36·8	504	55	1284
37·5	526	57·6	1433
39·5	581	58·1	1486
41·0	631	61·5	1703
43·0	702	62·0	1743
43·5	719	—	—
45·1	777	—	—
47·0	853	—	—
48·0	893	—	—

Graphical Treatment.

The oleum data were plotted on squared paper (to the scale of 1 cm. ≡ 4° C. ≡ 20 mm. Hg) and a smooth curve was drawn through each set of points with a flexible celluloid curve-tracer held by steel clamps.

These six curves gave the data exactly as they were obtained (in the form of $p-t$ curves, the composition being constant for practical purposes each curve), but for the curves must be spaced at regular intervals and it is preferable to plot for fixed values of the temperature.

The complete series of isothermal ($p-t$) curves for intervals of 10° C. is reproduced in Fig. 3. They were obtained for the most part from the original $p-t$ curves, simply by reading off the pressures corresponding to even decades of temperature, for each sulphur trioxide concentration, and then replotting as curves of constant temperature. This was not sufficient, however, for the region of higher pressures, because the $p-t$ curves are there nearly vertical, and the ordinates of temperature on which readings are required rarely intersect them. Two separate $t-c$ curves were therefore drawn again for pressures of 900 and 650 mm. From these were taken the values used to complete the higher region of Fig. 3. There is no reason to believe that the points obtained in this way are less trustworthy than the original points.

To this procedure one exception had to be made. When the logarithmic plots ($\log_{10} p-1/T$; see below) were inspected it was found that each set lay close to a straight or simple curve, except that for 21 % free trioxide which departed appreciably from the straight line of closest fit without falling as a whole as any other curve of single inflection. The result of this irregularity was that the final smoothed vapour pressures, when tested by plotting as logarithmic curves, showed this defect not only for 20 % but for other concentrations in that neighbourhood. It was therefore considered best in deriving the smoothed values to substitute, for the actual experimental pressure values for 21 % (but only in this case), those read from the logarithmic line of closest fit. This rather arbitrary procedure is largely justified by the concordance it introduces into the smoothed values at and near 20 % free trioxide.

There is a certain doubt about the lower parts of the isotherms for 160° and 170°. Neither curve can pass through the origin, on account of the appreciable vapour pressure of 100 % sulphuric acid at these

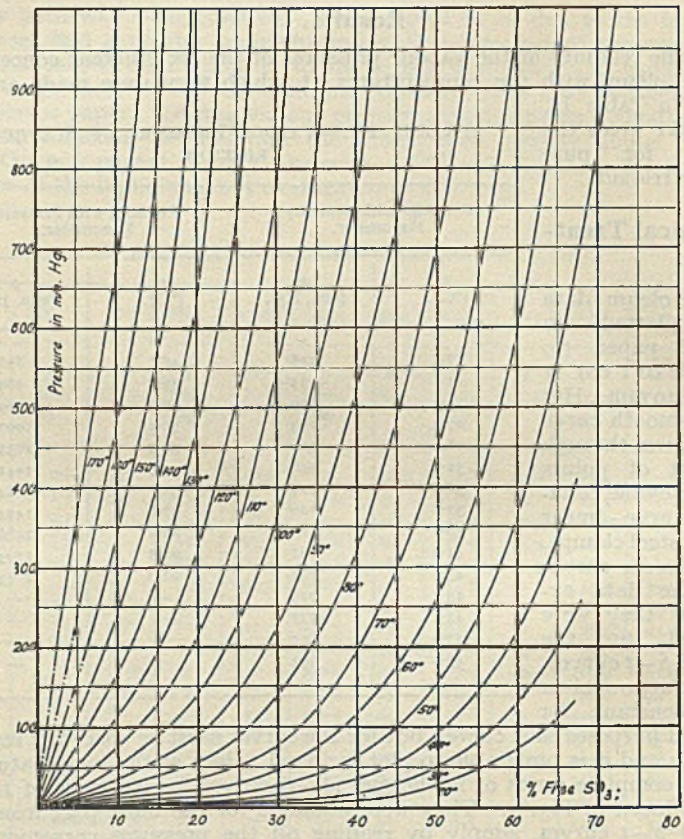

FIG. 3.—Smoothed values of vapour pressure of oleum.

TABLE IV.—VAPOUR PRESSURE OF OLEUM, AT INTERVALS OF 10° C. AND 5 % FREE SO_3. (READINGS FROM $p-c$ CURVES (FIG. 3).)

t (°C.).	% Free SO_3.													
	5	10	15	20	25	30	35	40	45	50	55	60	65	70
20	—	—	—	—	—	—	—	—	16	28	46	73	111	164
30	—	—	—	—	—	—	12	17	30	50	82	128	197	300
40	—	—	—	—	—	15	22	35	55	89	162	217	330	500
50	—	—	—	12	16	25	40	63	100	153	230	354	545	816
60	—	—	15	20	28	46	74	115	173	257	384	579	880	—
70	—	16	25	35	50	75	119	192	290	426	628	954	—	—
80	12	24	37	57	84	135	209	313	469	688	—	—	—	—
90	18	34	60	89	140	220	339	504	728	—	—	—	—	—
100	23	52	89	138	225	351	515	794	—	—	—	—	—	—
110	35	76	128	209	334	530	840	—	—	—	—	—	—	—
120	54	114	194	316	459	—	—	—	—	—	—	—	—	—
130	78	167	294	460	752	—	—	—	—	—	—	—	—	—
140	112	240	396	650	—	—	—	—	—	—	—	—	—	—
150	162	334	558	—	—	—	—	—	—	—	—	—	—	—
160	236	470	824	—	—	—	—	—	—	—	—	—	—	—
170	360	655	—	—	—	—	—	—	—	—	—	—	—	—

temperatures. These pressures have not been directly measured, but extrapolation of the results of Thomas and Barker [4] leads to the rough values for the total pressures of 7·0, 12·5 and 21·0 mm. at 150°, 160° and 170° C. respectively.

Heats of Vaporisation.

Fig. 4 shows the experimental data plotted as $\log_{10} p$ against 1/T.

They should fall on straight lines, the slopes of which are $Q/2{\cdot}303R$ (Q being the molecular heat of vaporisation) so that Q can be found in calories, for each line, as 4·573 × the determined slope of the line.

These plots were made to the largest practicable scale on paper (40 × 70 cm.) and the locations of the best-fitting straight lines were found by a convenient approximate graphical method of Least Squares. On the whole the fit is fairly good, but the two weakest oleums show, for the lower range of pressure, a departure from the straight line in the sense of excessive pressure which is difficult to account for. It is found only when both temperature and concentration are at their lowest and shows a certain gradation with concentration. There seems to be no source of experimental error from which a graded effect of this kind could arise and it seems more likely that the two logarithmic lines for 6·9 and 12·8 % are actually curved, in correspondence with a decrease in the latent heat of evaporation which occurs in these two cases, to a greater or less extent, as the temperature falls. Since, however, the readings at higher pressures were more important as results and were also proportionately less liable to the effect of some constant error—as, for instance, inaccuracy of the gauge—it was decided that in fixing the positions of the straight lines all readings of pressures below 12 mm. should be discarded.

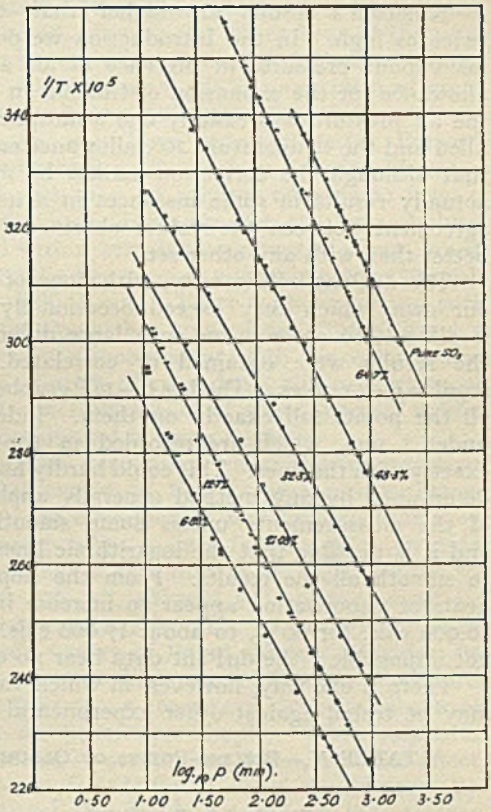

FIG. 4.—Vapour pressures of oleum and sulphur trioxide; logarithmic curves.

The molar latent heats of vaporisation of the trioxide from the several varieties of oleum, including the pure trioxide, are as follows: 6·4 % free trioxide—12,100 cal.; 12·7 %—11,300 cal.; 21·1 %—12,190 cal.; 32·3 %—12,500 cal.; 48·2 %—11,190 cal.; 64·7 %—10,240 cal.; trioxide—10,485 cal. There is a certain variation in the figures, visible in Fig. 4 as a slight lack of parallelism of the lines, which is by no means necessarily due entirely to experimental error.

[4] *J.C.S.*, 1925, **127**, 2820.

Discussion.

It has already been pointed out that the existing sets of data agree very badly with each other. The new set agrees well with none of them. The figures cover a wider field than any of the old.

The data of McDavid and Chadwick are only for pressures below 60 mm. On the whole they are lower, but the difference is not regular; at 40°, 50° and 90° they agree well with the new data but diverge widely at the intermediate temperatures.

Knietsch's results are higher than ours—sometimes more than twice as high. In the Introduction we pointed out that he measured his vapour pressures in presence of air and seems to have made no allowance for the expansion of this air on heating. If we assume that the air pressure was exactly one atmosphere when the manometer was filled and the temperature 20°, allowance can be made. It thus appears that although the correction cannot be more than a rough one, and actually results in some instances in a negative vapour pressure, the agreement between the values obtained in this way and our own is better than with any other set.

The duPont values agree with none of the others, least of all with our own, which they exceed occasionally by more than 100 %. It is difficult to account for such large differences without knowing how the results were obtained or correlated. When plotted they give regular $p-t$ curves. The log $p-1/T$ graphs are straight lines and nearly all the points fall exactly on them. Indeed, points for the pressures under 1 mm. which are recorded in the duPont table also coincide exactly with the lines. This could hardly happen with such low pressures determined by any method generally applicable over the whole range of the measurements unless some smoothing had been carried out, and it is possible that the logarithmic lines themselves have been used to smooth all the results. From the slopes of these lines the latent heats of vaporisation appear to increase in a regular way from about 10,000 cals. for 60 % to about 17,000 cals. for 10 %. Such values are not impossible; the duPont data bear no evidence of inconsistency.

There is one way, however, in which vapour pressure measurements may be tested against other experimental results. The boiling points of certain oleums were found directly by Knietsch. In Table V the experimental and the deduced values are compared. Those derived from our own results were read from the curves of Fig. 3 directly, those from duPont's had necessarily to be found by extra polation, since their measurements were limited to 500 mm. For this purpose the log $p-1/T$ curves of their data were used—a legitimate procedure since the data fit them closely.

TABLE V.—Boiling-Points of Oleum.

% Free SO_3.	Directly Determined by Knietsch (°C.).	From Vapour Pressure Curves (Ardeer).	Extrapolated from duPont Data.
3·6	212	—	—
9·6	170	175	137
26·2	125	128	115
42·8	92	94·5	75
63·2	60	60	53

Knietsch's figures and our own agree very well, but these derived from the duPont data depart so widely that the method of derivation

can account only for a small fraction of the difference. Our data, therefore, withstand the few tests that can be put to them.

The latent heats of vaporisation are somewhat unexpected. For sulphur trioxide the most trustworthy values are probably those obtained from vapour pressure data by Berthoud,[5] who found 10,580 cal. for the whole interval 25-44° C., and by Smits,[6] who found 10,100 cal. between 17° and 90° C. With these our figure of 10,480 cal. is in fair agreement, but those for the oleums tend to rise as the percentage of free trioxide falls, and to reach a maximum at about 30 % of pure trioxide. A rise is to be expected, because the latent heat of the pure trioxide must be less than that of very dilute oleum by the heat of mixing trioxide with great excess of sulphuric acid. It is doubtful how great this heat of dilution actually is. From Knietsch's investigation of the heats of dilution of various oleums in large excess of water, Porter[7] obtains certain figures (k) representing the heat in calories liberated when 1 g. of water is mixed with m g. of sulphur trioxide to form a certain oleum. The differential heat of mixing—*i.e.* the heat evolved when 1 g. of trioxide is mixed with a very large amount of oleum, must be dk/dm and for the quantity the figures give approximately 1500 cal. for 73 % and 3000 cal. for 18 % oleum. There is, however, no sure ground here for comparison, for Porter has pointed out that Knietsch's vapour pressure measurements are inconsistent with his calorimetric data and indicate the heat of dilution of trioxide in any proportion of sulphuric acid to be zero. A redetermination of these thermal values by direct methods would be useful, and is being made.

The vapour pressures have one peculiarity which is not altogether unexpected. If the isothermal curves of Fig. 3 representing change of pressure with concentration are examined, it will be seen that they cannot pass through the corresponding points for the pure trioxide without undergoing a marked change of curvature in the region 70-100 % free SO_3. The isothermals for 20°, 30°, 40° and 50° at least, must be S-shaped. This fact is interesting, and is quite in accordance with what we know of the associated nature of liquid sulphur trioxide; its very high specific heat, for instance, or its high value of Trouton's constant. On account of the association, the vapour pressure of the pure substance is lower than if its molecular condition were simple. When sulphuric acid is added the complex molecules are broken down, and the effect of diluting the trioxide with a non-volatile liquid, which would normally be to depress the vapour pressure sharply, is delayed by the increase in the activity of the trioxide. As more acid is added simple molecules of trioxide become more numerous and dilution causes the vapour pressure to fall in the usual way.

Summary.

The vapour pressures of oleum have been determined over a field which is limited generally by a concentration of 65 % free trioxide, and a pressure of 950 mm. and at particular points by a temperature of 170° C. The results agree with none of the published sets of oleum vapour pressures, but nevertheless appear to be reliable, and are in agreement with indirect estimates of the vapour pressure from certain other data. Some peculiar

[5] *Helv. Chim. Acta*, 1922, **5**, 513.
[6] *J. Chem. Soc.*, 1926, 1108.
[7] *Trans. Faraday Soc.*, 1917-18, **13**, 392.

features of the vapour pressure curves are discussed. The vapour pressures of sulphur trioxide have been redetermined from 17° to 62° C.

We are indebted to Messrs. Imperial Chemical Industries, Limited, for permission to publish this paper.

The Nobel Laboratories,
Ardeer.

THE PARTIAL PRESSURES OF NITRIC ACID-WATER MIXTURES FROM 0° – 20° C.

By G. L. Wilson and F. D. Miles.

Received 29th August, 1939.

These measurements were carried out because of two observations made in the course of experiments on the nitration of cellulose in nitric acid vapour.

The first was that the extensive series of vapour pressures collected and recalculated by Taylor [1] for nitric acid-water mixtures were not in agreement with two later series by Berl and Saenger [2] and Klemenc and Rupp.[3] The last two researches deal mainly only with 100 % nitric acid and although they agree with one another, they disagree with the older figures collected by Taylor. For instance, Klemenc and Rupp give 31 mm. at 12·5° whereas Taylor's value is 30 mm. at 15°.

For the total vapour pressure over nitric acid of 82 % by weight Klemenc and Rupp give 6·9 mm. at 0° and 23·4 mm. at 25° compared with 3·1 mm. and 15·5 mm. from Taylor's figures for the same temperatures; and for 71 % acid—2·2 mm. at 12·5° compared with 4·6 mm. according to Taylor.

The second observation was that dew was formed in an apparatus containing the vapours of nitric acid and water, at a pressure of about 5·9 mm. at 20° C., whereas the lowest total pressure of any nitric acid-water mixture at 20° given in Taylor's figures was 6·4 mm. (for a composition of about 60 %-65 %). To have accurate figures for both the composition and the pressure of the vapours is important in many industrial problems.

A static method of measuring the vapour pressure was preferred to a dynamic one as capable of greater accuracy. The total pressure of the liquid was found, some of it was then distilled and the distillate analysed. The two difficulties with nitric acid were its corrosive action and its liability to decomposition (colouring).

A special apparatus was devised for the measurements.

Experimental.

For purposes of our own work the pressures at 20° only were necessary, From these, calculated pressures for the other temperatures were derived. and a table constructed with a range of 0-20° and 50-100 % nitric acid. A few experiments at 0° were carried out to compare the results with the values calculated for that temperature.

[1] *Ind. Eng. Chem.*, 1925, 17, 633.
[2] *Monatshefte*, 1929, 53-54, 1042.
[3] *Z. anorg. Chem.*, 1930, 194, 59.

Material.—The nitric acid was prepared from 70 % A.R. HNO_3 by distillation with H_2SO_4 under reduced pressure. An all-glass apparatus, as shown in Fig. 1, was used and the one stopcock was moistened with phosphoric acid lubricant. The ground-joint was sealed with H_2SO_4. Distillations were conducted at room temperature and the vapour condensed at $-80°$; in this way a colourless acid was obtained, the strength of which was estimated by titration. Several distillations were necessary to reach 100 % nitric acid. In the last distillation H_2SO_4 was omitted in case slight splashing occurred, but in any event the acid was tested for sulphates. The nitrous acid content was practically nil.

Analysis.—When higher concentrations of acid were analysed some acid was introduced into a bulb by warming and then cooling it. After sealing off, the bulb was weighed and then broken under water and the solution titrated with methyl orange as indicator.

With concentrations of 99·5-100 % the titration method is not likely to be as sensitive as could be desired. The density was therefore determined. Now the density cannot well be used as an absolute measure of

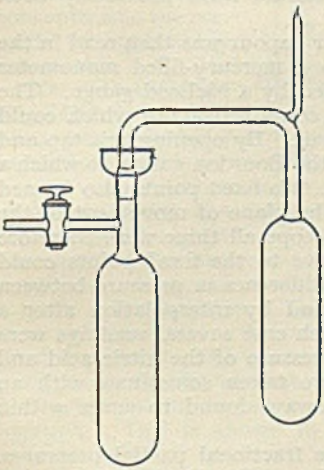

FIG. 1.

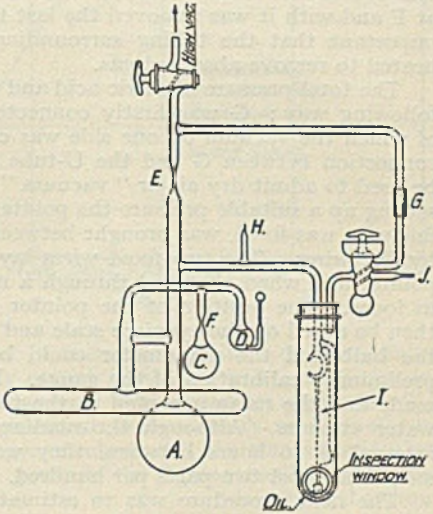

FIG. 2.

the purity, but if the curve connecting this quantity with the concentration (by titration) is drawn for a range of compositions the density forms a useful check on the concentration of any one acid. The average of all the titrations is, however, in effect the absolute standard.

Apparatus.—The apparatus is illustrated diagrammatically in Fig. 2. It embodied a Bourdon spoon gauge of the usual type which could be read to 0·10 mm. The remainder of the diagram explains itself.

Procedure.

About 100 c.c. of acid of requisite strength was placed in A and frozen by means of solid CO_2 in acetone. The apparatus was then evacuated. The gauge and the tube were connected during the evacuation because the gauge would fracture with any pressure difference higher than about 10 cm. of Hg between the two sides, but when the vacuum was more complete it was shut off.

The dissolved air present in the acid was withdrawn by repeated freezing and melting until a good vacuum was registered by a McLeod gauge, when the acid was frozen. It was also helpful to distil some acid

into B and back again. The apparatus was then ready to seal off at E. As a preliminary step the glass around the seals E and F was heated to drive off gas absorbed on it. After the pump had dealt with this the seal was made at E, the flexible rubber joint G allowing the necessary movement. G was detached and the apparatus could be removed to a thermostat. Firstly, however, the acid was poured over into B by tilting. (The oil used in I to steady the pointer is of such viscosity that it does not flow easily.)

The apparatus throughout the experiment was clamped to an iron rod which ran at right angles to the plane of the sketch and when in the thermostat was used as an axle about which to rock the tube so that the acid could be well mixed. A and B were in the thermostat while C, D and I hung over the front. No distillation into C, D or I took place, since the room temperature was higher than that of the thermostat (20° C.) in which a cooling-coil was fitted. In two instances when this may not have been true the results, although given, have been ignored. Arranged in this way, the apparatus was rocked for some time and then the bulb C was cooled and about 1 c.c. of acid collected. This bulb was sealed off at F and with it was removed the last trace of air or other gases. It was important that the tubing surrounding F should have previously been heated to remove absorbed gas.

The total pressure of nitric acid and water vapour was then read in the following way: G was firstly connected to a mercury-filled manometer of which the vacuum on one side was checked by a McLeod gauge. The connection between G and the U-tube also contained a tap which could be used to admit dry air or "vacuum" at will. By opening this tap and setting up a suitable pressure the pointer of the Bourdon gauge, to which a fine wire was fixed, was brought between the two fixed points also formed by fine wires. The two fixed wires lay in the plane of movement of the pointer and when observed through a microscope all three were therefore in focus. The position of the pointer relative to the fixed points could then be noted on the eyepiece scale and the difference in pressure between the bulb and the manometer could be found by interpolation after a preliminary calibration of the gauge. In each case several readings were made and the mean accepted as the total pressure of the nitric acid and water vapours. Although the readings were taken sometimes with an interval of 16 hours between, they were always found to agree within one, or at most two parts per hundred.

The next procedure was to estimate the fractional partial pressures. Some of the mixed vapours were condensed by cooling D while the apparatus was shaking. About 1-2 c.c. of liquid was condensed over a period of ½-1 hour and the degree of cooling just necessary for this was applied. When the required amount of acid had collected H was scratched with a glass-knife and connected to J by a rubber connection containing a T-piece with a tap. After connecting up and opening J the tip of H was broken off inside the connection, and air allowed to enter. The distillate was forced up into the small tube attached to D.

The small bulb, really a miniature Regnault bottle, had been standardised with water to the constriction before sealing on and the density of the acid was determined in it. The bulb was afterwards broken under water and the acid titrated. The weight of the empty bulb was obtained from the fragments of glass collected in a fused glass filter. The weighings of these small objects were all carried out on an assay balance to 0·1 mg.

Composition as shown by Density and Titration.

Mellor[4] quotes statements to the effect that 100 % nitric acid is unstable above − 40°. Our experience is in accordance with this. The acid,

[4] *Treatise on Inorganic and Theoretical Chemistry*, vol. 8.

however, could be kept for about a day at 0° and took an hour or two to develop more than a faint colouration at 20°. Below 99·5 % the decomposition is slower and 70 % acid is fairly stable if kept in the dark, preferably in full bottles. Probably the decomposition, as Veley and Manley suggested, takes place more readily in the vapour state. The nitrogen peroxide formed is very soluble in concentrated nitric acid and it was found better to concentrate colourless 70 % acid in several distillations at low temperature than to attempt to decolourise and use the plant 96 % acid. In our experience, to decolourise acid satisfactorily by blowing air through it the strength must be 88 % or less, for at such concentration the peroxide is appreciably less soluble.

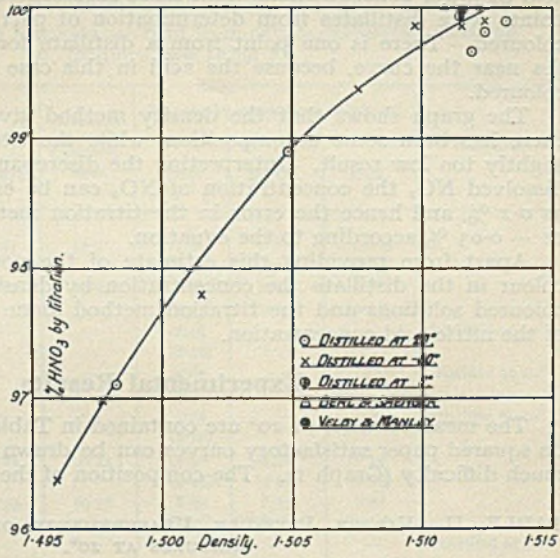

FIG. 3.

The distillates from the more concentrated acids being vapourised at 20° were invariably more or less coloured, the colouration being at the most about the same as that of N./1000 iodine solution. The effect of this decomposition on the results must be considered. As previously stated, the density was measured in the first place to check results by titration. With distillates above 99·5 %, however, it was found that the concentration by density read from our own density-titration curve no longer checked with the concentration by titration. This is shown in Fig. 3 where the figures available for the density of the more concentrated solutions of nitric acid are compared with the concentration by titration.

TABLE I.—ESTIMATED ERROR IN ANALYSIS DUE TO DECOMPOSITION OF NITRIC ACID IN DISTILLATES. ·5 % NO_2 FORMED.

	No decomposition.	Decomposition according to	
		Equation (*a*).	Equation (*b*).
Titration . .	97·33	97·29	97·40
Density . .	97·33	97·81	97·93

Suppose that the decomposition occurred according to equation (*a*) $2HNO_3 = H_2O + NO + NO_2 + O_2$, or (*b*) $4HNO_3 = 4NO_2 + 2H_2O + O_2$, and that it occurred during the distillation so that the total pressure reading was unaffected.

Then using the figures of Klemenc and Rupp [3] for the densities of mixtures of pure nitric acid with nitrogen peroxide, calculations could be made of the effect of decomposition on the titration and density. If 0·5 % by weight of peroxide were formed in a distillate by decomposition and this was not allowed for in the analytical calculations, the two methods

of estimation would give different results. Table I shows the figures which titration and density determinations would give and the results, if there were no decomposition, for the distillate from 81·2 % acid.

Of the points in Fig. 3 which lie above 99·5 %, those marked by "X," and representing values obtained directly from a supply of acid distilled at — 80°, are closer to the extrapolation of the curve obtained for pure acid at lower concentrations than those represented by "O." The latter points were distillates from determination of partial pressures and were coloured. There is one point from a distillate formed at 0° and it also lies near the curve, because the acid in this case also was only slightly coloured.

The graph shows that the density method gives a high result when there has been some decomposition, while the titration method gives a slightly too low result. Interpreting the discrepancy of 0·2 % as due to dissolved NO_2 the concentration of NO_2 can be estimated from Table I as 0·2 %, and hence the error in the titration method is only — 0·02 % or — 0·03 % according to the equation.

Apart from providing this estimate of the possible error caused by colour in the distillate the concentration by density was not used with coloured solutions and the titration method alone provided the measure of the nitric acid concentration.

Experimental Results.

The measurements at 20° are contained in Table II, and when plotted on squared paper satisfactory curves can be drawn through them without much difficulty (Graph 1). The composition of the original acid was used

TABLE II.—Vapour Pressure Measurements of Nitric Acid-Water Mixtures at 20°.

Composition by Weight.			Distillate Molecular Compositions.	Vapour Pressure (mm. Mercury).			Remarks.
Original Nitric Acid %.	Residual Nitric Acid %.	Distilled Nitric Acid %.		Total.	HNO_3.	H_2O.	
49·80	50·05	13·88	4·40	8·1	0·355	7·75	
—	59·53	40·70	16·40	7·7	—	—	Contained air
60·00	60·24	40·91	16·51	5·8	0·95	4·85	
69·64	69·60	77·76	49·96	5·8	2·90	2·90	
—	69·68	77·54	49·65	5·8	2·88	2·92	
69·80	—	—	—	5·95	—	—	Distilled at 0°
76·62	—	92·48	77·84	8·82	6·87	1·95	
78·80	78·50	94·59	83·34	11·5	9·58	1·92	
79·60	—	97·10	90·55	10·81	9·79	1·02	Fractionation *
81·60	—	97·51	91·80	13·6	12·49	1·11	
82·02	81·82	98·36	94·47	13·9	13·13	0·77	Fractionation *
86·13	—	98·90	96·25	19·05	18·34	0·71	
89·85	89·58	99·45	98·07	26·2	25·70	0·50	
91·45	—	99·66	98·80	29·55	29·11	0·35	
91·81	91·10	99·65	98·77	30·3	29·94	0·37	
94·49	—	99·81	99·33	36·32	36·08	0·24	
96·58	96·37	99·92	99·73	41·7	41·59	0·11	
97·43	97·00	99·75	99·17	41·7	—	—	Not reliable
99·78	99·75	—	—	47·8	—	—	
99·90	99·90	—	—	47·9	—	—	
99·80	—	—	—	47·8	—	—	

* These were done during cold weather and it is suspected that the room temperature may have fallen below 20°.

in plotting the results, since the change of composition was small. The experiments which were carried out at 0° are shown in Table III where the pressures given in brackets are calculated, in the manner shown later, from Graph 1.

TABLE III.—VAPOUR PRESSURE MEASUREMENTS OF NITRIC ACID-WATER MIXTURES AT 0°.

Vapour pressures in brackets are read from curves calculated from the 20° readings (see Table V).

Composition by Weight.			Distillate Molecular Composition.	Vapour Pressure (mm. Mercury).			Remarks.
Original Acid.	Residual Acid.	Distillate		Total.	HNO_3.	H_2O.	
69·80	—	79·27	52·21	1·60 (1·39)	0·835 (0·74)	0·765 (0·65)	
69·90	69·39	80·19	53·65	1·55 (1·37)	0·83 (0·74)	0·72 (0·63)	
76·62	—	—	—	2·42 (2·30)	—	—	Distilled at 20°
79·60	—	—	—	2·60 (3·04)	—	—	Distilled at 20°
81·60	—	—	—	3·70 (3·70)	—	—	Distilled at 20°
83·44	—	98·74	98·74	4·50 (4·49)	4·31 (4·30)	0·19 (0·19)	
91·45	—	99·93	99·76	8·39 (8·76)	8·37 (8·70)	0·02 (0·06)	
99·80	—	—	—	14·5	—	—	Distilled at 20°

Calculation of Vapour Pressures at other Temperatures.

The vapour pressures were required over a range of 0-20°. The values at other temperatures than 20° can be calculated by using Kirchhoff's equation—

$$\frac{dQ}{dN} = -2{\cdot}30\, RT^2 \frac{d}{dT}\left(\log \frac{P_0}{P}\right),$$

where $\frac{dQ}{dN}$ is the differential heat of mixing per mol. of a component.

P_0 = the vapour pressure of a pure component at $T°$ and
P = the partial pressure of the component in the mixture at $T°$.

For the temperature difference — 20° to 0° it will be sufficient to take

$$\frac{dQ}{dN} = \frac{-2{\cdot}30 \times 2 \times (283)^2}{20}\left\{\log\left(\frac{P_0}{P}\right)20° - \log\left(\frac{P_0}{P}\right)0°\right\}.$$

Of the terms contained in Kirchhoff's equation the values of P_0 (nitric acid) were calculated according to the equation

$$\log P = A - \frac{L}{2{\cdot}30RT}$$

where L = latent heat of nitric acid, R = gas constant, A = an unknown constant, T = absolute temperature, P = vapour pressure at temperature T.

The constant A and the latent heat were calculated from the measured vapour pressures of 100 % nitric acid at 0° and 20° and the intermediate

pressures at 5°, 10° and 15° could be calculated from them. The latent heat from the vapour pressure measurements, using the approximate formula above, was 9450 cal. per mol. while Berthelot's value (the only one in the literature) is 7250 cal. In view of this disagreement the latent

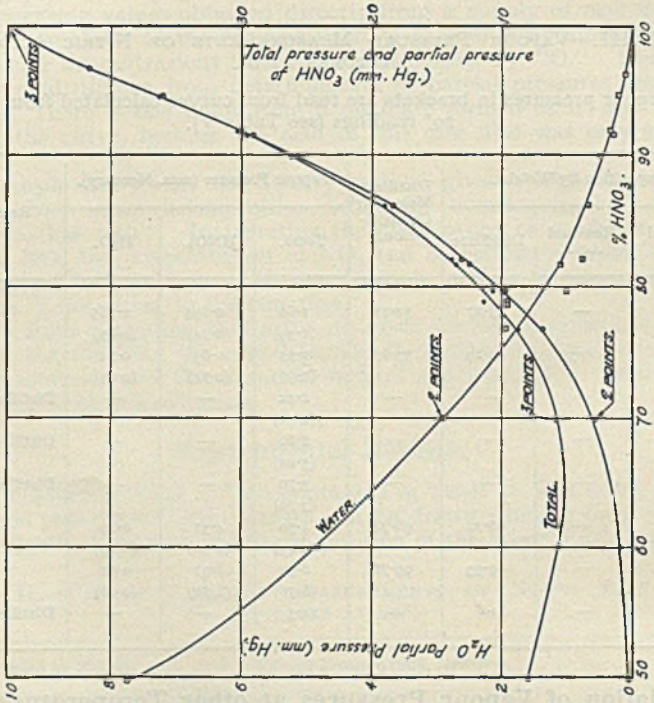

FIG. 4.—Partial pressures of aqueous nitric acid at 20° C.

heat of nitric acid was redetermined by a method which it is hoped to describe in full in connection with similar work in sulphur trioxide and oleum. Electrical heating was used in such a way that the rates of supply or electrical energy and of vaporisation could be balanced, so that the distillation was isothermal and the transference of heat between the distillation bulb and the calorimeter was almost negligible. The heat of vaporisation of nitric acid (99·91 %) at 20° was thus found to be 9415, and 9436 cal./g. mol. in two determinations, in good agreement with the figure obtained from the vapour pressure curves.

TABLE IV.—HEAT OF ADDITION OF 1 MOL. OF NITRIC ACID OR WATER TO A LARGE QUANTITY OF ACID OF THE STATED COMPOSITION AT 20°.

Composition % Nitric Acid.	Nitric Acid Cals. Per Mol.	Water Cals. Per Mol.
90	160	3140
80	860	2365
70	1760	1550
60	2680	750
50	3670	100(?)

The values for P_0 (water) are accurately known.

The differential heats of solution of nitric acid and water in nitric acids of various strengths had been determined in the course of other work which will be reported later. They are given in Table IV. The one result which is questioned is obtained by a rather hazardous extrapolation, but the heat is known to be small and the effect on the vapour pressure will be unimportant.

In this way, all the other terms of Kirchhoff's equation, P_0 (or P_5, P_{10}, P_{15}) can be calculated. Table V shows the values of the partial

TABLE V.—PARTIAL VAPOUR PRESSURES OF NITRIC ACID-WATER MIXTURES.

Temperature.	Constituent.	Composition of Acid (by Weight).					
		50 %.	60 %.	70 %.	80 %.	90 %.	100 %.
0°	Water	1·97	1·19	0·617	0·266	0·083	—
	Nitric acid } mm. Hg	0·095	0·195	0·76	2·89	7·81	14·7
	Total	2·06	1·39	1·38	3·16	7·89	14·7
5°	Water	2·80	1·73	0·92	0·409	0·132	—
	Nitric acid } mm. Hg	0·146	0·292	1·10	4·07	10·74	20·1
	Total	2·95	2·02	2·02	4·48	10·87	20·1
10°	Water	3·95	2·49	1·36	0·619	0·203	—
	Nitric acid } mm. Hg	0·222	0·428	1·57	5·63	14·56	27·1
	Total	4·17	2·92	2·93	6·25	14·76	27·1
15°	Water	5·48	3·52	1·97	0·92	0·309	—
	Nitric acid } mm. Hg	0·332	0·62	2·20	7·72	19·54	36·2
	Total	5·81	4·14	4·17	8·64	19·85	36·2
20°	Water	7·53	4·93	2·83	1·35	0·46	—
	Nitric acid } mm. Hg	0·49	0·89	3·08	10·49	26·03	48·0
	Total	8·02	5·82	5·91	11·84	26·49	48·0

pressures of nitric acid and water at 20° taken from the smoothed curve, and the values at 0°, 5°, 10° and 15° calculated from them as described above. The agreement of the observed readings at 0° and the calculated ones is satisfactory (see Table III) and reassures us that no appreciable error is introduced by the approximations of the Kirchhoff equation.

The difference between the new measurements and the older ones is quite considerable. Thus the distillates from 60, 70, 80 and 90 % nitric acid according to the older results have the respective compositions 34, 71·9, 92·1 and 98·95 %, while according to the new ones they are 38·9, 79·1, 96·5 and 99·5 %. This is no doubt due to the scarcity of experimental results for compositions above 70 % at the time when the older tables were constructed, which necessitated the use of extrapolation.

Summary.

The partial vapour pressures of nitric acid and water over nitric acid-water mixtures have been determined in a special apparatus over the range of compositions from 50 % to 100 % nitric acid, at 20° and 0°. The values at intermediate temperatures have been calculated from these. The heats of dilution of nitric acid (50-100 %) have been determined and a new value (much higher than the only available one due to Berthelot) has been obtained for the heat of vaporisation of pure nitric acid.

Our thanks are due to Messrs. Imperial Chemical Industries for permission to publish this paper.

The Nobel Laboratories,
Ardeer.

STUDIES IN ELECTRODE POLARISATION. PART II. THE INVESTIGATION OF THE RATE OF GROWTH OF POLARISATION POTENTIALS.

By A. Hickling.

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In recent years considerable interest has centred around the rate at which polarisation potentials are built up, particularly in connection with the problem of hydrogen overvoltage. The usual method of studying these changes has been to carry out polarisation at a constant current and to apply the voltage between the working electrode and a reference electrode, either with or without valve amplification, to some form of string galvanometer, the movement of which is photographed on a film moving at a constant speed. After suitable calibration, measurement of the track produced permits the construction of a graph of the polarisation potential plotted against the quantity of electricity passed.[1] This method, while capable of considerable accuracy, is attended by a number of difficulties which may be briefly summarised :

(*a*) Only minute polarising currents can be used, since at high speeds the inertia of the mechanical oscillograph becomes appreciable and causes distortion of the track.

(*b*) Rigorous precautions are necessary to remove all traces of depolarisers from the electrolytic cell, *e.g.* oxygen in studying hydrogen overvoltage, since these may change markedly the shape of the track obtained.[2]

(*c*) Since a single polarisation process only is studied in each experiment, it is necessary initially to have the electrode in a reproducible virgin state if the result is to have any general significance.

(*d*) The quantity of electricity passed is not directly recorded, and any fluctuation in the polarising current or the speed of the camera film will lead to an error in computing this quantity.

(*e*) The method is extremely laborious and time consuming, and requires a considerable quantity of rigidly mounted mechanical apparatus. Moreover, the required graph can only be obtained by measurement and calculation subsequent to each experiment, and direct visual observation of the building up of the polarisation potential is precluded.

The present method was devised to eliminate these difficulties. It utilises a cathode ray oscillograph as indicating instrument,[3] and by a

[1] Bowden and Rideal, *Proc. Roy. Soc. A*, 1928, **120**, 59 ; Baars, *Sitzungsber. Ges. Beförd. Naturw. Marburg*, 1928, **63**, 213 ; Brandes, *Z. physikal. Chem.*, 1929, **142**, 97 ; Erdey-Grúz and Volmer, *ibid.*, 1930, **150**, 203 ; Erdey-Grúz and Kromrey, *ibid.*, 1931, **157**, 213. For early work on the oscillographic study of polarisation processes, see Le Blanc, *Abhdlg. d. Buns.-Ges.*, 1910, No. 3 ; Reichinstein, *Z. Elektrochem.*, 1909, **15**, 734, 913 ; 1910, **16**, 916.

[2] *Cf.* Bowden and Rideal, *loc. cit.*[1]

[3] Butler and Pearson, *Trans. Faraday Soc.*, 1938, **34**, 1163, made use of a cathode ray oscillograph as indicating instrument for the study of the growth of polarisation potentials at high currents. Their method is fundamentally different from that to be described here, however, and in any general application is still open to most of the disadvantages listed ; moreover, it involves the photography of high speed transients.

special electrical circuit, free from moving parts, it is arranged that the polarisation process is repetitive, leading to a stationary image on the oscillograph screen showing directly the variation of polarisation potential with quantity of electricity passed. The presence of small quantities of depolarisers has no effect on the shape or slope of the section of the graph portrayed, but affects only its extent; furthermore, since the pattern obtained is the mean of a number of polarisations, it is largely independent of the initial state of the electrode. Direct visual examination of the effect of variable factors on the polarisation process is possible, and the results may be photographically recorded at leisure.

Experimental.

In the present method the polarising current is supplied from a high voltage direct current source, transmitted through a saturated diode which serves to maintain it substantially constant, and then passed into a condenser which is connected in series with the electrolytic cell. Connected across the condenser-cell section of the circuit is a thyratron valve, the trip voltage of which can be controlled by varying the grid potential. While the condenser is being charged, a steady current, which can be adjusted to any desired value, flows through the electrolytic cell, but when the condenser voltage reaches that required to trip the thyratron, the arrangement is short circuited and the condenser discharges, a quantity of electricity exactly equal to that originally passed flowing rapidly through the cell in the reverse direction; the process then repeats itself indefinitely. The voltage between the electrode of the cell which is being studied and a suitable reference electrode is amplified by means of a valve amplifier, and applied to the Y-deflecting plates of a cathode ray tube, while the voltage developed across the condenser (which is exactly proportional to the quantity of electricity passed at any time) is applied directly to the X-deflecting plates of the tube. Under these conditions, the track on the oscillograph screen represents directly the variation of potential of the working electrode with the quantity of electricity passed through the cell, and if the process is reproducible the track appears stationary. The occurrence of a stationary image implies that exactly the same change of potential is brought about on charging the electrode as on discharging it, *i.e.* that there is no irreversible loss of electromotively active material from the electrode. If the electrode is polarised and the pulsating current then switched on, the oscillograph track is usually found at first to move downwards, but in a few seconds becomes stationary; thus automatically only the reproducible portion of the polarisation curve is recorded. The presence of a depolariser which reacts irreversibly with the electromotively active material at the electrode, lowers the maximum polarisation potential which is recorded but cannot affect the shape or slope of that section of the polarisation curve which is portrayed, provided, of course, that the depolariser is not present in such large quantities as to prevent entirely the formation of a stationary image.

In this way the method serves to isolate that part of the polarisation curve which is unaffected by loss of electromotively active material and by accidental variation in the state of the electrode, and the results may therefore be presumed to be indicative of the true course of the polarisation process. The quantity of electricity passed at each pulse can be varied by changing the size of the series condenser, and hence any section, large or small, of the polarisation curve can be studied in detail.

The electrical circuit of the apparatus, constructed for the study of cathodic polarisation processes, is shown in Fig. 1. Current was supplied from an 800 V. rectifier, passed through a milliammeter and bright emitter valve V_1, the latter serving as a saturated diode, the current being adjustable by varying the filament current by means of the rheostat R_1, and then

passed into a condenser C connected in series with the electrolytic cell. The value of C was varied according to the quantity of electricity it was desired to pass in each pulse. Connected across the condenser and cell was the thyratron circuit which included a resistance R_2 of 125 ohms to

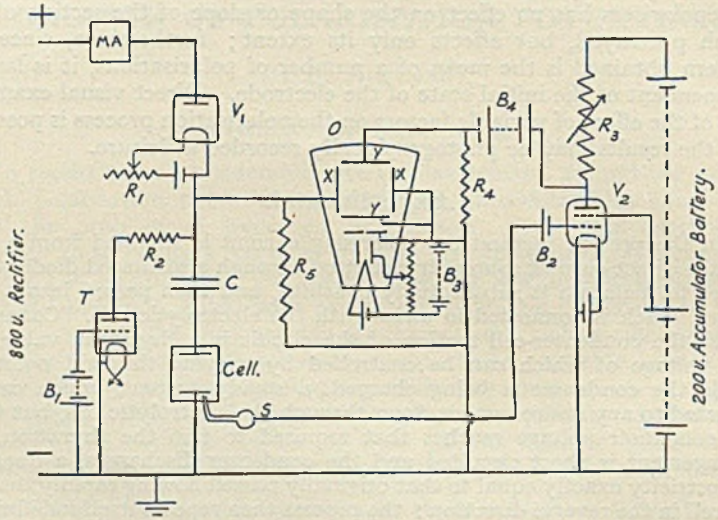

FIG. 1.

limit the discharge current. The thyratron T was an Osram GT1A, the heater being driven from a 4 V. transformer; by means of a grid bias battery B_1 the flashing over voltage of the thyratron was adjusted to approximately 60 V., this giving a convenient sweep on the oscillograph screen. The voltage developed between the cathode of the cell and a saturated calomel electrode S was applied between the grid and cathode of a screen grid valve V_2, the grid of which was kept negative under all conditions by means of a small biassing battery B_2. V_2 was an accumulator heated Triotron valve S213. Anode current was supplied to it from a 200 V. accumulator battery through a variable resistance R_3 of 125,000 Ω, the screen being maintained at a potential of 65 V. The amplification could be varied by adjustment of R_3 and had a maximum value of about 60. The cathode ray oscillograph tube O was a low voltage gas-focussed tube (Standard Telephone and Cables, 4050 BB) with a sensitivity of approximately 0·17 cm./V. Anode current was supplied to it from a 360 V. dry battery B_3. One of each pair of deflecting plates was connected to the anode which was earthed through the main negative lead of the circuit. The remaining X-plate was connected to the positive side of the condenser C, while the Y-plate was connected to the anode of V_2 through a backing battery B_4 which served to adjust the steady voltage on the plate. R_4 and R_5 were leakage resistances of 4 MΩ connected between each pair of deflecting plates. By switching arrangements not shown in the figure, it was arranged that a potentiometer-voltmeter could be connected to the

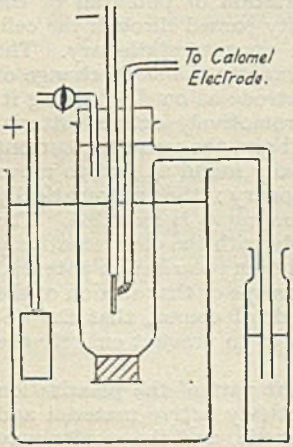

FIG. 2.

amplifier so as to give suitable reference lines at fractions of a volt on the oscillograph screen.

The form of the electrolytic cell is shown in Fig. 2. The anolyte was contained in a tall beaker and in it was immersed the cathode chamber which was stopped at its lower end with a tight filter paper plug to prevent mixing of anolyte and catholyte. The cathode compartment was fitted with a rubber bung carrying the cathode, the siphon connecting the cathode to the calomel electrode, and a glass tap for introduction of gas; a side tube led to a washbottle containing water. The anode was in general a piece of platinum foil, and the cathode was varied as described below.

Results.

Hydrogen Overvoltage.—In order to test the application of the method, the building up of hydrogen overvoltage was studied, since in this case the general nature of the process has been established by earlier workers.

A freshly amalgamated copper cathode, of 1 sq. cm. area, was used with N.-sulphuric acid as electrolyte. The acid solution was boiled out to get rid of dissolved air prior to introduction into the cell, and then steady electrolysis at 0·025 amp. was carried out for ten hours to displace the bulk of air in the cathode chamber and to polarise the electrode. The direct current was then stopped, the pulsating current switched on, and observations of the oscillograph tracks recorded under various conditions. The results are shown in Fig. 3 (Plate V). In Fig. 3A is shown the polarisation graph with a 0·05 μF. condenser in series with the cell and polarising currents of 10^{-3} and 10^{-4} amp./sq. cm. respectively; the reference potentials in this, and in all subsequent cases, are expressed on the hydrogen scale. It is to be noted that the potential varies linearly with the quantity of electricity passed, and is practically independent of current density. To explore a larger section of the polarisation curve, the capacity of the series condenser was increased to 0·1 μF. and the tracks again recorded. The results are shown in Fig. 3B and it is seen that the linearity of the polarisation process is maintained. The quantity of electricity delivered at each pulse can readily be worked out from a knowledge of the capacity of the series condenser and the voltage to which it is charged; this latter quantity is directly determined by comparing the horizontal deflection on the oscillograph with that produced by standard voltages. Hence the capacity of the double layer at the electrode, which is supposed to be involved in the building up of the hydrogen overvoltage, can be evaluated. Measurement of Figs. 3A and 3B give a value of 10-11 μF./sq. cm. Bowden and Rideal [2] obtained a value of 6 μF. for mercury and 7 μF. for freshly amalgamated silver under somewhat different conditions, while indirect measurements of the capacity by various methods give a value of ca. 20 μF. at a mercury surface.[4] It has been suggested [4] that the low values obtained by the direct methods of investigation are due to contamination of the surface studied, and this factor may be operative in the present experiments; it should be noted, however, that the same value was obtained in numerous experiments under a variety of conditions.

As has been previously stated, the shape and slope of the polarisation graph, as determined by the present method, should be independent of the presence of small quantities of air in the apparatus. To test this point, the value of the capacity of the series condenser was reduced to approximately 0·02 μF., so that a small section only of the graph was explored, and after the electrode had been polarised as above, air was slowly admitted to the cell; the current density was 10^{-4} amp./sq. cm. The track on the oscillograph screen moved slowly downwards, indicating

[4] See Proskurnin and Frumkin, *Trans. Faraday Soc.*, 1935, 31, 110.

decreasing polarisation, and three successive photographs were taken. These are reproduced in Fig. 3c. It is seen that although the maximum overvoltage obtained is different in each of the three cases, the linearity and slope of the graph is not appreciably affected by the presence of air.

Polarisation in the Deposition of Nickel.—Electrodeposition of Fe, Co, and Ni from solutions of their simple salts does not commence until the cathode potential is distinctly more negative than the reversible values.[5] This type of polarisation, which is apparently peculiar to these metals, is most markedly shown by Ni; thus, according to Glasstone,[6] the reversible potential of Ni in a N.-sulphate solution is — 0·23 V., but on electrolysis at room temperature deposition of metal does not commence until a cathode potential of about — 0·57 V. is reached. Foerster and Georgi[7] claim to have observed Ni deposition from a chloride solution at a cathode potential of — 0·40 V. at 18°, but it is doubtful whether it takes place much closer to the reversible potential even at very low current densities. Numerous suggestions have been made to account for this type of overvoltage,[8] and they fall generally into two classes: on the one hand, it has been postulated that the metal is deposited in some peculiarly active form which has a more negative potential than that of the metal in the normal stable state, while on the other hand, it has been suggested that the process of ionic discharge is slow and requires a certain energy of activation, *i.e.* a view essentially similar to that now adopted for the neutralisation of hydrogen ions. The present method would seem to afford a means of distinguishing between these two general views. If the overvoltage is due to some active form of Ni, then it is to be expected that in the initial building up of the polarisation the potential will either vary discontinuously with the quantity of electricity passed or else logarithmically if the active substance forms a solid solution in the cathode surface, while if the process of ionic discharge is slow, leading to the charging up of a double layer at the cathode surface, a linear variation of potential with quantity of electricity passed is to be anticipated.

To test this, an electrode of Ni wire of area 1 sq. cm. was used as cathode and solutions of Analar $NiSO_4$ in a buffer mixture of 0·5 N.-sodium acetate + 0·5N.-acetic acid (approx. p_H 4·6) employed as catholyte. The anode was of platinum foil and the anolyte was dilute sulphuric acid. Prior to each observation, the air in the cathode chamber was displaced by a current of hydrogen; steady electrolysis was then carried out for two minutes at the current density to be used subsequently, and finally the pulsating current was switched on and the oscillograph track observed. Some of the results obtained are shown in Fig. 4 (Plate V). In Fig. 4A is shown the polarisation graph using a current density of 10^{-3} amp./sq. cm. with a N.-$NiSO_4$ solution, there being a 4μF. condenser in series with the cell. The track on the oscillograph screen was very steady and showed little sign of decay even on admitting oxygen to the cell. It is to be noted that the graph is accurately linear up to a potential of about — 0·4 V., where it begins to round off, the potential then approaching asymptotically a

[5] Schweitzer, *Z. Elektrochem.*, 1909, **15**, 602; Schildbach, *ibid.*, 1910, **16**, 967; Foerster, *Abh. Bunsen-Ges.*, 1909, No. 2; Glasstone, *J.C.S.*, 1926, 2887.

[6] Glasstone, *loc. cit.*[5]

[7] Foerster and Georgi, *Z. physikal. Chem., Bodenstein Festband*, 1931, 543.

[8] See, for example, Le Blanc, *Trans. Faraday Soc. Soc.*, 1914, **9**, 251; Foerster, *Z. Elektrochem.*, 1916, **22**, 85; Smits, *Trans. Faraday Soc.*, 1924, **19**, 772; Kohlschütter, *Trans. Amer. Electrochem. Soc.*, 1924, **45**, 229; Glasstone, *loc. cit.*[5]; Thon, *Comptes rendus*, 1933, **197**, 1312.

constant value of rather less than $-0{\cdot}5$ V. The effect of variation of current density is shown in Fig. 4B, which was obtained with currents of 2, 1 and $0{\cdot}5 \times 10^{-3}$ amp. severally, other conditions being as before. The general features of the graphs are the same, but with decreasing current density the slope of the linear portion becomes rather less and the ultimate potential attained is slightly lowered. Decrease of the Ni ion concentration does not affect the general form of the graph, but the slope of the linear portion is increased, as is shown in Fig. 4C, which was obtained with a 0·1N.-$NiSO_4$ solution and a current density of 10^{-3} amp./sq. cm.

The results indicate quite conclusively that the essential process responsible for overvoltage in the deposition of Ni leads to a linear variation of potential with quantity of electricity passed up to the point at which metal commences to separate, and this is in conformity with the view that the polarisation is due to a slowness of ionic discharge leading to the charging up of a double layer at the cathode. The capacity of this double layer can be readily evaluated from the oscillograms, and is found to be 430-470 μF. per sq. cm. for a N.-$NiSO_4$ solution electrolysed at current densities of 2×10^{-3} to $0{\cdot}5 \times 10^{-3}$ amp./sq. cm. The precise physical significance of a double layer of so high a capacity cannot be assessed without accurate data on the accessible area of nickel under the conditions of experiment.

Summary.

1. A new method of studying the rate of growth of polarisation potentials is described which gives a stationary image on the screen of a cathode ray oscillograph showing directly the variation of potential with quantity of electricity passed.

2. The method has been tested by applying it to the study of the growth of hydrogen overvoltage at a mercury surface, and results in general conformity with those of previous workers have been obtained.

3. The growth of overvoltage in the deposition of nickel has been studied, and it is found that the potential varies linearly with quantity of electricity passed, up to the point at which separation of metal begins. The results support the view that this type of polarisation is due to slowness of the discharge of the metallic ions.

The author's best thanks are due to Mr. J. H. Bruce for many helpful suggestions.

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SYSTEMATICS OF BAND-SPECTRAL CONSTANTS. PART V.* INTERRELATION OF DISSOCIATION ENERGY AND EQUILIBRIUM INTERNUCLEAR DISTANCE OF DI-ATOMS IN GROUND STATES.

By C. H. Douglas Clark.

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1. Introduction.

Attempts are made in the present communication to find reliable means of calculating the dissociation energies of di-atoms in ground states. In the present incomplete state of the quantum-mechanical developments, the author has confined himself to empirical methods. The argument is necessarily based upon a limited number of experimental values, which appear, however, to be known with considerable certainty. Knowledge of ground state dissociation energies in conjunction with excitation energies may facilitate the calculation of dissociation energies from excited states. The first part of the paper deals with non-hydrides: in section 5 hydrides are considered.

Dissociation energy D is expressed in volts, no distinction being made between D_e and D_0 (from the zero vibrational level).

Expressions for D previously suggested vary according to the form chosen for the potential energy-nuclear distance function.

Morse,[1] using his exponential function, obtained the relation

$$D = 1{\cdot}23 \times 10^{-4}\, \omega_e^2/(4\omega_e x_e), \quad . \quad . \quad . \quad (1)$$

where ω_e, $\omega_e x_e$ are in cm.$^{-1}$. It appears that the estimates of D using this expression tend to be too high where comparison with experiment is possible.

Huggins[2] used a modified Morse potential energy function, and obtained a partly empirical relation which may be written

$$D = 7{\cdot}4 \times 10^{-7} M\omega_e^2/[(33 + 0{\cdot}72 M\omega_e x_e)^{\frac{1}{2}} - 7], \quad . \quad (2)$$

where $M = AA'/(A + A')$, A and A' being the weights of the two atoms concerned (O = 16). This relation tends to give lower and generally more accurate values of D than (1), but it applies only to molecular groups $n = 8$ to 14 in the KK period, where the average error in D is 0·7 volt.

Sutherland[3] has more recently used a potential function involving inverse powers of r, and has deduced a relation which may be written in the form

$$D = 3{\cdot}68 \times 10^{-6} M\omega_e^2 r_e^2/p, \quad . \quad . \quad . \quad (3)$$

where r_e is equilibrium internuclear distance in A, and p is the product of the attraction and repulsion exponents of r in the potential function.

* Parts I, II and III are in these *Transactions*, 1937, 33, 1390, and Part IV, 1938, 34, 1324.

[1] P. M. Morse, *Physic. Rev.*, 1929 (ii), 34, 57.

[2] M. L. Huggins, *J. Chem. Physics*, 1935, 3, 473; 1936, 4, 308.

[3] G. B. B. M. Sutherland, *Proc. Ind. Acad. Sci.*, 1938, 8, 341.

The value of Sutherland's product is approximately the same for di-atoms of similar electron structure in ground states.

The present author, in a preliminary note,[4] has suggested the relation

$$D = k/(r_e^3 n^{\frac{1}{2}}), \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where n is the group number of a non-hydride di-atom, and k is its period or sub-period dissociation constant. This relation also applies only to ground states.

Comparing (4) with the Morse-Clark formula (see Part IV), it appears that proportionality between ω_e and D is involved. If we calculate D from the relation $D = \omega_e/313$, however, an average error of 1·7 per cent. is found for the test cases LiLi, NN and OO, whereas (4) gives only 0·4 per cent. The constant in the Morse-Clark formula is slightly different for LiLi (*ss* type) from that for NN and OO (*pp* type), so that constancy of ω_e/D will not be exact. Moreover, the Morse-Clark constant takes a different value for di-atom ions in a given period. Out of a considerable variety of relations which have been tried, (4) appears to be the best, and it is also in conformity with the previous finding that Dr_e^3 is constant for carbon-carbon linkages.[5, 6]

2. Symmetrical (Elementary) Di-atoms of the KK Period.

Table I shows the results of calculation on three elementary di-atoms of the KK period, whose D values appear to be accurately determined.

TABLE I.

Di-atom.	n.	M.	r_e.	ω_e.	$\omega_e x_e$.	D (expt.).	ω_e/D.	Calculated Values. D(1).	D(2).	p(3).	k(4).	D(4).
LiLi .	2	3·5	2·670	351·4	5·18	1·14	308	0·7	—	9·9	**30·7**	1·14
NN .	10	7	1·094	2359·6	14·44	**7·35**	321	11·9	8·7	23·4	**30·4**	**7·39**
OO .	12	8	1·204	1580·3	11·99	**5·09**	311	6·4	4·8	20·9	**30·8**	**5·06**

D calculated by (1) does not give satisfactory agreement with experiment, whilst D(2) is closer for NN and OO. Sutherland's p separates the cases, p(LiLi) being different, whilst p(NN) > p(OO). The function $k = Dr_e^3 n^{\frac{1}{2}}$ is sensibly constant, giving mean $k = 30·6$, which therefore gives very good values of D(4).

Fox and Martin [6] find $p = 20·7$ for CC links, close to p(OO) = 20·9. Table II shows calculated values of D for FF and CC, assuming p(FF) = 20·7.

TABLE II.

Di-atom.	n.	M.	r_e.	ω_e.	$\omega_e x_e$.	k.	Calculated Values. D(1).	D(3).	D(4).
CC . .	8	6	1·31	1641·6	—	30·6	—	4·9	4·8
FF . .	14	9·5	1·33[7]	1081[8]	9·9	30·6	3·6	**3·5**	**3·5**

[4] C. H. D. Clark, *Nature*, 1939, **144**, 285.
[5] *Ibid.*, **143**, 800.
[6] J. J. Fox and A. E. Martin, *J. Chem. Soc.*, 1939, 884.
[7] C. H. D. Clark, *Nature*, 1934, **99**, 134.
[8] C. H. D. Clark, *Trans. Faraday Soc.*, 1935, **31**, 585.

The agreement between $D(3)$ and $D(4)$ is satisfactory in the two cases. The mean value $D(\mathrm{CC}) = 4{\cdot}85$ is lower than Mulliken's estimate,[9] 5·5, which is uncertain. $D(\mathrm{FF}) = 3{\cdot}5$ agrees fairly well with Desai's thermal value,[10] $3{\cdot}3 \pm 0{\cdot}1$. The higher figure is supported by the value from Morse's equation $D(1) = 3{\cdot}6$. Morse's equation gives a good fit for ClCl, but gives errors increasing from BrBr to II, so it may apply to FF.

3. Sutherland's Product as a Periodic Function.

The results of the preceding section suggest that Sutherland's product p, whilst closely alike for di-atoms of similar configuration, varies somewhat for a given configurational type with group number. Amongst the symmetrical di-atoms of KK*pp* type, it would appear that p reaches a maximum for $n = 10$, in common with other spectroscopic functions ω_e and k_e (bond constant).[11] This view appears somewhat strengthened when attention is paid to unsymmetrical KK di-atoms and to KK^+ di-atom ions.

From equations (3) and (4) we have

$$pk = 3{\cdot}68 \times 10^{-6} M\omega_e^2 r_e^5 n^{\frac{1}{2}}, \qquad (5)$$

which, since $k_e \propto M\omega_e^2$, is essentially a function of k_e, r_e and n. Values of pk are: NN 711, CO 692, and CN 667. If $p = 20{\cdot}7$ for CO and CN, $k = 33{\cdot}4$ and $32{\cdot}3$ respectively, values greater than the above KK constant 30·6; but if $p(\mathrm{CO}) = p(\mathrm{NN}) = 23{\cdot}4$, $k(\mathrm{CO}) = 29{\cdot}6$. (The remaining discrepancy may indicate a further variation of p with sub-group, NN being in the 10*s* and CO in the 10*b* sub-group of the classification,[12] but this possible refinement is not at present taken into account). We shall study the effect of a continuous variation of p with n in the KK and KK^+ periods for *pp* type di-atoms, taking $p = 21{\cdot}5$ in groups 9 and 11 on each side of the maximum, and so obtaining the $D(3)$ values of Table III. The values of $D(4)$ are obtained by keeping $k = 30{\cdot}6$ for all cases, and calculated values $D(1)$ and $D(2)$ are included for comparison. $D(\mathrm{J})$ and $D(\mathrm{S})$ refer to estimates quoted by Jevons[13] and Sponer[14] respectively, the values in brackets being generally less reliable.

TABLE III.

Di-atom	BeO	BeF	BO	CO^+	CN	NN^+	CO	NO	OO^+
n	8	9	9	9	9	9	10	11	11
Sub-group	*c*	*c*	*b*	*b*	*a*	*a*	*b*	*a*	*a*
$D(1)$	5·8	5·4	9·3	10·0	10·0	9·3	10·9	7·7	6·6
$D(2)$	4·6	4·7	7·2	7·5	7·6	6·9	8·2	5·7	4·8
$D(3)$	4·0	3·1	**5·7**	**7·1**	**6·5**	**7·2**	**6·5**	**6·1**	**6·3**
$D(4)$	**4·6**	**4·1**	**5·9**	**7·4**	**6·4**	**7·4**	**6·7**	**6·1**	**6·2**
$D(\mathrm{J})$	—	(6·0)	(6·6)	7·1	—	6·8	(10·0)	(6·1)	6·2
$D(\mathrm{S})$	(5·8)	—	—	—	6·7	6·3	(9·6)	5·3	6·4

[9] R. S. Mulliken, *Rev. Mod. Physics*, 1932, **4**, 1.
[10] M. S. Desai, *Proc. Roy. Soc., A*, 1932, **136**, 76.
[11] C. H. D. Clark, *Proc. Leeds Phil. Soc.*, 1935, **3**, 26.
[12] C. H. D. Clark, *Trans. Faraday Soc.*, 1935, **31**, 1017.
[13] W. Jevons, *Report on Band-Spectra of Diatomic Molecules* (*Appendix II.*), 1932, Camb. Univ. Press.
[14] H. Sponer, *Molekülspektren und ihre Anwendung auf chemische Probleme. I. Tabellen*, 1935, Berlin, Julius Springer.

As previously noticed, $D(1)$ tends to give rather too high values, and $D(2)$ is observed to be smaller than $D(1)$. $D(2)$ involves an empirical factor [2] of 0·8, which may not always be suitable, but the results are probably nearer the truth than those of $D(1)$. On the other hand, the generally satisfactory agreement between $D(3)$ and $D(4)$ previously found for CC and FF in this period is maintained. It is noteworthy that BeO and BeF give poor agreement, but since these di-atoms are of *sp* type, it appears that a different value of p should be used in calculating $D(3)$.

Comparing the results with the estimates $D(J)$ and $D(S)$ based upon experimental data, the mean of $D(3)$ and $D(4)$ agrees satisfactorily for CO^+, OO^+ and CN, less well for NN^+ and NO. There is striking divergence in the case of CO, but here the dissociation energy is still uncertain, in spite of extensive discussion of the data.[15] It appears well established that if the dissociation of both CN and CO is into unexcited atoms, $D(CO)$ should be greater than $D(CN)$ by about 3·2 volts. All the four methods of calculation used in compiling Table III, however, agree in making the difference much smaller than this. It may be pointed out that a difference of 3·2 is incompatible with even approximate equality of $p(CN)$ and $p(CO)$. The difficulty might be resolved if CN does not dissociate from the ground state into normal atoms.

Table III further suggests that the periodicity of dissociation energies follows a plan similar to that previously found for fundamental vibration frequencies,[11] with maximum values in group X, and decreasing values with increasing sub-group asymmetry: thus $D(CN) > D(BO) > D(BeF)$ in sub-groups IX*a*, IX*b* and IX*c* respectively. This would suggest $D(CO) < D(NN)$, which has not been so far proved by experiment. Apart from some uncertainty, the agreement between calculated and the most reliable experimental estimates may be judged generally satisfactory. The methods adopted afford considerable systemisation of the data on the related di-atoms of the KK and KK^+ periods, and provide evidence of the suggested periodicity of Sutherland's product.

The above considerations appear largely upheld by similar calculation in the KL and LK periods on *pp* type di-atoms, where we have the experimental result $D(SO) = 5{\cdot}053$. This with $r_e = 1{\cdot}489$ gives $p(3) = 21{\cdot}8$, and $k(4) = 57{\cdot}8$. If we keep k constant and assume a similar periodic variation of p with n to that used in the KK period, we obtain Table IV. We take $p = 24{\cdot}3$ for $n = 10$, $p = 22{\cdot}4$ for $n = 9$ and 11, with the above $p = 21{\cdot}8$ for $n = 12$.

TABLE IV.

Di-atom	AlO	CP	SiN	CS	SiO	PN	PO
Group	9	9	9	10	10	10	11
Sub-group	*b*	*a*	*a*	*b*	*b*	*s*	*a*
$D(3)$	4·1	5·3	5·0	5·1	5·4	5·8	5·5
$D(4)$	4·6	5·1	5·0	5·1	5·4	5·6	5·8

The agreement between $D(3)$ and $D(4)$ is again satisfactory, except in the case of AlO, where perhaps the less symmetrical sub-group 9*b* requires a lower p than 9a. Should the experimental $D(SO)$ be cor-

[15] G. Herzberg, *Chem. Rev.*, 1937, **20**, 145.

rected, this will affect the values of $D(3)$ and $D(4)$, but since ratios only are involved, it would appear that the measure of agreement between them would remain.

The methods of derivation of $D(3)$ and $D(4)$ appear quite independent, and the periodicity of p has not been suggested to cause them to agree, but to conform with the experimental results of Table I. It appears, however, that another relation of the form (5) is involved, connecting bond constant and internuclear distance.[4] Fox and Martin [6] have reached similar conclusions for C—C links, where $k_e r_e^5$ is found to be constant. This matter is receiving further consideration.

4. More Complex Non-hydride Di-atoms.

In Table V we have calculated as many values of $p(3)$ and $k(4)$ as possible from D(expt.) for di-atoms which contain no atom of the K period. The value of D(SS) is either 3·6 or 3·3 according to Olsson,[16, 17] whilst $r_e = 1{\cdot}88$. Other D values are taken from Sponer.[14]

TABLE V.

Di-atom	NaNa	PP	SS		ClCl	KK	BrBr	ICl	II
Period	LL	LL	LL		LL	MM	$\overline{\text{MM}}$	$\overline{\text{NL}}$	$\overline{\text{NN}}$
Group .	2	10s	12s		14	2	14	14	14
Type .	*ss*	*pp*	*pp*		*pp*	*ss*	*pp*	*pp*	*pp*
r_e .	3·07	1·88	1·88		1·983	3·91	2·28	2·315	2·660
D(expt.)	0·76	5·008	3·6	3·3	2·468	0·51	1·961	2·143	1·535
$p(3)$.	13·3	24·6	30·5	33·3	33·2	18·5	40·9	32·0	49·4
$k(4)$.	31·1	105·3	82·9	76·0	72·0	43·1	86·9	99·4	108·1

Table V indicates that for LL and higher periods k, like p, becomes sensitive to configuration type, being different for the *ss* di-atoms NaNa, KK from that for the *pp* cases ClCl, BrBr respectively. Amongst the LL*pp* cases, the $p(3)$ values support $D(\text{SS}) = 3{\cdot}3$ rather than 3·6, and $p(\text{PP}) = 24{\cdot}6$ appears erroneous. Further, $D(\text{SS}) = 3{\cdot}3$ gives $p(3) = 33{\cdot}3$, which agrees with $p(3) = 33{\cdot}2$ for ClCl. Values of $D(4)$ which agree with $k = 72$ are **3·4**, **3·1** for PP, SS respectively. Similarly, taking $k(\text{SeSe}) = k(\text{BrBr}) = 86{\cdot}9$, $r_e(\text{SeSe}) = 2{\cdot}15$,[17] and $k(\text{TeTe}) = k(\text{II}) = 108{\cdot}1$, $r_e(\text{TeTe}) = 2{\cdot}59$,[17] we obtain $D(4)$ equal to **2·5** and **1·8** for SeSe and TeTe respectively. Again, r_e(PP) lies near r_e(SS), so if we may take $r_e(\text{AsAs}) = r_e(\text{SeSe}) = 2{\cdot}15$, with $k = 86{\cdot}9$, we obtain $D(4)$ for AsAs as **2·8**. The D values found here for SeSe and TeTe are about 0·5 volt smaller than earlier uncertain assignments for these cases, whilst the value for AsAs agrees within 0·2 volt with the lower of the two possible values 4·0 and 2·6 found by Almy and Kinzer.[18]

5. Hydride Di-atoms.

It is characteristic of hydride di-atoms XH that the reduced atomic weight $M = A/(A + 1)$, where A is the atomic weight of X, does not

[16] E. Olsson, *Nature*, 1936, **137**, 745.

[17] E. Olsson, *The Band Spectra of Sulphur, Selenium and Tellurium*, 1938, Dissertation, Stockholm.

[18] G. M. Almy and G. D. Kinzer, *Physic. Rev.*, 1935, (ii), **47**, 721.

vary greatly for small changes in A, and approaches unity as A increases, whilst the reduced mass $\mu = 1{\cdot}65M$ approaches the value 1·65.

If we eliminate ω_e between the Morse-Clark formula (see Part IV) and Sutherland's relation (3), we obtain $pDr_e^4n = 3{\cdot}68 \times 10^{-6}MK^2_{qr}$, where K_{qr} is the sub-period constant of the formula. It then follows that for di-atoms whose values of p and M do not differ very greatly

$$D = l/(r_e^4n), \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where l is a sub-period constant. This formula may be expected to hold for hydrides, in place of (4) applicable to non-hydrides.

Isotopic di-atoms have D and r_e closely alike, so we may expect constancy of l in such cases, although M varies. Using Beutler's D values[19] for HH, HD, and DD, it is found that $l = 2{\cdot}7$ fits the three cases, a small increase in D from HH to DD being accompanied by a small decrease in r_e. Equation (4) should also be suitable for isotopic forms of non-hydrides.

We next apply (6) to the KH and LH periods, using the D values selected by Berriman and Clark,[20] based on careful comparison of available spectroscopic and thermal evidence. Some of the numbers may be subject to revision, but serve as a basis for discussion. In Table VI values of $p(3)$ and $l(6)$ are given.

TABLE VI.

Di-atom.	Period.	n.	Type.	D.	μ.	r_e.	$p(3)$.	$l(6)$.
LiH	KH	2	$s\sigma$	2·47	1·453	1·593*	6·6	**31·8**
BeH		3	$p\sigma$	3·22	1·495	1·340	7·8	**31·1**
BH		4		3·45	1·521	1·226	7·4	**31·2**
CH		5	$p\pi$	4·0	1·533	1·12	8·8	**31·5**
NH		6		4·47	1·550	1·041	7·9	**31·5**
OH		7		5·07	1·563	0·974	8·9	**31·9**
FH		8		6·36	1·578	0·915	7·9	**35·7**
NaH	LH	2	$s\sigma$	2·28	1·581	1·88	7·5	57
MgH		3	$p\sigma$	1·40	1·585	1·73	16·9	38
AlH		4		3·12	1·592	1·643	8·7	91
SiH		5	$p\pi$	3·27	1·593	1·53	10·3	90
PH		6		2·74	1·599	1·429	15·1	69
ClH		8		4·40	1·604	1·272	11·8	92

* Value for LiD.

From LiH to FH, D and r_e move in opposite directions, whilst p appears sensitive to structural change, apparently increasing slightly from $s\sigma$ to $p\pi$ types. On the other hand, l is remarkably constant throughout the whole period, except for FH, where perhaps D(FH)=6·36 is too high. The Morse formula (1) gives the following values of D: LiH 2·60, BeH 3·56, OH 5·26, FH 5·52. These numbers run within 0·3 volt of D for LiH, BeH and OH. If we take D(FH) = 5·52, we have $l(6) = 30{\cdot}9$, which is not far from the mean 31·5 of the KH period. If l(FH) = 31·5, we have $D(6) = \mathbf{5{\cdot}62}$, which in turn gives $p(3) = 8{\cdot}9$, in agreement with p(OH). A self-consistent scheme is thus obtained.

In the LH period, although r_e falls continuously from NaH to ClH, D does not move continuously in the opposite direction as in the KH period. This may suggest that some of the D values are wrong, which

[19] H. Beutler, *Z. physik. Chem.*, *B*, 1934, **27**, 287.
[20] R. W. Berriman and C. H. D. Clark, *Proc. Leeds Phil. Soc.*, 1938, **3**, 465.

appears borne out by the general irregularity of $p(3)$. The run of $l(6)$ suggests it to be a sub-period function depending on electron configuration. The l values for AlH, SiH and ClH lie near together, suggesting $l = 91$ for $p\sigma$ and $p\pi$ types in this period, in which case MgH and PH do not fit. If $l = 91$ for MgH, $D(6) = 3{\cdot}4$ and $p(3) = 7$, which fits better than 16·9 into the sequence; similarly, $l = 91$ for PH gives $D(6) = 3{\cdot}64$, $p(3) = 11{\cdot}3$, which lies near $p(\text{ClH}) = 11{\cdot}8$. From NaH to ClH, as from LiH to FH, p appears to increase with increasing n.

Results on the meagre data in higher hydride periods are not recorded in detail, but they tend to confirm the variation of l with electron type in a given period. Further, in the case of the only pair (AgH and CdH^+) of a given type ($\overline{N}Hs\sigma$) for which comparison is possible the l values coincide. In these higher periods, the evidence suggests that p may be periodic, in such a way that a maximum is reached in each period; thus, for example, p shows the following corresponding sequences: CuH 9·5, ZnH 21·7, BrH 13·4; AgH 12·2, CdH 32·6, IH 16·4.

The more certain period dissociation constants k and l are collected in Table VII, which shows that in the KK and KH periods the numbers are independent of sub-period type.

TABLE VII.

	Values of $Dr_e^3n^{\frac{1}{2}} = k$.				Values of $Dr_e^4n = l$.			
Period . .		KK	KL	LL		HH	KH	LH
Sub-period type	ss	30·6	—	31·1	$s\sigma$	2·7	31·5	57
	sp	30·6	—	—	$p\sigma$	—	31·5	91
	pp	30·6	57·8	72·0	$p\pi$	—	31·5	91

The views expressed in this communication may be capable of considerable extension as the experimental data are augmented. The work described in the present and preceding part of this series of papers appears to emphasise the importance of group number in interrelating spectroscopic constants.

Summary.

The applicability of the empirical relation $k = Dr_e^3n^{\frac{1}{2}}$, where D is dissociation energy, r_e equilibrium internuclear distance, n group number, and k a period (or sub-period) constant, has been tested for non-hydride di-atoms in ground states and compared with formulæ suggested by other authors (Morse, Huggins, Sutherland). Consistent results are obtained by Sutherland's and the author's formulæ, provided that the product occurring in Sutherland's expression has periodic character with group number, attaining maximum values in group X in each period. The results also confirm recent work of Fox and Martin on CC linkages.

The corresponding relation for hydride di-atoms is found to be $l = Dr_e^4n$. Consistent results are obtained by Sutherland's and the author's methods.

The results indicate that k is sensibly constant in the KK period for elementary di-atoms, and possibly for other cases, and that l is constant in the KH period, but that in other periods k, l are sensitive to electron configuration type.

Comparison with experimental data gives generally satisfactory results. A method is hereby suggested for the rapid approximation of D from r_e, whereby certain unknown dissociation energies are calculated.

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INFLUENCE OF ACIDITY ON CATALYTIC EXCHANGE OF HYDROGEN AND WATER.

By A. R. Bennett and M. Polanyi.

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The following note is concerned with a factual detail of a complex matter. Immediately following on their first observation [1] of the catalytic interchange of hydrogen and water on platinum black, Horiuti and Polanyi noted [2] that the rate of this reaction was slower in alkali than in acid. Hence they concluded that the rate was not determined by the process

$$\tfrac{1}{2}H_2 + Pt = Pt - H \quad . \quad . \quad . \quad . \quad (1)$$

which was at the time thought to be purely homopolar, but that it consists in

$$Pt - H + H_2O = Pt^- + HOH_2^+ \quad . \quad . \quad . \quad (2)$$

which, involving the separation of charges is of a nature to be influenced by potential changes accompanying variations in acidity. The significance of the acidity effect was contested by Butler [3] but maintained by Horiuti and Polanyi.[4] New evidence for the acid-alkali effect was presented by Eley and Polanyi [5] who, having found (similarly to Farkas and Farkas [6]) that there is little if any delay between the splitting up of a hydrogen molecule and its exchange with water, now concluded that it is not (2) but (1) which determined the rates, and that this is influenced by the interface potential in virtue of the polar nature of the Pt — H bond, as evidenced by the work of Slygin and Frumkin.[7] This contention, however, was not accepted by Horiuti and Okamoto [8] who doubted whether poisoning of the metal by impurities of the alkali, as observed in various electrolytes by Volmer and Wick,[9] could not, in conjunction with the activating effects of air, simulate a reversible effect of acidity which does not exist in reality.

Consequently, further experiments have now been undertaken to test the acidity effect using depoisoned alkali and removing the system from contact with air. The results contained in the present paper prove that this change of conditions has no influence: the acidity effect is observed exactly as before. Our experiments were completed when confirmation of the acidity effect also came from Horiuti and Ikusima [10] who, using depoisoned alkali and strong shaking, claim a 100-fold reduction of rate between N./10 HCl and N./1 KOH. Their communication, which seems to be of a preliminary nature, does not

[1] Horiuti and Polanyi, *Nature*, 1933, **132**, 819.
[2] *Ibid.*, 931. [3] Butler, *ibid.*, 1934, **133**, 26.
[4] Horiuti and Polanyi, *ibid.*, 1933, **132**, 931.
[5] Eley and Polanyi, *Trans. Faraday Soc.*, 1936, **32**, 1388.
[6] A. Farkas and L. Farkas, *ibid.*, 1937, **33**, 678.
[7] Slygin and Frumkin, *Acta Physicochimica U.R.S.S.*, 1935.
[8] Horiuti and Okamoto, *Trans. Faraday Soc.*, 1936, **32**, 1492.
[9] Volmer and Wick, *Z. physik. Chem.*, 1935, **172**, 429.
[10] Horiuti and Ikusima, *Proc. Imp. Acad. Tokyo*, 1939, **15**, 39.

mention what tests of reversibility were made and seems to imply that air was not excluded from reaching the catalyst when the liquid was changed; reference is made to further explanations which will be given in a later paper.

Experimental Method.

Materials.

Catalyst consisted of platinum foil 0·001 in. thick cut into squares of approximately 5 × 5 mm. and was cleaned by chromic acid and washed with distilled water.

N. Hydrochloric Acid.—Woolley's Pure Normal Hydrochloric acid was used.

N./10 Caustic Potash Solution.—Prepared by dissolving the requisite weight of Merck's pure KOH in distilled water. This was depoisoned by allowing to stand in contact with platinum black for some weeks.

Deuterium, obtained by electrolysis of alkaline D_2O from Norsk Hydro-Elektrisk Co., was purified by passing it through a heated palladium thimble. The D_2 concentration was assumed to be 100 %. For experiments in which 60 % D_2, 40 % H_2 was used the 100 % D_2 was diluted with pure H_2.

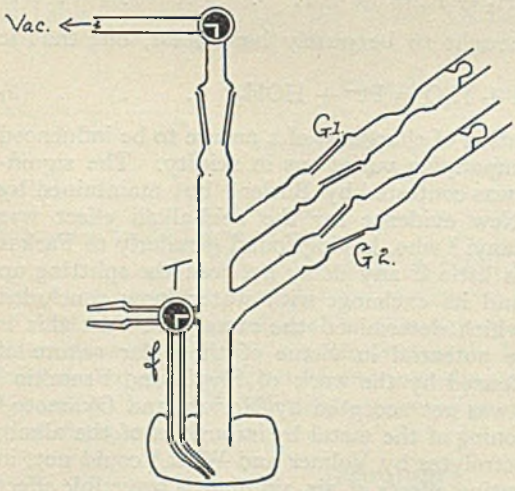

FIG. 1.

The Reaction Vessel before use was cleaned in chromic acid and washed thoroughly with distilled water.

The platinum foil cuttings which were used as the catalyst were placed in the reaction vessel shown in Fig. 1 and immersed to start with either in N./1 HCl or N./10 NaOH. The vessel (connected by a glass spiral with the vacuum apparatus) was filled with deuterium and shaken in horizontal direction at an amplitude of about ⅜ in., making 4-6 full turns per second. At the end of a run the liquid was removed under hydrogen through the capillary *f* and the two-way tap T; a new liquid which had been previously outgassed being then introduced through one of the breakable joints G1 or G2. The liquid was changed a second time under hydrogen through the joint not used in the first instance. This complete cycle was carried out twice; but experiments were also registered in which only one change could be made under hydrogen, because subsequently air came in by leakage or mistake. Such experiments showed that the presence of air has no appreciable effect on the phenomenon.

The deuterium used was 100 per cent. to start with, except in the experiments where the observation of the reaction $H_2 + D_2 = 2HD$ was intended, in which case an initial concentration of 60 % D was taken. Changes in concentration were observed by measuring the heat conductivity of the gas. For the $H_2 + D_2$ reaction the conductivity was read twice: before and after equilibriation on a hot wire.

Results.

In Table I one run is reproduced to show the details of the experimental conditions and the extent to which the exchange velocity constants k_e, calculated on the basis of a first order reaction, were reproducible. Table

TABLE I.

90 cm.² Platinum Foil. 10 c.c. N. HCl.
Initial Gas. 100 % D. Hydrogen Pressure 103-113 mm.

Date.	Temperature (°C.).	Time (t) (hr.).	% D at Time t.	k_e (hr.$^{-1}$).
24 I 39	19·4	3·31	46·6	0·230
25 I 39	18·1	4·29	37·7	0·227
25 I 39	18·5	3·17	48·2	0·230
26 I 39	18·0	3·37	44·8	0·240
27 I 39	0·0	5·03	46·0	0·155
27 I 39	0·0	3·93	52·4	0·165
28 I 39	0·0	2·67	66·0	0·156
30 I 39	0·0	3·67	54·4	0·166
30 I 39	19·0	2·10	62·0	0·229
30 I 39	17·2	2·10	59·8	0·246

II surveys the final results of a number of runs. It shows that the substitution of N./10 NaOH for N./1 HCl reduces the rate of exchange by a factor 4-12 at 0° and to a lesser extent at room temperature. This is accompanied by a marked increase in the temperature coefficient, resulting

TABLE II.*

a and *b* 90 cm.² Platinum Foil (Experiments 12 to 57).
c and *d* 150 cm.² Platinum Foil (Experiments 72 to 144).
Hydrogen Pressure 100-127 mm.

	Solution.	k_e(0° C.), hr.$^{-1}$.	k_e (20° C.), hr.$^{-1}$.	$\text{Log}_{10} B$.	E k.cal./mol.
a	N./10 KOH	0·040	0·134	6·3	9·8
	N. HCl	0·119	0·182	1·8	3·4
b	N. HCl	0·159	0·240	1·6	3·0
	N./10 KOH	0·013	0·037	4·7	8·4
c	N./10 KOH	0·065	0·179	5·6	8·4
	N. HCl	0·269	0·396	1·8	3·0
	N./10 KOH	0·056	0·146	4·8	7·7
d	N. HCl	0·357	0·525	2·0	3·2
	N./10 KOH	0·072	0·181	4·1	6·7
	N. HCl	0·271	0·449	2·6	4·1

* The value of k_e at 0° C. and 20° C., of B the temperature independent factor, and E the activation energy, were obtained graphically from the experimental values of k_e at various temperatures. The acid-alkali changes within the groups *a*, *b*, *c* and *d* were all effected in an atmosphere of H_2.

in an increase of the calculated activation energy on the average from 3·5 k.cal. in acid to 8·0 k.cal. in alkali. We cannot definitely conclude from our experiments as to what extent the rate of exchange was lowered by the physical factors limiting the rate of diffusion. This would reduce

the apparent effect of changes in acidity while at the same time diminishing the apparent activation energy of the faster reaction. Horiuti and Ikusima [10] have published a single series of observations from which by slight extrapolation a 22-fold reduction of rate in the range of N./HCl to N./10 KOH is apparent. This may perhaps indicate that even our ratio 12 is still somewhat reduced by the physical factors; but a more detailed consideration of our data, which need not be communicated here, does not make this appear likely.

In Table III some experiments are listed in which the first order

TABLE III.*

Experiments 12 to 15 and 22 to 25. 90 cm.² of Platinum Foil. Hydrogen Pressure 100 to 127 mm. Initial gas 62·0 % D_2, 38·0 % H_2.

Date.	Solution.	Temperature °C.	Time t (hr.).	% D, time t.	w_1/w_2.	k_d (hr.$^{-1}$).	k_c (hr.$^{-1}$).
15 12 38	N./10 KOH	21·3	3·23	36·8	0·84	0·162	0·055
16 12 38	,,	21·3	5·08	33·4	0·71	0·122	0·066
16 12 38	,,	21·0	4·71	34·8	0·76	0·118	0·059
17 12 38	,,	19·2	4·50	38·0	0·76	0·108	0·062
5 1 39	N. HCl	14·6	5·21	31·0	0·76	0·134	0·053
5 1 39	,,	15·4	4·48	30·0	0·79	0·162	0·053
6 1 39	,,	16·0	4·17	30·5	0·82	0·171	0·047
6 1 39	,,	16·9	5·20	27·0	0·83	0·160	0·036

* $k_c = 1/t \log w_2/w_1$ where w_1 is the resistance shift on equilibration of the final gas—w_2 is the resistance shift on equilibrating a gas of the same total D atom concentration with no HD present.

"conversion constant" k_c referring to the $H_2 + D_2 = 2HD$ reaction was also observed. The resistance shifts from which these are derived are of the order of 0·2 ohms only and the accuracy is correspondingly reduced. Nevertheless, the results leave no doubt that in our experiments the exchange was accompanied by a certain amount of conversion, its rate being $\frac{1}{3}$ to $\frac{1}{2}$ of the rate of exchange.

Discussion.

The communication of these experimental results seems no sufficient occasion to develop all the wider problems of which they form part. But a few remarks may be permitted concerning the new suggestion of Horiuti and Ikusima that the electrode processes on platinum proceed by the "electrochemical mechanism" of Horiuti and Okamoto. This mechanism would appear to be excluded for cathodically polarised electrodes of the metal palladium which is closely similar to platinum. Experiments quoted in this connection by Frumkin,[11] show that the overvoltage spreads by diffusion from one side of a thin palladium foil to the other: this effect proves that the evolution of hydrogen is not, or not principally, due to a lowering of an energy barrier caused by polarisation as in the electrochemical mechanism; but to an accumulation of hydrogen in the valley immediately preceding the significant energy barrier, and that hydrogen in the state corresponding to this valley is diffusible through palladium. To this may be added the experiments of Calvin and Dyas [12] showing that on platinum cathodically

[11] Frumkin, *Acta Physicochimica U.R.S.S.*, 1937, **7**, 475.
[12] Calvin and Dyas, *Trans. Faraday Soc.*, 1937, **33**, 1492.

polarised to not more than 0·01 volt, the rate of exchange is reduced to a fraction of the rate of $H_2 + D_2$ conversion—although according to the electrochemical mechanism such conversion should be negligible.

The conversion which we observed ourselves shows that even on unpolarised blank platinum a process of dissociation $H_2 = 2H$ preliminary to the formation of H^+—ions does take part in determining the rate of reaction.

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THE SIMPLEST ULTRACENTRIFUGE WITH PHOTOGRAPHIC RECORDING.[1]

By James W. McBain and Allen H. Lewis.

Received 13th October, 1939.

The directly air-driven transparent ultracentrifuges [2] require a highly skilled mechanician for their construction. Consequently the cost is more than that of the opaque analytical ultracentrifuges,[3] although still much less than that of the air-driven vacuum type of Beams and others. Furthermore, all of these transparent ultracentrifuges require expensive optical accessories. We have therefore simplified the directly air-driven rotor and dispensed with a camera, producing an ultracentrifuge with which useful results of fair accuracy can be attained in any laboratory with the necessary supply of air.

Briefly, the rotor is a solid piece of duralumin with a cover, holding slit non-conducting blocks each containing a capillary tube for the solution and resting upon a piece of ordinary photographic film. A run is made n dim light or under cover until the record is desired, whereupon the light is flashed on for one or more seconds. The record is thus obtained without stopping the rotor. The normal speed is 72,000 r.p.m., producing a force of 116,000 times gravity at the centre of the cell. A smaller rotor can produce any desired greater force. The present rotor may also be run as slowly as desired to measure sedimentation equilibrium. In this respect it is especially valuable for the study of virus.

Design of the Rotor.

The design of the rotor is illustrated in Figs 1 (Plate VI), 2, and 3. The rotor consists of a solid piece of duralumin, 7 cm. in diameter, with angle of cone 102°. The top surface is flat, exce'ɷ for a rim 4 mm. wide and 1 mm. high at the periphery. Two or more wells with perpendicular walls are milled into the rotor, each the same distance from the centre of rotation. These wells are 11·5 mm. wide, 10·5 mm. deep and 23 mm. long, with

[1] McBain and Lewis, *Science*, 1939, **89**, 611.

[2] McBain and O Sullivan, *J. Amer. Chem. Soc.*, 1935, **57**, 780, 2631; McBain and Lewis, presented at *Colloid Symposium*, 1939.

[3] McBain and Alvarez-Tostado, *Nature*, 1937, **139**, 1066; *J. Amer. Chem. Soc.*, 1937, **59**, 2489; McBain and Leyda, *Nature*, 1938, **141**, 913; *J. Amer. Chem. Soc.*, 1938, **60**, 2998; McBain, *J. Physic. Chem.*, 1938, **42**, 1063; *Chem. Rev.*, 1939, **24**, 289.

rounded ends. The cover is made of a single piece of duralumin, and is held to the rotor by a central screw. It has a maximum thickness of 3 mm. near the centre and tapers to be flush with the rim at the edge of the rotor. The under surface of the cover lies flush with the top surface of the rotor. The top surface of the cover is turned as shown in profile in Fig. 2, so that a ring uniformly 2 mm. in thickness is obtained just over the wells in the rotor. In this a slightly tapered hole 9 mm. in diameter, drilled from underneath, takes a glass or quartz window held by Duco cement. The threads of the central screw are ground until when the cover is tight the window is directly over the capillary tube. The cover also contains two small wrench holes for tightening the cover.

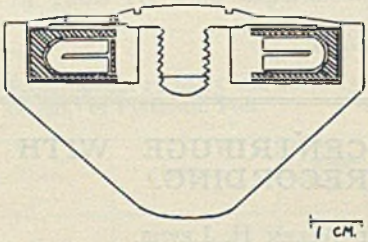

FIG. 2.—Cross-section through assembled rotor.

Two blocks of hard rubber were made to fit snugly into the wells. These blocks are half round at one end and cut off square at the other end. Into each is drilled a horizontal hole 7 mm. in diameter with a rounded bottom, leaving a wall of 3 mm. of hard rubber at the rounded end of the block. These holes are made so that thick-walled capillary tubes of 7 mm. external diameter fit snugly into them. The block which is to hold the tube in which measurement is to be made is sawn nearly in two lengthwise by a vertical cut to let a beam of light pass through. This produces two slits 0·6 mm. wide which are directly opposite each other, one in the centre of the top wall and the other in the centre of the bottom wall. If a small piece of photographic film is placed under the hard rubber block, the light beam places upon the film a shadow reproduction of the capillary tube and its contents. A tiny hole 0·5 mm. in diameter is drilled

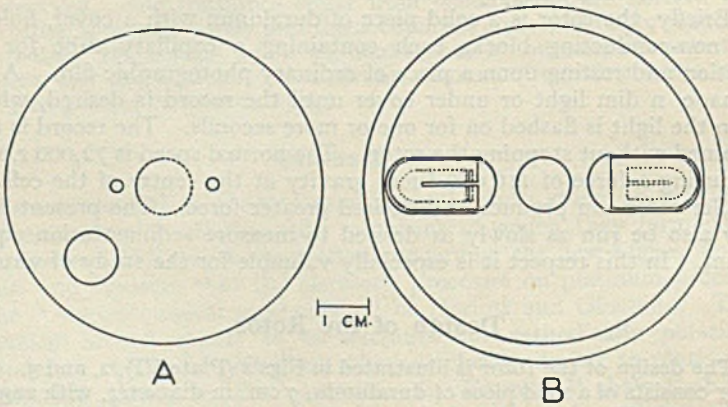

FIG. 3.—View from above, A, cover, and B, rotor containing cell and dummy.

through the cover just next to the window on the side toward the centre of the rotor. Part of the vertical beam of light passes through this hole and places a spot upon the film which is a known distance from the centre of rotation and is used as a reference point for measurement.

The capillary tubes are of glass or quartz of outside diameter about 7 mm. and inside diameter 1 mm. They are sealed at one end, and the open end is ground flat. They are filled with a capillary pipette and then, to prevent evaporation, sealed with a small piece of gummed label and Duco cement. The tubes are about 12 mm. long, thus being about 2 mm.

shorter than the hole in the rubber block into which they fit. A small piece of cork 1 mm. thick is placed over the flat end of the tube after it is placed in the rubber holder, to insulate it from any temperature changes.

A simple 7 cm. stator without central air inlet was used, with 15 air holes of 0·033 in. diameter.

Operation Characteristics of Rotors.

The relation between speed and the size and number of air ports was investigated by F. A. Leyda and Joseph Grebmeier, using a 5·8 cm. stator (Table I).

TABLE I.

Pressure (lbs./in.²).	Rotor Speed in Revolutions/Second.		
	12 Holes 0·028 in. diam.	24 Holes 0·028 in. diam.	12 Holes 0·033 in. diam.
50	675	780	840
75	725	855	980
100	770	920	1060
125	—	—	1120
150	840	1005	1165
200	860	1060	1180
225	885	—	1200
275	—	1115	—

Raising the number of flutes on the driving cone from 60 to 120 resulted in only a slight increase in speed. Nearly doubling the length of the flutes on the test rotor had practically no effect on the speed.

When the ratio of the number of flutes to the number of air ports is small, it must be an integer, such as 60/15 = 4, if smooth running is to be obtained. When the ratio is large, such as 120/16, it does not seem to matter.

Changing the angle of the rotor cone from 100° to 110° resulted in a marked increase in speed (Table II), and in the Bernoulli effect, but the rotor was not as stable. The instability was due to the greater Bernoulli effect and could be eliminated by use of a stator with adjustable central air inlet.

The simplest 7 cm. stator could be used for the larger proteins, but to eliminate vibration visible in the microscope, caused by turbulence of the air, six vertical baffles were attached to the aluminum ring of the stator, each approaching to 1 mm. from the edge of the rotor. In addition, six slanting pieces of metal were placed around the stator, alternating with the vertical baffles. The strips of metal simply rested against the stator at one end and against the top of the guard at the other.

TABLE II.—Effect of Angle of Cone Using a 90° Stator.

Pressure (lbs./in.²).	Speed in Revolutions/Second.		
	100° Cone.	102° Cone.	110° Cone.
50	840	870	980
75	980	1030	1160
100	1060	1150	1290

Use of Capillary Tubes.

Sectorial cells [2] may equally well be employed and made longer and thicker than those for the 37 mm. rotors, but they are much more complicated than ordinary capillary tubes. Objection might be made to these because they are cylindrical rather than radial and sectorial. However, they do in fact give almost perfect results. This must be due to streaming being confined to a few particle diameters on the outside of the

liquid, producing a very slow controlled and limited movement displacing upwards from the bottom an equal bulk of the total liquid. Thus not only are good boundaries formed and maintained, as observed by Elford, McIntosh and Selbie, and Ford, as well as ourselves, but they move at very nearly the exact theoretical rate.

Experimental Procedure.

The capillary tube was filled by means of a capillary pipette to about 1 mm. from the top, giving a column of solution about 8 mm. long. Zero time was taken when the air pressure to be used was reached, since the rotor accelerates to speed in a fraction of a minute. The speed of the rotor was measured in the dark by matching the note from an oscillator with that heard directly from the rotor. The temperature was likewise measured. After the run, the rotor was stopped in the dark, wrapped in black cloth and taken to the darkroom, where the film was developed.

Instead of making only one exposure, a movable slit can be used of sectorial shape with limited radius allowing only part of the tube to be photographed at each successive exposure.

Experimental Results.

Erythrocruorin of Earthworm Blood.[1]—With sharp boundaries such as those for so heavy a molecule ($s_{20} \times 10^{13}$ observed 59·6, Upsala value 60·9), measurement of the film (Fig. 4, A, B, Plate VI) can be made directly or with a travelling microscope with almost as great accuracy as with the microphotometer.

Carboxyhemoglobin.—On the other hand, with the smaller proteins, and only 116,000 times gravity, the boundaries are necessarily diffuse, in accordance with theory. Hence one must distinguish between the point of half-blackening of the film and that of half-concentration, the latter being a close approximation for the ideal for a sharp boundary. The effects were studied as follows.

Horse red blood cells saturated with carbon monoxide were centrifuged with 1 % NaCl five times at 0°, before adding distilled water to rupture the cells and centrifuging off the debris. After dialysis at 0°, some of the crystalline hemoglobin obtained was dissolved in 1 % KCl to study. Exposure was one second with blue light and the films were microphotometered. The point of half-blackening in the first four runs gave distinctly high values 4·8 to 5·6, mean $5{\cdot}2 \times 10^{-13}$, before the illumination was improved by placing a sectorial opening in the optical path to secure uniform illumination. The degree of blackening corresponding to half-concentration is simply determined by photographing in the same tube a solution of half concentration, the two films being developed together (Fig. 4*c*, *d*). It was found that the film had to be cut very carefully without exposure, either with a die, or most simply by cutting round an opaque form.

After adopting this technique the values for half-blackening were 6·10 and 6·21, but for half-concentration the results then obtained by L. H. Perry were 4·71 and 4·73 for $s_{20} \times 10^{13}$ as compared with Steinhardt's Upsala value 4·63.

Summary.

Details of the construction and operation of the simplest air-driven ultracentrifuge are given, and it is shown that the results are practically as good as those hitherto attained with any of the standard ultracentrifuges.

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NUCLEAR GOLD SOLS. II. MECHANISM OF FORMATION.

By A. Baker and F. L. Usher.

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It is well known that the size of the particles in gold sols prepared by chemical means depends partly on the reducing agents used in their preparation. Hydrazine and hydroxylamine, for example, give large particles of over 50 mμ radius in the absence of nuclei, whereas alkali thiocyanate or a solution of phosphorus in ether gives very small particles in the size range 1-6 mμ, sols of this kind being known as "nuclear." There are numerous experimental data relating to the conditions under which the different kinds of sols are produced and to their physical and chemical properties, but two questions of special interest remain unanswered; one relates to the cause of the dependence of particle size on the nature of the reducing agent, the other to the existence of a lower size limit. The present paper is concerned with the first of these problems.

The formation of a gold sol by chemical reduction involves crystallisation from a solution supersaturated with respect to gold, and therefore in experiments in which only the reducing agent is varied we should expect the relative size of the crystals to be determined by the relative speed of the reactions—the slower reaction giving fewer and larger crystals. This simple and obvious inference apparently contradicts what is observed when, for example, a dilute solution of a gold salt is treated on the one hand with hydroxylamine hydrochloride, and on the other with an ethereal solution of phosphorus; in the first case we get a coarse blue suspension by a reaction which is nearly instantaneous, and in the second a red nuclear sol by a reaction which at the ordinary temperature needs about a day for completion. It seems likely that this apparently anomalous behaviour is due to the occurrence, in the second case, of consecutive reactions differing greatly in velocity; we must therefore start by looking for evidence that reactions leading to the production of nuclear sols do in fact occur in at least two stages.

Faraday Sols.

When a solution of phosphorus in ether is added to a dilute and slightly alkaline solution of a gold compound (usually chloroauric acid), the liquid at once assumes a brown colour which, in about a day at room temperature, more rapidly if heated, changes to the normal colour of a Faraday sol. This colour change suggests the formation of some intermediate product, though it does not prove it, for the brown liquid may contain gold particles which afterwards undergo some structural change associated with change of colour. This question has been discussed[1] but not investigated. Attempts to find the composition of a coagulum from the brown liquid were inconclusive, because although

[1] Galecki, *Koll. Z.*, 1912, 11, 105; Zsigmondy and Thiessen, *Das kolloide Gold*, Leipzig, 1925, 120.

the coagula, after washing with ether, contained phosphorus, it is possible that some or all of it was derived from phosphorus precipitated along with the gold. The only way of removing this uncertainty is to use a method which does not involve the formation of colloidal phosphorus, a condition which would be satisfied by substituting for phosphorus in ether an aqueous solution of phosphine.

The action of phosphine on gold compounds was first described by Mrs. Fulhame [2] in 1794 as follows :—

" A piece of silk, which was immersed in a solution of nitro-muriate of gold in distilled water, and suspended in the air twelve hours to dry, was divided into three parts. One of these was exposed to a stream of phosphorated hydrogen gas ; the silk became brown . . . but no reduction took place. Another of these parts was wetted with alcohol, and exposed to the gas ; but no sign of reduction could be perceived. The remaining part was wetted with water, and was no sooner exposed to the gas than the reduction commenced over the whole silk, which was soon covered with a bright coat of reduced gold."

In 1811 Oberkampf [3] obtained from aqueous chloroauric acid a black precipitate which he regarded as gold phosphide, but which Rose [4] considered was metallic gold. The only other relevant observations were made in 1885 by Cavazzi,[5] who found that phosphine precipitated from solutions of gold chloride in alcohol or ether a black gold phosphide (AuP) which was decomposed by air, or by boiling with water or alkalis, forming metallic gold. He also stated that in aqueous solutions gold was obtained, owing to the action of cold water on the phosphide initially formed. The published information thus leaves little doubt that phosphine reduces gold compounds in aqueous solution to the metal, and suggests that the latter may be derived from a previously formed gold phosphide.

Experimental.

Phosphine was prepared (1) by boiling phosphorus with aqueous potassium hydroxide, and washing successively with concentrated hydrochloric acid and with water, and (2) by the action of water on phosphonium iodide and washing with water ; in each case the washed gas was passed over soda-lime, filtered through glass wool, and absorbed in water in a Pyrex flask. In the experiments to be described the results obtained were the same irrespective of the method of preparation of the phosphine.

(*a*) Addition of 50 c.c. of phosphine solution to 60 c.c. of a solution containing 15 mg. of gold as $KAuCl_4$ and $2{\cdot}5 \times 10^{-4}$ equivalent of sodium carbonate caused the instant formation of a red sol.

(*b*) When the above solutions were mixed in the reverse order a yellow sol was first formed, and this changed to reddish-brown in a few seconds ; the yellow colour was not regained on dilution. When the amount of gold was reduced to 10 mg. the duration of the yellow colour was increased to about 5 minutes.

(*c*) A more stable yellow sol (A) was made by adding a solution containing 8·5 mg. Au with a proportionate amount of alkali to a freshly prepared phosphine solution, the resulting sol containing 0·063 mg. Au per c.c. 20 c.c. of A, kept for 2 days in a stoppered flask containing air, changed into a red gold sol ; 20 c.c. kept for the same time in a similar flask under nitrogen remained yellow.

[2] Fulhame, *Essay on Combustion*, London, 1794, 63, 114.
[3] Oberkampf, *Ann. Chim. Phys.*, 1811, 80, 140.
[4] Rose, *Pogg. Ann.*, 1828, 14, 184. [5] Cavazzi; *Gazzetta*, 1885, 15, 40.

(*d*) When heated, sol A remained yellow until the boiling point was reached, and then quickly turned red.

(*e*) A mixture of sol A with a solution of $KAuCl_4$ turned red, whilst the same quantity of A exposed to air for the same time remained yellow.

(*f*) The dispersed material in sol A was analysed after coagulating with sodium chloride and washing the precipitate with water and finally with alcohol. The sol was prepared and coagulated and the precipitate dried in an atmosphere of nitrogen. After weighing, the precipitate was oxidised with nitric acid, and phosphorus was determined by the lead molybdate method,[6] in which the weight of the final product ($PbMoO_4$) is 142 times that of the phosphorus. Two analyses gave P 13·9 and 12·9 %; calc. for AuP 13·6 %. It is therefore probable that the gold in the yellow sol is present entirely as colloidal auric phosphide.

(*g*) A further analysis of the coagulum from a sol, originally yellow, which had been allowed to stand over a week-end in contact with air and had turned red, gave P 0·7 %. This coagulum was of the usual bluish-black colour of gold precipitated from a normal gold sol, whereas coagula from the yellow sols were brown. The black precipitates obtained by Oberkampf and by Cavazzi may have owed their colour to admixed gold; in our own experiments the colour of the phosphide precipitates was always brown when adequate precautions had been taken to prevent oxidation.

The experiments just described make it reasonably clear that the primary reaction between phosphine and an auric compound in aqueous solution gives auric phosphide, and that this may be converted into gold under conditions permitting oxidation, *e.g.* by the action of air, boiling water, or excess of gold salt. The reactions may be formulated thus:

$$(1)\ AuCl_3 + PH_3 = AuP + 3HCl;$$

$$(2)\ 4AuP + 5O_2 + 6H_2O = 4Au + 4H_3PO_4;$$

or

$$3AuP + 5AuCl_3 + 12H_2O = 8Au + 3H_3PO_4 + 15HCl.$$

According to Cavazzi, in the reaction with water, phosphine and hydrogen are formed in addition to phosphoric acid.

Gold sols made by the phosphine method are nuclear, and can in fact be obtained more finely disperse than any hitherto described. Chemically the reaction is of the kind expected, in that gold is formed only in the last of a sequence of (in this case two) reactions. The Faraday method, in the form described by Zsigmondy[7] is, however, the standard method of preparing nuclear sols, and it still remains to show what relations exist between Faraday sols and those made with phosphine. The first question that arises is whether auric phosphide is an intermediate product in the preparation of Faraday sols. Direct evidence on this matter is not to be had, since the presence of even a large proportion of phosphorus in the coagulum from a sol immediately after mixing the reactants is capable of more than one interpretation. A further difficulty is presented by the fact that auric phosphide sols prepared with phosphine are considerably more stable than are the sols made with a solution of posphorus in ether; the former are more slowly affected by air, and can be preserved under nitrogen unchanged for more than two months. The experiments described below give further information on these points.

(*h*) Auric phosphide sol was prepared and afterwards boiled in complete absence of air. The sol turned red within 15 minutes. A similar sol kept at 90° for 7 hours showed no change beyond a slight darkening of colour to yellowish-brown.

[6] Raper, *Biochem. J.*, 1914, 8, 649.
[7] Zsigmondy and Thiessen, *op. cit.*, 48

(*i*) 1 c.c. of a saturated solution of phosphorus in dry ether was added to 20 c.c. of an ether solution containing 1 mg. of Au as $HAuCl_4$. A yellow sol showing a marked Tyndall effect was formed. Half of this sol was shaken with an equal volume of water: the ether layer was decolorised and the aqueous layer became red. The other half of the yellow sol, when concentrated to one-third of its original volume, deposited a flocculent brown substance having the properties of auric phosphide.

(*j*) An ethersol of auric phosphide was prepared as in (*i*). Half of it was shaken with water and gave a red aqueous layer. The other half was shaken with an aqueous solution of phosphine: this gave a yellow aqueous layer. The ether layer was decolorised in both.

The results of these experiments, together with the facts previously established, enable a clear picture to be formed of the succession of events in the formation of nuclear sols whether made with phosphine or with ethereal phosphorus. Thus, when a dilute and slightly alkaline solution of a gold compound is mixed with excess of phosphine a yellow sol of auric phosphide is formed; a yellow hydrosol similar in all respects to the first is also formed by shaking with water the yellow ethersol produced by mixing ether solutions of phosphorus and chloroauric acid; finally, when either of these yellow hydrosols is subjected to the conditions normally prevailing during the preparation of a Faraday sol it is converted into a nuclear gold sol. There is, therefore, a strong probability that auric phosphide is formed as an intermediate product in the Faraday reaction, whilst failure to isolate it from the reaction mixture is adequately accounted for by the fact (*cf.* Experiment *j*) that oxidation of auric phosphide, though inhibited by phosphine, is not inhibited by phosphorus, and must, therefore, be proceeding at a very early stage, an inference supported by the rapid darkening of the mixture usually observed. The order of mixing (*i.e.* phosphorus is added to the gold compound) would also favour oxidation of the phosphide by the local excess of gold salt during mixing.

Faraday sols have been discussed at some length because of their historical interest and practical importance. The chemical mechanism suggested for their formation is at least highly probable; but the physical mechanism is obscure, owing to our ignorance of whether the initial reaction takes place in solution or is restricted to the surface of the phosphorus particles. This uncertainty, and the difficulty created by the presence of colloidal phosphorus, makes Faraday sols unsuited to further investigation. Sols made with phosphine are free from both these objections, but even they cannot be used in experiments designed to ascertain whether a definite physical connection exists between the particles of the supposed intermediate product and the gold particles finally produced. This question would be resolved if the number of gold particles in the final sol could be shown to be the same as that of the phosphide particles, and this could be done only if the amicroscopic particles were grown to a size large enough to enable them to be counted. The phosphide sols, however, are unstable in the absence of free phosphine, the presence of even a small trace of which would lead to the formation of fresh nuclei and thus nullify any attempt to count the particles.

Nuclear Sols made with Hydrogen Sulphide.

When a dilute solution of potassium chloroaurate is mixed with one of hydrogen sulphide in excess, a sol of gold (mainly auric) sulphide is formed; it is at first often turbid owing to the presence of some free

sulphur, but gives a clear yellow sol when boiled. The degree of dispersion of these sols increases with dilution, and when sufficiently dilute they are nuclear, *i.e.* they show only a very weak Tyndall effect, and give rise to nuclear gold sols. The conversion of a sulphide sol into a gold sol can be effected, as with the phosphide sols, by oxidation; but unlike the latter, sulphide sols are stable towards air and are unaffected by boiling, even when free from hydrogen sulphide. They can, therefore, be used for finding what relation exists between the number of sulphide particles and the number of particles in gold sols formed from them.

Auric sulphide sols can be converted into gold sols by treatment with potassium chloroaurate, ammonium persulphate, hydrogen peroxide, or ozone; in these reactions the concentrations must be kept low, since all the sulphur appears as sulphuric acid, the coagulating effect of which is added to that of the electrolyte already present and of any which may be derived from the oxidising agent used. The following are examples of the preparation and properties of the sols. The initial sulphide sol was in every case freed from hydrogen sulphide by boiling and by subsequently bubbling filtered air through the liquid for 30 minutes.

Reaction with Chloroaurate.—3 mg. of Au as $KAuCl_4$ were added to 50 c.c. of a Au_2S_3 sol containing 1 mg. Au and $3{\cdot}5 \times 10^{-4}$ equivalent Na_2CO_3. After 15 minutes the solution became pink, and the colour increased in depth for several days, gradually acquiring a smoky shade. After 8 days slight surface coagulation was visible, and after 1 month the gold was almost completely coagulated. More dilute sols were red, not smoky, but even these coagulated spontaneously in a few weeks. If alkali was omitted the sequence of changes was the same, but coagulation set in earlier. Dilute red sols formed by this reaction are amicronic, but owing to their instability are useless for the purpose in view.

Reaction with Ammonium Persulphate.—20 c.c. of a Au_2S_3 sol to which was added 1 mg. of $(NH_4)_2S_2O_8$ showed no change on standing overnight at room temperature. The sol was then boiled; it turned pink, with a brown tinge, in 10 minutes. The colour was not changed by further boiling. The sol showed only a very faint Tyndall effect.

Reaction with Hydrogen Peroxide.—1 c.c. of 6 % H_2O_2 (Merck's Perhydrol diluted) was added to 25 c.c. of Au_2S_3 sol containing 0·1 mg. Au. No immediate reaction occurred in the cold, but on boiling the liquid became red in 10 minutes. When Na_2CO_3 was added in amount sufficient to neutralise the acid formed oxidation occurred slightly less readily. The reaction was not obviously affected by decreasing the concentration of gold, but was greatly retarded by decreasing that of H_2O_2. These sols, when dilute, are amicronic and stable.

Reaction with Ozone.—Ozonised oxygen was passed at room temperature through Au_2S_3 sol containing 0·01 mg. Au per c.c. The sol slowly (20 mins.) turned pink, and finally became bluish-purple. The Tyndall effect, which was very faint, indicated that the blue colour was due neither to the production of large particles nor to coagulation. When boiled for 2 minutes the sol became pure red. Similar behaviour has been noticed in sols prepared by reduction methods, when the reduction has been incomplete, and in such cases the blue or purple colour is usually attributed to a gold oxide. This explanation is supported by the observation that a red gold sol made by the phosphine method was turned purple by passing ozonised oxygen through it; the red colour was regained on boiling, and the Tyndall effect remained unchanged throughout.

Particle Concentration in Sulphide Sols.

The particles in gold sulphide sols cannot be directly counted. Their size decreases with increasing dilution of the parent solutions, the largest "equivalent gold particle" (*i.e.* one containing the same amount of gold as the sulphide particles) having a radius of 2·5 mμ. The particles are, therefore, too small to count in the ultramicroscope, and must be grown before their number or size can be determined. It has been shown already that gold sulphide reacts rather slowly with potassium chloroaurate; it seems probable that the slowness is due entirely to the solid reaction, and that the surface of the particle is converted into gold very quickly. This view is borne out by the observation that the sulphide particles behave exactly like gold nuclei when an attempt is made to grow them by reducing a chloroaurate solution in their presence with hydroxylamine. Table I gives the results of determining in this manner the number of sulphide particles per c.c. in five different sols of concentration varying from 0·08 to 0·0008 mg. Au per c.c. The measurements were made by the method described in Part I of this series.[8] The first column gives the relative dilution of the particular sol used, and the second the calculated number of nuclei in the undiluted sol. These numbers should not vary with dilution if the sulphide particles do in fact act as the sole nuclei of condensation; if, on the other hand, the number of gold particles produced depends on some other factor, the observed numbers would be constant, and the calculated numbers would therefore be directly proportional to the dilutions.

TABLE I.

(c = Au per c.c. of undiluted Au_2S_3 sol; v = relative dilution; n = number of particles per c.c. of undiluted sol.)

c = 0·08 mg./c.c.		c = 0·02 mg./c.c.		c = 0·01 mg./c.c.	
v	n	v	n	v	n
1·0	$6·0 \times 10^{13}$	1·0	$3·3 \times 10^{13}$	1·0	$2·6 \times 10^{13}$
1·5	$5·6 \times 10^{13}$	1·025	$3·2 \times 10^{13}$	1·33	$2·6 \times 10^{13}$
2·0	$6·7 \times 10^{13}$	1·47	$3·4 \times 10^{13}$	1·67	$2·5 \times 10^{13}$
2·5	$6·8 \times 10^{13}$	1·5	$3·0 \times 10^{13}$	2·0	$2·4 \times 10^{13}$
		2·0	$2·8 \times 10^{13}$		
		2·2	$2·9 \times 10^{13}$		

c = 0·004 mg./c.c.		c = 0·0008 mg./c.c.	
v	n	v	n
1·0	$1·3 \times 10^{13}$	1·0	$5·0 \times 10^{12}$
1·25	$1·4 \times 10^{13}$	1·4	$4·3 \times 10^{12}$
1·75	$1·1 \times 10^{13}$	2·0	$4·5 \times 10^{12}$
2·5	$1·1 \times 10^{13}$	3·0	$4·5 \times 10^{12}$

The tabulated figures show that the number of gold particles formed, in each of the five sols, is proportional to the amount of sulphide sol used; it may therefore be assumed that this number is also that of the sulphide

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

particles present. The average deviation from the mean, averaged for the five sols, is 6·2 %, which is well within the permissible experimental error.

Particle Concentration in Gold Sols derived from Sulphide Sols.

Theoretically any one of the four oxidising agents previously named could be used to convert the sulphide sols into gold sols with a view to comparing their particle concentrations. In practice only hydrogen peroxide has been found satisfactory, since sols made with the others show too great a tendency to coagulate spontaneously. The sulphide sol containing 0·02 mg. Au per c.c. was converted into a gold sol by boiling some of the diluted sol with very dilute hydrogen peroxide. The original sol had particles of equivalent radius 2·0 mμ. When the conversion into gold was complete the resulting sol was suitably diluted, the particles were grown, and the size of the nuclei determined in the usual way. The results of two series of such measurements are in Table II.

TABLE II.

Relative Dilution.	Particle Radius.	Relative Dilution.	Particle Radius.
1·0	2·0 mμ	1·0	2·0 mμ
1·43	2·0	1·5	2·1
2·14	2·2	2·0	2·1

It is seen from these measurements that when a gold sulphide sol is oxidised by hydrogen peroxide to form a gold sol, the amount of gold in each particle, and consequently the number of particles, remains unchanged. It is difficult to imagine that this could happen unless each sulphide particle is converted into a gold particle by the removal of sulphur; and although no such proof is possible when the other oxidising agents are used, there is no reason to assume a different mechanism of conversion in their case.

Conclusion.

In all the methods of making nuclear sols examined, the chemical reaction leading to the formation of gold has been found to occur in at least two stages; the first is the formation of nuclei containing other elements besides gold; the second stage consists in the removal of these elements from the particles, leaving gold. Nothing definite is known about the reactions of gold salts with reducing agents such as hydrazine and hydroxylamine, which do not form nuclear sols; there is no evidence at present that insoluble particles, other than gold, are formed in them at any stage. With such non-nuclear reducing agents the formation of colloidal gold is apparently more rapid than it is with nuclear reducing agents (*e.g.* phosphorus, phosphine, hydrogen sulphide), but it may be surmised that the reactions which produce the first insoluble particles (gold) in the former case are slower than those which produce the first insoluble particles (auric phosphide, auric sulphide) in the latter. In the one reaction that permits exact investigation the number of the resulting gold particles has been shown to be determined by that of the antecedent nuclei, and it is reasonable to suppose that this will be true of all reactions of a similar kind in which the final gold-

producing reaction is topochemical. This would imply that the number and size of colloidal gold particles are independent of the velocity of the final reaction by which the metal is produced, but are determined rather by the velocity of that reaction which first produces an insoluble substance. The reaction between a gold salt and hydrogen sulphide is ionic, and instantaneous in the sense that every encounter between the reacting molecules is effective; if this is true also of the reactions with phosphorus and phosphine, the difference in size between the particles produced by the nuclear and non-nuclear types of reducing agent is seen to be in harmony with the generally recognised relation between crystal size and degree of supersaturation.

Summary.

1. The reduction of gold salts by phosphine and by hydrogen sulphide under certain conditions leads to the formation of nuclear gold sols. Under other conditions these reactions may give rise to sols of auric phosphide and auric sulphide, the properties of which are described.

2. The reactions of gold salts with phosphorus in ether (Faraday's method), phosphine, and hydrogen sulphide occur in at least two stages, one of which consists in the formation of an insoluble gold compound, and the last of which consists in a topochemical conversion of this into gold.

3. It is suggested that the difference in the size of gold particles produced by nuclear and non-nuclear types of reducing agent is determined by the speed of the reaction which first produces an insoluble substance, rather than by the overall speed of the complete process.

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THE INFLUENCE OF INTERFACIAL CURVATURE ON SOLUBILITY.

By R. Stevenson Bradley.

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If curvature occurs at the interface between two liquids, then, as is well known, the solubility is altered. It is of interest to consider the behaviour in the light of a change in energy due to molecular interaction without referring explicitly to the surface pressure due to curvature. The change in energy arises owing to the difference in molecular environment between a molecule at a plane and curved surface, and the method has the advantage that the enquiry can be pursued down to very small droplets. With such droplets, *e.g.* those which form on nuclei, there is considerable doubt as to the applicability of Kelvin's equation. The results apply not only to the solubility of liquids in liquids, but also to the condensation of vapours on nucleating particles or in capillary systems.

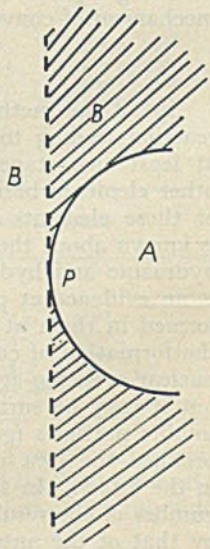

Fig. 1.

Suppose that we have a sphere of liquid A of radius r containing q_A molecules per c.c., immersed in a liquid B containing q_B molecules

per c.c. Let the law of force between two molecules of A be of the form $\frac{\lambda_n}{x^n} - \frac{\lambda_m}{x^m}$, and between a molecule of A and one of B be $\frac{\lambda_v}{x^v} - \frac{\lambda_u}{x^u}$. Consider a molecule of A at the surface of the sphere at P, Fig. 1. Then the difference in energy of this molecule when the interface is plane and when it is curved is given by $E_A - E_B$, where E_A is the energy of a molecule at P due to the shaded portion filled with A, and E_B that due to the shaded portion filled with B. The shaded region is supposed to extend round the sphere to ∞ except for the dotted boundary. This energy can be accurately expressed.

The potential of a molecule distant c from the centre of a sphere of radius r is, in absolute value,[1]

$$\theta(m) - \theta(n) = \frac{2\pi q\lambda_m}{c(m-1)(m-3)}\left[\frac{1}{(m-5)(c+r)^{m-5}} - \frac{c}{(m-4)(c+r)^{m-4}} - \frac{1}{(m-5)(c-r)^{m-5}} + \frac{c}{(m-4)(c-r)^{m-4}}\right] - \theta(n), \quad (1)$$

where $\theta(n)$ is obtained by replacing m by n in $\theta(m)$.

In our problem c may be put equal to $r + d$, where d is the molecular diameter, giving the energy, due to the sphere A,

$$\beta(m) - \beta(n) = \frac{2\pi q_A\lambda_m}{(r+d)(m-1)(m-3)}\left[\frac{1}{(m-5)(d+2r)^{m-5}} - \frac{(r+d)}{(m-4)(d+2r)^{m-4}} - \frac{1}{(m-5)d^{m-5}} + \frac{(r+d)}{(m-4)d^{m-4}}\right] - \beta(n) \quad (2)$$

where $\beta(n)$ is obtained by replacing m by n in $\beta(m)$.

Now the energy of a molecule at the surface of an infinite plane with liquid extending to infinity underneath is

$$\gamma(m) - \gamma(n) = \frac{2\pi q_A\lambda_m}{(m-1)(m-3)(m-4)d^{m-4}} - \gamma(n),$$

where $\gamma(n)$ is obtained by replacing m by n in $\gamma(m)$. Hence

$$E_A/q_A = f(m) - f(n) = \frac{2\pi\lambda_m}{(r+d)(m-1)(m-3)}\left[\frac{1}{(m-4)(m-5)d^{m-5}} - \frac{1}{(m-5)(d+2r)^{m-5}} + \frac{(r+d)}{(m-4)(d+2r)^{m-4}}\right] - f(n), \quad (3)$$

where $f(n)$ is obtained by replacing m by n in $f(m)$.

Similarly

$$E_B/q_B = f(u) - f(v) \text{ and } E_A/q_A - E_B/q_B = f(m) - f(n) - f(u) + f(v). \quad (4)$$

When $r \gg d$,

$$E_A/q_A - E_B/q_B = \phi(m) - \phi(n) - \phi(u) + \phi(v),$$

where $$\phi(m) = \frac{2\pi}{r}\,\frac{\lambda_m}{(m-1)(m-3)(m-4)(m-5)d^{m-5}}.$$

But the interfacial energy of A is given by[2]

$$\sigma_A = \frac{N^2\rho_A^2}{M_A^2}\left[\frac{\lambda_m}{(m-1)(m-3)(m-4)(m-5)d^{m-5}} - \frac{\lambda_n}{(n-1)(n-3)(n-4)(n-5)d^{n-5}}\right] \quad (5)$$

[1] Bradley, *Phil. Mag.*, 1932, **13**, 853: cf. equation above fig. 2.
[2] *Icid.*, 1931, **11**, 846.

where N is Avogadro's number, ρ_A is the density of A and M_A its molecular weight, *i.e.*

$$q_A = \frac{\rho_A N}{M_A}.$$

Hence $$E_A - E_B = \frac{2\pi}{rN}(\sigma_A M_A/\rho_A - wM_A/\rho_A),$$

where w is the work of adhesion, *i.e.* $w = \sigma_A + \sigma_B - \sigma_{AB}$, and the energy difference per g. mol.

$$E = \frac{2\pi}{r}\frac{M_A}{\rho_A}(\sigma_{AB} - \sigma_B) \quad . \quad . \quad . \quad . \quad (6)$$

If the osmotic work of transference of a differential element from the droplet to a plane surface be equated to the surface work we obtain in the usual way an increase in solubility (S) given by $S = S_0 e^{E/RT}$, where S_0 is the solubility over a plane and S that over a sphere of radius r.

Hence $$\log\frac{S}{S_0} = \frac{2\pi}{RTr}\frac{M_A}{\rho_A}(\sigma_{AB} - \sigma_B) \quad . \quad . \quad . \quad (7)$$

which is identical with Kelvin's result except for the second term, which is usually small, *e.g.* for a liquid volatilising into a vacuum.

This derivation has the advantage that it is possible to estimate exactly (if the premises are correct) the divergence from the formula when r is small. For solid crystalline particles, however, for which it is often applied there is no justification for the application, owing to the existence of edges and corners, in fact strictly speaking the energy of activation varies continuously over a crystalline face of a small solid particle.

In order to estimate the extent of divergence for very small droplets we may neglect the repulsive terms and put $m = u = 7$, the value given by wave mechanics. Then when $r = 10d$ formulæ (6) gives a value only 7·6 % in excess of the true result obtained from equation (3), and when $r = 5d$ the excess is only 12·9 %. The same remarks apply to the vapour pressure of a droplet.

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THE MOLECULAR STATE OF INORGANIC LIQUIDS.

By A. R. Morgan and S. T. Bowden.

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Although the osmotic properties of inorganic substances in aqueous solution have been the subject of extensive investigation, few measurements have been made upon non-aqueous solutions of non-polar and dipolar inorganic compounds. In connection with other investigations in this laboratory we were led to examine the properties of arsenic trichloride, phosphorus trichloride, sulphur monochloride, phosphorus oxychloride, sulphuryl chloride and thionyl chloride for the purpose of ascertaining the molecular condition of these substances in non-polar

media. Inasmuch as the ebullioscopic measurements of previous workers [1] led to erroneous results owing to the volatility of the solute, the cryoscopic method was employed in the present determinations.

Experimental.

Since the liquids suffer ready hydrolysis on exposure to the atmosphere they were allowed to stand for a short time over freshly activated silica gel (in order to adsorb traces of free hydrogen chloride) prior to distillation in an all-glass apparatus, which incorporated a long Dufton column and

TABLE I.

Substance.	Weight of Solute (g).	Depression.	Molecular Weight.
Arsenic trichloride $M = 181·3$ . . .	0·583	0·96	180
	1·214	1·97	182
	0·445	0·72	182
	0·986	1·58	184
			Mean 182
Phosphorus trichloride $M = 137·4$ . .	0·308	0·60	152
	0·664	1·31	150
	1·175	2·31	150
	1·006	2·01	148
	1·389	2·73	150
			Mean 150
Sulphur monochloride $M = 135·0$ . .	0·730	1·55	139
	0·983	2·07	140
	0·369	0·80	136
	0·885	1·90	137
	1·434	3·06	138
			Mean 138
Phosphorus oxychloride $M = 153·4$ . .	0·223	0·39	169
	0·623	1·09	169
	0·958	1·70	167
	0·481	0·89	160
	1·187	2·15	163
			Mean 166
Sulphuryl chloride $M = 135·1$ . . .	1·079	2·26	141
	1·367	2·82	143
	0·442	0·95	137
	0·702	1·49	139
			Mean 140
Thionyl chloride $M = 119·1$ . . .	0·246	0·56	130
	0·610	1·41	127
	1·060	2·45	128
	0·765	1·88	120
	1·310	3·16	122
			Mean 125

condensing unit provided with guard-tubes of anhydrous calcium chloride and silica gel. Each liquid was subjected to at least three fractionations under ordinary pressure, but sulphur monochloride was fractionated under reduced pressure in order to avoid thermal decomposition. The boiling-points and densities of the pure liquids were as follows: arsenic trichloride, b.p. 129·0°/771 mm., $d_{4°}^{25°}$ 2·1497; phosphorus trichloride, b.p. 75·7°/758 mm., $d_{4°}^{25°}$ 1·5659; sulphur monochloride, b.p. 42·0°/23 mm., $d_{4°}^{25°}$ 1·6714; phosphorus oxychloride, b.p. 105·9°/762 mm., $d_{4°}^{25°}$ 1·6676; thionyl

[1] Oddo and Serra, *Gazz. Chim. Ital.*, 1899, **31**, 222.

chloride, b.p. 76·5°/766 mm., $d_4^{25°}$ 1·6290 ; sulphuryl chloride, b.p. 69·2°/754 mm., $d_4^{25°}$ 1·6570. Benzene (purified for molecular weight determinations) was distilled over phosphorus pentoxide (free from trioxide) before use as solvent.

The cryoscopic apparatus consisted of a Beckmann tube provided with a three-holed rubber stopper carrying a calibrated thermometer, a delivery tube for the admission of nitrogen, and a glass stirrer. The stirrer was arranged to operate through an air-tight device, while a slow stream of rigorously dried nitrogen was passed through the apparatus. The gas was led out through the side-tube of the Beckmann vessel, which was also fitted with a guard-tube of calcium chloride to prevent backward diffusion of moisture. The measurements were carried out in accordance with the orthodox procedure with due regard to the precautions adopted in the case of highly reactive solutions.[2] The final concentrations employed, however, were rather higher than is customary in cryoscopic work in order to detect, if possible, the incidence of association. The cryoscopic constant of benzene was determined from the depressions produced by pure naphthalene under the same experimental conditions. The mean value, $K = 52·3$, was employed in calculating the results shown in Table I.

Discussion.

The molecular state of the pure liquids has been studied by Vaubel,[3] but as may be seen from Table II, the values of the association factor

TABLE II.—ASSOCIATION FACTORS.

	Vaubel.	Ramsay and Shields.	Walden.	Longinescu.	Present Work.
$AsCl_3$ . . .	1·50	—	0·83	0·83	1·00
PCl_3 . . .	1·48	1·02	0·97	1·17	1·09
S_2Cl_2 . . .	1·37	0·95	1·27	1·44	1·02
$POCl_3$ . . .	—	1·00	0·99	0·99	1·08
$SOCl_2$ . . .	—	1·08	0·80	1·09	1·05
SO_2Cl_2 . . .	—	0·97	1·09	0·80	1·03

obtained by this investigator are higher than would be anticipated from the general properties of the liquids. The association factors calculated from the surface energy equations of Ramsay and Shields [4] and Walden [5] are in good agreement in the case of all the liquids with the exception of sulphur monochloride. The values computed from the empirical equation of Longinescu [6] correspond fairly well with those obtained by the other methods.

The cryoscopic measurements show that the observed molecular weight does not change appreciably with the concentration of the solution. Although the calculation of the association factors on this basis depends on the premise that no interaction occurs between solvent and solute, there is little doubt that these values are more reliable than those calculated from the surface energy relations. In fact, we find no discrepancy in the case of sulphur monochloride, which behaves as a perfectly normal liquid. The depressions produced by phosphorus

[2] Bowden, *J. Chem. Soc.*, 1939, 37.
[3] Vaubel, *J. prak. Chem.*, 1904, **69**, 138.
[4] Ramsay and Shields, *J. Chem. Soc.*, 1893, **63**, 1087.
[5] Walden, *Z. physik. Chem.*, 1909, **65**, 129.
[6] Longinescu, *J. Chim. physique*, 1903, **1**, 289.

trichloride and phosphorus oxychloride are slightly lower than the ideal, and these deviations may be due to internal pressure differences between solvent and solute or to slight association of the solute.

It has been found by Sugden and his co-workers [7] that the parachor of several of the above substances is independent of the temperature of measurement and that these liquids, therefore, are essentially normal. Moreover, measurements in this laboratory reveal that the variation of viscosity with temperature conforms to the Andrade exponential formula [8] in the case of arsenic trichloride, sulphur monochloride and phosphorus oxychloride. Although such conformity does not in itself prove that association is absent, it does imply that there is no change of association with temperature. In the case of phosphorus trichloride, sulphuryl chloride and thionyl chloride, however, there is appreciable departure from the exponential relation, and this is doubtless to be referred to the difference in the associative tendency of the molecules at different temperatures.

Summary.

Molecular weight determinations on non-polar and dipolar inorganic chlorides in benzene solution indicate that the liquids behave as normal solutes with the exception of phosphorus trichloride and phosphorus oxychloride which show slight deviations from ideality. The results are briefly discussed in the light of the various formulæ for calculating association factors, and also from the standpoint of the exponential formula for the variation of viscosity with temperature.

[7] Sugden, Reed and Wilkins, *J. Chem. Soc.*, 1925, **127**, 1525.
[8] Andrade, *Phil. Mag.*, 1934, **17**, 497, 698.

THE THERMODYNAMICS OF INTERFACES IN SYSTEMS OF SEVERAL COMPONENTS.

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Part I. Plane Interfaces.

1. Introduction.

The thermodynamics of an interface separating a simple liquid from its vapour offer little difficulty and are well known. The physical chemist's interest, however, is directed largely to variations of composition. The thermodynamical formulæ for an interface separating a solution from its vapour or for an interface separating two liquid phases of at least two components are considerably more complicated. The classical treatment is, of course, that of Gibbs,[1] and it has the mathematical elegance characteristic of all Gibbs' work, but it must be admitted that this treatment is not readily assimilated. The characteristic feature of Gibbs' treatment is the introduction of a mathematical surface. Each extensive property of the system, such as its free energy, its entropy, its content of each component, is then imagined to be composed of three

[1] Gibbs, *Collected Works*, vol. 1, pp. 219 *seq.* (Longmans, 1928).

parts: the first is the contribution of the one bulk phase on the supposition that its properties remained homogeneous as far as the mathematical surface; the second is the similar contribution of the other bulk phase; the residual part of the extensive property is assigned to the mathematical surface. Thus to the mathematical surface are assigned a free energy, an entropy, a quantity of each component, but of course no volume. Although this method of treatment is mathematically accurate it has two features, closely related to each other, which make it particularly difficult to visualise. The first is that the actual values of the several extensive properties assigned to the mathematical surface depend to a marked degree on the exact position of the mathematical surface in the physical interfacial layer. In fact the mathematical surface can be so placed as to make a selected one of these extensive properties have an arbitrarily chosen value, such as zero.[2] The second unnatural feature is that the mathematical surface having by definition no volume, does not correspond to our physical picture of an interfacial layer. Experience indicates that it is much less difficult to use Gibbs' formulæ than to understand them.

In contrast to Gibbs' abstract treatment of surfaces, several Dutch physicists, notably Van der Waals and Bakker,[3] have made important contributions to the theory of surfaces by treating the surface as a layer of small but finite uniform thickness. Their treatment applies to a system of a single component, that is to the surface separating a simple liquid from its vapour. Verschaffelt[4] has supplied a treatment of surfaces between phases of several components, which explicitly recognises the finite thickness of the surface layer. This treatment shares the elegance of Gibbs' analysis, while avoiding the abstraction of his mathematical surface. The present treatment agrees in principle with that of Verschaffelt, but differs from it particularly in my choice of a set of independent variables, which I believe to be convenient in practice. In Part I, following Verschaffelt, I shall suppose the interface to be plane. In Part II I shall discuss briefly the applicability of the formulæ to curved interfaces.

2. Definitions.

Fig. 1 represents two homogeneous bulk phases, α and β, between which lies the surface layer σ. The boundary between σ and α is the plane AA′, that between σ and β the parallel plane BB′. All properties of σ are uniform in directions parallel to AA′, but not in the direction normal to AA′. At and near AA′ the properties are identical with those of the phase α; at and near BB′ they are identical with those of the phase β. Subject to these conditions there is freedom of choice in placing the planes AA′ and BB′. It will be possible and therefore natural, though not essential, so to place the planes AA′ and BB′ that the uniform distance between them is submicroscopic and usually less than 10^{-6} cm.

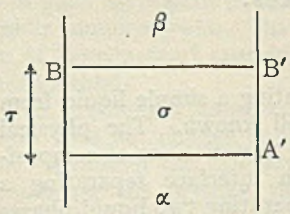

FIG. 1.

[2] See Guggenheim and Adam, *Proc. Roy. Soc. A*, 1933, **139**, 218.
[3] See *Handb. Experimentalphysik*, 1928, **6**.
[4] Verschaffelt, *Acad. roy. Belgique*, Bull. classe sciences, 1936, **22**, No. 4, pp. 373, 390, 402.

Since the surface layer σ is a material system with a well-defined volume and material content, its thermodynamic properties require no special definition. We may speak of its temperature, free energy, composition and so on just as for a homogeneous bulk phase. The only functions that call for special comment are the pressure and the surface tension. In any homogeneous bulk phase the force across any unit area is equal in all directions and is called the pressure. But in σ the force across unit area is not the same in all directions. If, however, we choose any plane of unit area parallel to AA′ and BB′, then the force across it has the same value for all positions of the plane whether it lie in α, β or σ; this value of the force across unit area is called the pressure P. Suppose, on the other hand, we choose a plane perpendicular to AA′ and extending above AA′ and below BB′; let this plane have the form of a rectangle of height h (parallel to AB) and of thickness l (perpendicular to the plane of the paper). Then the force across this plane will be equal to $Phl - \gamma l$, where P is the above-defined pressure and γ is the interfacial tension. If the height of this plane is chosen to extend exactly from AA′ to BB′, then the force across it will be equal to $P\tau l - \gamma l$, if the height AB is denoted by τ. Let the surface layer have an area A, a perimeter s and a volume V^σ so that

$$V^\sigma = \tau A. \qquad (2,1)$$

Suppose the area to be increased to $A + \mathrm{d}A$, the perimeter to $s + \mathrm{d}s$, the thickness to $\tau + \mathrm{d}\tau$ and the volume to $V^\sigma + \mathrm{d}V^\sigma$, the *material content remaining unaltered.* Then the work done on σ consists of $-pA\mathrm{d}\tau$ by the forces across AA′ and BB′ and $-(P\tau s - \gamma s)\mathrm{d}A/s$ by the forces parallel to the planes AA′ and BB′. The total work done on σ is therefore

$$\begin{aligned} &- PA\mathrm{d}\tau - (P\tau s - \gamma s)\mathrm{d}A/s \\ &= - P(A\mathrm{d}\tau + \tau\mathrm{d}A) + \gamma\mathrm{d}A \\ &= - P\mathrm{d}V^\sigma + \gamma\mathrm{d}A. \qquad (2,2) \end{aligned}$$

This expression takes the place of $-P\mathrm{d}V^\alpha$ for a homogeneous bulk phase α.

3. Free Energy of Surface Layer.

For the most general variation of the free energy F^α of a homogeneous bulk phase we have the well-known formula

$$\mathrm{d}F^\alpha = - S^\alpha\mathrm{d}T - P\mathrm{d}V^\alpha + \Sigma_r\mu_r\mathrm{d}n_r^\alpha, \qquad (3,1)$$

where S denotes entropy, T temperature, P pressure, V volume, μ_r chemical potential of the component r, and n_r number of moles of component r. The first term on the right gives the dependence of F on temperature, the second its dependence on volume and the remaining terms its dependence on composition. For a surface phase σ the dependence of the free energy F^σ on the temperature and the composition will be exactly parallel to that for a bulk phase; this may be taken as practically the definition of entropy and chemical potentials. But for the dependence of F^σ on size and shape we must replace $-P\mathrm{d}V$ by the expression (2, 2). We thus obtain the formula

$$\mathrm{d}F^\sigma = - S^\sigma\mathrm{d}T - P\mathrm{d}V^\sigma + \gamma\mathrm{d}A + \Sigma_r\mu_r\mathrm{d}n_r^\sigma. \qquad (3,2)$$

There is no need to add superscripts to T, P, μ_r, because these must have values uniform throughout α, β and σ in order that there may be thermal, mechanical and physico-chemical equilibrium.

4. Analogue of Gibbs-Duhem Relations.

In formula (3, 2) let us now set

$$dT = 0, \quad dV^\sigma = -V^\sigma d\lambda, \quad dA = -A d\lambda, \quad dn_r^\sigma = -n_r^\sigma d\lambda, \quad (4, 1)$$

and obtain

$$dF^\sigma = -d\lambda(-PV^\sigma + \gamma A + \Sigma_r \mu_r n_r^\sigma). \quad . \quad . \quad (4, 2)$$

This substitution corresponds physically to decreasing the extent of the surface layer σ by simply cutting off a portion at its edge, so that what remains is exactly like the original system except that it is reduced in extent in the ratio $(1 - d\lambda) : 1$. It is therefore obvious that F^σ will also be reduced in the same ratio. It is equally obvious that P, γ, μ_r remain unaltered. (In mathematical terminology: at constant temperature and thickness F^σ is homogeneous of first degree in V^σ, A and n_r^σ and of zero degree in P, γ, μ_r.) Thus the conditions (4, 1) imply the simultaneous conditions

$$dF^\sigma = -F^\sigma d\lambda, \quad dP = 0, \quad d\gamma = 0, \quad d\mu_r = 0. \quad . \quad (4, 3)$$

Substituting the value of dF^σ into (4, 2) we obtain

$$-F^\sigma d\lambda = -(-PV^\sigma + \gamma A + \Sigma_r \mu_r n_r^\sigma) d\lambda, \quad . \quad (4, 4)$$

and equating coefficients of $d\lambda$

$$F^\sigma = -PV^\sigma + \gamma A + \Sigma_r \mu_r n_r^\sigma \quad . \quad . \quad . \quad (4, 5)$$

or

$$F^\sigma + PV^\sigma - \gamma A = \Sigma_r \mu_r n_r^\sigma. \quad . \quad . \quad . \quad (4, 6)$$

(Alternatively formula (4, 6) can be derived mathematically from (3, 1) by using Euler's theorem.) Formula (4, 6) is the analogue of

$$F^\alpha + PV^\alpha = \Sigma_r \mu_r n_r^\alpha \quad . \quad . \quad . \quad . \quad (4, 7)$$

for a homogeneous bulk phase.

If we define the Gibbs functions G^α and G^σ by

$$G^\alpha = F^\alpha + PV^\alpha, \quad . \quad . \quad . \quad . \quad (4, 8)$$

$$G^\sigma = F^\sigma + PV^\sigma - \gamma A, \quad . \quad . \quad . \quad (4, 9)$$

then we deduce from (3, 1) and (4, 6)

$$dG^\sigma = -S^\sigma dT + V^\sigma dP - A d\gamma + \Sigma_r \mu_r dn_r^\sigma, \quad . \quad (4, 10)$$

$$G^\sigma = \Sigma_r \mu_r n_r^\sigma. \quad . \quad . \quad . \quad . \quad (4, 11)$$

These two formulæ are the analogues of the formulæ

$$dG^\alpha = -S^\alpha dT + V^\alpha dP + \Sigma_r \mu_r dn_r^\alpha, \quad . \quad . \quad (4, 12)$$

$$G^\alpha = \Sigma_r \mu_r n_r^\alpha. \quad . \quad . \quad . \quad . \quad (4, 13)$$

for a homogeneous bulk phase. Thus the partial molar derivatives of G^α are the μ_r^α's and the partial molar derivatives of G^σ are the μ_r^σ's.

If we differentiate (4, 6) we obtain

$$dF^\sigma + PdV^\sigma + V^\sigma dP - \gamma dA - A d\gamma = \Sigma_r \mu_r dn_r^\sigma + \Sigma_r n_r^\sigma d\mu_r. \quad (4, 14)$$

If we subtract (4, 14) from (3, 1) we obtain

$$S^\sigma dT - V^\sigma dP + A d\gamma + \Sigma_r n_r^\sigma d\mu_r = 0, \quad . \quad . \quad (4, 15)$$

which is the analogue of the Gibbs-Duhem formula

$$S^\sigma \mathrm{d}T - V^\sigma \mathrm{d}P + \Sigma_r n_r^\sigma \mathrm{d}\mu_r = 0. \quad . \quad . \quad . \quad (4, 16)$$

If we divide (4, 16) throughout by A we obtain the more convenient form

$$s^\sigma \mathrm{d}T - \tau \mathrm{d}P + \mathrm{d}\gamma + \Sigma_r \Gamma_r \mathrm{d}\mu_r = 0, \quad . \quad . \quad (4, 17)$$

where s^σ is the entropy per unit area and Γ_r is the number of moles, of the component r in unit area of surface layer, defined respectively by

$$s^\sigma = S^\sigma/A, \quad \Gamma_r = n_r^\sigma/A. \quad . \quad . \quad . \quad (4, 18)$$

It will be remembered that τ is the thickness of the surface layer, that is to say the length AB in Fig. 1.

5. Independent Variables.

We can rewrite (4, 17) in the form

$$-\mathrm{d}\gamma = s^\sigma \mathrm{d}T - \tau \mathrm{d}P + \Sigma_r \Gamma_r \mathrm{d}\mu_r. \quad . \quad . \quad (5, 1)$$

This tells us how the interfacial tension varies when the temperature, pressure and chemical potentials vary, but these variables are not all independently variable. It will be more useful if we can obtain a formula for $\mathrm{d}\gamma$ expressed in terms of independent variables.

The state of a single homogeneous bulk phase (apart from its quantity) may be completely defined by its temperature T, its pressure P, and its composition. If there are r components, the composition is conveniently defined by the r mole fractions x_r of which only $r - 1$ are independent because of the identity

$$\Sigma_r x_r = 1. \quad . \quad . \quad . \quad . \quad (5, 2)$$

Alternatively the state of the single phase might be defined by the $r + 2$ quantities T, P, μ_r of which only $r + 1$ are independent because of the Gibbs-Duhem relation (4, 16).

If we have two homogeneous phases α and β of r components, then the state of each separately may be defined by the variables $T, P, x_2, x_3, \ldots x_r$. If the two phases are in equilibrium there will be one condition of thermal equilibrium (equality of T^α and T^β), one condition of mechanical equilibrium (equality of P^α and P^β), and r conditions of chemical equilibrium (equality of μ_r^α and μ_r^β), one for each component. Thus the number of independent variables is reduced from $2(r + 1)$ to $2(r + 1) - (r + 2)$ or r. We may, for example, take these to be T, $x_2^\alpha, x_3^\alpha, \ldots x_r^\alpha$, in which case P is not an independent variable.

Let us now return to our original system consisting of the two bulk phases α and β and the surface layer σ. At equilibrium all the properties of the surface layer σ other than its extent are determined by the states of the phases α and β. Thus the number of independent variables for the whole system is r, and these can be taken as T, $x_2^\alpha, x_3^\alpha, \ldots x_r^\alpha$. Thus only r out of the $r + 2$ differentials on the right of (5, 1) are independent. It must therefore be possible to eliminate $\mathrm{d}P$ and one other.

We must remember that the present treatment is confined to plane surface layers. If we allowed curved surfaces, there would no longer be equality of P^α and P^β, and so we should have an extra degree of freedom.

6. Special Notation.

At this stage it is convenient for the sake of brevity to introduce a special notation. Suppose ϕ^α to be any intensive property of the phase α. Then we may regard ϕ^α as a function of T, P, x_2^α, x_3^α, . . . x_r^α. We shall now introduce the operator D defined as follows:

$$\mathrm{D}\phi^\alpha = \frac{\partial\phi^\alpha}{\partial x_2}\mathrm{d}x_2^\alpha + \frac{\partial\phi^\alpha}{\partial x_3}\mathrm{d}x_3^\alpha + \ldots + \frac{\partial\phi^\alpha}{\partial x_r}\mathrm{d}x_r^\alpha, \qquad (6, 1)$$

so that

$$\mathrm{d}\phi^\alpha = \frac{\partial\phi^\alpha}{\partial T}\mathrm{d}T + \frac{\partial\phi^\alpha}{\partial P}\mathrm{d}P + \mathrm{D}\phi^\alpha. \qquad (6, 2)$$

In words $\mathrm{D}\phi^\alpha$ is the part of the variation of ϕ^α due to variation of composition when T, P are kept constant.

When we use this notation we have

$$\mathrm{d}\mu_r^\alpha = -s_r^\alpha\mathrm{d}T + v_r^\alpha\mathrm{d}P + \mathrm{D}\mu_r^\alpha, \qquad (6, 3)$$

where s_r^α, v_r^α are the partial molar entropy and the partial molar volume of r in the phase α. Similarly in the phase β we have

$$\mathrm{d}\mu_r^\beta = -s_r^\beta\mathrm{d}T + v_r^\beta\mathrm{d}P + \mathrm{D}\mu_r^\beta. \qquad (6, 4)$$

Using this same notation, we can write the Gibbs-Duhem relations in the forms

$$\Sigma_r x_r^\alpha \mathrm{D}\mu_r^\alpha = 0, \qquad (6, 5)$$

$$\Sigma_r x_r^\beta \mathrm{D}\mu_r^\beta = 0. \qquad (6, 6)$$

7. Transformation of Formulæ.

The variation of the chemical potential of each component r in the phases α and β are determined by (6, 3) and (6, 4) respectively. The conditions for physico-chemical equilibrium between the two phases are of the form

$$\mu_r^\alpha = \mu_r^\beta. \qquad (7, 1)$$

Hence for variations at which equilibrium is maintained, we have

$$\mathrm{d}\mu_r^\alpha = \mathrm{d}\mu_r^\beta. \qquad (7, 2)$$

If we multiply (7, 2) by x_r^β, substitute from (6, 3) and (6, 4) and add for all r we obtain, using (6, 6),

$$-\Sigma_r x_r^\beta(s_r^\alpha - s_r^\beta)\mathrm{d}T + \Sigma_r x_r^\beta(v_r^\alpha - v_r^\beta)\mathrm{d}P + \Sigma_r x_r^\beta \mathrm{D}\mu_r^\alpha = 0. \qquad (7, 3)$$

If we substitute from (6, 3) into (5, 1) we obtain

$$-\mathrm{d}\gamma = (s^\sigma - \Sigma_r\Gamma_r s_r^\alpha)\mathrm{d}T - (\tau - \Sigma_r\Gamma_r v_r^\alpha)\mathrm{d}P + \Sigma_r\Gamma_r\mathrm{D}\mu_r^\alpha. \qquad (7, 4)$$

If we now eliminate $\mathrm{d}P$ between (7, 3) and (7, 4) we obtain

$$-\mathrm{d}\gamma = \left\{(s^\sigma - \Sigma_r\Gamma_r s_r^\alpha) - (\tau - \Sigma_r\Gamma_r v_r^\alpha)\frac{\Sigma_r x_r^\beta(s_r^\alpha - s_r^\beta)}{\Sigma_r x_r^\beta(v_r^\alpha - v_r^\beta)}\right\}\mathrm{d}T$$
$$+ \Sigma_r\left\{\Gamma_r + x_r^\beta\frac{\tau - \Sigma_r\Gamma_r v_r^\alpha}{\Sigma_r x_r^\beta(v_r^\alpha - v_r^\beta)}\right\}\mathrm{D}\mu_r^\alpha. \qquad (7, 5)$$

This somewhat formidable looking formula can be considerably abbreviated by using a suitable notation. If we denote by h^β the heat absorbed and by e^β the volume expansion when one mole of the phase β is formed reversibly at constant temperature and at constant pressure

by taking the required amounts of the various components from the phase α, then clearly

$$h^\beta = T\Sigma_r x_r^\beta(s_r^\beta - s_r^\alpha), \quad . \quad . \quad . \quad (7, 6)$$

$$e^\beta = \Sigma_r x_r^\beta(v_r^\beta - v_r^\alpha). \quad . \quad . \quad . \quad (7, 7)$$

Similarly, if we denote by h^σ the heat absorbed and by e^σ the volume expansion when unit area of the surface layer σ is formed reversibly at constant temperature and at constant pressure by taking the required amounts of the various components from the phase α, then clearly *

$$h^\sigma = T(s^\sigma - \Sigma_r \Gamma_r s_r^\alpha), \quad . \quad . \quad . \quad (7, 8)$$

$$e^\sigma = \tau - \Sigma_r \Gamma_r v_r^\alpha. \quad . \quad . \quad . \quad . \quad (7, 9)$$

If we use these new symbols, (7, 5) reduces to

$$-\,\mathrm{d}\gamma = \left(h^\sigma - \frac{e^\sigma h^\beta}{e^\beta}\right)\frac{\mathrm{d}T}{T} + \Sigma_r\left(\Gamma_r + \frac{e^\sigma x_r^\beta}{e^\beta}\right)\mathrm{D}\mu_r^\alpha. \quad . \quad (7, 10)$$

Finally, we can eliminate one of the $\mathrm{D}\mu_r^\alpha$, say $\mathrm{D}\mu_1^\alpha$'s, by means of (6, 5). We thus obtain

$$-\,\mathrm{d}\gamma = \left(h^\sigma - \frac{e^\sigma h^\beta}{e^\beta}\right)\frac{\mathrm{d}T}{T} + \Sigma_r'\left\{\left(\Gamma_r - \frac{x_r^\alpha \Gamma_1}{x_1^\alpha}\right) + \frac{e^\sigma(x_1^\alpha x_r^\beta - x_r^\alpha x_1^\beta)}{e^\beta x_1^\alpha}\right\}\mathrm{D}\mu_r^\alpha, \quad (7, 11)$$

where Σ_r' denotes that $r = 1$ is omitted from the-summation.

We have now obtained an exact formula expressing $\mathrm{d}\gamma$ in terms of the r independent variables $\mathrm{d}T$, $\mathrm{D}\mu_2^\alpha$, $\mathrm{D}\mu_3^\alpha$, . . . $\mathrm{D}\mu_r^\alpha$. This formula embraces all the information one can want regarding the variation of the interfacial tension. It will have been noticed that the two bulk phases α and β have not been treated on a par; formula (7, 11) relates $\mathrm{d}\gamma$ to the $\mathrm{D}\mu_r^\alpha$, not to the $\mathrm{D}\mu_r^\beta$. In applications to a liquid-vapour interface it will be usual to take the liquid phase as α, while in the case of a liquid-liquid interface it is immaterial which of the two liquid phases one takes as α. From here on it will then be assumed that the phase α is liquid.

If we denote activity coefficients in the liquid phase α by f_r^α, then we have

$$\mathrm{D}\mu_r^\alpha = RT\mathrm{D}\log x_r^\alpha f_r^\alpha, \quad . \quad . \quad . \quad (7, 12)$$

from which we see that the $\mathrm{D}\mu_r^\alpha$'s are experimentally measurable quantities. If the vapour phase in equilibrium with the phase α (this may or may not be the phase β) may be regarded as a perfect gas and we denote partial vapour pressures over the phase α by p_r^α, we also have

$$\mathrm{D}\mu_r^\alpha = RT\mathrm{D}\log p_r^\alpha. \quad . \quad . \quad . \quad (7, 13)$$

This formula will remain valid even if the vapour is not a perfect gas provided we let p_r^α denote the fugacities rather than the partial vapour pressures. On this understanding we substitute (7, 13) into (7, 11) and obtain finally

$$-\,\mathrm{d}\gamma = \left(h^\sigma - \frac{e^\sigma h^\beta}{e^\beta}\right)\frac{\mathrm{d}T}{T} + \Sigma_r'\left\{\left(\Gamma_r - \frac{x_r^\alpha \Gamma_1}{x_1^\alpha}\right) + \frac{e^\sigma(x_1^\alpha x_r^\beta - x_r^\alpha x_1^\beta)}{e^\beta x_1^\alpha}\right\}RT\mathrm{D}\log p_r^\alpha. \quad (7, 14)$$

* The quantities which I have denoted by h^β, e^β, h^σ, e^σ would be more reasonably denoted by $h^{\alpha\beta}$, $e^{\alpha\beta}$, $h^{\alpha\sigma}$, $e^{\alpha\sigma}$, or better still by $h^{\alpha\to\beta}$, $e^{\alpha\to\beta}$, $h^{\alpha\to\sigma}$, $e^{\alpha\to\sigma}$. My choice of the shorter symbols has been made to facilitate printing.

Either of formulæ (7, 11) and (7, 14) may be regarded as the fundamental formula of the present treatment.

If both the phases α and β are liquid it can happen that e^β is zero. The equilibrium between α and β is then independent of P, and so we are obliged to retain P as an independent variable; the coefficient of P in (7, 3) vanishes, and so we cannot eliminate P between (7, 3) and (7, 4). However, the vanishing of e^β implies that the tightness of packing of the molecules is the same in phases α and β (*i.e.* equal partial molar volumes in the two phases) and one may then with some confidence expect the same tightness of packing in σ. In this case, e^σ is also zero, wherever one places the plane BB′; thus the coefficient of $\mathrm{d}P$ in (7, 4) is zero. If then we eliminate $\mathrm{D}\mu^\alpha$ from (7, 4) by means of (6, 5), we now obtain in place of (7, 11) the simpler result

$$-\mathrm{d}\gamma = h^\sigma \frac{\mathrm{d}T}{T} + \Sigma_r'\left(\Gamma_r - \frac{x_r^\alpha \Gamma_1}{x_1^\alpha}\right)\mathrm{D}\mu_r^\alpha, \quad . \quad . \quad (7, 11a)$$

and correspondingly, in place of (7, 14),

$$-\mathrm{d}\gamma = h^\sigma \frac{\mathrm{d}T}{T} + \Sigma_r'\left(\Gamma_r - \frac{x_r^\alpha \Gamma_1}{x_1^\alpha}\right) RT\mathrm{D}\log p_r^\alpha. \quad . \quad (7, 14a)$$

8. Invariance of Fundamental Formula.

Although the quantities Γ_r, h^σ and e^σ have simple physical meanings, their values will depend on the positions assigned to the planes AA′ and BB′ which bound the surface layer. It can be shown, however, that formula (7, 11) remains invariant when either of the planes is shifted.

Let us first consider a shift of the plane AA′ a distance $\delta\tau$ away from BB′. Then Γ_r becomes increased by the number of moles in a cylinder of α of height $\delta\tau$, of unit cross-section, and consequently of volume $\delta\tau$. If, therefore, C^α denotes the total number of moles of any kind per unit volume in α, then Γ_r becomes increased by $x_r^\alpha C^\alpha \delta\tau$. Similarly, Γ_1 becomes increased to $x_1^\alpha C^\alpha \delta\tau$. Hence $(\Gamma_r - \Gamma_1 x_r^\alpha / x_1^\alpha)$ remains invariant. Furthermore, it is clear from their definitions that h^σ and e^σ remain invariant when the plane AA′ is shifted. Hence formula (7, 11) is invariant with respect to a shift of the plane AA′.

Let us now consider a shift of the plane BB′ a distance $\delta\tau$ away from AA′. In this case, if C^β denotes the total number of moles of any kind per unit volume in the phase β, Γ_r becomes increased by $x_r^\beta C^\beta \delta\tau$; at the same time h^σ becomes increased by $h^\beta C^\beta \mathrm{d}\tau$ and e^σ becomes increased by $e^\beta C^\beta \delta\tau$. If we substitute into (7, 11) it becomes immediately evident that the coefficients of $\mathrm{d}T$ and of each $\mathrm{D}\mu_r^\alpha$ all remain invariant.

We see then that the coefficients of $\mathrm{d}T$ and each $\mathrm{D}\mu_r^\alpha$ in (7, 11) or (7, 14) have values independent of the positions assigned to AA′ and BB′.

9. Temperature Coefficient of Interfacial Tension.

If we consider variations of temperature at constant composition of the (liquid) phase α, the pressure and the composition of the (gaseous or liquid) phase β being adjusted so as to maintain equilibrium, then all the $\mathrm{D}\mu_r^\alpha$ are zero. Formula (7, 11) or (7, 14) now reduces to

$$T\frac{\mathrm{d}\gamma}{\mathrm{d}T} = h^\sigma - \frac{e^\sigma h^\beta}{e^\beta}. \quad . \quad . \quad . \quad (9, 1)$$

A formula equivalent to (9, 1) has been obtained by Verschaffelt[4] for the special case of a simple liquid-vapour interface. For the general case of several components this formula is, so far as I know, new.

It has been verified in the previous section that the right side of (1) is invariant with respect to displacement of the plane BB′, while each term is separately invariant with respect to displacement of the plane AA′. If the plane BB′ can be so placed that e^σ vanishes, then (9, 1) reduces to

$$T\frac{\mathrm{d}\gamma}{\mathrm{d}T} = h^\sigma, \quad . \quad . \quad . \quad . \quad . \quad (9, 2)$$

but the physical significance of this arbitrary choice of the plane BB′ is far from obvious. Only in the special case referred to at the end of section 7 is formula (9, 2) valid wherever BB′ be placed.

10. Dependence of Superficial Tension on Composition.

For variations of composition at constant temperature formula (7, 14) reduces to

$$-\mathrm{d}\gamma = \sum_r{}' \left\{\left(\Gamma_r - \frac{x_r{}^\alpha \Gamma_1}{x_1{}^\alpha}\right) + \frac{e^\sigma(x_1{}^\alpha x_r{}^\beta - x_r{}^\alpha x_1{}^\beta)}{e^\beta x_1{}^\alpha}\right\} RT\mathrm{D}\log p_r. \quad (10, 1)$$

In the simple case of only two components this reduces further to

$$-\mathrm{d}\gamma = \left\{\left(\Gamma_2 - \frac{x_2{}^\alpha \Gamma_1}{x_1{}^\alpha}\right) + \frac{e^\sigma(x_2{}^\beta - x_2{}^\alpha)}{e^\beta x_1{}^\alpha}\right\} RT\mathrm{D}\ \log p_2. \quad (10, 2)$$

It has been verified in section 8 that the right side of (10, 1) is invariant with respect to displacements of the planes AA′ and BB′. If the plane BB′ can be so placed that e^σ vanishes, then (10, 1) reduces to

$$-\mathrm{d}\gamma = \sum_r{}' \left(\Gamma_r - \frac{x_r{}^\alpha \Gamma_1}{x_1{}^\alpha}\right) RT\mathrm{D}\log p_r. \quad . \quad (10, 3)$$

If, moreover, the plane AA′ can be so placed that Γ_1 vanishes, then (10, 3) reduces further to

$$-\mathrm{d}\gamma = \sum_r{}' \Gamma_r RT\mathrm{D}\log p_r. \quad . \quad . \quad . \quad (10, 4)$$

However, I believe that these algebraic contractions are achieved only at the cost of physical clarity (*Anschaulichkeit*) with respect to the meaning of the Γ_r's. Only in the special case referred to at the end of section 7 is formula (10, 3) valid wherever BB′ be placed.

11. Inert Components.

It is conceivable that certain components present in the phase β have a uniform concentration throughout β down to a certain plane where they fall abruptly to zero and remain zero across it and inside α. It will then be natural to choose this plane as BB′ the boundary between β and σ. These components may be called inert components, and will be denoted by the subscript i; the remaining components will be denoted by the subscript a. The number of components of the two classes will also be denoted by i and by a respectively. By using this notation formula (7, 4) becomes

$$-\mathrm{d}\gamma = (s^\sigma - \Sigma_a \Gamma_a s_a{}^\alpha)\mathrm{d}T - (\tau - \Sigma_a \Gamma_a v_a{}^\alpha)\mathrm{d}P + \Sigma_a \Gamma_a \mathrm{D}\mu_a{}^\alpha, \quad (11, 1)$$

since all the Γ_i's are by supposition zero. Similarly, the Gibbs-Duhem relation (6, 5) becomes

$$\Sigma_a x_a^\alpha \mathrm{D}\mu_a^\alpha = 0, \quad . \quad . \quad . \quad . \quad (11, 2)$$

since by supposition all the x_i^α's are zero. By means of (11, 2) we can eliminate one of the $\mathrm{D}\mu_a^\alpha$'s, say $\mathrm{D}\mu_1^\alpha$ from (11, 1). We obtain

$$-\mathrm{d}\gamma = (s^\sigma - \Sigma_a \Gamma_a s_a^\alpha)\mathrm{d}T - (\tau - \Sigma_a \Gamma_a v_a^\alpha)\mathrm{d}P + \Sigma_a'\left(\Gamma_a - \frac{x_a^\alpha \Gamma_1}{x_1^\alpha}\right)\mathrm{D}\mu_a, \quad (11, 3)$$

or in terms of h^σ and e^σ defined in section 7,

$$-\mathrm{d}\gamma = h^\sigma \frac{\mathrm{d}T}{T} - e^\sigma \mathrm{d}P + \Sigma_a'\left(\Gamma_a - \frac{x_a^\alpha \Gamma_1}{x_1^\alpha}\right)\mathrm{D}\mu_a. \quad . \quad (11, 4)$$

The number of differentials on the right of (11, 4) is $(a + 1)$, whereas the number of degrees of freedom of the whole system is $(a + i)$. Hence, as long as there is at least one inert component so that $i \geqslant 1$, the differentials on the right of (11, 4) are all independent. The physical explanation is that (11, 4) is a relation involving only properties of the phases α and of the interfaces σ; no properties of the phase β occur explicitly in (11, 4). The inert components present only in β are therefore available for adjusting the pressure P on the phase α without any need of altering its temperature or its composition. It is easily verified that each term on the right of (11, 4) is invariant with respect to displacements of the plane AA′. In the present case the plane BB′ is naturally fixed.

The treatment just described is particularly applicable to the interface between a liquid solution and the gaseous phase above it, when some of the gaseous constituents can be treated as inert components. The applications of formula (11, 4) are obvious. For example, we have for the temperature coefficient of γ at constant pressure and composition of the phase α

$$-\left(\frac{\partial \gamma}{\partial T}\right)_{P, x_a} = \frac{h^\sigma}{T}. \quad . \quad . \quad . \quad (11, 5)$$

Similarly, for the pressure coefficient of γ at constant temperature and composition of the phase α,

$$\left(\frac{\partial \gamma}{\partial P}\right)_{T, x_a} = e^\sigma. \quad . \quad . \quad . \quad . \quad (11, 6)$$

Finally, for variations of composition at constant temperature and pressure, we have

$$-\mathrm{d}\gamma = \Sigma_a'\left(\Gamma_a - \frac{x_a^\alpha \Gamma_1}{x_1^\alpha}\right)\mathrm{D}\mu_a = \Sigma_a'\left(\Gamma_a - \frac{x_a^\alpha \Gamma_1}{x_1^\alpha}\right) RT\mathrm{D}\log p_a^\alpha. \quad (11, 7)$$

The formulæ of this section are mostly familiar,* but the restrictive conditions for their validity seem to be less widely recognised.

12. Relation to Gibbs' Formulæ.

We have already verified that our formulæ remain invariant when either or both the planes AA′ and BB′ are shifted, as long as the inhomogeneous layer is contained between AA′ and BB′. Let us now

* The expression $(\Gamma_a - \Gamma_1 x_a^\alpha / x_1^\alpha)$ occurring in (11, 3), (11, 4) and (11, 7) is equivalent to Guggenheim and Adam's $\Gamma_a^{(1)}$ or to Gibbs' $\Gamma_{a(1)}$.

consider what happens if we move one of these planes towards the other until part of the inhomogeneous layer is on the outer side of the former plane. It is quite easy to see that all our formulæ can be made to remain unaltered, provided we alter our definitions of the symbols. We must now define F^α not as the free energy of the actual phase α up to the plane AA′, but as equal to the free energy of a fictitious phase α supposed to remain homogeneous right up to AA′. Similarly, we define F^β not as the free energy of the actual phase β down to the plane BB′, but as equal to the free energy of a fictitious phase β supposed to remain homogeneous right down to BB′. Finally, we define F^σ as the excess of the free energy F of the whole system over and above $F^\alpha + F^\beta$ as just defined. We give analogous definitions to S^α, S^β, S^σ; V^α, V^β, V^σ; n_r^α, n_r^β, n_r^σ.

As long as the planes AA′ and BB′ enclose the inhomogeneous layer, the new definitions of the thermodynamic functions relating to the surface are exactly equivalent to the ones used initially. The latter are certainly easier to visualise and are in this respect preferable. The only advantage of the former is that they allow us to place the two planes AA′ and BB′ as near to each other as we please, regardless of the structure of the surface layer, without affecting the validity of our formulæ. In particular we may, if we choose, make the planes AA′ and BB′ coincide. If we do this V^σ and τ become zero, some of the n_r^σ's and Γ_r^σ's may become negative and our formulæ reduce to those of Gibbs.

We may therefore describe Gibbs' formulæ as formally included in those of the present treatment. However, I believe that the mathematical elegance of Gibbs' formulæ is attained only at the cost of a certain obscurity in the physical significance of the symbols used. In the formulæ of the present treatment all the symbols have a simple physical definition with respect to an arbitrary pair of parallel planes enclosing the inhomogeneous layer.

In conclusion, it is interesting to note that Gibbs himself realised the existence of alternative formulations and recognised the possibility that the formulation, which he himself developed, might for certain purposes be less convenient than some alternative formulation.[5] I therefore hope the reader will regard the treatment, which I have described, as an attempt to follow the guidance of Gibbs without, however, following blindly.

I am indebted to Professor N. K. Adam, F.R.S., for his helpful and constructive criticism.

Part II. Curved Interfaces.

1. Introduction.

The object of Part II of this paper is to study the following question. What conditions are sufficient to justify the application to curved interfaces of the formulæ already derived for plane interfaces? As answer to this question we shall find that the formulæ strictly derived for plane interfaces may be applied to curved interfaces with an accuracy adequate for experimental purposes, provided that *the thickness of the inhomogeneous layer is small compared with its radii of curvature.*

[5] Gibbs, *loc. cit.*[1] Footnote on p. 267.

I shall first give a direct and simple derivation of this condition. We shall then see that this condition is in fact assumed implicitly by every experimenter when he measures a superficial tension and that when it is not satisfied the superficial tension and related properties of the interface become ill-defined. In conclusion, I shall discuss briefly Gibbs' treatment of the same subject.

2. Interfacial Tension of Curved Interface.

For the sake of simplicity let us first consider a system consisting of two homogeneous bulk phases α and β connected by a surface layer σ having the form of a circular cylindrical shell. Fig. 2 shows a cross-section of the phases α and β separated by the surface layer σ, bounded by the circular cylinders AA′ and BB′ with common axis O. There is complete homogeneity in the direction normal to the diagram. The properties of the surface layer σ are supposed identical at all points the same distance from the axis through O. Throughout the phase α and extending up to AA′ there is a uniform pressure P^α; throughout the phase β, and extending down to BB′, there is a uniform pressure P^β. Between AA′ and BB′ the pressure P_r parallel to the radii of the cylinders AA′ and BB′ varies continuously, but not necessarily monotonically, from the value P^α to the value P^β.

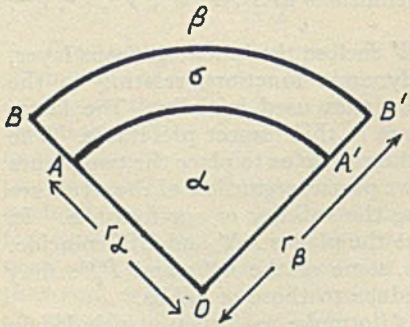

FIG. 2.

In the previous discussion of plane surfaces it was pointed out that the geometrical planes AA′ and BB′ could be placed an arbitrary distance apart, provided that the inhomogeneous layer was contained between them. For the present discussion of curved surfaces it is on the contrary essential that the circular cylindrical surfaces AA′ and BB′ should be placed as near together as is consistent with the condition that the inhomogeneous layer be contained between them. According to this condition we may usually expect the distance AB to be about 10^{-7} or 10^{-6} cm. I shall denote by r distances measured radially from O, and in particular by r_α and r_β, the distances OA and OB respectively.

Whereas the force per unit area across any element of surface inside either homogeneous phase is independent of the orientation of the element (Pascal's Law), this is not the case in the inhomogeneous layer σ. It is convenient to denote the force per unit area in the direction parallel to the surfaces AA′ and BB′ by $P_r - Q$. Both P_r and Q are functions of r. Q is zero at $r = r_\alpha$ and at $r = r_\beta$, but at least somewhere between Q is greater than zero. [It is conceivable that Q might be negative somewhere between $r = r_\alpha$ and $r = r_\beta$, but its average value in this range is unquestionably positive.]

According to elementary statics the mechanical equilibrium of the matter enclosed by AA′B′B requires that for all values of r

$$\mathrm{d}(P_r r) = (P_r - Q)\mathrm{d}r, \qquad (2, 1)$$

or

$$\mathrm{d}P_r = -Q\mathrm{d}r/r. \qquad (2, 2)$$

If we integrate (2, 2) from r_β to r_α we obtain

$$P^\alpha - P^\beta = \int_{r_\alpha}^{r_\beta} \frac{Q}{r} \mathrm{d}r. \quad . \quad . \quad . \quad (2, 3)$$

We now define quantities $\bar{r}$, γ, γ' by

$$2\bar{r} = r_\alpha + r_\beta, \quad . \quad . \quad . \quad . \quad . \quad (2, 4)$$

$$\gamma = \int_{r_\alpha}^{r_\beta} Q \mathrm{d}r, \quad . \quad . \quad . \quad . \quad . \quad (2, 5)$$

$$\gamma' = \bar{r} \int_{r_\alpha}^{r_\beta} \frac{Q}{r} \mathrm{d}r. \quad . \quad . \quad . \quad . \quad . \quad (2, 6)$$

According to (2, 6) we can rewrite (2, 3) in the form

$$P^\alpha - P^\beta = \gamma'/\bar{r}. \quad . \quad . \quad . \quad . \quad (2, 7)$$

If now $(r_\beta - r_\alpha) \ll r_\alpha$, so that we may ignore the distinction between r_α, r_β, $\bar{r}$, then we may also ignore the distinction between γ and γ', and instead of (2, 7) we may write

$$P^\alpha - P^\beta = \gamma/\bar{r}. \quad . \quad . \quad . \quad . \quad (2, 8)$$

Under these conditions either γ or γ' may be regarded as the interfacial tension.

For the sake of simplicity we have confined our attention to an interface in the form of a circular cylinder. For a spherical interface we should have found by analogous reasoning, instead of (2, 8),

$$P^\alpha - P^\beta = 2\gamma/\bar{r}. \quad . \quad . \quad . \quad . \quad (2, 9)$$

For an interface of arbitrary shape the geometry is somewhat more complicated and the general formula obtained is

$$P^\alpha - P^\beta = \gamma\left(\frac{1}{\rho_1} + \frac{1}{\rho_2}\right), \quad . \quad . \quad . \quad (2, 10)$$

where ρ_1, ρ_2 are the principal radii of curvature of the interface.

Formula (2, 10) is well known and, moreover, forms the basis of the experimental determinations of superficial tension. The quantities ρ_1, ρ_2 and $P^\alpha - P^\beta$ are measured, and then γ is calculated according to (2, 10). The best known method, that of the capillary rise, has already been discussed elsewhere [6] in relation to formula (2, 10). The point which I wish to emphasise is that, since formula (2, 10), like formulæ (2, 8) and (2, 9), implies ignoring the difference between lengths such as r_α, r_β, it follows that *the very measurement of interfacial tension implies that the thickness of the surface layer be small compared with its radii of curvature.*

3 Discussion of Pressure Difference.

Although the pressure difference $P^\alpha - P^\beta$ is fundamental in the measurement of γ, and so also one may say in the definition of γ, I shall show that this pressure difference is in certain other respects insignificant for the properties of the interface. I shall use the symbol τ to denote the thickness of the surface layer, hitherto denoted by $r_\beta - r_\alpha$. Let us consider a numerical example. We will suppose that $\tau = 10^{-7}$ cm. and that $\gamma = 50$ dynes/cm. Since the treatment requires that both principal radii of curvature satisfy the inequality $\rho \gg \tau$, if we aim at an accuracy

[6] Guggenheim, *Modern Thermodynamics*, p. 169 (Methuen 1933).

of the order 1 %, then ρ must not be less than 100 τ or 10^{-5} cm. According to formula (2, 10) we conclude that $P^\alpha - P^\beta$ is at most 10^7 dynes/cm.^{2} or 10 atmospheres. I have chosen a very unfavourable case and usually $P^\alpha - P^\beta$ will be only a small fraction of an atmosphere. Thus the product $(P^\alpha - P^\beta)$ cannot be greater than 1 dyne/cm. or 1 erg/cm.^{2}.

According to formula (2, 2) of Part I the total work done on a plane surface layer when its volume and area are altered is

$$-P\mathrm{d}V^\sigma + \gamma\mathrm{d}A. \quad . \quad . \quad . \quad . \quad (3, 1)$$

We could apply this formula also to a curved surface were it not for an ambiguity in the meaning of P. Since, however, we have verified that $(P^\alpha - P^\beta)\tau$ or $(P^\alpha - P^\beta)V^\sigma/A$ is at most 2 % of γ and usually much smaller, we may safely ignore this ambiguity. Thus (3, 1) is sufficiently accurate if P denotes P^α or P^β or any intermediate pressure. In virtue of the validity of (3, 1) for curved as well as plane interfaces, any of the formulæ of Part I are equally valid to the same degree of accuracy.

4. Dependence of Interfacial Tension on Curvature.

Let us now turn to the question of how the interfacial tension depends on the curvatures. We shall see that when the question is precisely defined it answers itself. In asking the question it is not sufficient to state that we vary the curvatures; we require also to state what we keep constant. For the question to be useful it should apply to the actual conditions of the experimental measurement of interfacial tension. For definiteness let us consider the capillary rise method. The values of the temperature T and the potentials μ_r are uniform throughout the system,* and so, whatever be the size and shape of the capillary, these variables have the same values at the curved surface where the surface tension is measured, as in the bulk phases. Hence to be useful the question should be worded: how does γ depend on ρ_1, ρ_2 for given values of T and the μ's. According to equation (5, 1) of Part I the variation of γ under these restrictions is given by

$$\mathrm{d}\gamma = \tau\mathrm{d}P. \quad . \quad . \quad . \quad . \quad (4, 1)$$

In its present application the ambiguity in the exact meaning of P does not matter, since we have already verified that $P^\alpha - P^\beta$ is negligible. If now we consider a curved interface, say in a capillary, in equilibrium with a plane interface and we integrate (4, 1) from the pressure at the plane surface to the pressure at the curved interface (either side of it) we again find that the integral of the right side is always negligible. Consequently γ has effectively the same value for the curved surface as for the plane surface with which it is in equilibrium. This is a statement of a principle usually assumed whenever an interfacial tension is measured. It is experimentally verified by the fact that within the experimental accuracy the same value is found for the interfacial tension when capillaries of different size are used, but this verification can be realised only for capillaries with diameters considerably greater than the lower limit 10^{-5} cm., allowed by the theory.

* For this statement to be true it is necessary that a gravitational term $M_r gh$ be included in μ_r, where M_r denotes molar mass, g gravitational accleration and h height. But it is physically obvious that the interfacial tension cannot depend on the height except through the pressure and composition. Such gravitational terms may therefore safely be omitted from the $\mathrm{d}\mu_r$'s in the formulæ relating $\mathrm{d}\gamma$ to the $\mathrm{d}\mu_r$'s.

5. Gibbs' Treatment.

The problem, which I have discussed, is treated by Gibbs [7] in a manner which appears to be quite different and more rigid. I have found Gibbs' treatment difficult and the more carefully I have studied it the more obscure it appears to me. The essence of Gibbs' treatment is that he replaces the term

$$\gamma \mathrm{d}A \quad . \quad . \quad . \quad . \quad . \quad (5, 1)$$

for a plane interface by terms of the form

$$\gamma \mathrm{d}A + C_1 \mathrm{d}\left(\frac{1}{\rho_1}\right) + C_2 \mathrm{d}\left(\frac{1}{\rho_2}\right), \quad . \quad . \quad . \quad (5, 2)$$

and assumes implicitly that, provided the radii of curvature are not too small, we may assign to C_1 and C_2 the values appropriate to a plane surface. It is then obvious from symmetry that $C_1 = C_2$, and so (5, 2) can be written in the simpler form

$$\gamma \mathrm{d}A + C \mathrm{d}\left(\frac{1}{\rho_1} + \frac{1}{\rho_2}\right), \quad . \quad . \quad . \quad . \quad (5, 3)$$

where C is independent of ρ_1, ρ_2. So far so good. Gibbs then sets out to prove that his geometrical surface can be so placed that C vanishes. The reasoning adduced is far from simple, and Gibbs' meaning is not even always clear. I am convinced that Gibbs was himself aware of the difficulty of being precise in this particular piece of reasoning. On page 226 he discusses the variation of a plane interface by bending it and uses the sentence "also at and about the surface let the state of the matter *so far as possible be the same* as at and about the plane surface in the initial state of the system." The words which I have written in italics are, I venture to say, in their vagueness unlike Gibbs' usual style. The whole treatment of Gibbs, as well as that of the present paper, postulates complete equilibrium throughout the whole system. It is therefore impossible to conceive of a variation of an interface apart from a variation in at least one of the bulk phases. It is clear that Gibbs realised this difficulty and tried to overcome it by flexible wording.

On the following page Gibbs claims to show that the position required for his geometrical surface to make C vanish will be either inside the non-homogeneous layer or at most at a distance from it comparable to the thickness of the layer. He here uses the words "on account of the thinness of the non-homogeneous film," and I feel convinced that this *thinness* is an essential assumption common to Gibbs' treatment and that outlined above. If then, as I believe, the assumption $\tau \ll r_\alpha$ is essential, it seems to me preferable to introduce it at the outset and so considerably simplify the whole argument.

Summary.

Part I.—

Following Verschaffelt the thermodynamic properties of a plane interface are derived by treating the interface as having a finite thickness. Formulæ are derived for the dependence of the interfacial tension on the temperature and the composition of one of the two bounding phases; the pressure, not being an independent variable, is eliminated. It is shown that the formulæ are invariant with respect to the thickness arbitrarily assigned to the interfacial layer. The treatment is correlated with that of Gibbs.

[7] Gibbs, *Collected Works*, vol. 1, pp. 225-228.

Part II.—

It is shown that the formulæ derived in Part I for plane interfaces may safely be applied to curved interfaces provided that the thickness of the inhomogeneous layer is negligibly small compared with its radius of curvature, a condition usually fulfilled in practice. When this condition is not fulfilled, the formulæ cease to be applicable and at the same time the normal methods of measuring interfacial tension break down and the very meaning of interfacial tension becomes ill-defined.

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CONTACT ANGLES OF "BUILT-UP" MULTILAYERS.

By J. J. Bikerman.

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1. Introduction.

The formation of "built-up" X, Y, or Z multilayers was recently[1] correlated to the wettability of the solid surfaces concerned; when this increased the transition $X \rightarrow Y \rightarrow Z$ took place. As a measure of wettability the angle α of sliding of a water drop on the multilayer was used. It was shown that in a first approximation the product $W \tan \alpha$, W being the weight of the sliding drop, was a constant for a given multilayer and could be taken as a measure of its hydrophilic character.

In the present work the wettability of a surface is determined by measuring the wetting angles θ formed by the solid, a water drop on it, and air. When θ was over 94° X films were deposited. Y films were observed when θ was greater than 80° and less than 92°. Smaller θ values favoured Z depositions.

2. Experimental Technique.

(*a*) Water-line Corrosion of Multilayers.

For measuring the contact angle θ a new method was devised which is especially convenient for multilayers but may, with slight modification, also be adapted to determination of contact angles on other solid surfaces (see the last paragraph of 2 (*b*)).

TABLE I.

Time in mins.	*θ in deg.*
0	90
5	76
10	72
15	51
20	42
30	42

If a water drop be put on a multilayer deposited on a chromium-plated slide it changes form within a few seconds. A fraction of a second after it has touched the surface the contact angle viewed with a projection microscope may be, say, 90°, but it diminishes rapidly. A typical example is given in Table I referring to a film of 38 monolayers of barium stearate.

The reason, or one of the reasons, for this decrease of θ was apparent when the drop was thrown off the slide. It left on the multilayer a coloured trace in the form of a narrow ring. As the thickness of a multilayer can be

[1] J. J. Bikerman, *Proc. Roy. Soc. A*, 1939, **170**, 130.

determined from its interference colour it was possible to estimate the depth of the circular "groove"; it turned out to be about 3 molecules. The width of the groove varied with the substance of the multilayer; it was less than 0·001 cm. for calcium stearate films, about 0·002 cm. for barium stearate, etc.

Obviously it was a case of "water-line corrosion."[2] Soap films which are practically insoluble in water are corroded along the water-film-air boundary because soaps lower the surface tension of water and are drawn into the water-air interface. The reduction of the surface tension thus produced caused a reduction of the contact angle in agreement with the well-known equation

$$\cos\theta = \frac{\gamma_{SG} - \gamma_{SL}}{\gamma_{LG}}, \quad . \quad . \quad . \quad . \quad (1)$$

where γ_{SG}, γ_{SL}, and γ_{LG} are the interfacial tensions between solid and gas, solid and liquid, and liquid and gas respectively. A lowering of γ_{LG} causes a lowering of θ. The validity of equation (1) is discussed in 4 (*c*).

Water droplets on multilayers having large contact angles (*e.g.* octadecyl acetate) usually evaporated very slowly, whilst those on the multilayers of hydrophilic octadecyl amine disappeared within a few minutes. Presumably water penetrates into hydrophilic films and spreads over the whole area of the multilayer, thus increasing the area from which evaporation takes place.

Droplets on mixed multilayers (for instance of 6 molecules of octadecyl amine + 2 molecules of calcium stearate + 6 amine + 2 stearate + 6 amine + 2 stearate + 6 amine + 4 stearate) produced no rings.

(*b*) Computation of Contact Angles.

The diameter Δ of the circular groove left by a drop was found to agree with the initial value θ of the wetting angle and not with the value observed shortly before throwing off the drop.

The general relation between Δ and θ is difficult to calculate, as the fundamental equation of capillarity

$$-h\rho g + \gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right) = \text{const.}, \quad . \quad . \quad . \quad (2)$$

leads at once to elliptic integrals; h is the vertical distance of a point on the drop surface from the summit of the drop, ρ the density of water minus the density of air, g the acceleration due to gravity, γ the surface tension, and R_1 and R_2 the principal radii of curvature. If, however, the drop may be assumed to be a spherical segment, then

$$\Delta_0 = 2R\sin\theta, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where R denotes the radius of the sphere (or the radius of the curvature of the drop); Δ_0 is Δ for drops having a spherical curvature. As it is more difficult to determine the curvature of a drop than its volume v, R may be expressed in terms of v. The volume of a spherical segment is

$$v = \pi R^3(\tfrac{2}{3} - \cos\theta + \tfrac{1}{3}\cos^3\theta). \quad . \quad . \quad . \quad (4)$$

From (3) and (4) the relation

$$\frac{\Delta_0{}^3}{v} = \frac{24\sin^3\theta}{\pi(2 - 3\cos\theta + \cos^3\theta)} \quad . \quad . \quad . \quad (5)$$

is obtained. The numerical values of the right hand function were calculated for several values of θ, and the table obtained was used for evaluation of θ from Δ_0 and v.

[2] See *e.g.* U. R. Evans, *Metallic Corrosion*, 1937, pp. 178, 296; M. Volmer and Mahnert, *Z. physik. Chemie*, 1925, **115**, 239.

It is obvious, and also follows from (2), that the deviation of the drop shape from that of a spherical segment diminishes when the volume v is reduced. To apply (5), the ratio Δ^3/v was therefore measured for several drops of various sizes and then extrapolated to $v = 0$.

For the case of $\theta = 90°$ the graphical extrapolation to $v = 0$ can be checked by calculation. Equations (3) and (4) neglect gravitation altogether. Gravitation flattens the drops which, in the second approximation, may be considered to be (at $\theta = 90°$) halves of ellipsoids of revolution; introducing their radii of curvature (a and b being the half-axes) (2) becomes

$$-h\rho g + \gamma\left(\frac{1}{a} + \frac{a}{b^2}\right) = \frac{2\gamma b}{a^2}. \quad . \quad . \quad . \quad (6)$$

On the other hand,

$$v = \tfrac{2}{3}\pi a^2 b. \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Setting $h = b$ and $\Delta/2 = a$ we obtain at small values of v and after utrioducing $r^3 = a^2b = 3v/2\pi$

$$\Delta - 2r = \frac{\rho g r^3}{6\gamma - \rho g r^2}, \quad . \quad . \quad . \quad . \quad (8)$$

and

$$\frac{\Delta^3}{v} = \frac{6}{\pi}\left(2 + \frac{3\rho g r^2}{6\gamma - \rho g r^2}\right). \quad . \quad . \quad . \quad . \quad (9)$$

In deducing (9) it is assumed that the contact angle is independent of the size of the drop. As the experimental curves of the function $\Delta^3/v = f(v)$ were quite similar to the theoretical curve this assumption appears to be justified.[3]

The method outlined above can be applied to other solid surfaces. If the liquid contains non-volatile matter, Δ is the diameter of the circle covered by residue. If the liquid evaporates without leaving marks it may be sprayed over with ignited talc which slides down to the circumference of the drop.

(c) Precision of the Results.

The drops were driven out from a calibrated micro-syringe [4] and the volume v of the drop was read directly; the error involved, except for the very small drops,[5] was negligible. The diameter Δ of the corrosion ring was measured at a magnification of 20 with a scale and the precision depended chiefly on the degree of deviation of the ring from the truly circular shape. If the drops were not too small two apparently identical drops gave on good surfaces values of Δ^3/v, agreeing within 1 %, and as the error of extrapolation is less than 0·5 %, the true value of Δ_0^3/v is known to 1·5 %, corresponding to an error of $\pm$ 15′ in the values of contact angles.

The differences between the contact angles on two different slides coated with supposedly identical multilayers were much larger and often exceeded 2°.

The values of Δ used for calculations were those of external diameters of the ring marks. If the internal diameters were taken all the values of θ would be raised by 1 % or more; indeed they would become greater than the contact angles observed with a projection microscope directly after deposition of drops.

[3] See F. E. Bartell and Merrill, *J. physic. Chem.*, 1932, **36**, 1178.

[4] In this case the difficulties which Bartell and Hatch (*ibid.*, 1935, **39**, 11) encountered when placing drops on solids were insignificant.

[5] The range of volumes used was 0·001 to 0·020 c.c.

3. Results.

A selection of the results obtained is given in Table II. The first column indicates the number, the type, and the composition of the "built-up" monolayers on chromium plated slides. The second and third

TABLE II.

Multilayer.	p_H.	Buffer.	Δ_0^3/v.	θ.
40 X octadecyl acetate . .	7·4	Phosphate .	2·79	101·2°
38 X calcium stearate . .	9·1	Borate .	3·12	97·5°
38 (X + Y) calcium stearate .	—	Borate .	3·56	92·6°
38 Y barium stearate . .	7·4	Phosphate .	3·87	89·5°
38 Y barium stearate . .	7·4	Phosphate .	3·93	89·1°
38 Y barium stearate . .	7·4	Phosphate .	4·00	88·2°
44 Y barium palmitate . .	7·4	Phosphate .	4·30	85·5°
38 Y octadecyl amine . .	7·4	Phosphate .	5	80°

columns refer to the underlying solution from the surface of which the monolayers were taken up. The meaning of Δ_0^3/v and θ is explained in 2 (*b*).

The multilayer described as 38 (X + Y) calcium stearate was a mixture of X and Y deposited films (see the previous paper [1]); the slide was dipped 22 times, and the area of film consumed corresponded to a deposition of 38 monolayers. The three values for barium stearate illustrate the differences between multilayers taken off the surfaces of apparently identical solutions.

4. Discussion.

(*a*) Wetting Angle and Deposition of Multilayers.

Table III contains the rule based on the explanation recently advanced [1] for the three types of deposition of multilayers on solid slides.

TABLE III.

	Multilayers.		
	X.	Y.	Z.
A monolayer is taken up in the course of	dipping only	both dipping and withdrawal	withdrawal only
if the contact angle (measured in the liquid) is	always greater than 90°	over 90° at dipping and below 90° at withdrawal	always below 90°

It deals with receding and advancing contact angles, which may be compared with the equilibrium contact angles listed in Table II. It is seen that Y layers are only deposited when the equilibrium wetting angle is near 90°, so that the receding angle (*i.e.* during withdrawal) may easily become $< 90°$ and the advancing angle (*i.e.* at dipping) $> 90°$. At the speeds used in the multilayer technique the range of θ values giving Y

layers extends from about 80° * to 92°. It is asymmetrical about 90° presumably because, in agreement with Blodgett's advice,[6] the dipping is carried out swiftly (whereby the difference between the equilibrium angle θ and the advancing angle is large) and the withdrawal slowly (thus diminishing the difference between θ and the receding angle).

(*b*) Wetting Angles and Chemical Composition.

Langmuir [7] considers the wetting angles to be determined by the most external radical of the molecule of the solid, *i.e.* for substances treated here, by the CH_3 group. As the wetting angles differ from substance to substance, it is suggested that the outer layer of a "built-up" film contains some "overturned" molecules so that some hydrophilic groups also are exposed. Since it was shown in the previous paper [1] that the multilayers usually had no specific structure the hypothesis of Langmuir cannot be accepted. Evidently the wetting angle of a substance is related to its whole chemical structure in the same manner as are its other physical properties.

(*c*) Wetting Angles and Interfacial Tensions.

The following observation casts some doubt upon the general validity of the usual theory of contact angles. A water drop placed on a hydrophobic surface † forms a wetting angle of, say, 100°. If a drop of ether hanging on a glass rod is brought near, the shape of the water drop does not change although, with a projection microscope, ether vapours can be seen descending onto the water surface.

According to (1) constant θ involves constant $(\gamma_{SG} - \gamma_{SL})/\gamma_{LG}$. Since diffusion of ether through the drop to the solid-liquid interface would take some time, γ_{SL} may be assumed to be unaffected by ether. Then the improbable result follows that the alterations of γ_{SG} and γ_{LG} just compensate each other. It appears more likely that, in consequence of the roughness of solid surfaces, an air-water surface continues underneath the drop so that γ_{SL} and γ_{LG} are interdependent.

It also follows from (1) that alteration of γ_{LG} alone cannot reverse the sign of cos θ, *i.e.* cannot make obtuse a contact angle which is acute, and *vice versa*. In the course of "water-line corrosion" of multilayers (see **2** (*a*)) angles which immediately after deposition of the drops were *e.g.*, 101° decreased gradually to, *e.g.*, 59° without any discontinuity at 90°. From the point of view of equation (1) this behaviour would suggest that the decay of θ is not due to a lowering of γ_{LG}. It is, however, also possible that equation (1) is not always correct.

Summary.

(1) A new method of determining large wetting angles is described. It is based on the measurement of the marks left by drops on solid surfaces.

(2) Wetting angles between air, water, and "built-up" multilayers are measured. They confirm the view that Y films are deposited when the

* Octadecyl amine tends to give Z multilayers.

[6] K. Blodgett, *J. Amer. Chem. Soc.*, 1935, **57**, 1007.

[7] I. Langmuir, *Science*, 1938, **87**, 493.

† It may be the surface of a multilayer or of paraffin wax.

angle is near 90°, whilst more hydrophobic surfaces give rise to X, and less hydrophobic ones to Z deposition.

(3) Langmuir's hypothesis connecting wetting angles with molecular orientation, and the usual theory of contact angles are briefly discussed.

The experiments here reported were carried out in the Department of Colloid Science, The University, Cambridge. I thank Professor E. K. Rideal and Dr. J. H. Schulman for suggestions and encouragement, and the Metal Box Co. Ltd. for financial assistance.

AN ACCURATE DIRECT READING MANOMETER FOR CORROSIVE AND OTHER GASES.

By R. Spence.

Received 4th December, 1939.

The ordinary U-tube type of mercury manometer is still the most convenient means of measuring gas pressures up to one atmosphere. Extremely accurate results may be obtained if a cathetometer is used and if the proper corrections for temperature and variation of gravitational constant are made. The simplicity, accuracy, and reliability of such instruments fully meet with the requirements of modern gas kinetics. There are, however, several limitations. Firstly, the gases under investigation may react chemically with the manometric liquid, as for example in the case of the halogens. Secondly, the existence of a free mercury surface introduces an additional variable into the reaction system, frequently of major importance, namely, an indeterminate partial pressure of mercury vapour. Thirdly, there is generally a considerable dead-space between the gas reservoir and the surface of the manometric liquid which normally varies with change of pressure. In experiments on gas kinetics, this dead-space must be accurately known.

Various kinds of Bourdon gauge of glass or quartz which avoid some of these difficulties have been in use for many years. The quartz spiral manometer of Bodenstein and Dux [1] has a very small dead-space and when used as a null-instrument is quite accurate. It is, however, rather delicate and is somewhat expensive to make. Moreover, extra time and labour are involved in adjusting the balancing-pressure and reading the manometers. This is sometimes important in a fast reaction. The same considerations apply in the case of the Bourdon spoon gauge, which is, in general, more liable to collapse under sudden changes in pressure. Glass "click" gauges have been used to a considerable extent. They are easy to make but they are very delicate and they require the usual balancing-pressure system. A number of direct reading manometers of glass or quartz have been described, which are in general elaborate and expensive and they do not equal the mercury manometer in regard to range, accuracy, or reliability. As a rule, the movement of a diaphragm or Bourdon coil is shown on a screen or recorded on a photographic film by means of an optical lever.[2] The

[1] Bodenstein and Dux, *Z. physik. Chem.*, 1913, **85**, 305.

[2] Lewis and Style, *Nature*, 1937, **139**, 631. Lockspeiser, *J. Sci. Instr.*, 1930, **7**, 145.

ideal instrument would possess the range of scale, accuracy and dependability of the mercury manometer whilst the gases under investigation would come into contact only with glass or quartz and there would be a negligible or small, constant dead-space.

In the hope of constructing an instrument which would approach more closely to these requirements, some experiments were carried out with glass bellows, and an attempt was made in the first instance to utilise the electronic ultra-micrometer as an indicator. Changes in capacity due to displacements of the order of 10^{-6} cm. can be detected by the ultra-micrometer,[3] and several such instruments have been described which are comparatively stable and which show a linear relationship between voltage or current and displacement.[4] Manometric readings to 0·1 mm. Hg over a range of 1 atm., however, correspond to an accuracy of the order of 0·01 % which unfortunately could not be attained in practice using the ultra-micrometer. Moreover, a scale of 10^4 divisions would involve the use of a potentiometer rather than a galvanometer or ammeter and this would greatly increase the cost and complexity of the apparatus. In the final arrangement, therefore, the glass bellows was filled with mercury as shown in Fig. 1. The bellows was sealed into a close-fitting glass tube and a change of pressure of 1 atmosphere in the annular space produced a displacement of the mercury meniscus in the 1 mm. capillary side tube of about one-fifth of the normal barometric height. The degree of accuracy is therefore about one-fifth of that attainable with the U-tube manometer.

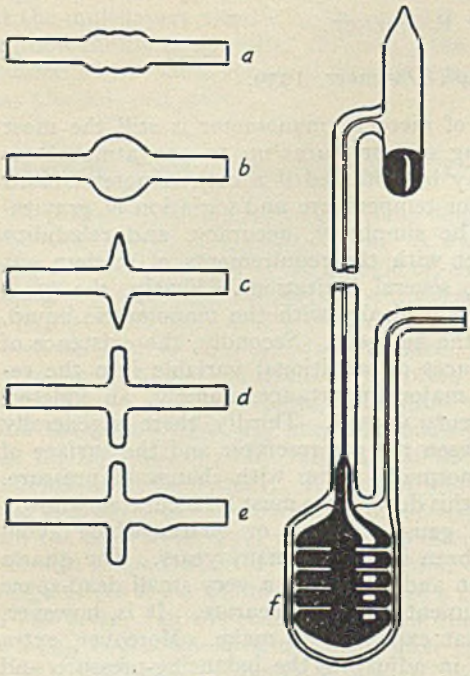

FIG. 1.

Construction.

A length (about 15 cm.) of Pyrex glass tubing (external diameter 0·55 cm., internal diameter 0·35 cm.) was heated in the middle, allowed to thicken slightly, and then blown out to about 1 cm. diameter. By repeating the process twice, about 1·5 cm. of 1 cm. tubing was produced (Fig. 1*a*). This was blown to form a larger bulb (Fig. 1*b*), the wall of which was practically uniform in thickness. Gentle pressure on the ends of the tubing gave a disc (Fig. 1*c*), which was now blown at the edge to a "pancake" shape (Fig. 1*d*). A second pancake was produced in exactly the same way (Fig. 1*e*) not more than 0·5 cm. from the first one, and by directing a very sharp flame on to the short length of connecting tubing, it was gradually thickened and shortened and the bellows were finally pushed close together but without touching at any point. Five such

[3] Dowling, *Phil. Mag.*, 1923, **46**, 81.
[4] Schmidt, *Hochfrequenztechnick und Elektroakustic*, 1933, **41**, 96. Spencer-Smith, *J. Sci. Instr.*, 1935, **12**, 316.

bellows were completed, one side arm was sealed off, and the end walls were blown out (Fig. 1*f*) so as to fit the containing tube as closely as possible. It is advisable to test the bellows thoroughly by repeated sudden evacuation on either side. The remainder of the instrument was constructed as shown in Fig. 1*f*, the interior of the 1mm. capillary tube being slightly ground to prevent sticking of the mercury. After having been thoroughly cleaned, the instrument was evacuated and filled with highly purified mercury. The level of the mercury column could be adjusted by means of the small reservoir at the top.

Calibration.

A thermos flask filled with ice forms a convenient means of keeping the bulb at constant temperature and the displacement of the mercury meniscus can be read off on a travelling microscope or cathetometer. There is no detectable hysteresis effect, and exactly the same straight line relationship between pressure and meniscus displacement was obtained again after an interval of four months. The constants of this equation were obtained from the data by the method of least squares.

MANOMETER 1. DEAD SPACE 8·75 C.C.

EQUATION : $p_{\text{cm. Hg}} = 5{\cdot}02d$ cm. $- 16{\cdot}71$.

d.	$p_{\text{obs.}}$	$p_{\text{calc.}}$
16·320	65·26	65·21
13·460	50·85	50·86
10·914	38·01	38·07
8·468	25·81	25·80
5·880	12·82	12·81
4·236	4·55	4·55

The travelling microscope used gave readings accurate to 0·05 mm. corresponding to 0·25 mm. Hg. Visual readings of the mercury U-manometer have about the same degree of accuracy so that the agreement between $p_{\text{obs.}}$ and $p_{\text{calc.}}$ can be regarded as satisfactory. A finer and more uniform capillary and a good cathetometer would, of course, considerably improve the accuracy.

If set up in the same way as an accurate thermometer, with enclosed scale, calibrated at 0°, the manometer could be used as a direct-reading instrument. Visual readings to 0·2 mm. would be accurate to 1 mm. Hg. which is sufficient for many purposes. The instrument possesses the advantage of comparatively small size, the movement of the mercury meniscus is practically instantaneous and free from oscillation, whilst pressure measurement involves only a single scale reading. Although designed primarily for work involving chemically reactive gases, it should also find useful application in the case of inert gases.

Summary.

A glass manometer is described in which the relation between scale reading and pressure is linear. The dead space is small and practically constant (variation 1·25 % for 1 atm). and pressures up to 1 atmosphere can be readily determined to within 0·25 mm. Hg. The instrument is specially suited for the study of gas reactions.

Physical Chemistry Department,
The University, Leeds.

THE PROPERTIES OF DETERGENT SOLUTIONS. PART X. SOME FURTHER OBSERVATIONS ON ELECTROPHORETIC MOBILITIES IN DETERGENT SOLUTIONS.

By J. Powney and L. J. Wood.

Received 15th December, 1939.

In a previous paper [1] we described some measurements of the electrophoretic mobility of mineral oil (Nujol) in alkalies and in solutions of certain surface-active substances. This work has now been extended to include the study of the influence of temperature, chain-length and added electrolytes on the electrophoretic mobility. In addition to oil drops, suspensions of wax, ilmenite and calcium laurate have been investigated. The experimental technique was the same as that used in the previous investigation except that the electrophoresis cell and microscope were placed in an air thermostat to enable measurements to be made at higher temperatures.

Results and Discussion.

Influence of Temperature and Chain-Length.

In considering the influence of temperature upon electrophoretic mobilities in solutions of paraffin chain salts the following factors have to be taken into account:

(*a*) change of viscosity of the dispersion medium,
(*b*) change of state of aggregation of the solution,
(*c*) change of degree of adsorption of the long chain ions.

The second and third factors have also to be considered in connection with the effect of chain-length on mobilities.

For particles suspended in water Freundlich [2] has pointed out that the change of mobility with temperature should depend only on the change of viscosity of the water according to the simple relationship $u_1\eta_1 = u_2\eta_2$, where u represents the mobility of the particle and η the viscosity of the water. In the present work it has been confirmed that this holds for suspensions of Nujol and paraffin wax in water over the temperature range 25° to 60°.

The abrupt transition from single ions to micelles which occurs in solutions of paraffin chain salts at certain critical concentrations is reflected in a sudden change of properties such as density, electrical conductivity, surface and interfacial activities. The critical concentrations at which these changes occur are known to depend on temperature and chain-length.[3] The preliminary data given in the previous paper [1] showed that the aggregation to form ionic micelles is also reflected in the electrophoretic behaviour of oil drops dispersed

[1] Powney and Wood, *Trans. Faraday Soc.*, 1940, **36**, 57.
[2] Freundlich, *Colloid and Capillary Chemistry*, London, p. 248.
[3] *Cf.* Hartley, *Aqueous Solutions of Paraffin-chain Salts*, Paris, 1936.

in such solutions. The additional mobility data now obtained confirm that the critical concentration rises with decreasing chain-length and increasing temperature.

The mobilities of oil drops in sodium laurate solutions at 25° and 60° C. are shown in Fig. 1 together with data for ilmenite ($FeO . TiO_2$) particles in similar solutions at 25° C. The commencement of aggregation of the laurate ions is indicated by minima which occur at a concentration of approximately 0·35 % at 25° C. and 0·6 % at 60°. The view that these minima are related to a sudden change in constitution of the sodium laurate solution is supported by the fact that the minima

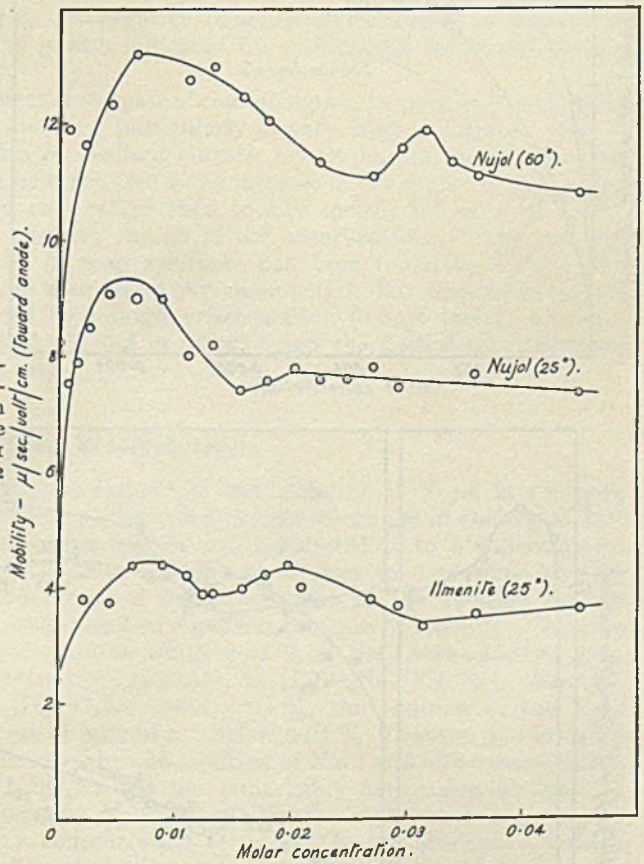

FIG. 1.—Electrophoretic mobilities in sodium laurate solutions (0·01 Molar = 0·222 %).

for both Nujol and ilmenite, two very different types of particles, occur at similar concentrations. Inflections in the curves are also shown by Nujol in sodium myristate and sodium palmitate solutions at 60° C. (Fig. 2) at concentrations which decrease with increasing chain-length. The minimum in the sodium palmitate curve is at a somewhat higher concentration than might be anticipated from available data for the critical concentrations of unhydrolysed paraffin chain salts of similar chain-length. This is undoubtedly due to the fact that sodium palmitate is considerably hydrolysed in solution [4] at 60°.

[4] Powney and Jordan, *Trans. Faraday Soc.*, 1938, **34**, 363.

For an unhydrolysed long chain salt such as sodium tetradecyl sulphate (Fig. 3, *a* and *b*) the inflections in the mobility curve also occur very close to the critical concentration as determined from surface and

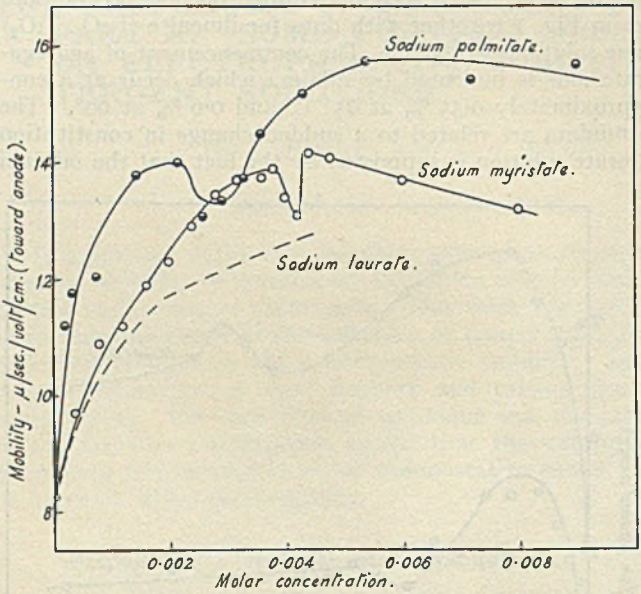

FIG. 2.—Electrophoretic mobilities of Nujol in sodium myristate and sodium palmitate solutions at 60° C.

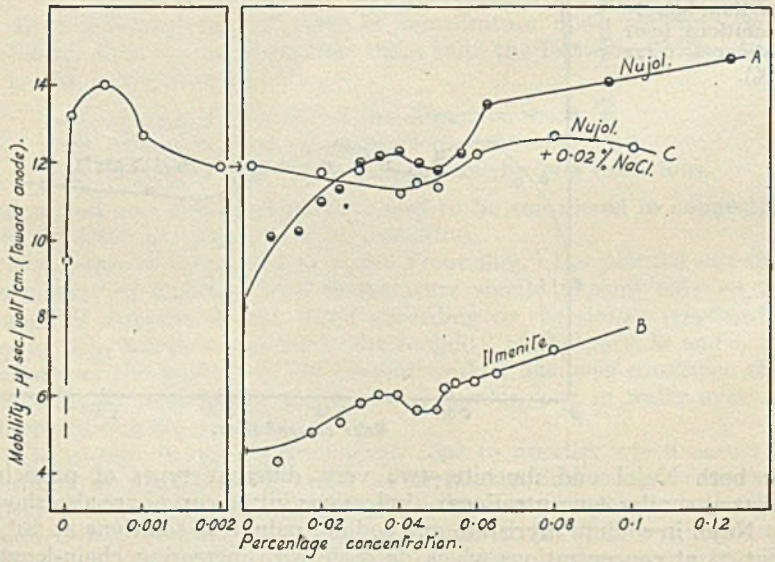

FIG. 3.—Electrophoretic mobilities in sodium tetradecyl sulphate solutions at 60° C.

interfacial tension and conductivity data.[5] As was found with sodium laurate, the nature of the particle does not in any way determine the position of the mobility minimum.

[5] Powney and Addison, *Trans. Faraday Soc.*, 1937, **33**, 1243, and 1938, **34**, 372.

Since it is highly probable that the increase in the mobility of oil drops on the addition of paraffin chain salts is due to the adsorption of long chain ions, increase of temperature will indirectly affect the mobility by decreasing the degree of adsorption. Thus, for Nujol in sodium laurate solutions at 60° C. the observed mobilities are only about 75 % of the values calculated from corresponding data determined at 25° on the assumption that change of viscosity is the only factor. This difference is probably due to a decrease in the adsorption of laurate ions at the higher temperature, as check measurements show that the viscosity of paraffin chain salts at the concentrations used in this investigation does not differ from that of water at the same temperature by more than 1 %. A negative temperature coefficient of adsorption of long chain ions is also indicated by surface and interfacial tension measurements.[5]

The general effect of increase of chain-length is to give rise to somewhat higher values of mobility, particularly in very dilute solutions. This is shown by the data for sodium laurate, myristate, and palmitate given in Fig. 2 and can be attributed to an increase in the degree of adsorption of the long chain ions rather than to any specific influence of chain-length upon the effective charge of the adsorbed ions. The mobility of carbon particles in soap solutions has been found by Urbain and Jensen[6] to increase with increasing chain-length, but their observations have been confined to a single concentration (0·0036 molar) which in some instances is above and in others below the critical concentrations of the long chain salts.

Influence of Added Electrolytes.

In our previous discussion[1] of the mobility of Nujol in solutions of paraffin chain salts we described the sharp change in the region just below the critical concentration and attributed it to a superimposed sodium ion effect. It was thought of interest to determine whether increasing the concentration of sodium ions in the solution by the addition of NaCl would lead to a general decrease of mobility. A series of experiments was made in which 0·02 % of NaCl was added to solutions of sodium tetradecyl sulphate, $C_{14}H_{29}SO_4Na$ (Fig. 3*c*). For concentrations of $C_{14}H_{29}SO_4Na$ above 0·03 %, the addition of the NaCl results in a decrease of mobility. Below 0·03 %, however, the mobility is considerably increased by the addition of NaCl and at a concentration of 0·0005 % $C_{14}H_{29}SO_4Na$ has the remarkably high value of 14μ/sec./volt/cm. With 0·00002 % $C_{14}H_{29}SO_4Na$ the mobility is 10, a figure only attained at a concentration of 0·01 % in the absence of sodium chloride. The values at low concentrations were obtained by successive dilutions of the emulsions with the stock aqueous Nujol emulsion and with NaCl so as to keep the concentrations of both of these constant. The persistently high mobilities could not be due to any time factor in attaining adsorption equilibrium since at each dilution at least an equal amount of Nujol was added and therefore at least half the Nujol droplets in the new mixture were freshly added to the surface active solution. No irregularities outside the usual experimental error were found in the mobilities of the individual Nujol droplets.

These high values are all the more surprising since the addition of

[6] Urbain and Jensen, *J. Physic. Chem.*, 1936, **40**, 821.

NaCl to Nujol in pure water causes a considerable decrease in mobility.[1] Neutral salts are known to increase the interfacial activity of paraffin chain salt solutions,[7] and it is possible that the high mobilities are due to an increased adsorption of long chain ions at the surface of the oil drops. The interfacial activities of the extremely dilute solutions of sodium tetradecyl sulphate used are, however, quite low and would not appear to account entirely for the very high electrophoretic mobilities observed under similar conditions. In the first part of this investigation [1] it was also shown that the high mobility of Nujol in very dilute solutions of the cation-active salt dodecyl pyridinium chloride could not be correlated with the interfacial activity of the solution.

TABLE I.

NaCl (%).	Mobility (μ/sec./volt/cm.).
Zero	8·4 *
0·001	9·2
0·005	10·4
0·02	12·3
0·05	13·5
0·1	13·3

* By interpolation from Fig. 3*a*.

A further series of measurements was carried out to determine the quantity of sodium chloride necessary to produce an optimum effect at a low concentration (0·001 %) of $C_{14}H_{29}SO_4Na$. These are given in Table I and indicate that 0·02 to 0·05 % sodium chloride is necessary.

Influence of Nature of Particle.

(*a*) **Liquid and Solid Paraffin.**—Since the mobility of liquid paraffin in surface active solutions is dependent upon the formation of oriented interfacial films of long chain ions, it was thought of interest to investigate whether a transition of the particle from the liquid to the solid state would influence its mobility, possibly by effecting a change in the degree or in the nature of the adsorption. For this purpose a series of measurements on a sample of paraffin wax (congealing point 49°) in 0·1 % $C_{14}H_{29}SO_4Na$ was made at increasing temperatures from 37° to 60°. The data obtained are shown in Table II and it will be noted that no significant changes of mobility occur at the melting-point of the wax. The product $u\eta$, whree η is the viscosity of the dispersion medium in centipoises, shows a small but definite decrease with increasing temperature of the same order as was found with Nujol in sodium laurate solutions described above.

TABLE II.

Temperature (°C.).	Mobility (μ/sec./volt/cm.).	η.	$u\eta$.
37·1	11·5	0·69	7·9
42·1	12·2	0·63	7·7
45·7	12·3	0·59	7·3
50·5	13·2	0·54	7·2
55·5	13·2	0·50	6·6
59·7	14·6	0·47	6·9

(*b*) **Calcium Laurate.**—The mobility of another type of particle, namely calcium laurate, has been studied and the value for a suspension in water at 25° C. found to be 3·8 μ/sec./volt/cm. towards the anode, which is approximately the same as that found for other hydrophobic particles such as Nujol and paraffin wax.

[7] Robinson, *Wetting and Detergency*, London, 1937, p. 137, and Powney and Addison, *Trans Faraday Soc.*, 1937, **33**, 1253.

(*c*) **Ilmenite.**—The behaviour of ilmenite particles in sodium laurate and sodium tetradecyl sulphate solutions has been mentioned above and is illustrated in Figs. 1 and 3. A stock suspension was prepared in the following manner. A sample of "Air-floated Ilmenite Black," supplied by Messrs. British Titan Products Co., Ltd., was first treated with sodium hexametaphosphate to remove traces of divalent metal salts which were found to be present. The ilmenite was then thoroughly washed with conductivity water and dried. Two grams of the material were shaken up with a litre of conductivity water and allowed to stand for $4\frac{1}{2}$ hours. About 700 c.c. were then carefully decanted and kept as the stock suspension. For use it was diluted with an equal volume of a solution of alkali or detergent. The particles had a diameter of approximately 1-2 μ. The mobility of ilmenite particles suspended in water is approximately half that of oil drops in water and this ratio persists in sodium laurate and sodium tetradecyl sulphate solutions

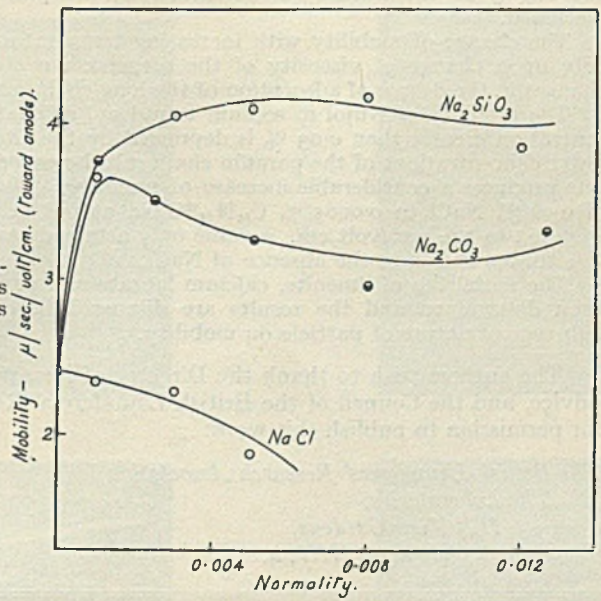

FIG. 4.—Electrophoretic mobilities of ilmenite particles at 25° C.

at all the concentrations examined. It might have been expected that at the higher concentrations where the surfaces are probably fairly well covered with long chain ions the potential of the particles would be dependent only on the charge of the ions and independent of the nature of the "core" of the particle. At any given temperature, however, the mobility of ilmenite in solutions of paraffin chain salts attains but never rises above the water value for hydrophobic particles such as Nujol. A tentative explanation is that in the case of ilmenite particles the long chain ions are oriented in the opposite direction to those on oil drops, *i.e.*, the polar heads will be oriented towards the ilmenite surface leaving the particles as a whole with a hydrophobic exterior of hydrocarbon chains, the resulting mobility being that found for an oil drop. It is not clear why the mobility is not further increased by the adsorption of a second long chain ion film to give a value characteristic of a normal oil drop in paraffin chain salts solutions. This may possibly be due to some restriction in the formation of a bimolecular film.

Some measurements have also been made of the mobility of ilmenite in sodium chloride, sodium carbonate and sodium metasilicate solutions and the results are plotted in Fig. 4. These are qualitatively the same as those obtained for Nujol in similar solutions and described in our previous paper.[1] The mobility rises rapidly with increasing hydroxyl ion concentration but is lowered slightly by increasing sodium ion concentration. Although there are slight divergences there is again a tendency for the ilmenite particles to have one-half the mobility of Nujol drops under the same conditions.

Summary.

Additional data concerning the electrophoretic mobility of oil drops in solutions of paraffin chain salts are recorded. The maximum mobilities in such solutions are obtained at concentrations which decrease with increasing chain-length. The abrupt changes of mobility which occur in the region of the critical concentration of the paraffin chain salt are discussed.

The change of mobility with increasing temperature is dependent not only upon change of viscosity of the dispersion medium but also upon changes in the degree of adsorption of the long chain ions at the interfaces.

The mobility of Nujol in sodium tetradecyl sulphate solutions of concentration greater than 0·03 % is depressed by the addition of NaCl. At lower concentrations of the paraffin chain salt, however, the added electrolyte produces a considerable increase of mobility. Thus, on the addition of 0·02 % NaCl to 0·0005 % $C_{14}H_{29}SO_4Na$ at 60° C. the mobility rises from 8·3 to 14μ/sec./volt/cm., a value only attained at two hundred times this concentration in the absence of NaCl.

The mobilities of ilmenite, calcium laurate and paraffin wax have also been determined and the results are discussed in connection with the nfluence of nature of particle on mobility.

The authors wish to thank the Director of Research for his valuable advice, and the Council of the British Launderers' Research Association for permission to publish this work.

The British Launderers' Research Association,
The Laboratories,
Hill View Gardens,
Hendon, N.W. 4.

REVIEW OF BOOK.

Chemical Spectroscopy. By W. R. Brode. (Chapman & Hall, 1939.) Pp. xii + 494. Price 36s. net.

This should prove a useful book for students whose interests are in spectroscopy as a "profession." This activity exists in the United States to a degree not always appreciated in this country.

Judged by these standards, the distribution of subjects—absorption, emission, qualitative and quantitative analysis and so forth—is probably correct. Much the same applies to the instrumental sections, where apparatus is described in detail. Throughout, the aim seems to me to give the reader information of considerable precision within a very limited range of ideas.

As a laboratory guide, the volume can be recommended.

F. I. G. R.

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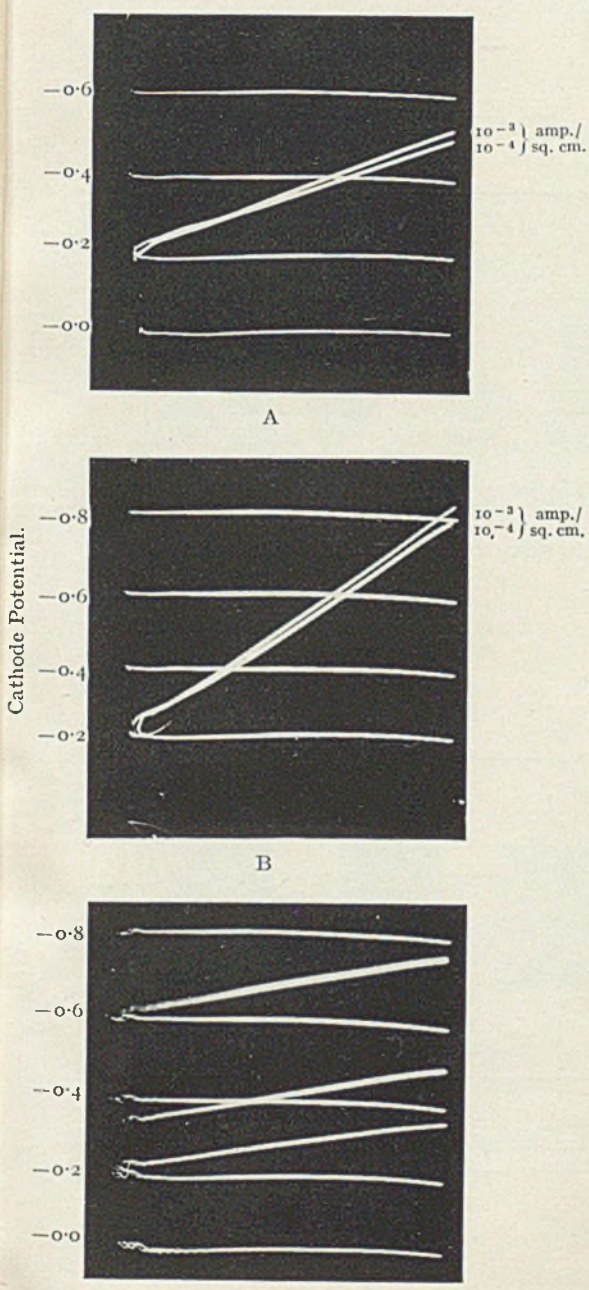
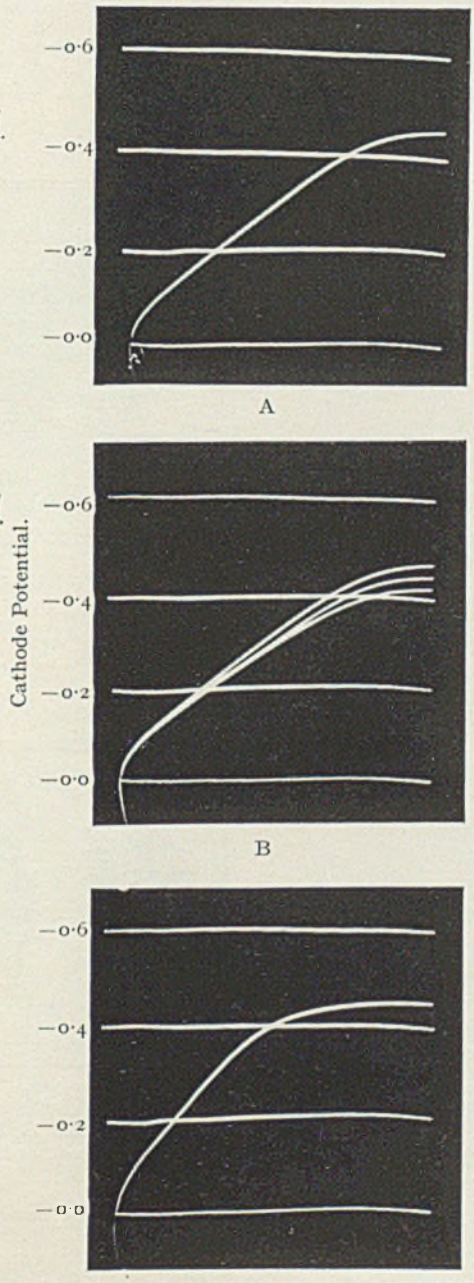
PLATE V.



C
Quantity of Electricity.

FIG. 3.



C
Quantity of Electricity.

FIG. 4.

[*See page* 367.

PLATE VI.

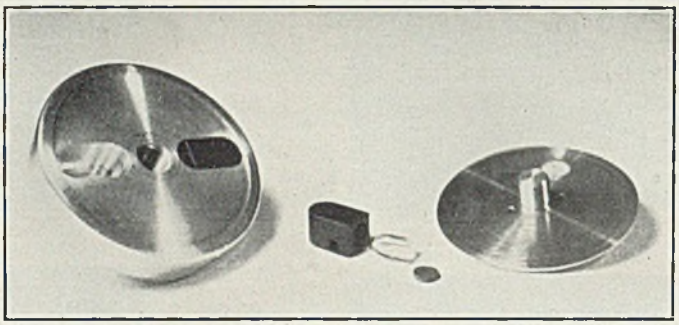


FIG. 1.—Photograph of rotor, showing cell and hard rubber block.

[*See page* 381.

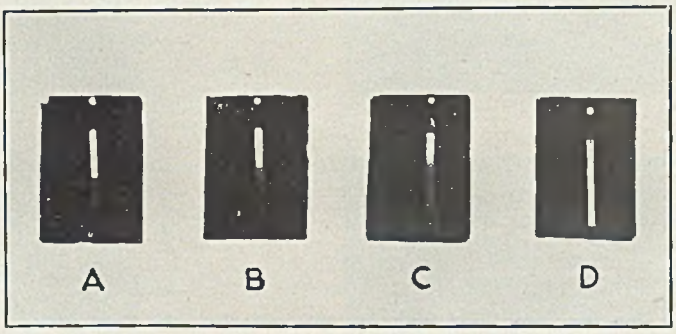


FIG. 4.—A, B, sedimentation of erythrocruorin of earthworm blood; C, carboxyhemoglobin, and D, half-concentration, about 0·5 %, of carboxyhemoglobin (boundary near top of liquid).

[*See page* 384.

Transactions of the Faraday Society

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

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